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Study of Changes in Phase Equilibrium in Three-Component Deep Eutectic Solvents “Tetra Atomic Alcohol – Urea – Salt of a Quaternary Ammonium Base” Depending on the Preparation Method

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Abstract. The paper presents the results of a comparative study of two different methods for preparing three-component systems of deep eutectic solvents (DESs) based on tetra atomic alcohol, urea and a salt of a quaternary ammonium base. To study the phase equilibrium of mixtures of hydrogen bond donors and acceptors, two-component mixtures of different molar ratios of components, from 1:10 to 10:1 mole fractions, were prepared, followed by determination of the melting/crystallization temperature and construction of phase equilibrium diagrams of the components. Based on the results of a study of phase equilibrium diagrams of two component systems and the established coordinates of eutectic points, a phase equilibrium diagram of a three-component system was constructed. A study of two methods for preparing a three-component DES mixture (preparation of binary systems with the addition of a third component and a method of simultaneous mixing of three components) showed that the most correct is the simultaneous mixing of all three components, based on a theoretical calculation of the composition of a three-component mixture from two-component mixtures of eutectic composition.

Keywords: deep eutectic solvents, donor-acceptor interaction, eutectic, phase diagram, two-component and three-component systems.

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Исследование изменения фазового равновесия в трехкомпонентных глубоких эвтектических растворителях «четырёхатомный спирт – карбамид – соль четвертичного аммониевого основания» в зависимости от способа приготовления

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Аннотация. В работе представлены результаты сравнительного исследования двух разных способов приготовления трехкомпонентных систем глубоких эвтектических растворителей на основе четырёхатомного спирта, карбамида и соли четвертичного аммониевого основания. Для исследования фазового равновесия смесей доноров и акцепторов водородных связей были приготовлены двухкомпонентные смеси различного мольного соотношения компонентов, от 1:10 до 10:1 мольных долей, с последующим определением температуры плавления/кристаллизации и построением диаграмм фазового равновесия компонентов. На основе результатов исследования диаграмм фазового равновесия двухкомпонентных систем и установленных координат точек эвтектики была построена диаграмма фазового равновесия трехкомпонентной системы. Исследование двух способов приготовления трехкомпонентной смеси ГЭР (приготовление бинарных систем с добавлением третьего компонента и способ одновременного смешения трех компонентов) показало, что наиболее верным является одновременное смешение всех трех компонентов, основанное на теоретическом расчете состава трехкомпонентной смеси из двухкомпонентных смесей эвтектического состава.

Ключевые слова: глубокие эвтектические растворители, донорно-акцепторное взаимодействие, эвтектика, фазовая диаграмма, двухкомпонентная и трехкомпонентная система.

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Introduction

In the last decade, deep eutectic solvents (DESs) have attracted enormous attention from researchers from various fields of science due to their unique nature and properties, such as low melting/crystallization point, non-toxicity, biodegradability and biocompatibility, ease and low cost of preparation, low cost, thermal stability, possibility of use as "green" solvents, chemical compatibility with water, etc. [1–9]. DESs are formed by self-association or complexation of a hydrogen bond donor and acceptor. DESs were first presented in 2003 by Abbott et al. in [10–16].

Despite the growing interest in DESs, there is very little information about the mechanism of donor-acceptor interaction between the components of DES. In addition, most of the publications are devoted to studies of two-component DESs, while there is practically no information about studies of three-component DESs.

Previously, we developed acid oil-displacing compositions based on several DESs [17–20]. The research results presented in this article will form the basis for the creation of a new oil-displacing composition based on DES.

The paper presents the results of a comparative study of two different methods for preparing three-component DES systems based on tetra atomic alcohol, urea and a salt of a quaternary ammonium base.

Experimental

To study the phase equilibrium of mixtures of hydrogen bond donors and acceptors, two-component mixtures of different molar ratios of components, from 1:10 to 10:1 mole fractions, were prepared. To do this, samples of components pre-weighed on an analytical balance were placed in mortars, where they were mechanically mixed and ground until completely homogeneous. The resulting homogeneous mixtures of components were placed in dry flasks and heated in a sand bath with constant stirring until transparent melts formed. After this, the flasks with the melts were placed in a thermostat heated to a temperature of 80 °C for 4–6 hours, and then cooled to room temperature.

For each melt, characterized by a different molar ratio of components, the melting or crystallization temperatures were determined (in the case of a liquid form of the melt at room temperature). The melting point was determined using a "Stuart SMP 30" instrument. To do this, the resulting solid melts were ground into powder in a mortar, and then a small amount of finely ground dry melt was placed in a thin-walled glass capillary sealed at one end. The initial temperature was set approximately 5 °C below the expected melting point, and then the glass capillary was heated at a rate of 1 °C/min. The temperature at which the last crystal of the melt passed into the liquid phase was recorded as the melting point of the mixture under study.

To determine the crystallization temperature in the range from room temperature to minus 30 °C, samples were placed in a thermostat (cryostat) filled with a cooling mixture with a temperature 3–5 °C lower than the expected crystallization temperature and the temperature at which crystals began to form was visually assessed. The crystallization temperature was determined using a setup consisting of a glass bottle with the test sample placed in the cryostat coolant, a thermocouple inserted into the sample volume, and a temperature change recorder. When the phase state of the sample under study changes, the recorder recording the cooling shows a break in the cooling curve corresponding to the phase transition temperature (State All-Russian Standard 18995.5–73).

Based on the results obtained from studying the melting and crystallization temperatures, phase equilibrium diagrams were constructed in the coordinates "melting/crystallization temperature" – molar ratio of the mixture components.

Results and discussion

All chemicals used in the experimental work were of analytical grade and were used without further purification. To obtain three two-component and one three-component DES systems underlying the future oil-displacing composition, the following substances were used: tetra atomic alcohol (pentaerythritol), urea and a salt of a quaternary ammonium base (choline chloride).

For the study, two-component mixtures with different molar ratios of components were prepared: pentaerythritol and choline chloride (DES_1), choline chloride and urea (DES_2), pentaerythritol and urea (DES_3). Based on the analysis of previously constructed phase equilibrium diagrams, the coordinates of the eutectic points were established: eutectic temperature and molar ratio of components (Table 1).

From table 1 it can be seen that each system (DES_1, DES_2 and DES_3) is characterized by one eutectic point at a certain ratio of components: DES_1–50 % mol. pentaerythritol and 50 % mol. choline chloride; DES_2–33 % mol. choline chloride and 67 % mol. urea; DES_3–40 % mol. pentaerythritol and 60 % mol. urea. The melting/crystallization temperatures of the eutectic composition at the eutectic point were 98, 18 and 96 °C for DES_1, DES_2 and DES_3, respectively.

Based on two-component systems of eutectic composition, three-component mixtures were prepared by adding a third component (pentaerythritol, urea and choline chloride). Moreover, the principle of preparing the mixtures was similar to that described above; component 1 was the two-component eutectic composition DES_1, DES_2 and DES_3, and the second component was pentaerythritol, urea and choline chloride, respectively, for DES_1, DES_2 and DES_3. Three-component mixtures of different molar ratios of components and the construction of diagrams of their phase equilibrium made it possible to determine the eutectic point for the prepared three-component systems, characterized by the lowest melting/crystallization temperature at a certain molar ratio of components. Three-component systems are designated below in the text as DES_4, DES_5 and DES_6 (Table 2). Table 2 and Fig. 1–5 show the phase diagrams of DES_4, DES_5, DES_6 and DES_7.

Fig. 1 shows the phase diagram of the binary system DES_4 based on DES_1 (50 % mol. pentaerythritol and 50 % mol. choline chloride) and urea.

A study of the phase diagram of the DES_4 binary system showed that the DES_4 system has one eutectic point with a component ratio of 20 % mol. DES_1 and 80 % mol. urea. The melting point of

Table 1. Composition and physicochemical characteristics of two-component DES systems: DES_1, DES_2 and DES_3

DES	Composition of DES substance	Component ratio, % mol.	Molecular weight, g/mol	Melting temperature, °	Density, g/cm^3
DES_1	PER: ChCh	50:50	275.5	98	1.2458
DES_2	ChCh: U	33:67	201.5	18	1.2158
DES_3	PER: U	40:60	198.0	96	1.2346

Note: PER – pentaerythritol, U – urea and ChCh – choline chloride.

Table 2. Physico-chemical characteristics: DES_4, DES_5, DES_6 and DES_7

DES	Component	Component ratio, %. mol.	Melting point of the mixture at the eutectic point, °
DES_4	DES_1: U	20.0:80.0	70.2
DES_5	DES_3: PER	70.0:30.0	minus 14
DES_6	DES_2: ChCh	30.0: 70.0	70
DES_7	PER: U: ChCh	27.0:51.5:21.5	minus 14.5

Note: PER – pentaerythritol, U – urea and ChCh – choline chloride.

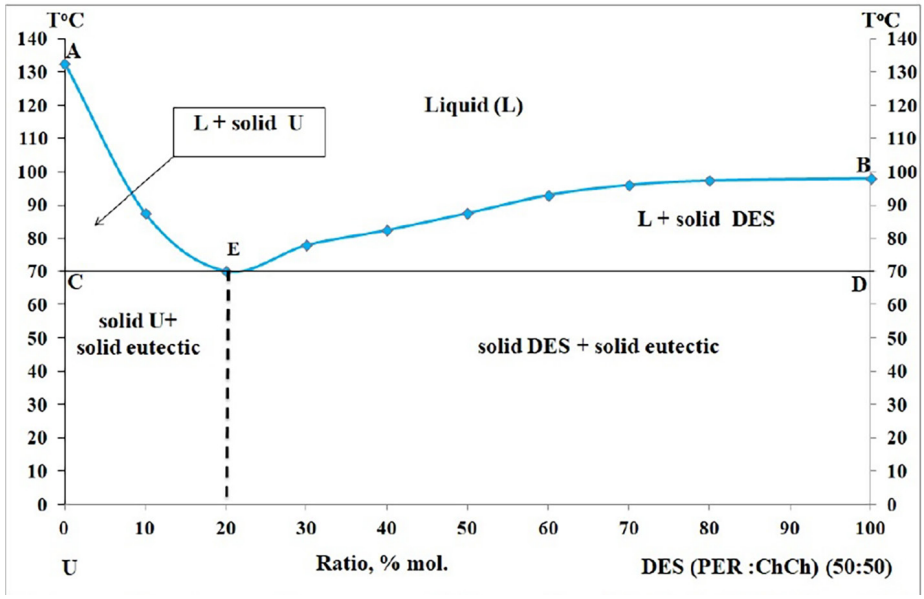


Fig. 1. Phase diagram of the binary system DES_4: L – region of existence of liquid (melt), (L + solid. U and (L + solid. DES) – regions of coexistence of the liquid phase and solid urea and DES based on pentaerythritol and choline chloride, respectively; (solid. U + solid. DES) – region of existence of a mechanical mixture of solids (urea and DES based on pentaerythritol and choline chloride, respectively. AEB and CED – liquidus and solidus lines, respectively, E – eutectic point.

the DES_4 mixture of eutectic composition is 70.2 °C, which is significantly lower than the melting temperatures of DES_1 and urea. The formation of hydrogen bonds is a key intermolecular force leading to a decrease in the melting point [21], which confirms the formation of DES. The presence of one eutectic point and the absence of other extrema on the liquidus line indicate the absence of the formation of chemical compounds.

Fig. 2 shows the phase equilibrium diagram of a mixture of DES_5 based on DES_2 (67 % mol. urea and 33 % mol. choline chloride) and pentaerythritol.

The DES_5 system is characterized by one eutectic point with a component ratio of 70 % mol. DES_2 and 30 % mol. pentaerythritol. The pour point of the DES_5 mixture of eutectic composition is minus 14 °C.

Fig. 3 shows the phase diagram of the DES_6 system based on DES_3 (40 % mol. pentaerythritol and 60 % mol. urea) and choline chloride.

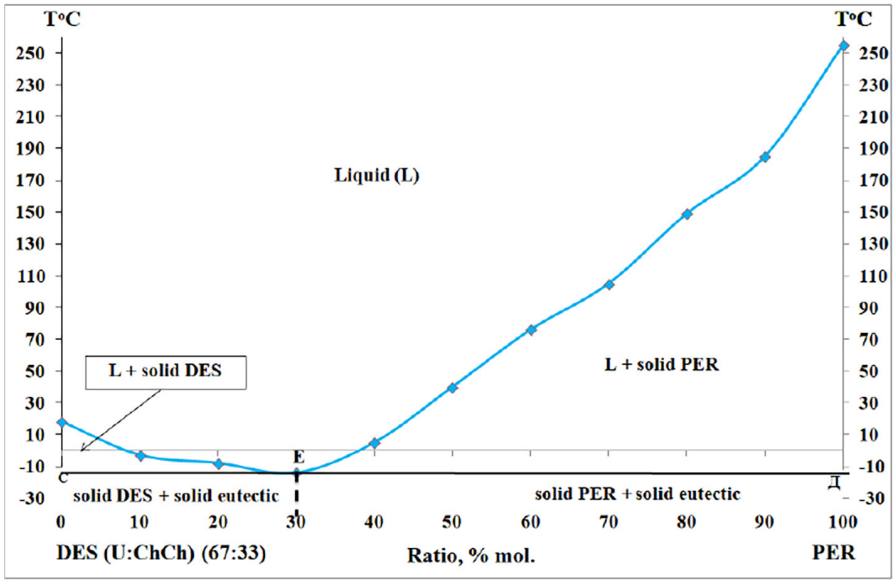


Fig. 2. Phase diagram of the fusibility of the binary system DES_5: L – region of existence of liquid (melt), (L + solid. PER and (L + solid. DES) – regions of coexistence of the liquid phase and solid pentaerythritol and DES based on urea and choline chloride, respectively; (sol. PER + solid. DES) – region of existence of a mechanical mixture of solids (pentaerythritol and DES based on urea and choline chloride, respectively. AEB and CED – liquidus and solidus lines, respectively, E – eutectic point.

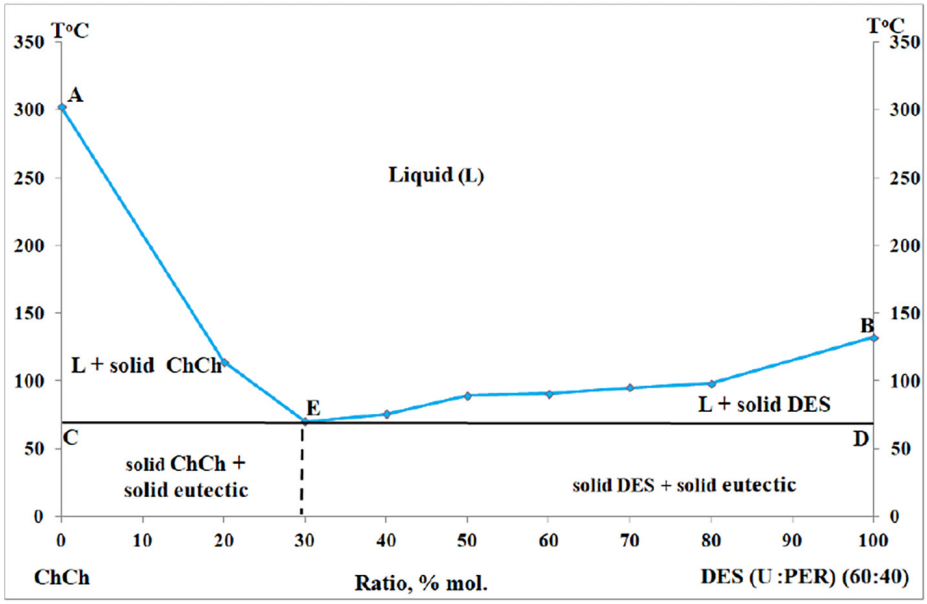


Fig. 3. Phase diagram of the triple DES_6 system: L – region of existence of liquid (melt), (L + solid. ChCh and (L + solid. DES) – regions of coexistence of the liquid phase and solid choline and DES based on pentaerythritol and urea, respectively; (sol. ChCh + solid. DES) – region of existence of a mechanical mixture of solids (choline chloride and DES based on pentaerythritol and urea, respectively. AEB and CED – liquidus and solidus lines, respectively, E – eutectic point.

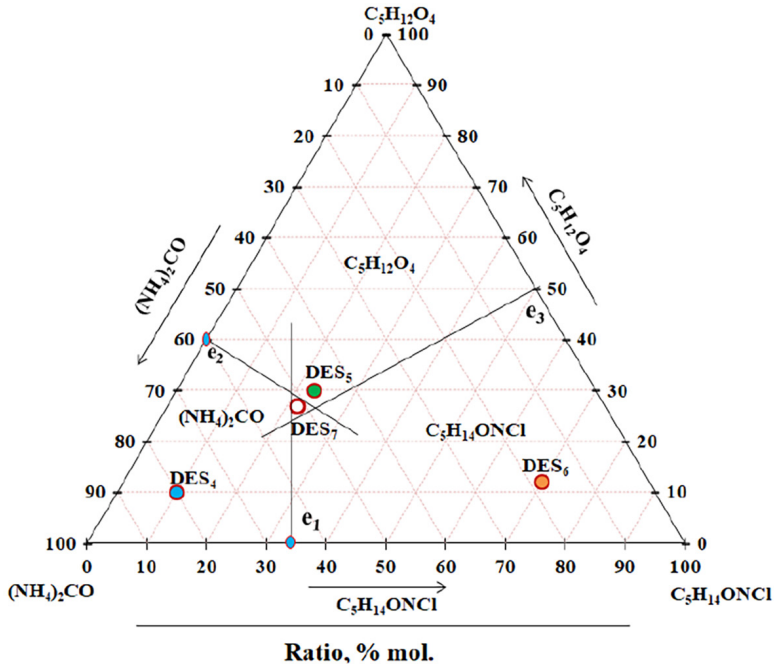


Fig. 4. Phase diagram of the ternary system DES based on pentaerythritol, urea and choline chloride: e_1, e_2 and e_3 are monovariant cotectic lines of simultaneous crystallization of two phases, which begin in double phases and converge in a triple eutectic. DES_4, DES_5, DES_6 and DES_7 – triple (in terms of the number of components) eutectic of invariant simultaneous crystallization of three phases from the melt.

The binary system DES_6 based on DES_3 and choline chloride is characterized by one eutectic point for a composition of 30 % mol. DES_3 and 70 % mol. Choline chloride. The melting point of a mixture of eutectic composition is 70 °C.

The study of phase equilibrium diagrams of the two-component systems DES_1, DES_2, DES_3 allowed us to theoretically calculate the eutectic composition and synthesize the three-component system DES_4, DES_5, DES_6 and DES_7 (Fig. 4, Table 2). The ratio of components in such a theoretically calculated three-component system was 27.0 % mol. pentaerythritol, 21.5 % mol. choline chloride and 51.5 % mol. urea. Determination of the melting point of the theoretically calculated and synthesized eutectic mixture showed that it is characterized by a lower temperature than the melting point of each of the two-component systems of the eutectic composition and is minus 14.5 °C.

The diagram (Fig. 4) also shows the experimentally determined eutectic points of the mixtures DES_4, DES_5 and DES_6. It can be noted that the coordinates of the experimentally determined eutectic points of three-component systems obtained by mixing two-component mixtures with a third component do not coincide with the coordinates of the theoretically calculated eutectic point, which was experimentally characterized by the lowest melting point of minus 14.5 °C.

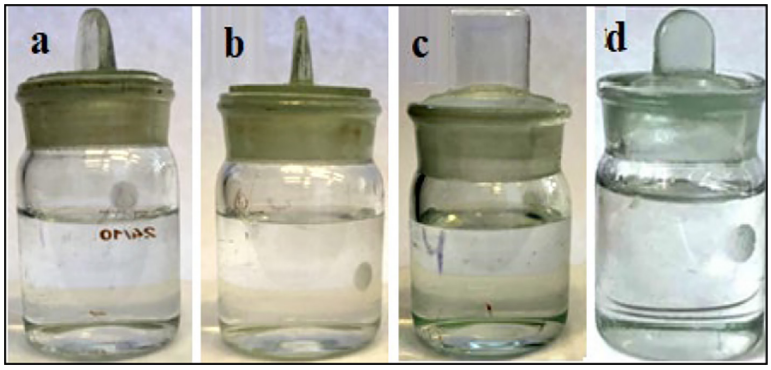
Thus, the above studies have shown that the method of preparing three-component mixtures of DES has a significant impact on the formation of complex compounds, but the most correct is the simultaneous mixing of all three components, based on a theoretical calculation of the composition of a three-component mixture from two-component mixtures of eutectic composition.

For the theoretically calculated composition corresponding to the eutectic mixture of DES_7, a mechanism of donor-acceptor interaction of the components of the three-component system is proposed.

Fig. 5 shows the appearance of the resulting melts of mixtures of the eutectic composition DES_4, DES_5, DES_6 and DES_7 at temperatures above their melting temperatures.

Fig. 6 shows the proposed scheme of donor-acceptor interaction of the components of the three-component system of DES_7.

In DES_7, based on pentaerythritol, urea and choline chloride, a molecular complex is formed due to donor-acceptor interaction, in which choline chloride is an electron pair acceptor in relation to pentaerythritol and urea, urea and pentaerythritol are hydrogen bond donors.



Note: photographs of DES mixtures were taken at temperatures above their melting/crystallization temperatures.

Fig. 5. Melts of eutectic composition DES: a – DES_4; b – DES_5; c – DES_6; d – DES_7

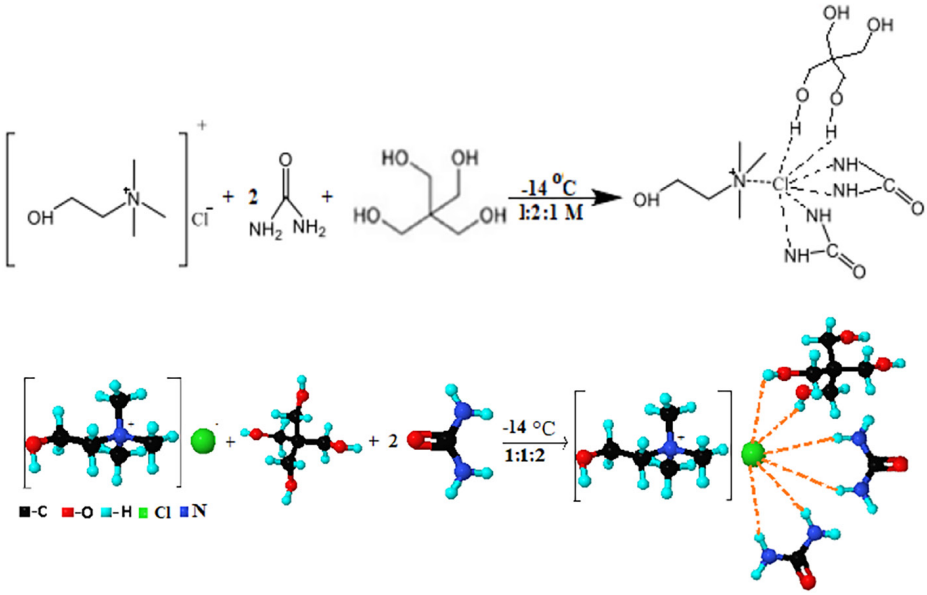


Fig. 6. Proposed scheme of donor-acceptor interaction of components of the three-component system of DES_7

Conclusion

Thus, based on the eutectic compositions of two-component DES systems, a phase equilibrium diagram of a three-component DES system was constructed using two methods. The results of the study showed that the method of preparing three-component mixtures of DES has a significant impact on the formation of complex compounds, but the most correct is the simultaneous mixing of all three components, based on a theoretical calculation of the composition of a three-component mixture from two-component mixtures of eutectic composition. This is confirmed by the almost identical values of the melting temperature of the theoretically calculated and obtained eutectic temperature of the three-component DES system, which is characterized by a lower temperature than the melting temperature of each of the two-component systems of the eutectic composition and is minus 14.5 °C.

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References

[1] Xu P., Zheng G.-W., Zong M.-H., Li N., Lou W.-Y. Recent Progress on Deep Eutectic Solvents in Biocatalysis. *Bioresour. Bioprocess. 2017.* 4, article number: 34.

[2] Khandelwal S., Tailor Y.K., Kumar M. Deep Eutectic Solvents (DESs) as Eco-friendly and Sustainable Solvent/Catalyst Systems in Organic Transformations. *J. Mol. Liq. 2016.* 215, 345–386.

[3] Radosevic K., Cvjetko Bubalo M.C., Gaurina Src ek V.G., Grgas D., Landeka Dragicevic T.L., Radojcic Redovnikovic I.R. Evaluation of Toxicity and Biodegradability of Choline Chloride Based Deep Eutectic Solvents. *Ecotoxicol. Environ. Saf. 2015.* 112, 46–53.

[4] Halder A.K., Cordeiro M.N.D. Probing the Environmental Toxicity of Deep Eutectic Solvents and Their Components: An in silico Modeling Approach. *ACS Sustainable Chem. Eng. 2019.* 7, 10649–10660.

[5] AlOmar M.K., Alsaadi M.A., Hayyan M., Akib S., Ibrahim R.K., Hashim M.A. Lead removal from water by choline chloride based deep eutectic solvents functionalized carbon nanotubes. *J. Mol. Liq. 2016.* 222, 883–894.

[6] Pollet P., Davey E.A., Urena-Benavides E.E., Eckert C.A., Liotta C.L. Solvents for Sustainable Chemical Processes. *Green Chem. 2014.* 16, 1034–1055.

[7] Altunina L.K., Stasyeva L.A., Kuvshinov V.A., Sholidodov M.R., Kozlov V.V., Kuvshinov I.V. Acid Oil-Displacing Composition of Prolonged Action Based on Deep Eutectic Solvents. *Chemistry for Sustainable Development. 2023.* 31, 135–147.

[8] Shahbaz K., Mjalli F.S., Hashim M.A., AlNashef I.M., Prediction of the surface tension of Deep Eutectic Solvents. *Fluid Phase Equilib. 2012.* 319, 48–54.

[9] Smith E.L., Abbott A.P., Ryder K.S. Deep eutectic solvents (DESs) and their applications. *Chem. Rev. 2014.* 114, 11060–11082.

[10] Abbott A.P., Boothby D., Capper G., Davies D.L., Rasheed R.K. Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. *Journal of the American Chemical Society 2004.* 126(29), 9142–9147.

[11] Abbott A.P., et al. Eutectic-based ionic liquids with metal-containing anions and cations. *Chem. – Eur. J. 2007.* 13, 6495–6501.

[12] Sholidodov M.R., Altunina L.K., Kozlov V.V., Chernova U.V. Deep Eutectic Solvents as a Basis for Chemical Oil-Displacing Compositions. *AIP Conference Proceedings 2022.* 2509, 020177.

[13] Abbott A.P., Capper G., Davies D.L., Rasheed R.K., Tambyrajah V. Novel solvent properties of choline chloride/urea mixtures (Electronic supplementary information (ESI) available: spectroscopic data). *Chem. Commun 2003.* 70–71.

[14] Li X., Choi J., Ahn W.-S.S., Row K.H. Preparation and Application of Porous Materials based on Deep Eutectic Solvents. *Crit. Rev. Anal. Chem. 2018.* 48, 73–85.

[15] Wang XiuLi, Lu Y., Shi L., Yang D., Yang Y. Novel low viscous hydrophobic deep eutectic solvents liquid-liquid microextraction combined with acid base induction for the determination of phthalate esters in the packed milk samples. *Micro. chem. J. 2020.* (159), 105332, DOI: 10.1016/j.microc.2020.105332.

[16] Xueyi Song, Junjie Yuan, Chen Yang, Gaofeng Deng, Zhichao Wang, Jubao Gao, Carbon dioxide separation performance evaluation of amine-based versus choline-based deep eutectic solvents. *Renewable and Sustainable Energy Reviews. 2023.* 184, 113499. DOI: 10.1016/j.rser.2023.113499.

[17] Sholidodov M.R., Altunina L.K., Kozlov V.V., Kuvshinov V.A., Stas'eva L.A., Saidentsal A.R. Acidic oil-displacing system based on deep eutectic solvents and surfactants: development, physical and chemical studies, evaluation of its effect on the composition and properties of oil. *J. Sib. Fed. Univ. Chem. 2023.* 16(3), 337–349.

[18] Sholidodov M.R., Altunina L.K., Kozlov V.V., Kuvshinov V.A., and Stas'eva L.A. Low freezing acid oil-displacing composition based on surfactants and deep eutectic solvents for the Arctic. *Bashkir Chemical J. 2023.* 30(1), 34–42.

[19] Sholidodov M.R., Kozlov V.V., Altunina L.K., Kuvshinov V.A. and Stas'eva L.A. Laboratory testing of acidic EOR oil-displacing compositions based on surfactants, inorganic acid adduct and polyols. *J. Sib. Fed. Univ. Chem. 2022.* 15(2), 186–196. DOI: 10.17516/1998–2836–0283.

[20] Altunina L.K., Kuvshinov V.A., Stasyeva L.A., Kuvshinov I.V., Kozlov V.V., Sholidodov M.R. Advanced compositions for increasing oil recovery on the principles of «green chemistry». *AIP Conference Proceedings. 2022.* 2509, 020015.