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Experimental investigation and modeling of thermophysical and extraction properties of choline chloride + DL-malic acid based deep eutectic solvent

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Abstract: The ability of non-toxic and biodegradable deep eutectic solvent (DES) choline chloride + DL-malic acid in mole ratio 1:1, for the breaking of the azeotropes heptane + methanol and toluene + methanol by means of liquid–liquid extraction was evaluated. Ternary liquid–liquid equilibrium experiments were performed at 298.15 K and at atmospheric pressure. Densities, viscosities and refractive indices of DES + methanol and water + DES systems were experimentally determined over a wide temperature range and at atmospheric pressure. Additionally, the viscosities of DES + glycerol mixture were determined at temperatures up to 363.15 K to check how much the addition of glycerol decreases high viscosities of DES. The results indicate that the addition of small amounts of water or glycerol as a third component significantly decreases the viscosity of the investigated deep eutectic solvent. Based on the selectivity and distribution ratio values, the extraction ability of the investigated deep eutectic solvent, in comparison with the conventionally used solvents, yields promising results. Non-random two-liquid (NRTL) and universal quasichemical (UNIQUAC) models were satisfactorily applied for correlation of experimental phase equilibrium data for two ternary mixtures.

Keywords: deep eutectic solvents; choline chloride; DL-malic acid; quantitative ¹³C-NMR spectroscopy; liquid–liquid equilibria; modelling.

INTRODUCTION

Over the last century, major concerns have been related to rapid industrial development, resulting in depletion of oil reserves and large amount of hazardous waste which is affecting natural resources. Sustainable alternatives to the existing

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processes need to link long-term productivity with high efficiency, taking into consideration all twelve principles of “green” chemistry established by Anastas and Warner.¹

In the field of green chemistry, non-toxic organic solvents, the so-called green solvents, have attracted major attention. The aim is to create a solvent with low toxicity and volatility that is biodegradable and made from naturally occurring substances. One class of the new green solvents having these appealing properties are called deep eutectic solvents (DESs). Eutectic mixtures are typically formed of solid components having a melting point higher than that of a mixture. The work of Smith *et al.*² provides a good review of possible types of eutectic mixtures and their constituents. What makes these mixtures attractive is the easiness of their preparation: they are formed simply by stirring and continuous heating of their compounds. DES costs depend on the costs of the usually inexpensive naturally occurring constituents. Also, the purity of DES only depends on the purity of its constituents since the synthesis of DES has 100 % reaction mass efficiency,^{3–5} and no further purification of a formed DES is needed. Finally, the properties of DESs can be adjusted by selecting the proper ratio of the hydrogen bonding pairs and nature of the building participants.⁶

With discovery of the eutectic mixtures in 2003, numerous studies and articles related to this topic have appeared. There are various investigations of potential application of DESs. Some recent review articles analyzed the previous achievements in this field in detail and proposed further research ideas.^{2,5,7–9} Depending on the starting compounds and properties of the obtained DES, different names of mixtures have been used in the literature. For example, in literature one can find a term low transition temperature mixtures (LTTMs) which have only a glass transition temperature,^{6,10} natural deep eutectic solvents (NADESs) made of primary metabolites,^{11,12} or the usual, deep eutectic solvents (DESs).

In this work, the eutectic mixture of naturally occurring and biodegradable compounds choline chloride and DL-malic acid is studied in mole ratio 1:1. To the best of our knowledge there are no studies regarding characterization of this DES and its application in the separation of azeotropes by means of liquid–liquid extraction. Capability of the analyzed DES to separate azeotropes such as heptane + methanol and toluene + methanol was investigated through experimental determination of liquid–liquid equilibria (LLE) of the ternary mixtures heptane + methanol + DES and toluene + methanol + DES. Since many compounds form azeotropes, the separation of azeotropes in industrial processes is a topic of big interest. In petrochemical processes alcohols added as oxygenate additive to gasoline cause formation of alkane/alcohol azeotrope,¹³ *e.g.*, methanol/heptane while methanol/toluene mixture is widely encountered in the pharmaceutical industry.¹⁴ Thus, there is a demand for new extraction solvents with high distribution ratios and high selectivity. In order to test the extraction properties of the inves-

tigated DES, the binodal curves and tie lines were experimentally determined for the investigated ternary systems and from these data distribution coefficients and selectivities were calculated. Non-random two-liquid¹⁵ (NRTL) and universal quasichemical¹⁶ (UNIQUAC) models were applied with a success for correlation of experimental equilibrium data for both investigated systems.

Upon the extraction of heptane/toluene from the ternary mixture, the remaining mixture is composed of methanol and DES, so the knowledge of its thermodynamic properties is of interest. Thus, densities, viscosities and refractive indices of DES + methanol mixture were measured at temperatures between 298.15 and 323.15 K. Due to a high viscosity of the studied DES, the influence of water or glycerol addition into DES on its thermodynamic properties was also investigated. Densities and viscosities of water + DES were measured at temperatures between 298.15 and 363.15 K, while refractive indices were measured at temperatures up to 343.15 K due to the apparatus limitations. For the mixture DES + glycerol (choline chloride:DL-malic acid:glycerol 1:1:0.5) viscosities were determined between 298.15 and 363.15 K. All measurements were performed at atmospheric pressure and with a temperature step of 5 K.

EXPERIMENTAL

Chemicals

DES was prepared by mixing choline chloride (HBA) with DL-malic acid (HBD) in mole ratio 1:1. Choline chloride (0.99 mass fraction) and DL-malic acid (0.99 mass fraction) were purchased from Acros Organics and dried under vacuum (applied pressure was around 5 mbar) before use. DES synthesis was performed simply by mixing two solids in the stirring-equipped conical Pyrex vial and heating it up to 353.15 K with continuous stirring for about 45 min, until a transparent liquid is obtained. The molar masses and phase transition temperatures of pure components and DES are listed in Table I, where DES molar mass is calculated as a mean value of molar masses of individual components. In order to determine the glass transition temperature of DES, the calorimetric measurements were carried out using a Micro Cal MC-2 sensitive differential scanning calorimeter (DSC) and the standard DA-2 software package for data acquisition and Origin software for DSC data analysis. The structure of the synthesized DES was checked by Bruker Avance III 500 NMR spectrometer (500.26 MHz for ¹H, 125.8 MHz for ¹³C, with 5mm BBO probe head) and presented in Fig. 1. Having in mind that the synthesized DES is highly hygroscopic, it was dried under vacuum (pressure of around 5 mbar) before use, according to the procedure applied on ionic liquids (ILs) which is described in detail in our previous work.¹⁷ Water content of investigated DES

TABLE I. Molar masses and phase transition temperatures of pure components and DES

Component	CAS number	Molar mass, kg·kmol ⁻¹	Phase transition temperature, K
Choline chloride	67-48-1	139.62	575.15–578.15 ^a
DL-Malic acid	6915-15-7	134.09	404.5–406.5 ^b
DES (1:1)	–	136.86	218 ^c , 216.67 ^d

^aMelting and decomposition temperature [Chemical book-material safety data sheet]; ^bmelting temperature [Chemical book-material safety data sheet]; ^cglass transition temperature, this work; ^dFrancisco *et al.*¹⁸

was measured with Karl Fisher titration method using Metrohm KF titrator (798 MPT Titrimo, 703 TI Stand, 728 Stirrer) and water standard 1 % (1mg/g H₂O) supplied from Merck. Obtained water content in the investigated DES was less than 1.2 wt. %.

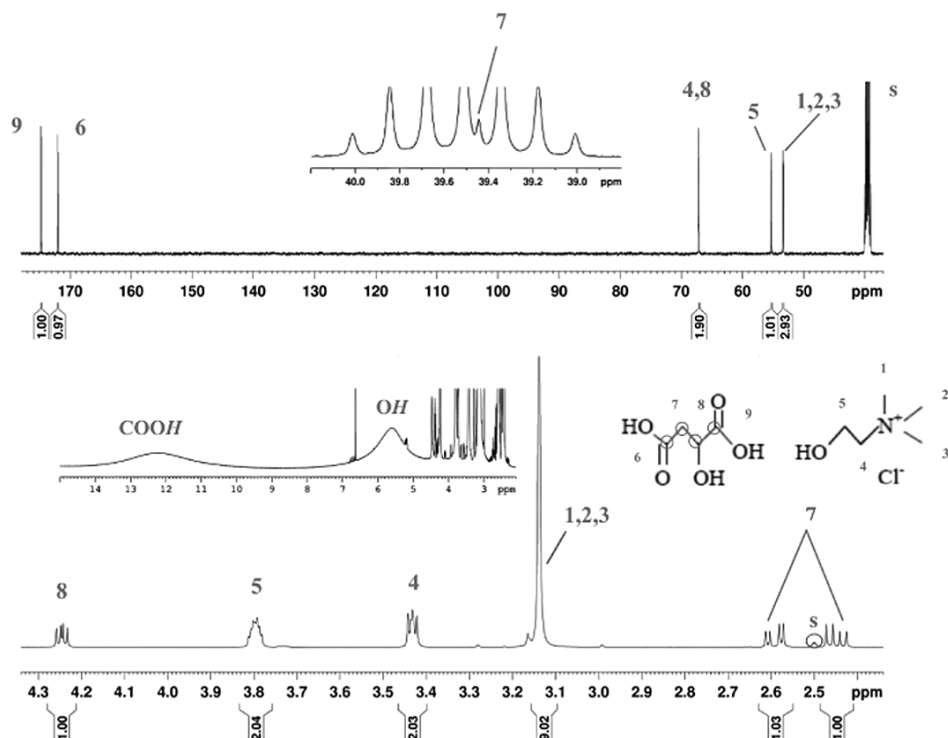


Fig. 1. a) Quantitative ¹³C- (125.80 MHz) and b) ¹H-NMR (500.26 MHz) spectra (DMSO-*d*₆, 298.15 K) of pure DES synthesized by heating method at 353.15 K (s means solvent). The structure and numbering of both compounds are depicted.

Thermodynamic properties

Ternary liquid–liquid equilibrium (LLE) experiments were performed at 298.15 K and 0.1 MPa in a glass beaker filled with water. The experiments consisted of two parts: *i*) determination of the phase boundary, *i.e.*, binodal curves and *ii*) determination of the coexisting LLE lines, the so-called tie-lines.

Binodal curves were determined using a well-known synthetic cloud-point method combined with a titration technique.¹⁹ Experiment starts with the preparation of the binary mixtures of DES + heptane or toluene in the immiscible region in the stirring-equipped conical Pyrex vial. The third component (methanol) is added by titration, with continuous stirring, until a mixture becomes homogenous (disappearance of turbidity). The composition of the ternary mixture in the moment when it becomes clear and transparent liquid belongs to a binodal curve.

For the determination of the tie-lines, ternary mixtures heptane + methanol + DES or toluene + methanol + DES of a known composition were made in the immiscible region (area below binodal curve). The mixture was vigorously stirred for about one hour and left to settle

for 24 h in the thermostatic bath at 298.15 K. As a result, two phases in equilibrium were obtained, upper phase (rich in heptane in the first case or toluene in the second case) and a bottom phase (rich in DES). Samples are taken from both phases. Quantitative analysis of the upper layer is performed by quantitative ^{13}C -NMR spectroscopy and the analysis of the bottom layer is performed by combining NMR and thermogravimetry.

Temperature in the thermostatic bath and during the experiments was monitored using a Pt100 temperature probe, with an accuracy of ± 0.03 K. Temperature uncertainty estimated from the repeated measurements was less than ± 0.5 K. Mixtures were prepared gravimetrically using a Mettler AG 204 balance. A 2 L glass beaker filled with silicone oil, as a thermostatic liquid, was used as a thermostat bath in all experiments.

Density, ρ , measurements were performed using an Anton Paar DMA 5000 digital vibrating U-tube densimeter, refractive index n_D was measured using an automatic Anton Paar RXA 156 refractometer and viscosity measurements were made using a digital Stabinger viscometer (model SVM 3000/G2). The detailed explanation of the apparatus can be found elsewhere.²⁰ Pure DES viscosity was measured employing the Anton Paar modular compact rheometer MCR 102 with Peltier temperature control device P-PTD200/56/AIR. A Mettler AG 204 balance, with a precision 10^{-7} kg, was used for the precise measuring of the mass composition of the mixtures, using the cell and the procedure described previously.²¹ The uncertainty of the mole fraction calculation was less than $\pm 10^{-4}$. The experimental uncertainty of density measurements was $\pm 4 \times 10^{-2} \text{ kg} \cdot \text{m}^{-3}$. The uncertainty of the refractive index data measurements was ± 0.00009 units. Dynamic viscosity measurements were performed with the relative uncertainty ± 1 %.

Modelling of LLE

The experimental tie-line data for the two investigated ternary mixtures were correlated using the non-random two-liquid (NRTL)¹⁵ and universal quasi-chemical (UNIQUAC)¹⁶ thermodynamic models. Here DES was treated as one component, as it was stated also previously in the literature for other combinations of eutectic mixtures.^{10,22}

The activity coefficients in NRTL model were calculated using the following equation:

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (1)$$

where

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad (2)$$

$$\frac{\Delta g_{ij}}{R} = A_{ij} + B_{ij} T \quad (3)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}), \quad (\alpha_{ij} = \alpha_{ji}) \quad (4)$$

Here, Δg_{ij} describes the energy interactions between components i and j and α_{ij} is the non-randomness parameter. Generally there are five adjustable parameters A_{ij} , A_{ji} , B_{ij} , B_{ji} and α_{ij} , but in this work the adjustable parameters were treated as temperature independent ($B_{ij} = B_{ji} = 0$). For non randomness parameter α_{ij} value 0.2 is adopted,²³ so only A_{ij} and A_{ji} parameters were optimized.

The UNIQUAC calculates activity coefficients as a sum of residual γ^R and combinatorial γ^C contributions as follows:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (5)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^m x_j l_j \quad (6)$$

$$\ln \gamma_i^R = q_i \left[1 - \ln \sum_{j=1}^m \theta_j \tau_{ji} - \sum_{j=1}^m \frac{\theta_j \tau_{ij}}{\sum_{k=1}^m \theta_k \tau_{kj}} \right] \quad (7)$$

where

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right) \quad (8)$$

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^m x_i r_i} \quad (9)$$

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^m x_i q_i} \quad (10)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (11)$$

Here, Δu_{ij} and Δu_{ji} describe interaction energy between molecules i and j , but in this work two adjustable interaction parameters were optimized and given in the form a_{ij} and a_{ji} .

Lattice coordination number z is equal to 10, and relative volume r_i and surface area q_i of the pure component i were taken from literature.²⁴ r_i and q_i for DES were calculated as a sum of the group volume R_k and group surface area Q_k parameters given in literature²⁵ as follows:

$$r_i = \sum_k v_k^i R_k \quad \text{and} \quad q_i = \sum_k v_k^i Q_k \quad (12)$$

where v_k^i is the number of groups of type k in molecule i . Procedure for r_i and q_i determination was explained in the literature for other DES components.¹⁰ Table II gives r_i and q_i values for the compounds investigated in this work.

TABLE II. UNIQUAC volume and surface area structural parameters for investigated pure components

Component i	r_i	q_i
Heptane	5.174	4.396
Toluene	3.9228	2.968
Methanol	1.4311	1.432
DES	5.52375	5.162

The estimation of binary interaction parameters was performed through the minimization of the composition based objective function:

$$OF = \sum_i \sum_\alpha \sum_k \left(x_{ik}^{\alpha(\text{exp})} - x_{ik}^{\alpha(\text{cal})} \right)^2 \quad (13)$$

where i is the number of components in the mixture, α number of phases and k number of tie-lines; superscripts exp and cal refer to experimental and calculated values of mole fractions.

With this minimization function it is possible to obtain the binary interaction parameters along with the following equilibrium condition:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (14)$$

To evaluate the quality of the correlation the root-mean-square deviation (rmsd) of the composition, σ , has been calculated as follows:

$$\sigma = 100 \sqrt{\frac{\sum_i \sum_\alpha \sum_k \left(x_{ik}^{\alpha(\text{exp})} - x_{ik}^{\alpha(\text{cal})} \right)^2}{6k}} \quad (15)$$

RESULTS AND DISCUSSION

Experimental LLE results, given as mole fractions of the components in the raffinate and the extract phase, selectivity and distribution ratio values for the two investigated systems heptane + methanol + DES and toluene + methanol + DES are reported in Table III. For the evaluation of the DES extraction efficiency, distribution coefficient β and selectivity S values, the following equations are used:

$$\beta_2 = \frac{x_2^{II}}{x_2^I} \quad (16)$$

$$S = \frac{\beta_2}{\beta_1} = \frac{x_2^{II} x_1^I}{x_2^I x_1^{II}} \quad (17)$$

where x_1^I and x_2^I are the mole fractions of heptane/toluene and methanol in the upper phase (raffinate layer), respectively, and x_1^{II} and x_2^{II} are the mole fractions of heptane/toluene and methanol in the bottom phase (extract layer) (Table III). The distribution coefficient β_2 indicates how well is a desired component (methanol) distributed between raffinate and an extract layer. Selectivity S indicates the extraction efficiency of the DES, showing the easiness of a solute (methanol) extraction from a diluent (inert, heptane or toluene). High values for the distribution coefficient and selectivity are desirable.

Figure 2 presents binodal curves and the tie lines for the systems heptane + methanol + DES (Fig. 2a) and toluene + methanol + DES (Fig. 2b), respectively.

From Fig. 2 it is obvious that the immiscibility region is wider for the mixture with heptane. It is evident that heptane and toluene are not miscible with DES, while wide immiscibility region between heptane and methanol (Fig. 2a) is a result of the methanol and heptane heterogeneous azeotrope formation.

TABLE III. Experimental tie line compositions, distribution ratio and selectivity values for the ternary systems heptane (1) + methanol (2) + DES (3) and toluene (1) + methanol (2) + DES (3) at 298.15 K and at atmospheric pressure; x_1 is the mole fraction of heptane/toluene, x_2 is the mole fraction of methanol, and x_3 is the mole fraction of DES; – means dividing by zero

Heptane (1) + Methanol (2) + DES (3)							
Heptane-rich phase			DES-rich phase			β	S
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}		
1.0000	0.0000	0.0000	0.0000	0.2943	0.7057	–	–
1.0000	0.0000	0.0000	0.0000	0.5000	0.5000	–	–
1.0000	0.0000	0.0000	0.0000	0.6496	0.3504	–	–
1.0000	0.0000	0.0000	0.0000	0.7570	0.2430	–	–
1.0000	0.0000	0.0000	0.0038	0.8452	0.1510	–	–
Toluene (1) + Methanol (2) + DES (3)							
Toluene-rich phase			DES-rich phase			β	S
x_1^I	x_2^I	x_3^I	x_1^{II}	x_2^{II}	x_3^{II}		
0.9940	0.0060	0.0000	0.0000	0.1995	0.8005	33.450	–
0.9862	0.0138	0.0000	0.0129	0.4018	0.5853	29.102	2229.0
0.9615	0.0385	0.0000	0.0332	0.5294	0.4374	13.764	398.37
0.9346	0.0654	0.0000	0.0546	0.6502	0.2952	9.9388	169.98
0.9200	0.0800	0.0000	0.0658	0.6777	0.2565	8.4674	118.40

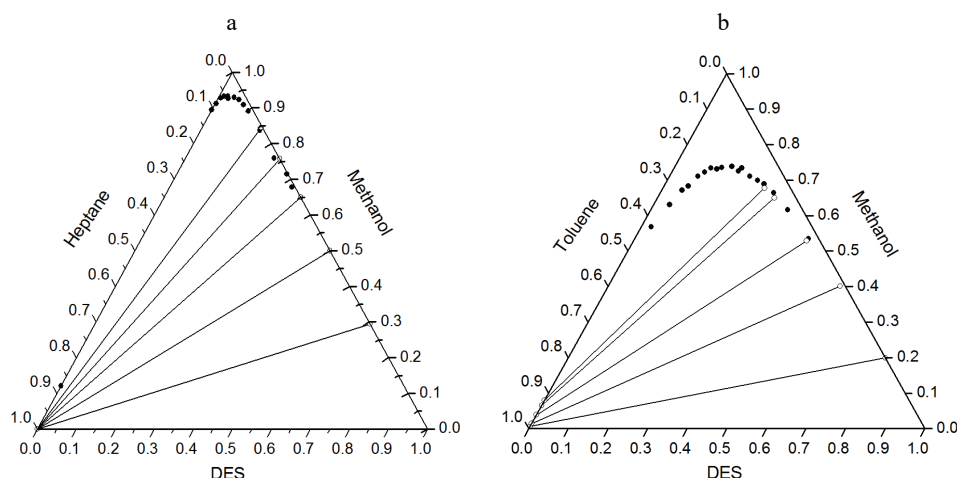


Fig. 2. Experimental ternary LLE diagrams at 298.15 K for: a) heptane (1) + methanol (2) + DES (3); b) toluene (1) + methanol (2) + DES (3); Filled circles represent cloud points.

The quantitative analysis of the bottom layer was performed by combining NMR and thermogravimetry. The mole fraction of heptane/toluene is obtained from the NMR spectra, while the DES mole fraction is obtained by evaporating the volatile components. Methanol mole fraction in the bottom layer is obtained from the simple equation in which the sum of mole fractions of all three components equals 1. The integrals' ratio of the ^{13}C signals is used for the quantitat-

ive analysis of the layers by NMR, because in the $^1\text{H-NMR}$ spectra methanol's CH_3 signal was partly overlapped with the choline methyl-groups. Recently published work of Florindo *et al.*²⁶ shows that the small amounts of impurities can be formed during the synthesis of a pure DES. The authors noticed the different characteristics of DESs synthesized by two different methods, grinding and heating. It was found that heating might promote the formation of esters in DES.

From the selectivities and distribution coefficients given in Table III, it can be concluded that DES presents the promising candidate for the separation of both alkane/alcohol and aromatic/alcohol azeotropes. For the system heptane + methanol + DES, Table III indicates that neither DES nor methanol are present in the raffinate layer (heptane rich phase). According to the distribution coefficient, DES shows excellent selectivity towards methanol and methanol-carrying capacity. DES is also not present in the raffinate layer of the system toluene + methanol + DES, while methanol is present in small traces (max 0.0800 mole fraction). For this azeotrope DES also shows very good selectivity and methanol-carrying capacity, especially at low methanol concentrations. These high values of both selectivity and distribution coefficient can be explained by the structure of HBD. As stated in the literature,²⁷ the OH bond in the carboxylic group is more strongly polarized than that of the alcohols, thus allowing stronger hydrogen bonding with methanol. This is the reason for the high distribution coefficient values. Also, DL-malic acid with three OH groups enhances methanol extraction, which explains very high selectivity values. Since in the DES rich phase heptane or toluene are not present, or are occurring in traces, pure methanol could be obtained by distillation from extract layer. Heptane as a non-polar molecule can form dispersion forces. Toluene can form both dipole-dipole and dispersion forces since it is characterized by a weak dipole moment (0.4 D^*)²⁵. Polar methanol (dipole moment is 1.7 D)²⁵ forms strong hydrogen bonds, as well as a weaker dipole-dipole and dispersion forces. In the heptane + methanol + DES system tie lines show that practically there is no mixing between heptane and methanol since methanol is strongly bonded to DES *via* hydrogen bonds, so the dispersion forces between methanol and heptane are not strong enough to coexist with hydrogen bonds. On the other hand, methanol can form dipole-dipole forces with toluene which are strong enough to coexist with hydrogen bonds. This leads to a small miscibility between methanol and toluene which reduces immiscible region in the ternary mixture toluene + methanol + DES.

To the best of our knowledge there are no data dealing with toluene + methanol azeotrope separation, applying the liquid-liquid extraction, although there are some other separation techniques reported in the literature.^{14,28} Heptane + methanol mixture was previously analyzed in the literature using some ILs.^{13,29} Comparison of the selectivity of the applied DES to the ILs studied in the litera-

* $1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$

ture for the system heptane + methanol and for the same ethanol content in the raffinate layer implies that DES is also a highly efficient extracting agent, since the indefinitely high selectivity values are obtained here, as in the mentioned literature. Having in mind high S values, a few extraction stages would be required to obtain highly pure extract in an industrial process. Additionally, considering high β values, an extraction process would not require huge amounts of solvent. Taking into account the low cost of this solvent industrial application, the investigated DES is certainly capable of meeting most of the principles of green chemistry.

The experimental tie-line data for the two investigated ternary mixtures were correlated using the non-random two-liquid (NRTL)¹⁵ and universal quasi-chemical (UNIQUAC)¹⁶ thermodynamic models. Table IV represents the obtained parameters and deviations for NRTL and UNIQUAC models. As it can be seen, the excellent rmsd is obtained for both models, but better matching is obtained for system heptane (1) + methanol (2) + DES (3).

TABLE IV. Binary interaction parameters obtained for NRTL and UNIQUAC equations for two ternary mixtures, heptane (1) + methanol (2) + DES (3) and toluene (1) + methanol (2) + DES (3), along with root-mean-square deviation (σ) of the composition defined with Eq. (15)

i	j	NRTL			$\sigma / \%$	UNIQUAC		$\sigma / \%$
		A_{ij}	A_{ji}	α_{ij}		a_{ij}	a_{ji}	
Heptane	Methanol	957.2361	1000	0.200	–	497.601	426.143	–
Heptane	DES	600.4378	958.9947	0.200	0.5492	–14.823	455.532	0.2768
Methanol	DES	–978.777	358.9334	0.200	–	–486.665	–797.657	–
Toluene	Methanol	66.384	485.424	0.200	–	606.365	–1.944	–
Toluene	DES	663.5102	825.515	0.200	0.9395	2.070	528.376	1.2306
Methanol	DES	–890.103	–993.024	0.200	–	–159.789	287.702	–

Thermodynamic and transport properties of pure DES and its mixtures were also investigated here. Considering that in the DES rich phase toluene or heptane are present only in trace amounts, the extract layer can be approximated as a binary mixture of DES and methanol. For further processing of this mixture it is important to know its thermodynamic properties. Table S-I of the Supplementary material to this paper lists experimental values of densities, viscosities and refractive indices of the DES + methanol mixture in the given temperature range, while in Fig. 3 densities and viscosities at selected temperatures are presented. Densities of pure DES are in the range from $1.278119 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ at 298.15 K to $1.236060 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ at 363.15 K, which is higher comparing to similar liquids investigated in the literature. In the work of Yadav and Pandey³⁰ mixture of choline chloride + urea named as reline (mole ratio 1:2) is investigated and density is varying from 1.2001×10^{-3} to $1.1554 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ over the same temperature range. In the work of Yadav *et al.*³¹ choline chloride + glycerol mixture

named glyceline (mole ratio 1:2) is investigated and density is varying from 1.1943×10^{-3} to $1.1495 \times 10^{-3} \text{ kg} \cdot \text{m}^{-3}$ between 293.15 and 363.15 K. As expected, densities of all three DESs are found to decrease with the increase in temperature. The viscosity is in the range of 24492 to 300.95 mPa·s for the investigated DES, while for reline and glyceline it ranges from 1371.9719 to 19.9490 mPa·s and from 472.9671 to 19.5866 mPa s, at temperatures between 298.15 and 363.15 K, respectively. It can be concluded that DES investigated here has somewhat higher densities comparing to reline and glyceline and exhibits significantly higher viscosities, particularly in the low temperature range, but with temperature increase viscosity decreases notably. Despite this shortcoming, this work proves that high viscosity values of DES can be decreased to a significant extent by adding water or glycerol in small quantities.

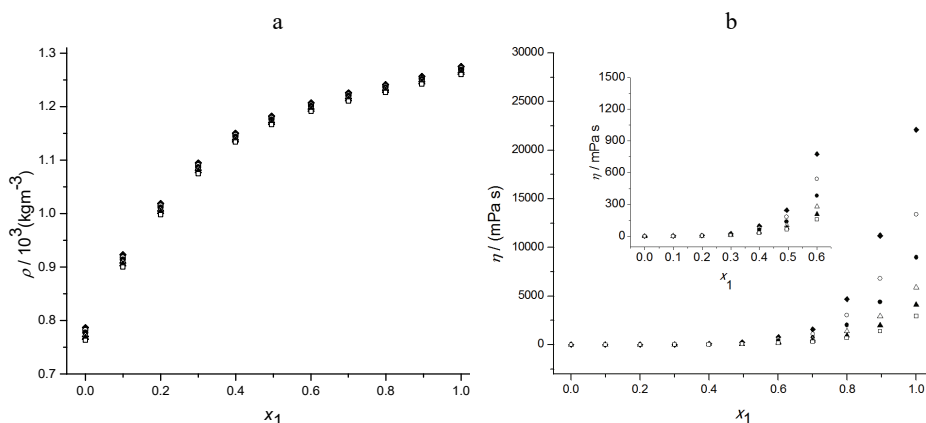


Fig. 3. Experimental values of: a) density and b) viscosity vs. DES mole fraction for the system DES (1) + methanol (2) where symbols refer to experimental data points at several temperatures: 298.15 K (\blacklozenge); 303.15 K (\circ); 308.15 K (\bullet); 313.15 K (Δ); 318.15 K (\blacktriangle) and 323.15 K (\square). Values for pure DES are obtained by rheometer.

While the temperature influence on densities of the DES + methanol mixture is insignificant (Fig. 3a), its influence on pure DES viscosities is considerable (Fig. 3b). At room temperatures DES viscosity is rather high (above 20 Pa s). However, both temperature raise and the addition of small amounts of methanol to pure DES highly reduce viscosities of the mixture. From equimolar mixture towards pure methanol, the influence of temperature on DES + methanol viscosities diminish.

Some authors³² have recently identified that the addition of the third component as a DES making compound reduces the high viscosity of the DES. Here we examined how the addition of water or glycerol to DES would affect its viscosity (Tables S-II and S-III of the Supplementary material).

The amount of added water did not exceed 0.5751 mole fraction since higher water content could rupture DES structure.³³ Glycerol was added in the choline chloride:DL-malic acid:glycerol mole ratio of 1:1:0.5). In Fig. 4 densities and viscosities of water + DES mixtures at selected temperatures are presented. Addition of water to pure DES reduces both density and viscosity. As the amount of water increases, viscosity decreases notably, especially at lower temperatures. Therefore, in order to reduce high viscosity of pure DES, water might be used as a third DES compound as proposed by Maugeri and Domínguez de María.³²

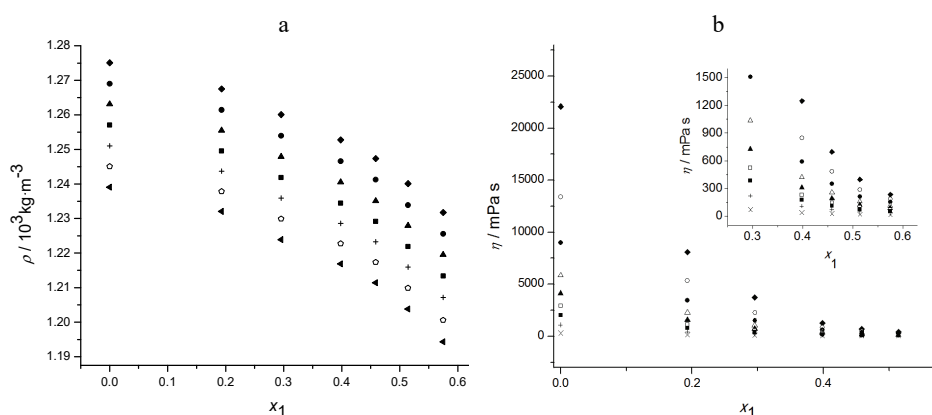


Fig. 4. Experimental values of: a) density and b) viscosity vs. water mole fraction for the system water (1) + DES (2) where symbols refer to experimental data points at several temperatures: 298.15 K (◆); 303.15 K (○); 308.15 K (●); 313.15 K (Δ); 318.15 K (▲); 323.15 K (□); 328.15 K (■); 338.15 K (+); 348.15 K (△); 358.15 K (◀) and 363.15 K (×). Values for pure DES are obtained by rheometer.

Fig. 5 depicts the changes of viscosities with temperature increase for the DES + glycerol mixture. When glycerol is added to DES in a choline chlo-

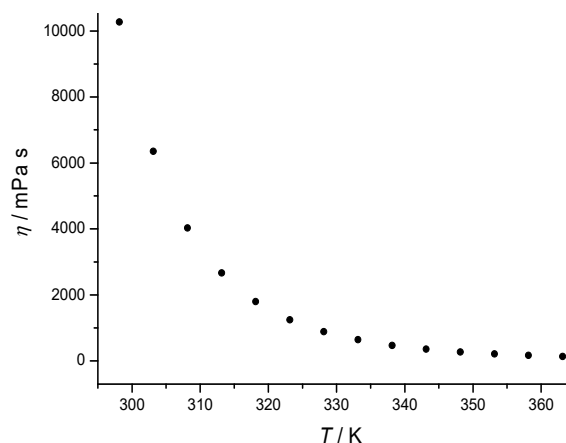


Fig. 5. Experimental values of viscosity vs. temperature for the system DES + glycerol (choline chloride:DL-malic acid:glycerol is in mole ratio 1:1:0.5) over the temperature range between 298.15 and 363.15 K.

ride:DL-malic acid:glycerol mole ratio of 1:1:0.5, at room temperature viscosities significantly decrease and with additional temperature increase further viscosity reduction is possible. In this regards, glycerol can also be proposed as a third DES compound.

It is already stated in the literature^{34,35} that ionic liquids and mixtures with glass transition temperature, such as DES investigated in this work, have slightly non-linear trend in $\ln \eta$ vs. $1/T$ plots. Although viscosities of the mixture choline chloride:DL-malic acid:glycerol analyzed here may be described by Arrhenius type model, viscosity–temperature profile can be more satisfactorily described with Vogel–Fulcher–Tamman model (VFT):³⁴

$$\ln \eta = A + B / (T - T_0) \quad (18)$$

where A , B and T_0 are empirical constants obtained as a result of fitting. From these parameters the energy of activation of viscous flow $E_{a,\eta}$ can be calculated as follows:

$$E_{a,\eta} = RB \left(\frac{T}{T - T_0} \right)^2 \quad (19)$$

Calculated parameters, energy of activation and evaluated goodness of fit statistic R^2 for the system DES + glycerol (choline chloride:DL-malic acid:glycerol is in mole ratio 1:1:0.5) are presented in ESI (Table S-IV of the Supplementary material).

Plots of $\ln \eta$ versus $1/T$ along with the fit line according to VFT model are presented in Fig. 6.

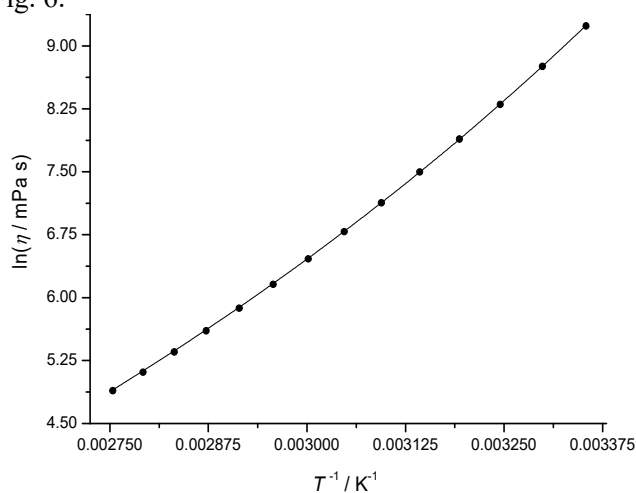


Fig. 6. Experimental values of $\ln \eta$ vs. T^{-1} for the system DES+Glycerol (choline chloride:dl-malic acid:glycerol is in molar ratio 1:1:0.5) over the temperature range between 298.15 K and 363.15 K. Line represents the fit for the Vogel–Fulcher–Tamman model.

CONCLUSIONS

In this work the efficiency of DES formed between choline chloride and DL-malic acid in a mole ratio 1:1 for the breaking of the azeotropes heptane + methanol and toluene + methanol was tested. Ternary liquid–liquid equilibrium experiments were performed at 298.15 K and at atmospheric pressure. It was found that DES selectivity towards methanol is rather high. Heptane or toluene were present in extract layers only in trace amounts, so the separation of methanol after the extraction can be performed simply by distillation, since DES is non-volatile. Comparing the efficiency of DES with some investigated ionic liquids it was found that DES exhibits higher selectivity and distribution ratio for heptane + methanol separation. Since there are no literature data about toluene + methanol separation through liquid–liquid extraction using DES or ILs, this work reveals that DES is also suitable for extracting alcohol from alcohol + aromate mixture. Better methanol partitioning is achieved in the system heptane + methanol + DES due to a non-polar nature of heptane. In this system hydrogen bonding between DES and methanol prevails over the weak dispersion forces between methanol and heptane.

Additionally, densities, viscosities and refractive indices of DES + methanol and water + DES mixtures were experimentally determined in a wide temperature range and at atmospheric pressure. Viscosities of DES + glycerol mixture in a mole ratio 1:1:0.5 (choline chloride:DL-malic acid:glycerol) were measured at different temperatures. Results show that water and glycerol can in small amounts significantly decrease the DES viscosity. The temperature increase decreases viscosity, however heating promotes the formation of esters inside DES. Therefore, in order to reduce high viscosities of DES, the introduction of the third component into DES, rather than temperature increase, is recommended.

Modelling of phase equilibrium was performed with NRTL and UNIQUAC correlative models. Both models show the excellent agreement with experimental data, while for system heptane + methanol + DES both models shown better performances.

SUPPLEMENTARY MATERIAL

Detailed experimental data are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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ИЗВОД
 ЕКСПЕРИМЕНТАЛНО ИСПИТИВАЊЕ И МОДЕЛОВАЊЕ ТЕРМОФИЗИЧКИХ И
 ЕКСТРАКЦИОНИХ СВОЈСТАВА ЕУТЕКТИЧКОГ РАСТВОРАЧА НА БАЗИ
 ХОЛИН-ХЛОРИДА + DL-ЈАБУЧНЕ КИСЕЛИНЕ

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Испитивана је способност нетоксичног и биодеграбилног еутектичког растварача (DES) холин-хлорид + DL-јабучна киселина у молском односу 1:1, за сепарацију азеотропа хептан + метанол и толуен + метанол применом екстракције течност–течно. Равнотежни експерименти течност–течно тернарних система изведени су на 298,15 К и на атмосферском притиску. Густине, вискозности и индекси рефракције DES + метанол и вода + DES система експериментално су одређене у широком температурном опсегу и на атмосферском притиску. Додатно, вискозности DES + глицерол смеше одређене су на температурама до 363,15 К у циљу провере утицаја додатка глицерола на смањење вискозности DES растварача. Резултати указују да додавање малих количина воде или глицерола као треће компоненте значајно смањује вискозност испитиваног еутектичког растварача. Добијене вредности селективности и дистрибуционог коефицијента, у поређењу са конвенционалним растварачима, указују на изузетну екстракциону способност испитиваног еутектичког растварача. NRTL и UNIQUAC модели задовољавајуће корелишу експерименталне равнотежне податке за две испитиване тернерне смеше.

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