

Effect of water addition on extraction ability of eutectic solvent choline chloride+1,2-propanediol for separation of hexane/heptane+ethanol systems

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Abstract—The ability of binary deep eutectic solvent choline chloride+1,2-propanediol (DES1; 1 : 3 mole ratio) and ternary deep eutectic solvent choline chloride+1,2-propanediol+water (DES2; 1 : 3 : 3 mole ratio) for breaking the azeotropes hexane/heptane+ethanol by means of liquid-liquid extraction was evaluated. Liquid-liquid equilibrium experiments were performed at 298.15 K, at atmospheric pressure, and data were correlated by NRTL and UNIQUAC models. Thermodynamic properties (density, viscosity, refractive index and speed of sound) of DES1 and DES2 were determined in temperature range from 288.15 K to 333.15 K and at atmospheric pressure. Extraction ability of the investigated eutectics yielded promising results in comparison with conventional solvents. Besides a high selectivity towards ethanol, an advantage of DES2 is its lower viscosity and higher distribution ratio values, which is an important aspect for a potential industrial application. Another advantage of both investigated eutectics is their easy and high recoverability from the extract layer based on their negligible vapor pressure.

Keywords: Deep Eutectic Solvents, Liquid-liquid Equilibria, Choline Chloride, 1,2-Propanediol, Azeotrope Separation

INTRODUCTION

With intensive industrial production, negative impact on environment is a big concern. Some of the point-source pollutants are commercially used volatile organic solvents. Constant efforts towards development of more sustainable and less hazardous industrial processes have led to remarkable scientific progress in the field of green industrial solvents and its applications in various industries, such as polymers, ionic liquids, aqueous biphasic systems and deep eutectic solvents. Besides low toxicity and low volatility, an important demand for industrial commercialization of such solvents is low price. Renewability of a solvent contributes in lower price, but also in environmental aspects since it prevents depletion of fossil feedstocks.

The new generation of green solvents which possess appealing properties are deep eutectic solvents (DES). The first discovered DES synthesized by Abbott et al. [1] was based on choline chloride and urea mixture in the molar ratio 1 : 2. From 2003 numerous studies concerning this topic have appeared. DESs are eco-friendly solvents with attractive properties which enable their wide potential use [2-9]. What makes these mixtures attractive is easiness of their preparation, low cost, low volatility, low toxicity, and biodegradability in most of the cases. Finally, properties of DESs can be adjusted by selecting the proper ratio of the hydrogen bonding pairs and nature of the building participants, and that tunability aspect is one of the most important [10]. Although the large-scale application of this type of solvent is still not realized, its extraction efficiency has been successfully tested on pilot scale [11].

This work investigates the ability of non-toxic and biodegradable deep eutectic solvent choline chloride+1,2-propanediol in the molar ratio 1 : 3 (DES1) for breaking the azeotropes hexane+ethanol and heptane+ethanol by means of liquid-liquid extraction (LLE). Liquid-liquid equilibrium experiments are the basis for determination of extraction efficiency, and according to the literature this experimental technique and separation processes in general are highly attractive topic [12-14].

Choline chloride is attractive compound because of its biodegradability, low cost and low toxicity. As an essential nutrient it can be extracted from biomass and is often regarded as a part of B complex vitamins [15]. Recently, a “green” process of catalytic conversion of cellulosic biomass into 1,2-propanediol with high yield was reported [16]. Both choline chloride and 1,2-propanediol possess harmless nature, which makes the investigated DES1 an attractive industrial solvent, and most importantly renewable.

To the best of our knowledge there are no studies regarding detailed thermodynamic characterization of the investigated DES1 and its application in the separation of azeotropes by means of liquid-liquid extraction. Besides numerous advantages over the traditional solvents, one of the major drawbacks of DESs is their high viscosity. Since LLE is a mass transfer operation, high solvent viscosity would require more energy intense mixing. Certain investigations showed that water can reduce DESs viscosity and that ternary DESs certainly could find its role as extracting agents. Dai et al. [15] reported the structure of choline chloride+1,2-propanediol deep eutectic solvent, as well as the influence of water addition on the supramolecular structure and hydrogen bonding within eutectic components [17,18]. Results have shown that water might also participate in the supramolecular structure of ternary eutectics as a third component as long as water content is below 50%. Dai et al. [17] confirmed that the polarity of examined DES increases

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Table 1. Information regarding sample description

Chemical	Supplier and initial purity	Purification method	Water content
Hexane	Fluka (≥ 0.99 wt)	None	
Heptane	Sigma-Aldrich (0.99 wt)	None	
Choline chloride	Acros Organics (0.99 wt)	Vacuum	<0.01 wt
1,2-Propanediol	Acros Organics (0.99 wt)	None	
Millipore water		None	
DES1 (choline chloride+1,2-propanediol 1:3)		None	<0.01 wt

by addition of water, which indicates that the extraction efficiency of such ternary eutectic might be improved.

Knowing this, we also examined the extraction ability of ternary eutectic mixture choline chloride+1,2-propanediol+water in the molar ratio 1 : 3 : 3 (DES2). Many compounds form azeotropes, so separation of azeotropes in industrial processes is of major interest. Thus, there is a demand for new extraction solvents with high distribution ratios and high selectivity. The binodal curves and tie lines were experimentally determined for the investigated DES1/DES2+azeotrope systems, and from these data distribution coefficients and selectivity values were calculated. Liquid-liquid equilibrium experiments were performed at 298.15 K and at atmospheric pressure. Thermodynamic characterization of solvents was also performed in a wide temperature range. Densities, viscosities, refractive indices and sound velocities of DES1 and DES2 were measured between 288.15 K and 333.15 K. All measurements were at atmospheric pressure and with a temperature step of 5 K. To check the possibility for solvent recovery, vapor pressures and saturation vapor densities were measured too, for both solvents from 298.15 K to 333.15 K. Additionally, NRTL and UNIQUAC models were applied for the correlation of the phase equilibrium data of two investigated systems.

MATERIALS AND METHODS

1. Experimental Section

Hexane and heptane were purchased from Fluka (≥ 0.99 mass fraction) and Sigma-Aldrich (0.99 mass fraction), respectively. Eutectic mixtures were prepared by mixing choline chloride with 1,2-propanediol in molar ratio 1 : 3 (mixture named as DES1) or choline chloride with 1,2-propanediol and water in molar ratio 1 : 3 : 3 (mixture named as DES2). Choline chloride (0.99 mass fraction) and 1,2-propanediol (0.99 mass fraction) were purchased from Acros Organics. Millipore water was used for DES2 synthesis. DES1 and DES2 synthesis was performed simply by mixing individual components in the stirring-equipped conical Pyrex vial and heating it up to 313.15 K with continuous stirring for about 15 minutes, until a transparent liquid is obtained. The molar masses of synthesized eutectic mixtures were calculated as follows: $M_{DES1} = (M_{Choline\ Chloride} + 3 \cdot M_{1,2-propanediol}) / 4 = 91.97 \text{ kg} \cdot \text{kmol}^{-1}$ and $M_{DES2} = (M_{Choline\ Chloride} + 3 \cdot M_{1,2-propanediol} + 3 \cdot M_{water}) / 7 = 60.27 \text{ kg} \cdot \text{kmol}^{-1}$. Due to high hydrophilicity of choline chloride it was dried under vacuum before use according to the procedure applied on ILs, which is described in detail in our previous work [19]. The water content in DES1 was confirmed by Karl Fischer titration method using a

water standard 1% (1 mg/g H₂O) supplied from Merck. The sample description can be found in Table 1.

2. 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 (Fig. S1). The experiments consisted of two parts: (i) determination of the phase boundary--binodal curves, and (ii) determination of the coexisting LLE lines--tie-lines.

Binodal curves were determined using a well-known synthetic cloud-point method combined with a titration technique [20]. The experiment started with the preparation of the binary mixtures of DES1/DES2+hexane/heptane in the immiscible region in the stirring-equipped conical Pyrex vial. The third component (ethanol) was added by titration, with continuous stirring, until a mixture became homogeneous (disappearance of turbidity). The composition of the ternary mixture in the moment when it becomes clear and transparent liquid belongs to a binodal curve.

The refractive indices of the mixtures from the binodal curves were measured with an Anton Paar RXA 156 refractometer at 298.15 K. Experimental results for binodal curves, along with refractive index data are reported in Table 2. The uncertainty of the mole fraction calculation was less than $\pm 1 \cdot 10^{-3}$. The uncertainty of the refractive index data measurements was ± 0.00009 units.

For the determination of the tie-lines, ternary mixtures hexane/heptane+ethanol+DES1/DES2 of a known composition were made in the immiscible region (area below binodal curve). The mixtures were vigorously stirred for about 15 minutes and centrifuged for 30 minutes at 1,000 rpm (Thermo scientific Heraeus Megafuge 16 Centrifuge) at 298.15 K. As a result, two phases in equilibrium were obtained: an upper phase (rich in hexane/heptane) and a bottom phase (rich in DES1/DES2) (Fig. S2). Samples were taken from both phases and refractive indices were measured for each phase. Tie-line compositions were determined via refractive index calculation, as it was successfully applied in the literature [6]:

$$n_D = A w_1 + B w_1^2 + C w_2 + D w_2^2 + E w_3 + F w_3^2 \quad (1)$$

$$w_3 = G \exp[H w_1^{0.5} + I w_1^3] \quad (2)$$

$$w_2 = 1 - w_1 - w_3 \quad (3)$$

where w_1 , w_2 and w_3 correspond to the mass fraction compositions of hexane/heptane, ethanol and DES1/DES2, respectively, and the parameters A to I are adjustable parameters and are reported in Table 3.

Temperature in the thermostatic bath and during the experi-

Table 2. Experimental binodal data and appropriate experimental refractive index data for the four ternary systems at 298.15 K and at atmospheric pressure (0.1 MPa)^a

Hexane (1)+Ethanol (2)+DES1 (3)				Hexane (1)+Ethanol (2)+DES2 (3)			
x ₁	x ₂	x ₃	n _D	x ₁	x ₂	x ₃	n _D
0.131	0.689	0.180	1.38549	0.168	0.668	0.164	1.37651
0.209	0.662	0.129	1.37903	0.063	0.579	0.359	1.39246
0.106	0.670	0.224	1.39112	0.141	0.656	0.203	1.37869
0.258	0.639	0.103	1.37604	0.117	0.637	0.246	1.38240
0.080	0.629	0.291	1.39918	0.208	0.660	0.132	1.37323
0.324	0.600	0.076	1.37314	0.086	0.623	0.290	1.38633
0.052	0.534	0.414	1.41536	0.278	0.617	0.105	1.37138
0.466	0.482	0.052	1.37227	0.061	0.586	0.353	1.39194
0.404	0.529	0.067	1.37306	0.538	0.421	0.040	1.36940
0.069	0.597	0.334	1.40747	0.021	0.418	0.561	1.41074
0.174	0.667	0.160	1.38270	0.027	0.495	0.478	1.40359
0.061	0.570	0.370	1.41047	0.314	0.603	0.083	1.37028
0.035	0.357	0.609	1.43219	0.430	0.521	0.050	1.36933
0.608	0.362	0.030	1.36960	0.574	0.394	0.032	1.36916
0.047	0.414	0.539	1.42619	0.048	0.549	0.403	1.39675
0.521	0.439	0.040	1.37049	0.451	0.504	0.045	1.36921
0.053	0.427	0.520	1.42435	0.035	0.525	0.440	1.39943
0.050	0.486	0.464	1.41892	0.386	0.545	0.069	1.36994
				0.236	0.646	0.118	1.37245
Heptane (1)+Ethanol (2)+DES1 (3)				Heptane (1)+Ethanol (2)+DES2 (3)			
x ₁	x ₂	x ₃	n _D	x ₁	x ₂	x ₃	n _D
0.142	0.703	0.155	1.38485	0.145	0.689	0.166	1.37879
0.115	0.702	0.184	1.38784	0.092	0.677	0.232	1.38332
0.178	0.695	0.128	1.38221	0.184	0.684	0.132	1.37716
0.224	0.671	0.105	1.38063	0.243	0.651	0.106	1.37670
0.066	0.665	0.270	1.39783	0.049	0.628	0.323	1.39052
0.086	0.694	0.220	1.39189	0.362	0.570	0.067	1.37709
0.296	0.621	0.083	1.37963	0.028	0.555	0.417	1.39848
0.427	0.517	0.056	1.37959	0.115	0.698	0.187	1.37978
0.038	0.595	0.367	1.40837	0.067	0.672	0.260	1.38528
0.351	0.578	0.071	1.37950	0.452	0.506	0.042	1.37747
0.533	0.436	0.031	1.37935	0.016	0.479	0.505	1.40619
0.031	0.565	0.405	1.41246	0.395	0.551	0.054	1.37702
0.012	0.441	0.547	1.42670	0.538	0.435	0.027	1.37846
0.050	0.624	0.326	1.40380	0.022	0.536	0.443	1.40086
0.021	0.509	0.470	1.41939	0.277	0.639	0.084	1.37619
				0.037	0.601	0.362	1.39376
				0.310	0.613	0.077	1.37689
				0.058	0.653	0.289	1.38768

^au(x)=±1·10⁻³; u(T)=±0.5 K; u(p)=0.005 MPa; u(n_D)=±0.00009; with 95 % level of confidence

ments was monitored using a Pt100 temperature probe with an accuracy of ±0.03 K, connected to magnetic agitator (supplier: Heidolph) (Fig. S1). 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 water was used as a thermostatic bath in all experiments. Experimental setup is presented in Fig. S1.

Thermodynamic characterization of eutectic solvents was performed measuring refractive index data using Anton Paar RXA 156 refractometer, density and sound velocity data using DSA 5000 M densimeter and viscosities by digital Stabinger viscometer (model SVM 3000/G2).

Density measurements were performed with the experimental repeatability ±8·10⁻² kg·m⁻³, and combined expanded uncertainty,

Table 3. Values of the adjustable parameters A to I for the system of Eqs. (1) to (3)

A	B	C	D	I	F	G	H	I
Hexane (1)+Ethanol (2)+DES1 (3)								
1.000	-4.121	4.130	0.610	0.763	2.161	-0.723	0.753	0.707
Hexane (1)+Ethanol (2)+DES2 (3)								
0.995	-4.180	5.724	1.058	0.314	1.666	-0.257	1.117	0.348
Heptane (1)+Ethanol (2)+DES1 (3)								
0.940	-4.821	-0.617	0.608	0.798	2.185	-0.765	0.678	0.785
Heptane (1)+Ethanol (2)+DES2 (3)								
0.826	-4.252	1.340	1.911	-0.529	0.815	0.496	1.994	-0.515

including the influence of sample purity, within $\pm 1 \text{ kg}\cdot\text{m}^{-3}$ with a 0.95 level of confidence. The relative uncertainty in dynamic viscosity measurements was estimated to be $\pm 2\%$. Repeatability in sound velocity measurements was $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$ and uncertainty within $\pm 1 \text{ m}\cdot\text{s}^{-1}$.

Headspace gas chromatography (HS-GS) was used to measure the vapor pressures (P_s) and saturated vapor densities (SVD) of DES1 and DES2 in the temperature range 298.15 K to 333.15 K. The microprocessor controlled HS-GC instrument automatically thermostated samples contained in septum-sealed glass vials to equilibrate the vapor and liquid for 60 min, pressurized the vials to pre-set pressure by inserting a hollow needle through the septum, and sampled the vapor for 0.01 min by allowing the pressure in the vial to drive an aliquot of the vapor through the needle and onto the analytical column. The apparatus was the following: GC-MS Thermo, GC is Focus, MS is PolarisQ, autosampler TriPlus, headspace TriPlusHS, and software used was Xcalibur Thermo. Estimated uncertainties were $\pm 7\%$ at 298.15 K, 308.15 K and 318.15 K, and $\pm 5\%$ at 328.15 K and 333.15 K; temperature uncertainty was $\pm 0.15 \text{ K}$.

3. Modeling

The experimental tie-line data for the investigated ternary mixtures were correlated using the non-random two-liquid (NRTL) [21] and universal quasi-chemical (UNIQUAC) [22] thermodynamic models. DES was treated as one component (pseudo-molecule) as it was stated in the literature for other combinations of eutectic mixtures [23,24]. Both, pseudo-molecular approach and modeling of individual DES components gave similar results since molar ratios of DES1 and DES2 are not affected in two phases in equilibrium. Choosing to model investigated mixtures as quaternary or five-component mixtures will introduce more binary interaction parameters and hence more complexity in the modeling, still obtaining similar results compared to pseudo-molecular approach. This is also explained by Naik et al. [25].

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

$$\ln \gamma_i = \frac{\sum_{j=1}^m \tau_{ji} G_{ji} x_j}{\sum_{l=1}^m G_{li} x_l} + \sum_{j=1}^m \frac{x_j G_{ij}}{\sum_{l=1}^m G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^m x_r \tau_{rj} G_{rj}}{\sum_{l=1}^m G_{lj} x_l} \right) \quad (4)$$

where

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad (5)$$

$$\frac{\Delta g_{ij}}{R} = A_{ij} + B_{ij} T \quad (6)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji}) \quad (7)$$

Δg_{ij} describes the energy interactions between components i and j and α_{ij} is the non-randomness parameter. In total there are five adjustable parameters A_{ij} , A_{ji} , B_{ij} , B_{ji} and α_{ij} , but in this work adjustable parameters were treated as temperature independent ($B_{ij}=B_{ji}=0$). For nonrandomness parameter α_{ij} value 0.2 is adopted [26], so only A_{ij} and A_{ji} parameters were optimized. Although in the literature the value 0.2 for the non-randomness parameter is mostly applied, we performed some preliminary tests where different values for non-randomness parameter (α_{ij}) were applied and we concluded that 0.2 value is optimal.

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

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (8)$$

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^m x_j l_j \quad (9)$$

$$\ln \gamma_i^R = q_i \left[1 - \ln \sum_{j=1}^m \theta_j \tau_{ji} - \sum_{j=1}^m \frac{\theta_j \tau_{ij}}{\sum_{k=1}^m \theta_k \tau_{kj}} \right] \quad (10)$$

where

$$\tau_{ij} = \exp\left(-\frac{\Delta u_{ij}}{RT}\right) = \exp\left(-\frac{a_{ij}}{T}\right) \quad (11)$$

$$\phi_i = \frac{x_i r_i}{\sum_{i=1}^m x_i r_i} \quad (12)$$

$$\theta_i = \frac{x_i q_i}{\sum_{i=1}^m x_i q_i} \quad (13)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (14)$$

Here, Δu_{ij} and Δu_{ji} describe interaction energy between molecules i and j . In this work two adjustable interaction parameters were

Table 4. UNIQUAC volume and surface area structural parameters for investigated pure components and eutectic mixtures

Component i	r_i	q_i
Hexane	4.4998	3.856
Heptane	5.1742	4.396
Ethanol	2.5755	2.588
DES1	4.5977	4.489
DES2	3.0215	3.165

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 a pure component i were taken from literature [27]. r_i and q_i for individual eutectic components were calculated as a sum of the group volume R_k and group surface area Q_k parameters given in literature [28] as follows:

$$r_i = \sum_k v_k^i R_k \text{ and } q_i = \sum_k v_k^i Q_k \quad (15)$$

where v_k^i is the number of groups of type k in a molecule i . Procedure for r_i and q_i determination for DES1 and DES2 was explained

in the literature for other DES combinations [23]. Table 4 gives r_i and q_i values for the compounds and eutectic mixtures investigated in this work.

The binary interaction parameters were estimated through minimization of the composition based objective function:

$$OF = \sum_i \sum_\alpha \sum_k (x_{ik}^{\alpha(exp)} - x_{ik}^{\alpha(cal)})^2 \quad (16)$$

where i is the number of components in the mixture, α is the number of phases and k is the 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 binary interaction parameters along with the following equilibrium condition:

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (17)$$

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

$$\sigma = 100 \sqrt{\frac{\sum_i \sum_\alpha \sum_k (x_{ik}^{\alpha(exp)} - x_{ik}^{\alpha(cal)})^2}{6k}} \quad (18)$$

Table 5. Experimental values of density, refractive index, viscosity and sound velocity for investigated DES1 and DES2 at temperature T and at atmospheric pressure (0.1 MPa)^a

T/K	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	n_D	$\eta / \text{mPa} \cdot \text{s}$	$u / \text{m} \cdot \text{s}^{-1}$	$10^{-3} \cdot \rho / \text{kg} \cdot \text{m}^{-3}$	n_D	$\eta / \text{mPa} \cdot \text{s}$	$u / \text{m} \cdot \text{s}^{-1}$
	Choline chloride+1,2-propanediol (1 : 3)				Choline chloride+1,2-propanediol+H ₂ O (1 : 3 : 3)			
288.15	1.07478	1.46278	119.12	1751.7	1.07421	1.44782	45.859	1803.8
293.15	1.07170	1.46137	89.383	1738.9	1.07113	1.44646	35.085	1791.8
298.15	1.06862	1.45995	68.432	1726.1	1.06803	1.44510	27.689	1779.6
303.15	1.06554	1.45853	53.339	1713.4	1.06491	1.44372	22.082	1767.4
308.15	1.06247	1.45708	42.261	1700.8	1.06178	1.44231	17.859	1755.1
313.15	1.05939	1.45561	33.925	1688.1	1.05863	1.44092	14.578	1742.7
318.15	1.05632	1.45418	27.714	1675.5	1.05546	1.43951	12.147	1730.2
323.15	1.05324	1.45275	22.880	1662.9	1.05227	1.43811	10.207	1717.5
328.15	1.05016	1.45131	19.111	1650.3	1.04906	1.43671	8.6840	1704.8
333.15	1.04707	1.45012	16.179	1637.7	1.04583	1.43543	7.4690	1692.0

^a $u(T) = 0.01 \text{ K}$; $u(p) = 0.005 \text{ MPa}$; $U_c(\rho) = \pm 1 \text{ kg} \cdot \text{m}^{-3}$; $u(n_D) = \pm 0.00009$; $u(\eta) = \pm 2\%$; $u(u) = \pm 0.1 \text{ m} \cdot \text{s}^{-1}$; with 95% level of confidence

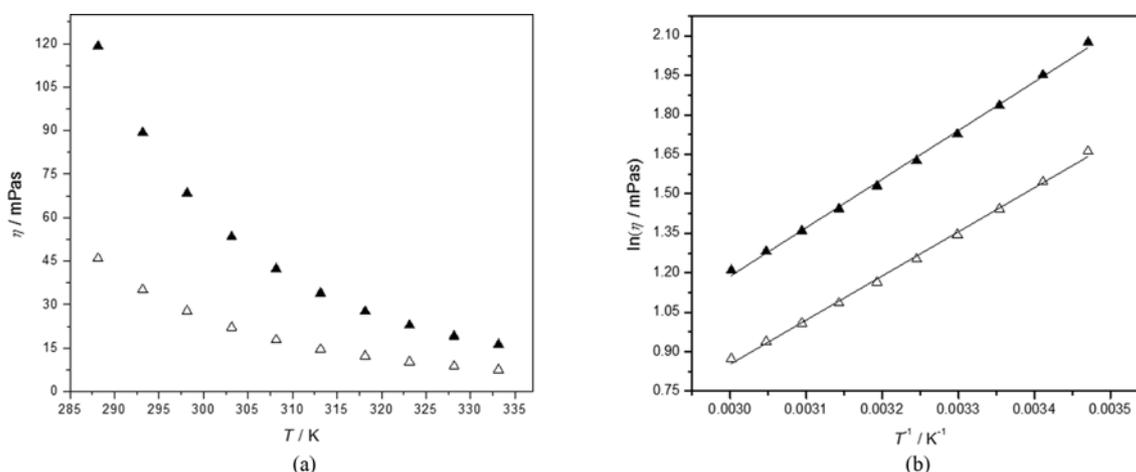


Fig. 1. Temperature dependence of viscosity for two investigated eutectics: (▲) DES1 and (△) DES2. (a) η vs. T and (b) $\ln \eta$ vs. T^{-1} .

RESULTS AND DISCUSSION

The results for density, viscosity, refractive index and sound velocity of both investigated solvents, DES1 and DES2, are given in Table 5.

Results presented in Table 5 reveal that all properties decrease with temperature increase. Comparing the viscosity values of DES1 and DES2, it is obvious that water addition significantly reduces DES2 viscosity, while for density this influence is negligible. Speed of sound values are slightly higher for DES2 comparing to binary eutectic named DES1. Since eutectics are multicomponent compounds, the nature of individual forming components and its molar ratio are affecting viscosity, besides temperature. Fig. 1 provides graphical presentation of water influence on viscosity behavior of ternary deep eutectic solvent over wide temperature range in comparison to binary eutectic.

Arrhenius equation satisfactorily fits $\ln\eta-T^{-1}$ dependences of both eutectics in the following forms: $\ln\eta=1846.853/T-4.354$ for DES1 and $\ln\eta=1677.840/T-4.181$ for DES2 (Fig. 1(b)).

From Fig. 1(a) it is obvious that water influence is greater at lower temperatures, and becomes less pronounced at high temperatures. This observation is advantageous for liquid-liquid extraction, since it is usually performed at lower temperatures. At lower temperatures addition of 14 mass% of water more than doubly reduces dynamic viscosity (Table 5). This is a significant reduction, and there is a room for further decrease by adding water till 25 mass% with no rupture of supramolecular structure of a ternary eutectic [17,18].

Experimental LLE results, given as mole fractions of the components in the raffinate and the extract phase, selectivity and distribution ratio values of four investigated systems hexane+ethanol+DES1/DES2 and heptane+ethanol+DES1/DES2 are reported in Table 6. For the evaluation of the DES1/DES2 extraction efficiency, distribution coefficient β and selectivity S values, the following equations were used:

$$\beta_2 = x_2^{\text{II}}/x_2^{\text{I}} \quad (19)$$

$$S = \frac{\beta_2}{\beta_1} = \frac{x_2^{\text{II}}x_1^{\text{I}}}{x_2^{\text{I}}x_1^{\text{II}}} \quad (20)$$

where x_1^{I} and x_2^{I} are mole fractions of hexane/heptane and ethanol in the upper phase (raffinate layer) and x_1^{II} and x_2^{II} are the mole fractions of hexane/heptane and ethanol in the bottom phase (extract layer) (Table 6). The distribution coefficient β_2 indicates how well a desired component (ethanol) is distributed between raffinate and an extract layer. Selectivity S indicates an extraction efficiency of the DES1/DES2, showing the easiness of solute (ethanol) extraction from a diluent (inert, hexane/heptane). High values for the distribution coefficient and selectivity are desirable.

These four investigated systems are considered as ternary mixtures even though eutectics are composed of two or three components. Dai et al. [18] explained the supramolecular structure of various eutectic mixtures, among them choline chloride+1,2-propanediol. Authors found that individual eutectic components are bonded via strong hydrogen bonds formed between -OH groups in 1,2-propanediol and chloride and a hydrogen bonds with -CH₂-OH in

Table 6. Experimental tie line compositions, distribution ratio and selectivity values for the four ternary systems at 298.15 K and at atmospheric pressure (0.1 MPa)^{a,b,c}

Hexane (1)+Ethanol (2)+DES1 (3)							
Hexane-rich phase			DES1-rich phase			β	S
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}		
0.979	0.021	0.000	0.001	0.100	0.899	4.8	4661.9
0.971	0.029	0.000	0.003	0.204	0.793	7.0	2276.8
0.959	0.041	0.000	0.008	0.299	0.693	7.3	874.2
0.928	0.071	0.001	0.016	0.395	0.589	5.6	322.7
0.907	0.092	0.001	0.031	0.483	0.486	5.3	153.6
0.851	0.147	0.002	0.045	0.538	0.417	3.7	69.2
0.809	0.188	0.003	0.071	0.595	0.334	3.2	36.1
Hexane (1)+Ethanol (2)+DES2 (3)							
Hexane-rich phase			DES2-rich phase			β	S
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}		
1.000	0.000	0.000	0.003	0.200	0.797		
1.000	0.000	0.000	0.010	0.340	0.650		
1.000	0.000	0.000	0.018	0.417	0.565		
0.987	0.013	0.000	0.032	0.496	0.472	38.2	1176.8
0.976	0.024	0.000	0.046	0.548	0.406	22.8	484.5
0.953	0.047	0.000	0.072	0.605	0.323	12.9	170.4
Heptane (1)+Ethanol (2)+DES1 (3)							
Heptane-rich phase			DES1-rich phase			β	S
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}		
0.986	0.000	0.014	0.001	0.168	0.831		
0.971	0.015	0.014	0.003	0.280	0.717	18.7	6041.8
0.959	0.027	0.014	0.008	0.380	0.612	14.1	1687.1
0.928	0.057	0.015	0.016	0.478	0.506	8.4	486.4
0.851	0.133	0.016	0.045	0.617	0.338	4.6	87.7
0.810	0.173	0.017	0.071	0.668	0.261	3.9	44.1
Heptane (1)+Ethanol (2)+DES2 (3)							
Heptane-rich phase			DES2-rich phase			β	S
x_1^{I}	x_2^{I}	x_3^{I}	x_1^{II}	x_2^{II}	x_3^{II}		
0.994	0.003	0.003	0.000	0.200	0.800	66.7	
0.978	0.018	0.004	0.003	0.350	0.647	19.4	6338.9
0.973	0.023	0.004	0.013	0.475	0.512	20.7	1545.7
0.942	0.054	0.004	0.022	0.535	0.443	9.9	424.2
0.920	0.075	0.005	0.035	0.591	0.374	7.9	207.1
0.881	0.113	0.006	0.058	0.645	0.297	5.7	86.7

^a x_1 is the mole fraction of hexane/heptane, x_2 is the mole fraction of ethanol, and x_3 is the mole fraction of DES1/DES2

^bEmpty cells denote very high S or β values

^c $u(x)=\pm 1 \cdot 10^{-3}$; $u(T)=\pm 0.5$ K; $u(p)=0.005$ MPa; with 95% level of confidence

choline chloride. Water can be added as a third component in eutectic mixture. The supramolecular complex structure of such ternary eutectic is preserved as long as the content of water is below 50 wt%, but further dilution produces a solution of the free

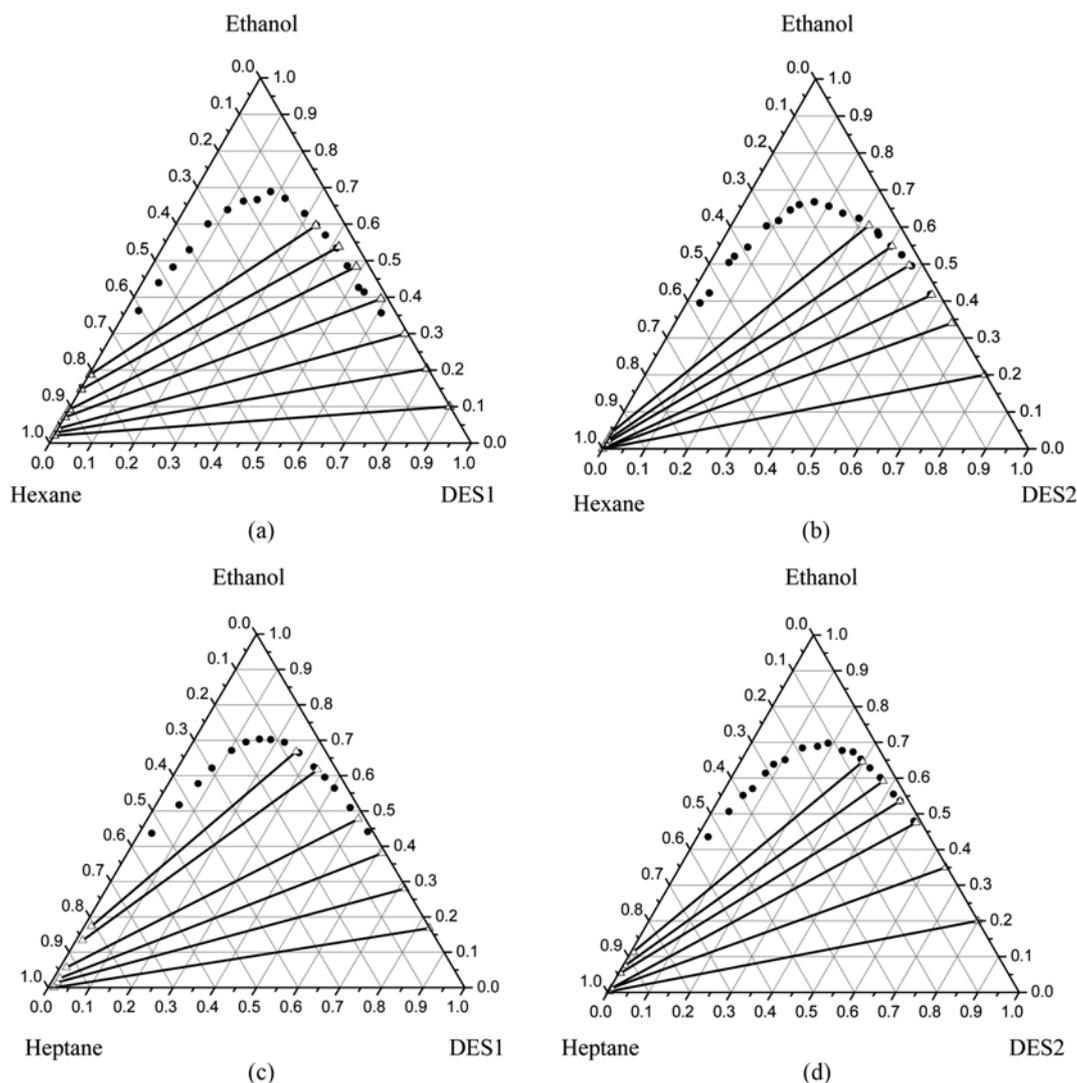


Fig. 2. Experimental ternary LLE diagrams at 298.15 K for: (a) hexane (1)+ethanol (2)+DES1 (3); (b) hexane (1)+ethanol (2)+DES2 (3); (c) heptane (1)+ethanol (2)+DES1 (3); (d) heptane (1)+ethanol (2)+DES2 (3); dots represent binodal curve, triangles and lines represent tie line along with compositions on both ends.

forms of the individual components in water [17]. These gradual changes in the structure of ternary eutectics during dilution may affect their physicochemical properties and also their application [17]. In this work water was added in the amount of around 14 wt%, to avoid rupture of the hydrogen bond network and stay far from the point where rupture of ternary eutectic supramolecular structure can occur. Hydrogen bond network preserves the compact structure of eutectics, and thus DES1 or DES2 (with 14 wt% of water) can be considered as one component.

As stated previously, our objective was to study the extracting ability of both DES1 and DES2 for the separation of azeotropes containing components of significantly different polarities such as hexane+ethanol and heptane+ethanol. Additionally, the goal was to check the assumption of Dai et al. [17] that water addition in eutectic solvent affects polarity increase, which could enhance its solubilizing capacity for polar compounds, e.g., ethanol in an azeotropic mixture. From this assumption higher selectivity of DES2

towards ethanol in hexane/heptane+ethanol azeotropic mixture is expected.

Fig. 2 presents binodal curves and the tie lines for the systems hexane+ethanol+DES1 (Fig. 2(a)) and hexane+ethanol+DES2 (Fig. 2(b)), heptane+ethanol+DES1 (Fig. 2(c)) and heptane+ethanol+DES2 (Fig. 2(d)), respectively.

From Fig. 2 it is evident that hexane or heptane are immiscible with both eutectics, while the immiscibility region is not influenced by introducing ternary eutectic in the azeotropic mixture. From the selectivity and distribution coefficient values given in Table 6, it can be concluded that both DES1 and DES2 present promising candidates for the separation of alkane/alcohol azeotropes. For four investigated systems, results indicate that an alkane is successfully separated for lower ethanol concentrations in the starting mixture as it is present in traces in the extract layer, while DES1/DES2 is found in traces in the raffinate layer for all experimental points. Extract layer is significantly more abundant with ethanol, which

agrees with high distribution coefficient and selectivity values in Table 6. These high values of both selectivity and distribution coefficient can be explained by the structure of the hydrogen bond donor, 1,2-propanediol. As stated in the literature [6], the OH bond in alcohol is strongly polarized, thus allowing strong hydrogen

bonding with ethanol. This is the reason for high distribution coefficient values. Also, 1,2-propanediol with two -OH groups enhances ethanol extraction which explains high selectivity values. Alkane as a non-polar molecule can form dispersion forces. Polar ethanol (dipole moment is 1.7 D [28]) forms strong hydrogen bonds, as

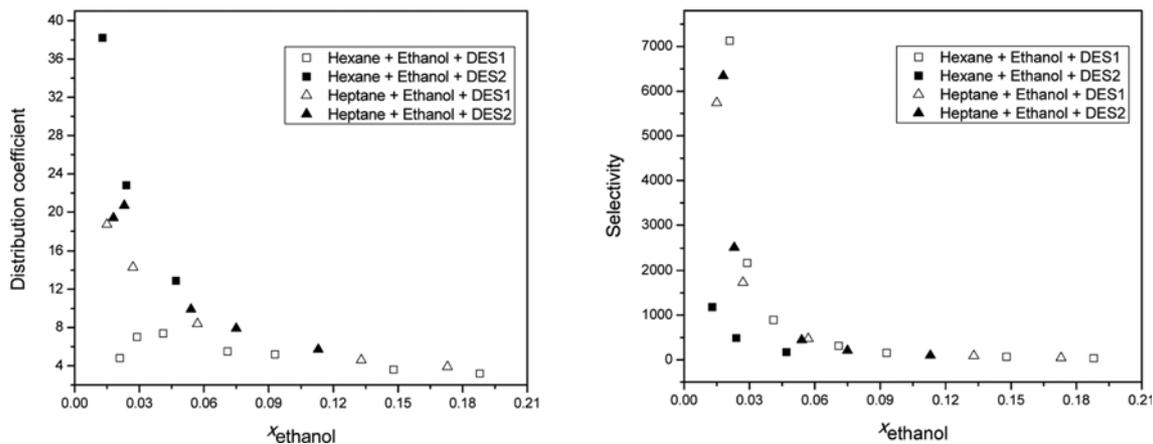


Fig. 3. Comparison of the distribution coefficient and selectivity values vs. ethanol mole fraction in the raffinate for the studied systems at 298.15 K.

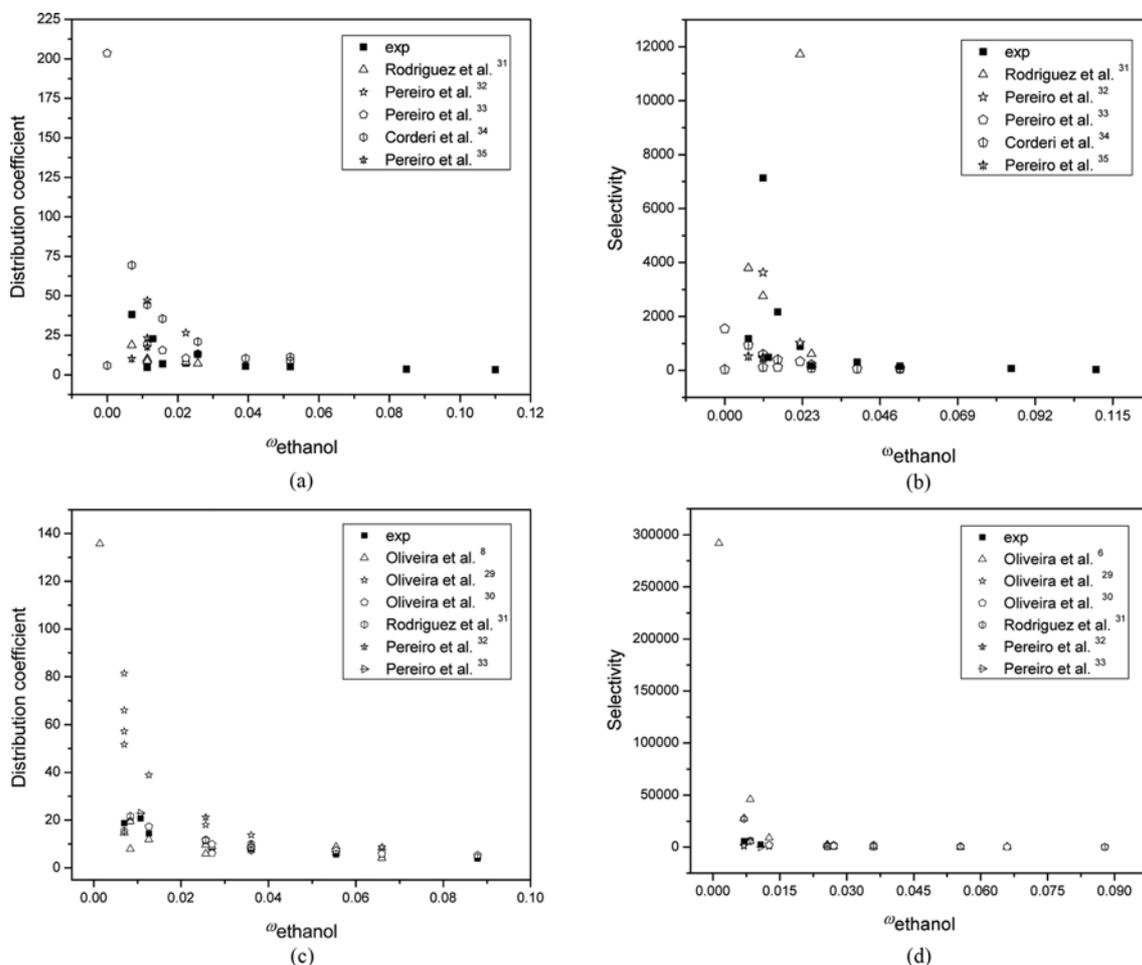


Fig. 4. Comparison of the distribution coefficient and selectivity values vs. ethanol mass fraction in the raffinate at 298.15 K for the systems with hexane (a) and (b); and for the systems with heptane (c) and (d).

well as a weaker dipole-dipole and dispersion forces. Ternary eutectic DES2 contains water, which raises polarity of eutectic and forms additional hydrogen bonds. Fig. 3 makes a comparison of the β and S values for four investigated systems, where the influence of water addition is visually presented, as well as influence of alkane in the extraction behavior.

Both distribution ratio and selectivity for the hexane+ethanol system are influenced by applied DES, though for heptane+ethanol system both parameters act similarly no matter of solvent applied. For the system with hexane it is evident from Fig. 3 that water addition in a DES structure raises distribution coefficient values. For selectivity, the following interesting behavior is noticed: for small ethanol concentrations DES2 exhibits complete separation of azeotrope components and results in pure hexane raffinate. For ethanol concentrations higher than 1.3 mol%, the opposite behavior is detected: DES1 reaches higher selectivity values. Note that notable solvent influence for all systems is present in the range of 6 mol% of ethanol in raffinate or less. Mass fractions are commonly used as composition data in process design. Thus, when the mass fraction is included in calculation of distribution ratio, β values for DESs are higher compared to the values given in Table 6. It is important to emphasize that these higher values are much more pronounced for DES2 solvent, which is another advantage of using ternary DES. Higher β values indicate lower solvent requirements and lower costs of the operation. Despite mass ratios being more common in process design, in this work molar ratios are used for the easiness of comparison with other published literature.

Comparing experimental results with literature, the success of the proposed extraction systems is confirmed and graphically presented in Fig. 4. For three of four investigated systems, very high β and S values were reached for certain mixture's compositions (below 1 mass% of ethanol in the raffinate) and those data cannot be seen on diagrams since they present points of complete separation of azeotrope components. For other data presented in Fig. 4, the investigated DES1 and DES2 express rather high extraction efficiency.

Table 7. Vapor pressures and saturation vapor densities for investigated solvents DES1 and DES2 in wide temperature range^a

Temperature	298.15 K	308.15 K	318.15 K	328.15 K	333.15 K
Vapor pressure, P_s /kPa					
DES1	<0.01	0.03	0.07	0.16	0.23
DES2	<0.01	0.03	0.07	0.15	0.22
Saturation vapor density (SVD)/g·m ³					
DES1	0.32	1.12	2.72	3.52	6.25
DES2	0.32	1.13	2.73	3.52	6.26

^aEstimated uncertainties $u(P_s)$ and $u(\text{SVD})$ are $\pm 7\%$ at 298.15 K, 308.15 K and 318.15 K, and $\pm 5\%$ at 328.15 K and 333.15 K; $u(T) = \pm 0.15$ K; with 95% level of confidence

Extraction parameter values of our DESs are as high as for eutectics investigated in the literature, while for the most of the ionic liquids studied in literature, the obtained results are more satisfactory.

To check the possibility for solvent recovery, vapor pressures were measured, along with saturation vapor densities of both DESs. Results show negligible differences for DES1 and DES2 (Table 7). This means that both solvents are practically nonvolatile and can be easily recovered from the extract layer.

Taking into account the low cost of these solvents and their recoverability, their potential industrial application is certainly capable of meeting most of the principles of green chemistry, while DES2 lower viscosity requires less energy for mass transfer and thus lower operational costs.

The experimental tie-line data for the investigated ternary mixtures were correlated using the nonrandom two-liquid (NRTL) [21] and universal quasi-chemical (UNIQUAC) [22] thermodynamic models. Table 8 presents the obtained parameters and deviations for NRTL and UNIQUAC models. As can be seen, good fit quality is obtained for both models, though UNIQUAC correlates the experimental tie lines more accurately than NRTL model.

Table 8. Binary interaction parameters obtained for NRTL and UNIQUAC equations for four investigated ternary mixtures and rmsd values

i	j	NRTL			UNIQUAC		σ (%)
		A_{ij}	A_{ji}	α_{ij}	a_{ij}	a_{ji}	
Hexane	Ethanol	34.29	383.34	0.200	9586.22	4658.73	1.348 ^a , 0.101 ^b
Hexane	DES1	935.00	910.00	0.200	270.61	-4669.05	
Ethanol	DES1	954.83	-823.00	0.200	-5350.06	-8968.32	
Hexane	Ethanol	107.45	707.19	0.200	-5413.87	-6422.02	2.651 ^a , 0.010 ^b
Hexane	DES2	952.97	864.38	0.200	-6610.31	6578.11	
Ethanol	DES2	-316.35	-879.57	0.200	2089.57	8471.12	
Heptane	Ethanol	183.02	560.93	0.200	-717.26	-7401.88	1.342 ^a , 0.002 ^b
Heptane	DES1	820.71	829.47	0.200	1529.93	1007.07	
Ethanol	DES1	-113.48	-155.64	0.200	-7969.92	-9072.17	
Heptane	Ethanol	294.49	358.49	0.200	581.01	-189.88	1.365 ^a , 1.596 ^b
Heptane	DES2	843.45	888.04	0.200	149.29	905.18	
Ethanol	DES2	817.03	-945.17	0.200	-326.30	611.53	

^aNRTL

^bUNIQUAC

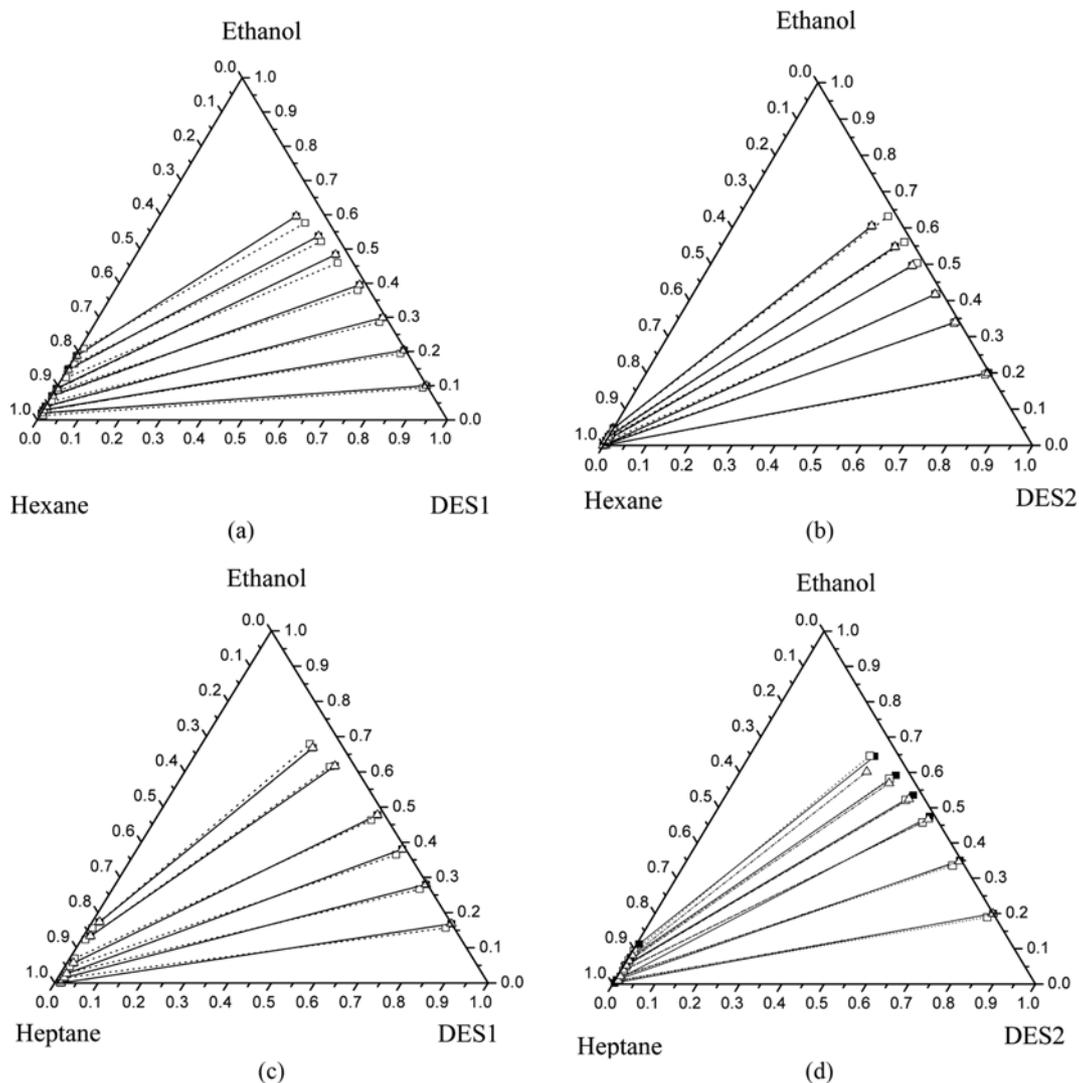


Fig. 5. Comparison of NRTL model (□) and UNIQUAC model (△) with experimental tie lines (■) for: (a) hexane (1)+ethanol (2)+DES1 (3); (b) hexane (1)+ethanol (2)+DES2 (3); (c) heptane (1)+ethanol (2)+DES1 (3); (d) heptane (1)+ethanol (2)+DES2 (3). Solid lines are experimental tie lines, dot lines represent NRTL and dash dot lines represent UNIQUAC model.

Fig. 5 shows the experimental tie line data together with the data calculated with NRTL and UNIQUAC models where the goodness of the fit can be visually observed.

CONCLUSIONS

We tested the efficiency of two eutectic solvents choline chloride+1,2-propanediol in molar ratio 1:3 (DES1) and choline chloride+1,2-propanediol+H₂O in molar ratio 1:3:3 (DES2) for breaking the azeotropes hexane+ethanol and heptane+ethanol. Ternary liquid-liquid equilibrium experiments were performed at 298.15 K and at atmospheric pressure. Also, additional thermodynamic properties, e.g., densities, viscosities, refractive indices and speed of sound, were determined for both DES1 and DES2 from 288.15 to 333.15 K and at atmospheric pressure. Density changes by water addition were not pronounced, while 14 mass% of water in ternary DES2 reduced dynamic viscosity of the solvent significantly

compared to DES1. This reduction is especially present at lower temperatures. Liquid-liquid extraction feasibility was investigated at 298.15 K. Both solvents, DES1 and DES2, exhibited rather high selectivity for ethanol and thus high extraction efficiency. For three of four systems, complete separation was achieved at low ethanol concentration in the starting mixture. Water addition in the ternary eutectic DES2 provoked complete separation of hexane+ethanol azeotrope at points with low ethanol concentrations in the raffinate layer (i.e. much higher comparing to DES1), but with increase of the ethanol concentration, selectivity values exhibited opposite behavior, decrease compared to binary eutectic selectivity. For heptane, solvent influence was not pronounced. Vapor pressures and saturation vapor densities, measured for DES1 and DES2, indicated that both solvents are practically non-volatile and can be easily recovered from the extract layer. Additional advantage of DES2 is its lower viscosity compared to DES1, as confirmed for a wide temperature range in this work.

Modeling of phase equilibrium was performed with NRTL and UNIQUAC correlative models. Both models showed good agreement with experimental data, where UNIQUAC gave better fit quality.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Effect of water addition on extraction ability of eutectic solvent choline chloride+ 1,2-propanediol for separation of hexane/heptane+ ethanol systems

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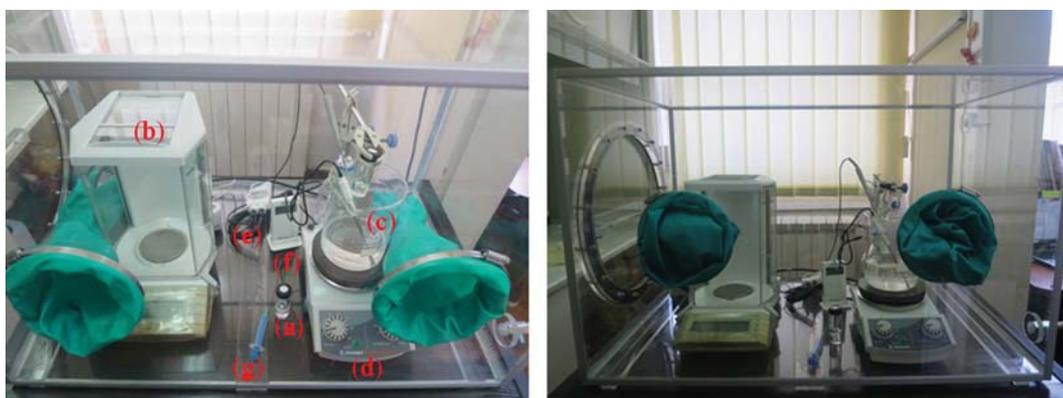


Fig. S1. Experimental apparatus for liquid-liquid equilibrium experiments: (a) conical Pyrex vial; (b) Mettler AG 204 balance; (c) thermostatic bath - 2 L glass beaker filled with water; (d) magnetic agitator (supplier: Heidolph); (e) Pt100 temperature probe; (f) thermostat; (g) syringe with long needle.

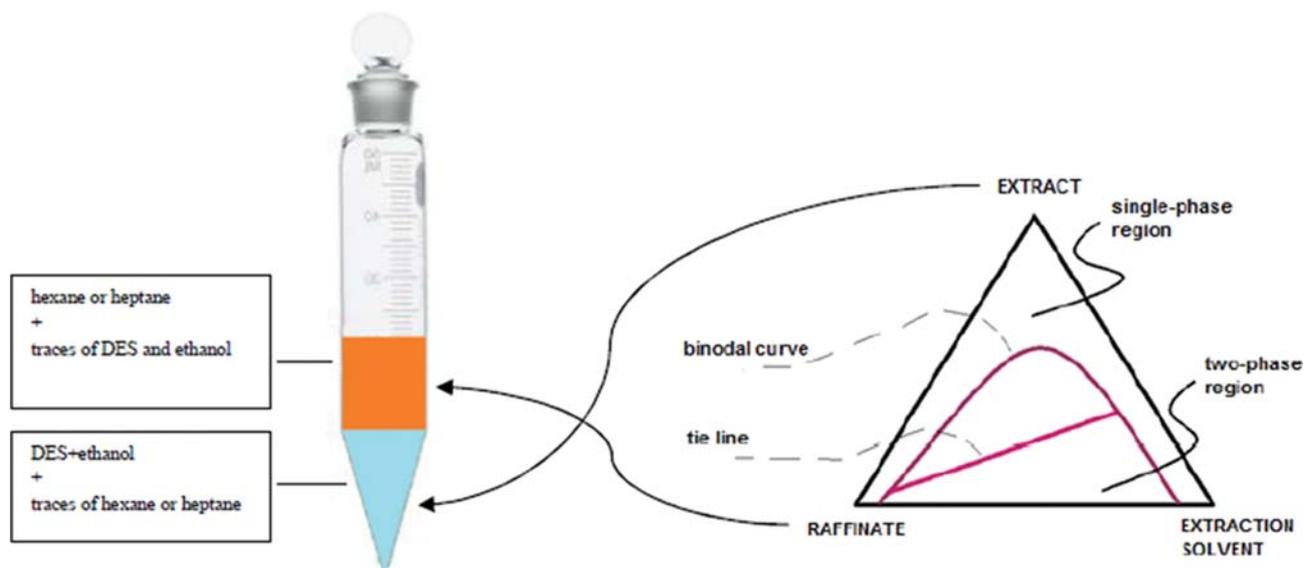


Fig. S2. Diagram of multiphase system and visual representation of the raffinate and extract layers.