Article

Liquid−Liquid Equilibrium of Alcohol (Ethanol or *n*-Propanol)−Ester (Ethyl or *n*-Propyl Propionate) Systems with a Deep Eutectic Solvent Based on Choline Chloride at 293.15 K

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ABSTRACT: Deep eutectic solvents (DESs) formed by choline chloride and urea or glycerol were tested for the separation of azeotropic mixtures. The case study was the separation of ethanol−ethyl propionate and *n*-propanol−*n*-propyl propionate. For this aim, the experimental data of liquid−liquid equilibria (LLEs) were obtained at temperature 293.15 K and atmospheric pressure. Liquid−liquid tie lines were determined using NMR spectroscopy and analyzed. The extraction performance of DESs was characterized with distribution coefficients and values of selectivity to alcohol. Comparison of selectivity values in systems containing alcohols and esters with another DES formed by choline chloride and malonic acid was carried out. The NRTL model for LLE data correlation was used. The model is shown to give rather good estimates for the selectivity values.
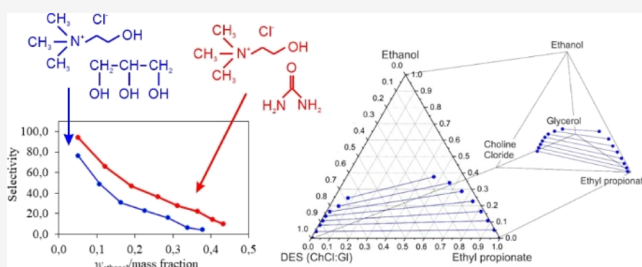
INTRODUCTION

Development of green chemistry (green technology) is an important current issue aimed at reducing the negative impact on the environment. In particular, much attention is paid to the search of new solvents. Ionic liquids are their representatives, but their "green" properties due to low biodegradability and biocompatibility are in doubt recently.[1,2] At the same time, deep eutectic solvents (DESs) are considered one of the most promising environmentally friendly and cost-effective alternatives to traditional volatile organic solvents and ionic liquids.[3,4] Typically, the DES is a liquid system at room temperature consisting of a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), which have a higher melting point than the DES formed by them.[5] Most DESs are easy to prepare, inexpensive, and biodegradable.[6] Application of DESs takes place in many fields of chemistry, such as electrochemistry, organic reactions, and enzymatic reactions, because of the green properties and variety of DESs.[7] The areas of research where DESs are successfully applied in recent studies are extraction and high-purity separation,[8,9] for instance, aromatic hydrocarbons and gas and biologically active compounds. Purification is of particular importance for the use of biodiesel, as glycerol is an undesirable byproduct and must be removed before biodiesel based on esters can be used as a fuel because the viscosity of glycerol contained in the mixture makes it difficult for the high-pressure injection system of a modern diesel engine and can cause damage.[10]

The separation of azeotropic mixtures and systems of close-boiling components is a crucial issue in chemical technology,

particularly in ester production. Esters are used in various fields of chemical industry and everyday life as solvents, aromatic additives, and in other applications. Recent applications are also related to the use in fuel technology; selected publications on this issue are cited below. For example, esters are considered promising candidates as components of second-generation biofuels because of the simple production from biomass waste.[11−13] They can be also considered as fuel additives for gasoline.[14,15] The most common components for the formation of DESs are choline chloride (ChCl) as HBAs and glycerol and urea as HBDs. The effect of various DESs based on ChCl and dimethylammonium chloride as HBAs and thiourea, glycerol, malonic acid, and urea as HBDs on the thermodynamic and transport properties in aqueous glucose solutions has been studied.[16] DESs composed of ChCl, urea, and glycerol have been applied to separate a mixture of toluene and heptane.[17] Lee and Park have obtained LLE data in the temperature range 298.2−313.2 K. Usage of the DES in the extraction of aromatic hydrocarbons from reformer and pyrolysis gasolines was investigated.[18] Larriba et al.[18] have considered six DESs based on ChCl formed by ethylene glycol, glycerol, levulinic acid, phenylacetic acid, malonic acid, and urea in the study of dearomatization of gasolines. Zhekenov et

Table 1. Information of the Chemicals

chemical name	source	initial mass fraction purity	purification method	final mass fraction purity[a]	analysis method
ethanol	Vekton	0.960	drying	0.990	GC[b]
n-propanol	Vekton	0.990	none		
ethyl propionate	Vekton	0.990	none		
n-propylpropionate	Vekton	0.990	none		
glycerol	Vekton	0.990	none		
urea	Vekton	0.980	none		
choline chloride	AppliChem	0.960	drying	0.980	NMR[c]

[a]Standard uncertainty is estimated to be 0.002 mass fraction. [b]Gas–liquid chromatography. [c]Nuclear magnetic resonance spectroscopy.

al.[19] have performed molecular dynamics simulation on three of the most commonly used DESs, which are composed of urea, ethylene glycol, and glycerol with ChCl. The authors describe the role of intermolecular and intramolecular hydrogen bonds and energy in the formation of these DESs. Zhang et al.[20] have proposed new methods based on an ultrasonically assisted deep eutectic solvent aqueous two-phase system for the extraction of ursolic acid from *Cynomorium songaricum*. For this aim, the authors have tested four DESs based on ChCl with glucose, glycerol, ethylene glycol, and urea. Baghlani and Sadeghi[21] have studied vapor–liquid equilibrium and LLE in the systems with DES based on ChCl and urea, ethylene glycol, and glycerol in the absence and presence of the water-soluble polymers polypropylene glycol 400, polyethylene glycol 400, and polyethylene glycol 10,000 at different temperatures; they have evaluated the ability of each DES component to form aqueous biphasic systems with polypropylene glycol. Experimental data on the density and dynamic viscosity of DESs consisting of ChCl and urea in a molar ratio of 1:2 and its aqueous mixtures in the temperature range from 293.15 to 363.15 K have been reported.[22] The effect of various DESs based on ChCl and ethylammonium chloride, with three different HBDs (urea, glycerol, and ethylene glycol), on the catalytic behavior and structure of heme-dependent biocatalysts has been studied.[23] It was found that these solvents can be promising media for biocatalytic processes of industrial interest. Yi et al.[24] have presented a new approach for extracting phenolic compounds from coal liquefaction oil using a DES based on ChCl and glycerol (1:1). It was found that this DES is able to extract up to 98.5% of phenolic compounds. The possibility of using a DES based on choline chloride and glycerol to separate the alcohol–ester system (1-phenylethanol–1-phenylethanol-acetate) has been demonstrated.[25] Unfortunately, the authors did not provide data on the phase equilibrium but indicated that the equimolar composition of the alcohol–ester mixture can be almost completely divided into four extraction procedures (recovery ester> 80%).

The phase equilibrium is commonly studied using two methods. Applying the isothermal titration together with the cloud point technique,[26] the solubility is investigated and the location of the binodal curve is determined, but in this case, it is not possible to estimate the compositions of the coexisting liquid phases. To determine LLE data (tie lines), various analytical techniques are applied. For this aim, the following experimental methods are most widely used: gas chromatography,[27] refractometry,[28] volumetric method,[29] microfluidics, and Raman microspectroscopy.[30] In this work, the NMR spectroscopy method is used.[31]

This article is a continuation of a series of studies devoted to the research of the phase equilibrium and extraction properties of deep eutectic solvents based on ChCl and various HBDs in alcohol–ester systems.[27,32–36] Now, we present the results of exploring the degree of separation of mixtures of alcohols and propionic acid esters (ethyl propionate and n-propyl propionate), using a DES based on ChCl and glycerol/urea. To correlate the experimental LLE data, the local composition model NRTL was used.

■ EXPERIMENTAL SECTION

Materials. Ethanol, n-propanol, ethyl propionate, n-propyl propionate, glycerol, and urea were purchased from "Vekton" (Russia). Choline chloride was obtained from AppliChem. Molecular sieves with pore diameter 3 Å are used to dry ethanol. The purity of ethanol was checked before each experimental study by gas chromatographic analysis. The choline chloride was kept under vacuum with heating. All the chemicals were used without further purification. All the chemicals used in this work, purity, and source are listed in Table 1.

Preparation of DESs. Choline chloride (0.7–0.8 g) was placed in vials (10 mL) and then placed in a vacuum dryer. The drying of choline chloride to remove water was carried out under vacuum (10 Pa) with heating up to 70 °C during 5 h. After drying, the mass of choline chloride was refined and glycerol or urea was added to the vial in the molar ratio equal to 1:2.[37] Substances were weighed on a Shinko VIBRA HT-120CE analytical balance (Japan) with an accuracy of 0.001 g. To obtain the DESs, vials were placed in a ultrasonic bath at a temperature of 40 °C for 3 h. Finally, colorless transparent DESs were prepared: DES (ChCl/Gl) and DES (ChCl/Ur). The water content in DESs was controlled by the Karl Fischer titration method. All samples of the DES were proved to contain less than 0.1 wt % water.

Apparatus and Procedure. Mixtures of alcohol, ester, and DESs of given compositions were placed in a thermostat at a fixed temperature and stirred with a magnetic stirrer for 3–4 h. Standard uncertainty of the temperature is 0.05 K. To reach phase equilibrium and complete liquid-phase splitting, the systems under the study were kept for 12 h. The compositions of two coexisting phases were analyzed using ^1H NMR spectroscopy. NMR analysis has been described in detail in our previous studies.[31,38–40] Figure 1 shows the ^1H NMR spectra of the studied DES. Peaks from protons in CH_2 and CH_3 groups of each compound in the organic and DES-rich phase were used for integration. Examples of ^1H NMR spectra for each phase of all studied systems are given in the Supporting Information, Tables S1–S8. Standard uncertainty of the composition determination was estimated to be 0.015 in mass fraction.
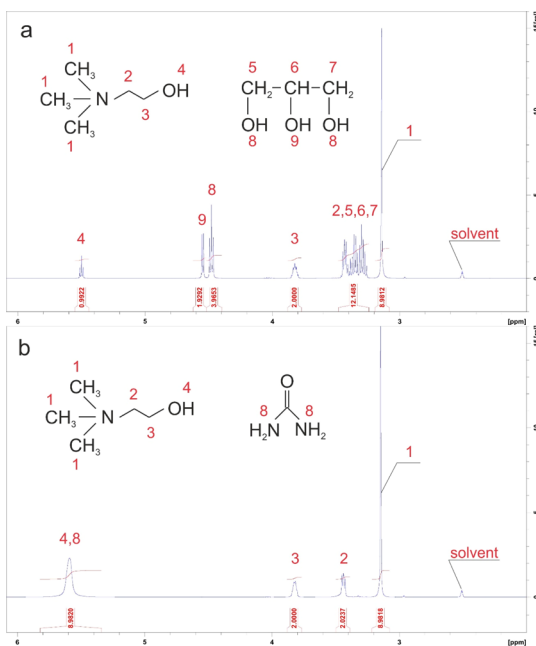
Figure 1. ^{1}H NMR spectra of the DES in dimethyl sulfoxide: (a) ChCl/Gl (1:2, mole ratio) and (b) ChCl/Ur (1:2, mole ratio).

CALCULATION

NRTL Model. The experimental data were correlated by the NRTL model.[41] We used the NRTL equation for the activity coefficients in the solution of n pseudo-components (DES was considered as a component) is the following form

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{m} x_j \tau_{ji} G_{ji}}{\sum_{i=1}^{m} x_i G_{ji}} + \sum_{j=1}^{m} \frac{x_j G_{ji}}{\sum_{i=1}^{m} x_i G_{ji}} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{ri} G_{ri}}{\sum_{i=1}^{m} x_i G_{ji}} \right) \tag{1}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \cdot G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \cdot (\alpha_{ji} = \alpha_{ij}) \tag{2}$$

where g_{ji} is the energy parameter, which characterizes the interaction between the components j and i; x denotes the mole fraction of the component, R is the gas constant, and T is the temperature, K. The physical meaning of the parameter α_{ji} is the nonrandomness of the system.

The objective function (OF) used to be minimized in this work is

$$\text{OF} = \sum_{k=1}^{n} \sum_{i=1}^{n} [(x_{ik}^{\text{exp}} - x_{ik}^{\text{cal}})_I^2 + (x_{ik}^{\text{exp}} - x_{ik}^{\text{cal}})_{II}^2] \tag{3}$$

The parameters estimated by this procedure are presented in Table 2.

The standard deviation σ was calculated using the equation

$$\sigma(\%)$$
$$= 100 \sqrt{\frac{\sum_{k=1}^{n} \sum_{i=1}^{3} [(x_{ik}^{\text{exp}} - x_{ik}^{\text{cal}})_I^2 + (x_{ik}^{\text{exp}} - x_{ik}^{\text{cal}})_{II}^2]}{2mn}} \tag{4}$$

where x is the mole fraction of the component, the subscripts i and k indicate components and tie lines, respectively, n is the number of tie lines, m is the number of components; and I and II denote organic and DES phases, respectively.

Table 2. Energy Parameter g_{ji} Obtained by Regression of Experimental Data on the LLE with NRTL Model

ij	Δg_{ji} J mol^{-1}	Δg_{ij} J mol^{-1}	α_{ji}
Ethanol (1)−Ethyl Propionate (2)−DES (ChCl/Gl) (3)			
1−2	−20,306	−27,032	0.3
1−3	4311	−9731	0.3
2−3	10,847	10,391	0.3
$\sigma = 0.45$			
n-Propanol (1)−n-Propyl Propionate (2)−DES (ChCl/Gl) (3)			
1−2	−20,800	−13,184	0.3
1−3	6361	−8360	0.3
2−3	12,734	10,657	0.3
$\sigma = 0.83$			
Ethanol (1)−Ethyl Propionate (2)−DES (ChCl/Ur) (3)			
1−2	−25,227	−16,351	0.3
1−3	4872	−11,075	0.3
2−3	15,416	11,192	0.3
$\sigma = 0.46$			
n-Propanol (1)−n-Propyl Propionate (2)−DES (ChCl/Ur) (3)			
1−2	−18,428	−34,823	0.3
1−3	8760	11,266	0.3
2−3	16,071	12,872	0.3
$\sigma = 0.42$			

The deviation did not exceed 0.83% (Table 2). The results of NRTL modelling are in good agreement with experimental data.

RESULTS AND DISCUSSION

LLE experimental data in quaternary alcohol−ester−DES (including ternary ester−DES subsystems) systems at 293.15 K and atmospheric pressure obtained using the ^{1}H NMR spectroscopy method are listed in Tables 3 and 4.

The molar ratio of the constituent components of the DES in the DES-enriched phase was found to be constant. In the organic phase, the ratio between the components becomes close to the initial stoichiometry only as the alcohol content increases. On the other hand, this is due to the low absolute values of the concentration of choline chloride in the organic phase that only leads to a high relative experimental uncertainty (see the concentration of choline chloride in the organic phase, Tables 3 and 4). Because the absolute value of the concentration of the DES in the organic phase is minimal (less 1.5%), this does not affect the DES phase, in which the ratio of the forming components is maintained. Because extraction occurs in the DES phase, this does not influence the process of extraction of alcohols from the systems under study. Accordingly, this makes it possible to accept the molar ratio of the DES components to be constant and allows considering the studied systems as pseudoternary ones; this simplifies the presentation of experimental data and the analysis of the topology of phase diagrams. As an example, a projection of 3D tie lines in the composition tetrahedron on the triangle is shown in Figure 2: the result is a ternary phase diagram with the vertices which refer to alcohol, ester, and DES.

Phase diagrams for both pseudo-ternary systems are presented in Figure 3.

The slope of tie lines increases both with increasing of chain length of ester and with a change in the HBD in the DES (from glycerol to urea). As can be seen from Figure 3, alkyl chain lengthening in alcohol (ester) causes an increase in heterogeneous area in the systems containing n-propanol and

Table 3. Experimental LLE Data for the System Alcohol−Ester−DES (ChCl/Gl 1:2) at 293.15 K and P = 101.3 kPa (w_1, w_2, and w_3−Mass Fractions of Alcohol, Ester, and Choline Chloride, Respectively[a], β is the Distribution Coefficient, and S is the Selectivity)

organic phase			DES phase					
w_1	w_2	w_3	w_1	w_2	w_3	$\beta_{alcohol}$	β_{ester}	S
Ethanol (1)−Ethyl Propionate (2)−Choline Chloride (3)−Glycerol (4)								
0.000	0.998	0.000	0.000	0.007	0.425			
0.051	0.945	0.000	0.041	0.010	0.412	0.803	0.011	75.8
0.108	0.883	0.001	0.075	0.013	0.386	0.701	0.014	48.6
0.164	0.820	0.002	0.101	0.017	0.373	0.615	0.020	30.5
0.226	0.744	0.007	0.128	0.018	0.365	0.565	0.025	22.8
0.288	0.657	0.018	0.152	0.022	0.354	0.529	0.033	16.0
0.339	0.564	0.038	0.190	0.049	0.325	0.562	0.086	6.5
0.379	0.466	0.067	0.240	0.072	0.302	0.632	0.155	4.1
n-Propanol (1)−n-Propyl Propionate (2)−Choline Chloride (3)−Glycerol (4)								
0.000	0.999	0.000	0.000	0.006	0.426			
0.084	0.914	0.000	0.025	0.004	0.416	0.305	0.004	67.9
0.147	0.846	0.000	0.044	0.005	0.411	0.302	0.006	49.3
0.219	0.769	0.001	0.062	0.007	0.400	0.284	0.009	32.9
0.287	0.694	0.003	0.070	0.007	0.399	0.244	0.010	25.6
0.349	0.623	0.007	0.086	0.012	0.400	0.247	0.019	13.2
0.417	0.542	0.013	0.092	0.011	0.403	0.221	0.021	10.8
0.488	0.427	0.026	0.109	0.010	0.386	0.224	0.024	9.4
0.520	0.369	0.044	0.130	0.012	0.377	0.250	0.034	7.4
0.541	0.293	0.065	0.152	0.016	0.365	0.282	0.053	5.3
0.577	0.199	0.095	0.177	0.020	0.368	0.306	0.102	3.0

[a]Standard uncertainties: $u(w)$ = 0.015, $u(P)$ = 1.5 kPa, and $u(T)$ = 0.05 K.

Table 4. Experimental LLE Data for the System Alcohol−Ester−DES (ChCl/Ur 1:2) at 293.15 K and at P = 101.3 kPa (Denotations[a] are the Same as those in Table 3)

organic phase			DES phase					
w_1	w_2	w_3	w_1	w_2	w_3	$\beta_{alcohol}$	β_{ester}	S
Ethanol (1)−Ethyl Propionate (2)−Choline Chloride (3)−Urea (4)								
0.000	0.999	0.000	0.000	0.007	0.521			
0.050	0.948	0.000	0.039	0.008	0.508	0.783	0.008	93.6
0.122	0.873	0.001	0.074	0.008	0.480	0.605	0.009	65.7
0.192	0.796	0.004	0.093	0.008	0.472	0.484	0.010	46.8
0.261	0.713	0.011	0.115	0.009	0.461	0.440	0.012	36.4
0.313	0.641	0.021	0.121	0.009	0.459	0.386	0.014	27.7
0.365	0.568	0.036	0.133	0.009	0.453	0.363	0.016	22.2
0.405	0.502	0.050	0.145	0.013	0.453	0.357	0.025	14.2
0.434	0.445	0.064	0.161	0.016	0.423	0.372	0.037	10.2
n-Propanol (1)−n-Propyl Propionate (2)−Choline Chloride (3)−Urea (4)								
0.000	1.000	0.000	0.000	0.003	0.540			
0.088	0.910	0.000	0.023	0.003	0.520	0.265	0.003	87.9
0.166	0.830	0.001	0.036	0.003	0.517	0.215	0.003	61.9
0.236	0.756	0.002	0.043	0.003	0.512	0.180	0.004	43.2
0.307	0.680	0.005	0.056	0.004	0.502	0.181	0.006	28.7
0.369	0.609	0.010	0.063	0.006	0.498	0.171	0.009	18.7
0.523	0.417	0.033	0.085	0.012	0.482	0.164	0.030	5.5

[a]Standard uncertainties: $u(w)$ = 0.015, $u(P)$ = 1.5 kPa, and $u(T)$ = 0.05 K.

n-n-propyl propionate in comparison with those including ethanol and ethyl propionate.

The correlation of the experimental LLE data was carried out using the Othmer−Tobias equation[42]

$$\log\left(\frac{1 - w_2^{I}}{w_2^{I}}\right) = a + b \log\left(\frac{1 - w_3^{II}}{w_3^{II}}\right) \tag{5}$$

the Hand equation[43]

$$\log\left(\frac{w_1^{I}}{w_2^{I}}\right) = a + b \log\left(\frac{w_1^{II}}{w_3^{II}}\right) \tag{6}$$

and the Bachman equation[44]

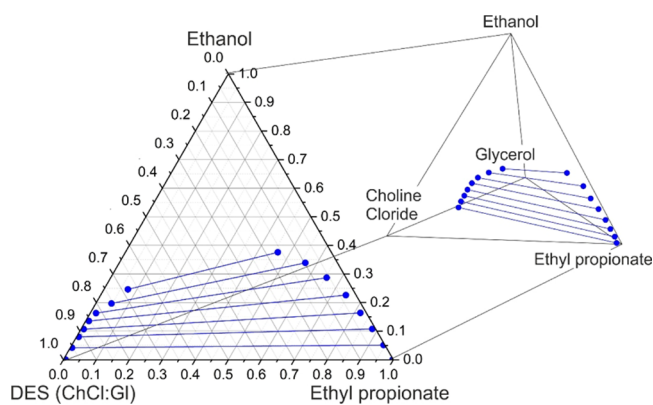$$w_2^{I} = a + b\left(\frac{w_2^{I}}{w_3^{II}}\right) \tag{7}$$

Figure 2. Schematic representation of tie lines in the composition tetrahedron in the ethanol−ethyl propionate−DES (ChCl/Gl) system at 293.15 K and their projections on the composition triangle.

where w_1^{I} is the mass fraction of alcohol and w_2^{I} is the mass fraction of ester in the organic phase, w_1^{II} is the mass fraction of alcohol and w_3^{II} is the mass fraction of the DES in the DES-rich phase, and a and b are adjustable parameters. Correlation results by the Othmer−Tobias, Hand, and Bachman equations (Table 5) show a linear dependence with a high correlation coefficient ($R^2 > 0.98$), which indicates a high internal consistency of the experimental LLE data measured in our work.

To estimate the efficiency of the alcohol extraction and check the ability of the model to describe LLE data, the distribution coefficient of the component (β_i) and the selectivity (S) were calculated, which are defined as follows

$$\beta_{\mathrm{alcohol}} = \frac{w_{\mathrm{alcohol}}^{\mathrm{II}}}{w_{\mathrm{alcohol}}^{\mathrm{I}}}, \qquad \beta_{\mathrm{ester}} = \frac{w_{\mathrm{ester}}^{\mathrm{II}}}{w_{\mathrm{ester}}^{\mathrm{I}}} \tag{8}$$

$$S = \left(\frac{w_{\mathrm{alcohol}}^{\mathrm{II}}}{w_{\mathrm{alcohol}}^{\mathrm{I}}}\right)\left(\frac{w_{\mathrm{ester}}^{\mathrm{I}}}{w_{\mathrm{ester}}^{\mathrm{II}}}\right) \tag{9}$$

The symbol w denotes the mass fraction of the component in phases I (organic phase) or II (DES phase). The values of selectivity and distribution coefficients are presented in Tables 3 and 4.

The selectivities for the systems studied in this work in comparison with the data for the systems with DES choline chloride/malonic acid (DES ChCl/Mal)[27] and several ionic liquids (ILs) are shown in Figures 4 and 5. As can be seen, the selectivity values for the systems with DES ChCl/Mal are much lower in comparison with those of DES ChCl/Gl and DES ChCl/Ur.

Additionally, as an example, Figures 4 and 5 illustrate data on the selectivity of alcohol extraction from azeotropic mixtures ethanol−n-hexane and n-propanol−n-hexane using some ILs.[45,46] In both cases (for both alcohols), a high selectivity value was found in the alcohol concentration range of less than 0.1. With an increase in alcohol concentration, the selectivity of ILs decreases significantly.

In the studied systems, in the case of DES ChCl/Ur, the slope of the curve is steeper than that of DES ChCl/Gl. This can be explained with the aid of the obtained distribution coefficients of alcohol and ester (Figure 6). These coefficients for alcohols do not significantly change in comparison with the distribution coefficients of esters. Thus, the change in the distribution coefficient of ethanol in the system with DES ChCl/Gl is higher than in the system with DES ChCl/Ur by an average of 30%. At the same time, the change in the distribution coefficient of the ester in the system with DES ChCl/Gl is higher than in the system with DES ChCl/Ur by an average of 2−2.5 times, despite the minimum absolute values.
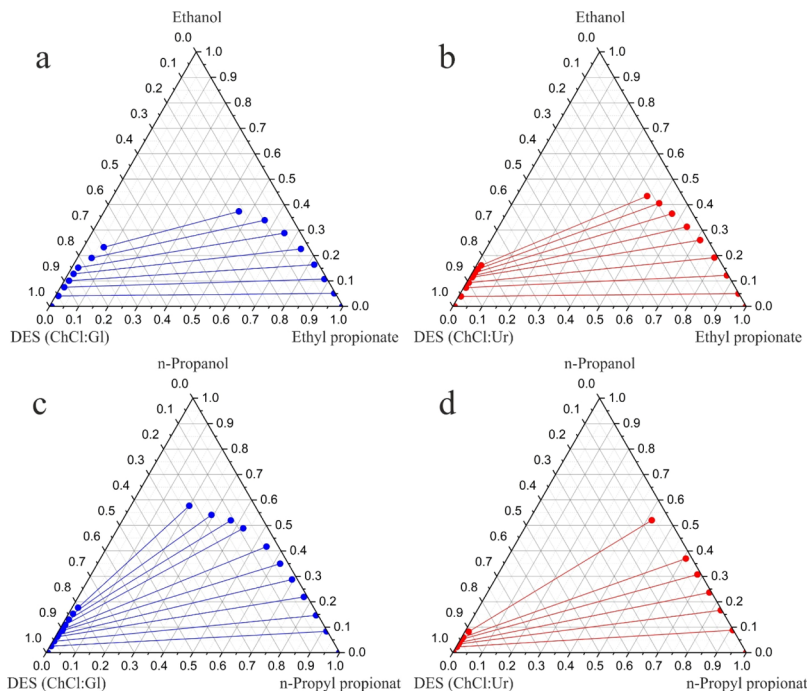

Figure 3. Experimental tie lines for the pseudoternary systems: (a) ethanol−ethyl propionate−DES (ChCl/Gl), (b) ethanol−ethyl propionate−DES (ChCl/Ur), (c) n-propanol−n-propyl propionate−DES (ChCl/Gl), and (d) n-propanol−n-propyl propionate−DES (ChCl/Ur) at 293.15 K and atmospheric pressure.

Table 5. Correlation Results Given by the Othmer−Tobias, Hand, and Bachman Equations for Describing LLE Data in the Pseudo Ternary Systems

	Othmer−Tobias			Hand			Bachman		
DES	a	b	R^2	a	b	R^2	a	b	R^2
				Ethanol−Ethyl Propionate−DES					
ChCl/Gl	0.6870	−0.4278	0.9900	0.7352	−0.4309	0.9931	1.4409	−0.5052	0.9955
ChCl/Ur	0.4734	−0.5991	0.9860	0.4454	−0.5083	0.9810	1.0274	−0.1329	0.9935
				n-Propanol−n-Propyl Propionate−DES					
ChCl/Gl	0.5311	−0.9024	0.9824	0.5874	−0.9067	0.9852	1.0210	−0.0674	0.9982
ChCl/Ur	0.5471	−1.0497	0.9957	0.5573	−1.0741	0.9964	1.0454	−0.0697	0.9997
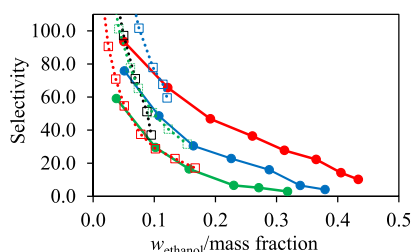
Figure 4. Selectivity values vs alcohol mass fraction at 293.15 K and 101.3 kPa for the pseudo-ternary systems: ethanol−ethyl propionate−DES [ChCl/Gl (●), ChCl/Ur (●), and ChCl/Mal (●)].[27] ethanol−n-hexane−IL ([Hmim][BF4] □[45] [MMIM][DMP] □[46] [EMIM]-[DEP] □[46] [BMIM][DBP] □[46]).
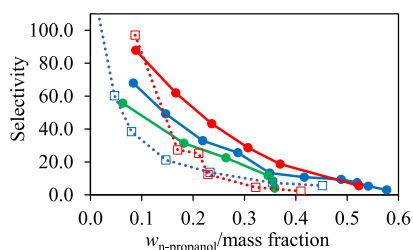

Figure 5. Selectivity values vs alcohol mass fraction at 293.15 K and 101.3 kPa for the pseudoternary systems: n-propanol−n-propyl propionate−DES. [ChCl/Gl (●), DES ChCl/Ur (●) and DES ChCl/Mal (●)].[27] n-propanol−n-hexane−IL [[Hmim][BF4] (□),[45] and [Hmim][OTf] (□).[45]

The dependence of the distribution coefficient of alcohol on its concentration in the organic phase in the systems under study has a local minimum. This is due to the slope of the tie lines, which allows us to suggest that the maximum alcohol concentration value does not refer to the plate point.

The use of 1H NMR and various 2D-NMR analyses (NOESY and HOESY) allowed us to study the nature of intermolecular interactions in DES ChCl/EG (1:4)[47] and DES

ChCl/Gl (1:3).[48] The NOESY spectrum of the pure DES showed the presence of strong interactions between the protons of the methyl and OH groups of ChCl with the protons of the OH groups of glycerol and ethylene glycol.

Wazeer et al.[47] have investigated the interaction of ethanol with DES ChCl/EG (1:4). On adding 40% wt ethanol, NOESY spectra showed strong interactions between OH groups of ethanol and OH groups of both ChCl and EG and weak interactions between methyl groups from ChCl and OH groups from ethylene glycol. Ethanol is suggested to form new hydrogen bonds between ChCl and EG, although the DES still exists under this condition. Addition of 60 % wt ethanol leads to interactions only between ethanol and ChCl and ethanol and EG, and no interactions were observed between the DES components.

The effect of water on intermolecular interactions in DES ChCl/Gl (1:3) was investigated by Hadj-Kali and co-authors.[48] They have obtained similar results that on adding 25% wt water, the interaction between methyl groups from ChCl and OH groups from glycerol weakened. Adding 50% wt water to the DES destroyed the interactions between the DES components.

These results indicate that DES ChCl/Gl (1:3) and DES ChCl/EG (1:4) retain their structures; however, interactions between DES components weaken.

The extraction alcohols from alcohol−ester systems using the DES suggests that the DES can disrupt the interaction of "alcohol−ester", forming a new and strong interaction "DES−alcohol". However, an increase in the alcohol concentration weakens the intermolecular interaction between the DES components themselves. It can be assumed that a small part of the choline chloride and HBD molecules interacting with alcohol and ester in the organic phase are not able to interact with each other, as a result of which the molar ratio of DES differs from the initial value. This is especially evident at low concentrations of alcohol in the organic phase. Increasing of the concentration of the DES components in the organic phase
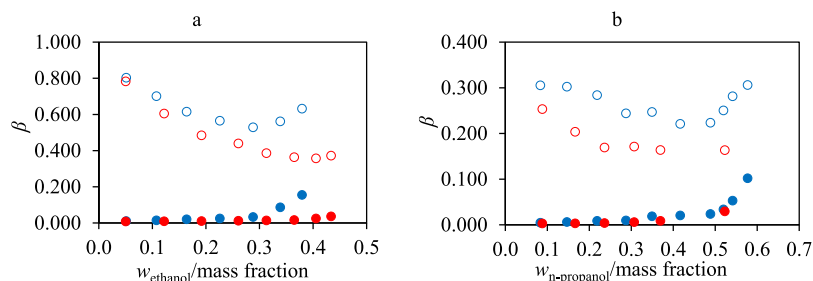

Figure 6. Distribution coefficient vs alcohol mass fraction in the systems: (a) ethanol−ethyl propionate−DES, (b) n-propanol−n-propyl propionate−DES. DES ChCl/Gl β_{ester} (●), $\beta_{alcohol}$ (○), and DES ChCl/Ur β_{ester} (●), and $\beta_{alcohol}$ (○).

results in that they are capable of interacting with each other again; finally, this leads to the initial molar ratio between parent compounds of DESs (1 mol ChCl and 2 mol glycerol or urea).

The molecular dynamic simulations on DESs based on choline chloride have been recently studied.[49] The obtained results have demonstrated that anion−HBD interactions play an important role and dominant interactions are depending on the anion type. It can be assumed that the extraction ability of DES ChCl/Gl is influenced by both the steric factor because of the presence of three OH groups and the intermolecular interactions between glycerol molecules. Perhaps, a more compact urea molecule provides a stronger H bond with the choline chloride molecule in DES ChCl/Ur.

■ CONCLUSIONS

The experimental data on LLE for the systems ethanol−ethyl propionate−DES (ChCl/Gl and ChCl/Ur) and n-propanol−n-propyl propionate−DES (ChCl/Gl and ChCl/Ur) were obtained at temperature 293.15 K and the atmospheric pressure. To quantify the concentrations, the ^{1}H NMR analytical method was used. The values of distribution coefficients and selectivity values were calculated on the basis of obtained data. A comparative analysis of the selectivity together with literature data on the systems including the DES formed by choline chloride and malonic acid was carried out. The DESs ChCl/Gl and ChCl/Ur allow us to achieve higher selectivity compared to the DES based on malonic acid. In the studied systems, the selectivity is characterized with the greatest value using DES ChCl/Ur. The correlation of experimental LLE data with the NRTL model showed their high consistency. The standard deviation did not exceed 0.83% for all systems studied.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.0c00659.

NMR spectra of the studied systems: organic and DES-rich phases (PDF)

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