Journal of chemical & engineering data

Article

Cite This: J. Chem. Eng. Data 2018, 63, 1877−1884

pubs.acs.org/jced

Study of Deep Eutectic Solvent on the Base Choline Chloride as Entrainer for the Separation Alcohol–Ester Systems

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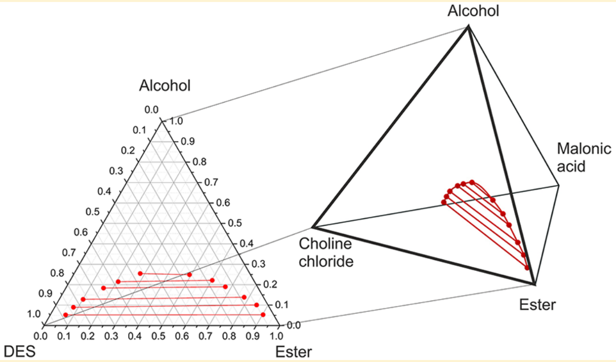
Supporting Information



ABSTRACT: Choline chloride-based deep eutectic solvent (DES) was tested for the separation of azeotropic mixtures of ethanol−ethyl acetate, *n*-propanol−*n*-propyl acetate and *n*-butanol−*n*-butyl acetate via liquid−liquid extraction. The mixture of choline chloride with malonic acid with a molar ratio of 1:1 was used. Extraction experiments were conducted with the ternary mixture ethanol−ethyl acetate−DES at temperatures 293.15, 303.15, and 313.15 K and with ternary mixtures *n*-propanol−*n*-propyl acetate−DES and *n*-butanol−*n*-butyl acetate−DES at 293.15, 303.15, 313.15, and 323.15 K. Liquid−liquid tie-lines for studied systems were determined. The extraction performance of DES was characterized with solute distribution coefficients and values of selectively respectively to alcohol. The influence of the alkyl chain length of the alcohol and ester on the phase equilibria was investigated. Experimental data were fitted using the nonrandom two liquids model.

■ INTRODUCTION

Distillation is a traditional method of separation, which, however is not fully applicable for mixtures of close boiling substances or azeotropes. Separation of azeotrope mixtures is a complicated task, which arises in various chemical processes in industry. The most suitable methods for the separation of such mixtures are the extraction and extractive distillation processes.[1,2] This technique includes the addition of a special agent for the removal of one of the components of an azeotrope by changing its fugacity.[3,4] The effectiveness of the extractive distillation strongly depends on the selection of appropriate extractive agent. The separation of an alcohol from an ester, which is complicated by formation of azeotrope between these substances, is a common problem in chemical technology connected with esterification reactions.[4,5]

Volatile organic solvents that are commonly used as conventional extractants in extractive distillation have a number of significant disadvantages, since they release volatile organic compounds and their use consumes a large amount of energy.[6] The need to reduce environmental pollution leads to increasing interest toward application of "green chemistry" technologies in the chemical industry. This leads to the growing of number of studies on the possibility of replacing the usual organic solvents with ionic liquids (ILs) because of their unique physic-chemical properties and low environmental impact. The low vapor pressure, incombustibility, thermal, and chemical stability, high solubility, and also high efficiency in changing the relative volatility of azeotropic mixtures make ILs a promising candidate for application in extractive distillation.[6−8]

The review of the application of ILs for separation of azeotrope mixtures can be found in the references.[3] Different ILs were reported as extractants for separation of alcohol−ester mixtures. In the ref 9 the authors present phase diagrams of ternary systems with 1-alkyl-3-methylimidazolium chloride and 1-allyl-3-methylimidazolium chloride and bromide. Liquid−liquid equilibrium (LLE) data are presented for mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim]BF4) or 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([C2OHmim]BF4) or 1-ethyl-2,3-dimethylimidazolium tetrafluoroborate ([edmim]BF4) or 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate ([C2OHdmim]BF4)−ethanol−ethyl acetate at 298.15 K in ref 10. In ref 11 LLE data for the ternary systems containing acidic IL−ethyl acetate−ethanol or acetic acid are reported, and the influence of the alkyl chain length on the LLE were studied at 313.2 K. In this work authors used several ILs: 1-methylimidazolium hydrogen sulfate ([hmim][HSO4]), 1-ethyl-3-methylimidazolium hydrogen sulfate ([emim][HSO4]), and 1-butyl-3-methylimidazolium hy-

Received: October 17, 2017
Accepted: April 25, 2018
Published: May 4, 2018

ACS Publications

DOI: 10.1021/acs.jced.7b00912

Table 1. Purities of the Chemicals

CASRN	substance	source	purity, mass fraction[a]	purification method	water content, mass fraction[a]	analysis method
141-78-6	ethyl acetate	Vecton	0.998	none	0	GC[b]
64-17-5	ethanol	Vecton	0.990	drying	<0.003	GC[b]
109-60-4	*n*-propyl acetate	Vecton	0.990	none	0	GC[b]
71-23-8	*n*-propanol	Vecton	0.990	none	0	GC[b]
123-86-4	*n*-butyl acetate	Vecton	0.990	none	0	GC[b]
71-36-3	*n*-butanol	Vecton	0.990	none	0	GC[b]
141-82-2	malonic acid	Vecton	0.980	drying	0	TGA[c]
67-48-1	choline chloride	AppliChem	0.980	drying	<0.005	TGA[c]

[a] Standard uncertainty is estimated to be 0.002 mass fraction. [b] Gas chromatography. [c] Thermogravimetric analysis.

drogen sulfate ([bmim][HSO_4]). In the ref 12 the data on LLE for ethyl acetate−ethanol−1-ethyl-3-methylimidazolium acetate at 288.15, 299.15, and 308.15 K is presented. The ternary LLE for four systems alcohol (*n*-propanol or *n*-butanol)−ester−1-ethyl-3-methylimidazolium hydrogen sulfate [emim][HSO_4] were studied at 313.2 K.[13]

At the same time, a number of recent studies demonstrate that ILs cannot be considered as completely "green" solvents.[14] In the last years, DES were proposed as green alternative to the ILs. DES have similar physicochemical properties but are composed from green and often biodegradable components.[15−17] Used as entrainers, DES allow effective and easy separation of purified substances from extragent due to extremely low vapor pressure. DES prepared on the base of choline chloride and glycerol were used for the separation of 1-phenylethanol and 1-phenyl-ethyl-acetate.[18] In ref 19 the authors have determined with the aid of gas−liquid chromatography the activity coefficients at infinite dilution in DES (choline chloride and glycerol in molar ratios of 1:1 and 1:2) for 23 solutes (aliphatic and aromatic hydrocarbons, alcohols, ketones, ethers, and esters). Unfortunately, in these studies the experiments on LLE were not performed although such data are necessary for the design of extraction processes.

The information on the phase equilibrium of various extraction agents allows one to make the right choice and optimize the separation and purification process. This was the motivation for performing an investigation of the LLE equilibrium of alcohol−ester−DES pseudoternary systems in our research. In this work we continue our systematic investigations of extractive properties of DES based on choline chloride that could be useful for the separation of various mixtures of industrial significance.[20] Now we present and discuss the data on LLE equilibrium for DES based on choline chloride and malonic acid in the separation of ethanol−ethyl acetate, *n*-propanol−*n*-propyl acetate and *n*-butanol−*n*-butyl acetate mixture at four temperatures: 293, 303, 313, and 323 K.

■ EXPERIMENTAL SECTION

Materials. Ethyl acetate (≥99 wt %), ethanol (≥99.0 wt %), *n*-propyl acetate (≥99 wt %), *n*-propanol (≥99.0 wt %), *n*-butyl acetate (≥99 wt %), *n*-butanol (≥99.0 wt %), and malonic acid (≥98 wt %) were purchased from Vecton and used without purification. Choline chloride ((2-hydroxyethyl)-trimethylammonium chloride) was obtained from AppliChem (≥98 wt %). The purity of organic liquids was determined by gas chromatography and is given in Table 1. Gas chromatograph "Chromatec Crystal 5000.2" (Russia) with thermal conductivity detector (TCD) and packed column Porapak R (1 m × 3 mm i.d.) was used. The moisture content and purity of the components of DES were analyzed with the simultaneous thermal analyzer Netzsch STA 449 F1 Jupiter equipped with the quadrupole mass-spectrometer Netzsch QMS 403C Aëolos.

Preparation of DES. Prior to use, water and other volatile substances were removed from the choline chloride by applying the reduced pressure (1 Pa) and heating up to 70 °C for 5 h. The DES were obtained via mixing HBA (choline chloride) and HBD (malonic acid) in the molar ratio equal to 1:1.[16] Components were weighed with the analytical balance Shinko VIBRA HT-120CE (Japan) with an accuracy of 0.001 g. Then the mixture of the solids was placed in the ultrasonic bath for 3−4 h with heating up to 40 °C. As a result, the clear liquid was prepared, which was cooled down and used in the LLE experiments.

LLE Determination. For investigation of LLE the ternary mixtures of known overall compositions were prepared in glass vessels (8 mL) and placed in the cell, which was thermostated with liquid thermostat to the desired temperature with standard uncertainty 0.05 K. The mixture was stirred for 3 h and then left undisturbed to allow phase separation. It was considered that the phase equilibrium was achieved after full separation of phases, when they became quite transparent. The composition of both phases was determined by analyzing the aliquots of the organic-rich and DES rich-phases using liquid state ^1H NMR spectroscopy with Bruker Avance III 500 MHz. To ensure the possibility of quantitative analysis of peak integrals of ^1H NMR spectra the following methodology was applied. The spin−lattice NMR relaxation times T1 for all chemical groups under consideration and for all investigated compounds were measured and were found to be in the range from 3 to 5 s. The relaxation delay applied during acquired NMR spectra (1 s) was high enough for quantitative analysis of peak integrals since the relaxation times have close values and the flip angle of pulse (30°) is relatively small. The error introduced by saturation was lower than 1%. Bruker TopSpin software was used for processing spectra. The phase correction was done manually. A polynomial baseline correction was done automatically. For quantitative analysis, the external standards were used: *n*-propanol in the case of ethanol−ethyl acetate and *n*-butanol−*n*-butyl acetate mixtures and *n*-butanol in the case of *n*-propanol−*n*-propyl acetate. Well separated peaks from protons in CH_2 and CH_3 groups of each compound in the mixture were used for integration. Chemical shifts of used peaks and their attribution to the components and chemical groups are listed in the Supporting Information Table S1.

The important problem that is connected with the use of DES is a control of the ratio of DES components during phase separation. In our experiments the maximal amount of ethanol in the feed mixture was 50 wt %. Accordingly, it could be expected that the maximum changes of the ratio of components in DES will occur for these mixtures. To check the stability of

DES composition we additionally analyzed the phases corresponding to this and close compositions. The results confirmed that the ratios of DES components in our experiments remain the same after phase separation. It is obvious that this conclusion will be valid for other polar substances, *n*-propanol and *n*-butanol. The detailed description of NMR analysis is given in the Supporting Information (Figure S1). The conclusion on the stability of DES corresponds to the results of the work[21] where the problem of preserving of DES composition during the LLE experiment was discussed. Using 2D NMR spectroscopy the authors also confirmed that the addition of lower than 60 wt % of ethanol does not lead to the disturbance of interactions between the components of the DES.

Moreover, previously we have measured the test mixtures with known composition with the help of NMR spectroscopy and gas chromatography, and the results were quantitatively the same for both methods (Table S2). This method was used previously in our works.[20,22] The standard uncertainty of NMR analysis averaged to be 0.005 mass fraction.

■ RESULTS AND DISCUSSION

LLE Data. Compositions of raffinate and extract at 293.15, 303.15, 313.15, and 323.15 K are presented for systems of DES with ethanol—ethyl acetate, *n*-propanol—*n*-propyl acetate and *n*-butanol—*n*-butyl acetate in Tables 2, 3, and 4, respectively. The systems with binary DES and two other components should be considered as quaternary systems. In our study we used the opportunity to simplify the representation and analysis of obtained data, and have presented the LLE for pseudoternary systems alcohol—ester—DES. In such an approach the LLE diagrams are formed by projections of quaternary data on the faces of composition tetrahedron (Figure 1).

Table 2. Experimental LLE Data for the Ternary System Ethanol (1)—Ethyl Acetate (2)—DES (3) at 293.15, 303.15, 313.15 K and at P = 101.3 kPa[a]

organic phase		DES phase			
w_1	w_2	w_1	w_2	$\beta_{ethanol}$	S
		293.15 K			
0.053	0.903	0.052	0.065	0.99	13.7
0.101	0.851	0.090	0.080	0.89	9.5
0.139	0.779	0.128	0.101	0.92	7.1
0.190	0.674	0.184	0.160	0.97	4.1
0.221	0.603	0.215	0.207	0.97	2.8
0.249	0.492	0.255	0.280	1.02	1.8
σ(NRTL) = 0.58%					
		303.15 K			
0.051	0.890	0.047	0.060	0.99	13.7
0.097	0.828	0.086	0.075	0.89	9.5
0.143	0.756	0.122	0.097	0.92	7.1
0.193	0.661	0.179	0.148	0.97	4.1
0.224	0.595	0.210	0.195	0.97	2.8
0.236	0.515	0.230	0.230	1.02	1.8
σ(NRTL) = 0.24%					
		313.15 K			
0.049	0.882	0.044	0.065	0.90	12.3
0.095	0.823	0.082	0.074	0.87	9.7
0.137	0.755	0.118	0.102	0.86	6.4
0.196	0.656	0.175	0.146	0.89	4.0
0.220	0.595	0.202	0.198	0.92	2.8
0.238	0.510	0.230	0.217	0.97	2.3
σ(NRTL) = 0.50%					

[a] Standard uncertainties $u(x)$ = 0.005, $u(P)$ = 1.5 kPa, $u(T)$ = 0.05 K, σ, standard deviation. Notation: w_1 and w_2 represent mass fractions of ethanol and ethyl acetate, respectively; β is a distribution coefficient, and S is a separation factor.

Table 3. Experimental LLE Data for the Ternary System *n*-Propanol (1)—*n*-Propyl Acetate (2)—DES (3) at 293.15, 303.15, 313.15, 323.15 K and at P = 101.3 kPa[a]

organic phase		DES phase			
w_1	w_2	w_1	w_2	$\beta_{n\text{-propanol}}$	S
		293.15 K			
0.084	0.884	0.034	0.035	0.41	10.4
0.155	0.789	0.063	0.037	0.41	8.6
0.220	0.713	0.088	0.045	0.40	6.3
0.262	0.648	0.115	0.056	0.44	5.1
0.282	0.606	0.134	0.068	0.48	4.2
0.319	0.526	0.156	0.078	0.49	3.3
σ(NRTL) = 0.58%					
		303.15 K			
0.074	0.884	0.030	0.041	0.40	8.6
0.145	0.802	0.050	0.039	0.35	7.1
0.209	0.723	0.077	0.042	0.37	6.3
0.251	0.660	0.102	0.052	0.41	5.1
0.267	0.625	0.114	0.060	0.43	4.4
0.310	0.545	0.146	0.069	0.47	3.7
σ(NRTL) = 0.53%					
		313.15 K			
0.071	0.894	0.024	0.033	0.34	9.0
0.137	0.816	0.049	0.037	0.36	7.9
0.195	0.738	0.073	0.041	0.38	6.8
0.238	0.682	0.092	0.046	0.38	5.7
0.255	0.655	0.103	0.051	0.41	5.2
0.290	0.579	0.131	0.062	0.45	4.2
σ(NRTL) = 0.47%					
		323.15 K			
0.066	0.884	0.021	0.035	0.32	8.0
0.124	0.816	0.044	0.037	0.35	7.7
0.182	0.743	0.066	0.043	0.36	6.3
0.221	0.691	0.084	0.044	0.38	6.0
0.243	0.665	0.095	0.051	0.39	5.1
0.273	0.590	0.123	0.059	0.45	4.5
σ(NRTL) = 0.71%					

[a] Standard uncertainties $u(w)$ = 0.005, $u(P)$ = 1.5 kPa, $u(T)$ = 0.05 K, σ, standard deviation. Notation: w_1 and w_2 represent mass fractions of *n*-propanol and *n*-propyl acetate, respectively, β is a distribution coefficient, and S is a separation factor.

On the basis of experimental results, the LLE tie-lines were plotted (see Figures 2, 3, and 4). The reliability of the experimental tie-line data was validated by the Othmer—Tobias[23] correlation and Hand equation.[24] Results were fitted with the second order equation, which is appropriate for describing the experimental trend. The value of correlation factor ($R^2 > 0.99$) indicates a high degree of consistency of the LLE data measured in our work.

The efficiency of extraction of solvents was characterized with the distribution coefficient of the component (β_i) and the selectivity (S), which are defined as follows:

$$\beta_i = \frac{w_i^{\mathrm{II}}}{w_i^{\mathrm{I}}} \tag{1}$$

Table 4. Experimental LLE Data for the Ternary System *n*-Butanol (1)−*n*-Butyl Acetate (2)−DES (3) at 293.15. 303.15. 313.15, 323.15 K and at P = 101.3 kPa[a]

organic phase		DES phase			
w_1	w_2	w_1	w_2	$\beta_{n\text{-butanol}}$	S
293.15 K					
0.121	0.879	0.029	0.029	0.24	7.3
0.191	0.767	0.044	0.029	0.23	6.0
0.255	0.682	0.053	0.028	0.21	5.1
0.310	0.615	0.064	0.033	0.21	3.8
0.351	0.559	0.069	0.034	0.20	3.2
0.374	0.526	0.076	0.039	0.20	2.8
σ(NRTL) = 0.61%					
303.15 K					
0.114	0.875	0.028	0.026	0.25	8.2
0.196	0.771	0.043	0.028	0.22	6.0
0.264	0.683	0.057	0.027	0.22	5.5
0.320	0.621	0.069	0.030	0.22	4.5
0.363	0.570	0.075	0.033	0.21	3.6
0.385	0.531	0.079	0.037	0.21	3.0
σ(NRTL) = 0.38%					
313.15 K					
0.126	0.873	0.027	0.024	0.21	7.7
0.205	0.767	0.042	0.025	0.21	6.3
0.266	0.678	0.048	0.027	0.18	4.5
0.323	0.616	0.055	0.032	0.17	3.3
0.358	0.569	0.059	0.035	0.17	2.7
0.391	0.538	0.066	0.038	0.17	2.4
σ(NRTL) = 0.48%					
323.15 K					
0.115	0.885	0.020	0.020	0.17	7.7
0.203	0.769	0.031	0.019	0.15	6.2
0.273	0.686	0.044	0.023	0.16	4.8
0.324	0.614	0.050	0.022	0.15	4.2
0.362	0.567	0.056	0.024	0.16	3.7
0.392	0.541	0.059	0.026	0.15	3.1
σ(NRTL) = 0.40%					

[a] Standard uncertainties $u(w)$ = 0.005, $u(P)$ = 1.5 kPa, $u(T)$ = 0.05 K, σ, standard deviation. Notation: w_1 and w_2 represent mass fractions of *n*-butanol and *n*-butyl acetate respectively, β is a distribution coefficient, and S is a separation factor.

$$S = \left(\frac{w_i^{\mathrm{I}}}{w_i^{\mathrm{II}}}\right)\left(\frac{w_j^{\mathrm{II}}}{w_j^{\mathrm{I}}}\right) \tag{2}$$

Symbol w denotes the mass fraction of component i in phases I (organic-rich) or II (DES-rich). The calculated distribution coefficients of esters and alcohols and selectivity respectively alcohol for investigated systems are listed in Table 2−4 and presented in Figure 5−8.

Figures 5−8 demonstrate that distribution coefficients decrease in the raw alcohols from ethanol to butanol. This can be attributed to the decreasing polarity of the −OH group in alcohol with increasing of length of alkyl radical. Additionally, it can be derived that the distribution coefficients slightly depend on the temperature. It can be proposed that the absence of temperature dependence is connected with very low enthalpy of transfer of alcohol and ester from organic to the DES phase. Accordingly, it means that the introduction of alcohol to the DES does not break the hydrogen bonds between malonic acid and choline chloride. It can be proposed that hydrogen bonds are formed between −OH groups of alcohol and the HO−CH_2−CH_2− part of choline chloride.

Literature data on the LLE of similar mixtures with ILs allow comparing the performance of DES-based choline chloride and malonic acid with ILs. Figure 9 shows the selectivity in the ethanol−ethyl acetate system at the temperature range 288.15−299.15 K. The selectivity of IL [emim]BF_4, [C_2OHmim]BF_4, [edmim]BF_4, and [C_2OHdmim]BF_4 studied in ref 10 at 298 K is in the range 1−3.5. Also, the figure shows the data for [emim][Ac] at temperatures 288.15 and 299.15 K studied in ref 12. The selectivity for [emim][Ac] demonstrates the fast decay with increasing ethanol fraction, and values in the range of ethanol concentrations from 0.05 to 0.25 are significantly below the selectivity of the DES investigated in this work.

Figure 10 shows the selectivity for the ethanol−ethyl acetate system at 313 K. Three ILs [emim][HSO4], [hmim][HSO_4], and [bmim][HSO_4] were studied in ref 11; two of them ([emim][HSO4] and [hmim][HSO_4]) show higher selectivity values than DES.

n-Propanol−*n*-propyl acetate and *n*-butanol−*n*-butyl acetate systems were studied only in ref 13. The liquid equilibrium liquid was studied for the [emim][HSO_4] at a temperature of 313.2 K. In both cases, both for extraction of *n*-propanol and for *n*-butanol extraction, higher results are shown (Figures 11,12) in comparison with those for DES.

The differences of separation performance between IL and the studied DES can be explained on the basis of the suggestion that the molecular cross-interaction of alcohols with ILs and DES in the liquid phase is connected with hydrogen bond formation between the OH group of the alcohol, cation, and anion of an extractant. In the case of DES, hydrogen bond formation between the OH group of the alcohol and choline chloride is concurrent with the H-bonding formation process between malonic acid and choline chloride. As a result, hydrogen bonding between alcohol and extractant is the key factor that influences alcohol−ester separation.

Modeling of LLE. The experimental results were correlated by nonrandom two-liquid (NRTL) model.[25] The NRTL equation for the activity coefficients in the solution of n components is used in the following form:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{m} x_j \tau_{ji} G_{ji}}{\sum_{i=1}^{m} x_i G_{ji}} + \sum_{J=1}^{m} \frac{x_j G_{ij}}{\sum_{i=1}^{m} x_i G_{ij}} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{i=1}^{m} x_i G_{ij}} \right) \tag{3}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} = \frac{\Delta g_{ji}}{RT}. \quad G_{ji} = \exp(-\alpha_{ji}\tau_{ji}). \quad (\alpha_{ji} = \alpha_{ij}) \tag{4}$$

where g_{ji} is the energy parameter. which characterizes interaction between components j and i; x denotes the mole fraction of component. The physical meaning of parameter α_{ji} is the nonrandomness of the system. The optimization tool for calculating NRTL parameters that minimize the composition values was the following objective function (OF):

$$\mathrm{OF} = \sum_{k=1}^{n} \sum_{i=1}^{n} [(x_{ik}^{\mathrm{exp}} - x_{ik}^{\mathrm{cal}})_{\mathrm{or}}^2 + (x_{ik}^{\mathrm{exp}} - x_{ik}^{\mathrm{cal}})_{\mathrm{d}}^2] \tag{5}$$

The parameters estimated by this procedure are presented in Table 5.

The standard deviation σ was determined using the following equation:

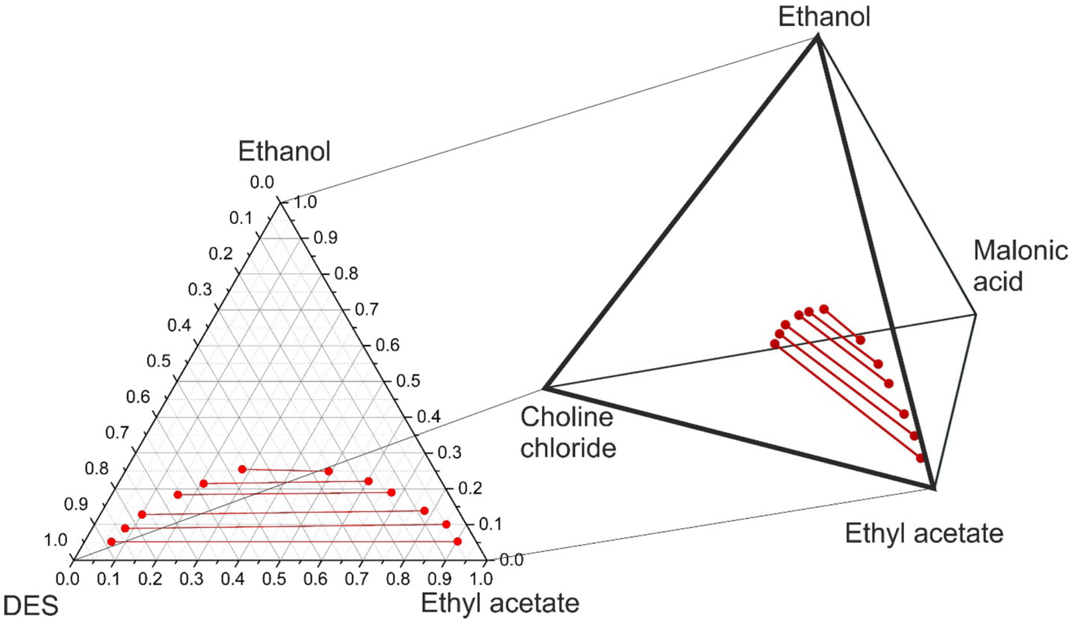


Figure 1. Schematic representation of the face of the concentration tetrahedron in the ethanol-ethyl acetate-choline chloride-malonic acid system at 293.15 K.

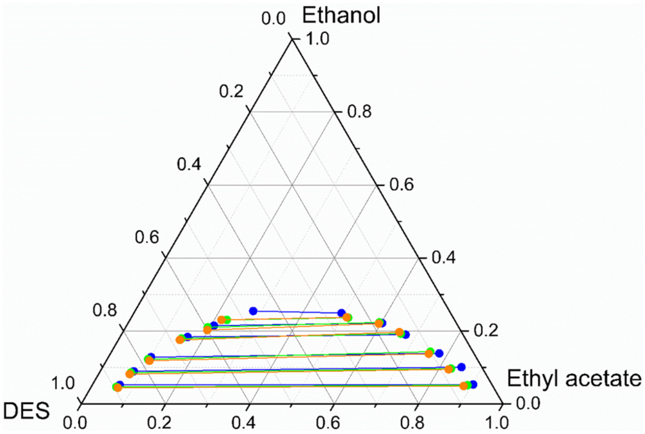


Figure 2. Tie-lines for the pseudoternary system ethyl acetate–ethanol–DES at 293.15 K (blue ●), 303.15 K (green ●), 313.15 K (yellow ●).

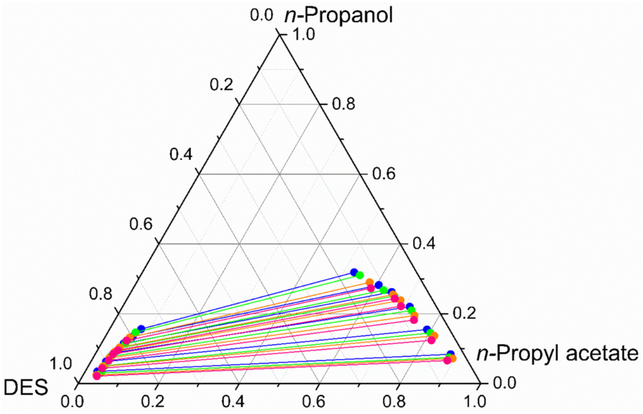


Figure 3. Tie-lines for the pseudoternary system *n*-propanol–*n*-propyl acetate–DES at 293.15 K (blue ●), 303.15 K (green ●), 313.15 K (yellow ●), 313.15 K (red ●).

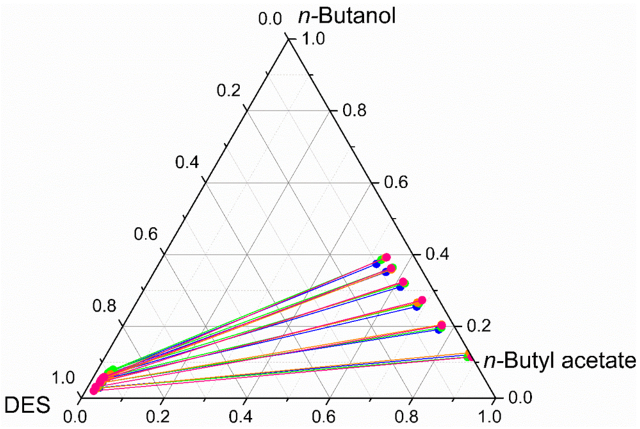


Figure 4. Tie-lines for the pseudoternary system *n*-butanol–*n*-butyl acetate–DES at 293.15 K (blue ●), 303.15 K (green ●), 313.15 K (yellow ●), 313.15 K (red ●).

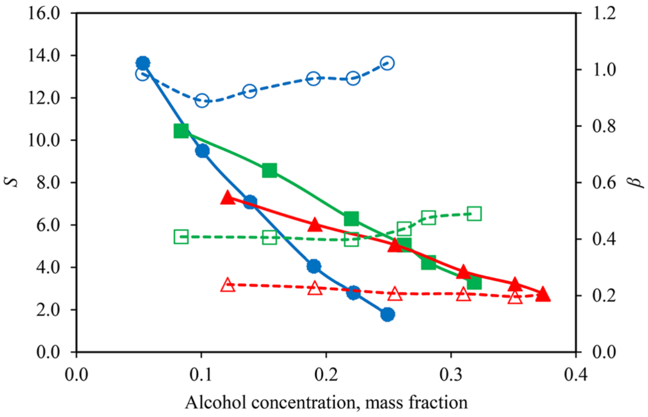


Figure 5. Dependence of selectivity (S) and distribution coefficient (β) on alcohol concentration in raffinate for LLE with DES at 293.15 K. Ethanol: S (blue ●), β (blue ○). *n*-Propanol: S (green ■), β (green □). *n*-Butanol: S (red ▲), β (red △).

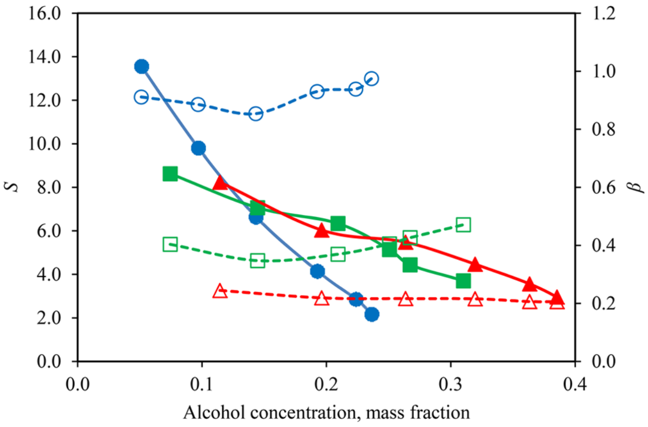


Figure 6. Dependence of selectivity (S) and distribution coefficient (β) on alcohol concentration in raffinate for LLE with DES at 303.15 K. Ethanol: S (blue ●), β (blue ○). n-Propanol: S (green ■), β (green □). n-Butanol: S (red ▲), β (red △).

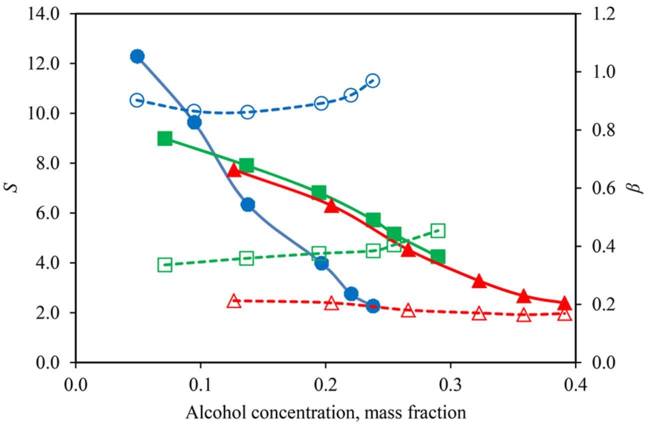


Figure 7. Dependence of selectivity (S) and distribution coefficient (β) on alcohol concentration in raffinate for LLE with DES at 313.15 K. Ethanol: S (blue ●), β (blue ○). n-Propanol: S (green ■), β (green □). n-Butanol: S (red ▲), β (red △).

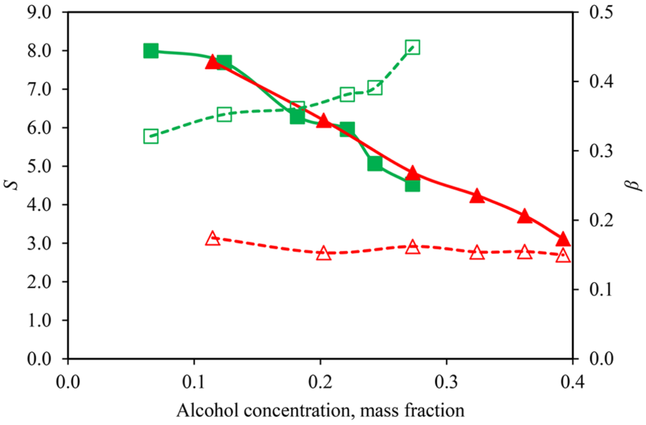


Figure 8. Dependence of selectivity (S) and distribution coefficient (β) on alcohol concentration in raffinate for LLE with DES at 323.15 K. n-Propanol: S (green ■), β (green □). n-Butanol: S (red ▲), β (red △).

$$\sigma(\%) = 100\sqrt{\frac{\sum_{k=1}^{n}\sum_{i=1}^{4}(x_{ik}^{\mathrm{exp}} - x_{ik}^{\mathrm{cal}})_{\mathrm{or}}^{2} + (x_{ik}^{\mathrm{exp}} - x_{ik}^{\mathrm{cal}})_{\mathrm{d}}^{2}}{2mn}} \quad (6)$$

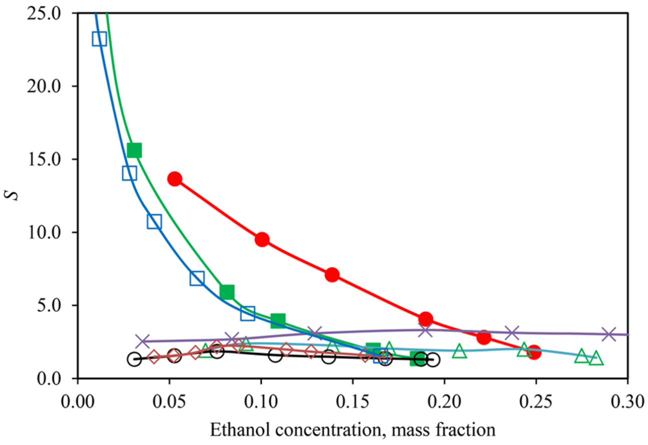


Figure 9. Dependence of selectivity of ethanol concentration in raffinate for LLE: DES this work (red ●), $[emim]BF_4$[10] (red ◇), $[C_2OHmim]BF_4$[10] (purple ×), $[edmim]BF_4$[10] (○), and $[C_2OHdmim]BF_4$[10] (green △) at 298.15 K; [emim][Ac][12] 288.15 K (green ■),[emim][Ac][12] 299.15 K (blue □).

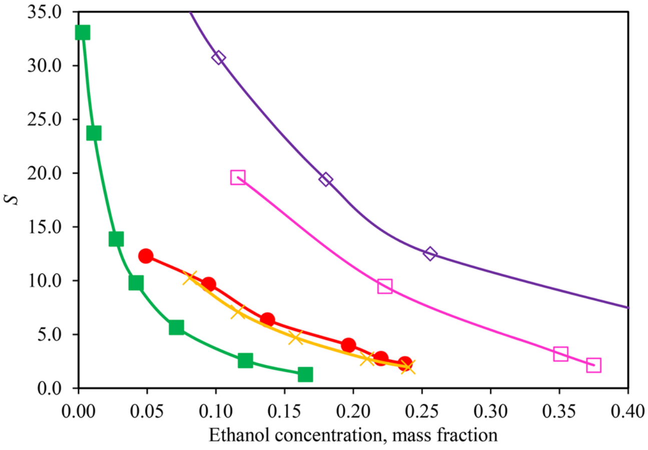


Figure 10. Dependence of selectivity on ethanol concentration in raffinate for LLE: DES this work (red ●), $[emim][HSO_4]$[11] (red □), $[hmim][HSO_4]$[11] (blue ◇), $[bmim][HSO_4]$[11] (yellow ×),at 313.15 K and [emim][Ac][12] (green ■) at 308.15 K.

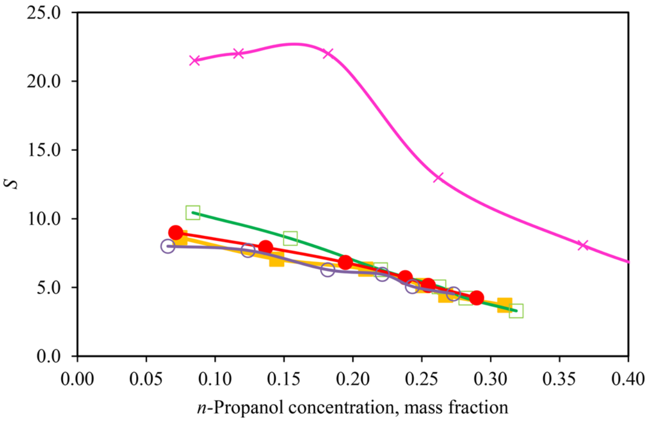


Figure 11. Dependence of selectivity on n-propanol concentration in raffinate for LLE with DES (293.15 (yellow ■), 303.15 (green □), 313.15 (red ●), 323.15 (purple ○)), $[emim][HSO_4]$ 313.15 K[13] (pink ×).

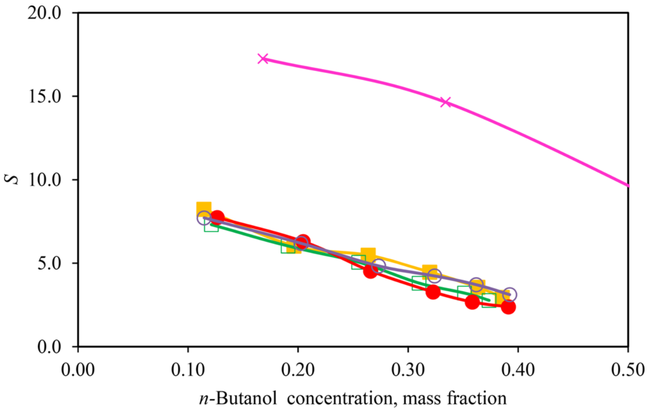


Figure 12. Dependence of selectivity on *n*-butanol concentration in raffinate for LLE with DES (293.15 (yellow ■), 303.15 (green □), 313.15 (red ●), 323.15 (purple ○)), [emim][HSO_4] 313.15 K[13] (pink ×).

Table 5. Energy Parameters g_{ji} Obtained by Simulation of Experimental Data on LLE Equilibrium with the NRTL Model

ij	Δg_{ji} J mol^{-1}	Δg_{ij} J mol^{-1}	α_{ji}
	Ethanol (1)−Ethyl Acetate (2)−DES (3)		
1−2	526	−6630	0.3
1−3	7037	−9145	0.3
2−3	6808	5773	0.3
	n-Propanol (1)−*n*-Propyl Acetate (2)−DES (3)		
1−2	9437	−7832	0.3
1−3	3081	−1887	0.3
2−3	30862	9820	0.3
	n-Butanol (1)−*n*-Butyl Acetate (2)−DES (3)		
1−2	−1242	−20894	0.3
1−3	2061	−11965	0.3
2−3	17381	11643	0.3

,where x indicates mole fraction of component, subscripts i and k indicate components, n is a number of tie-lines, m is a number of components; *or*, *d* represent the organic and DES phases, respectively.

Since the temperature dependence of the liquid−liquid equilibrium is not pronounced clearly, simulation was performed at the average temperature of the studied range of each system. Thus, optimization of the model for the ethyl acetate−ethanol−DES system was reported at 303 K. At the same time, the deviation for each of the temperatures did not exceed 0.6% (Table 2). The results of NRTL modeling are in good agreement with experimental data. The deviation for the systems *n*-propanol−*n*-propyl acetate−DES did not exceed 0.8% (Table 3) and that for the *n*-butanol−*n*-butyl acetate−DES did not exceed 0.7% (Table 4).

■ CONCLUSIONS

The deep eutectic solvent based on choline chloride and malonic acid was prepared. LLE data were obtained for the systems ethanol−ethyl acetate−DES, *n*-propanol−*n*-propyl acetate−DES and *n*-butanol−*n*-butyl acetate−DES at 293.15, 303.15, 313.15, and 323.15 K and atmospheric pressure. The influence of the alkyl chain on the alcohol and ester on the phase equilibria was studied. The results show that DES based on choline chloride and malonic acid is a very effective extracting agent for the separation of alcohol from ester. The values of the selectivity and the distribution coefficient show that DES can serve as an inexpensive and green alternative to some ILs for the separation of the alcohol−ester system. Experimental results were simulated according to the NRTL model and were in good agreement with the results of this model.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00912.

Determination of the mass fraction from NMR data; additional tables (PDF)

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Funding

This study was supported by the Russian Foundation for Basic Research (research Grant No. 16-33-60128 mol_a_dk).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to NIST ThermoData Engine group for the data on the properties of considered system. The experimental work was facilitated by the equipment of Magnetic Resonance Research Centre and Center of Thermal Analysis and Calorimetry at St. Petersburg State University.

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