

Separation of toluene from a toluene/n-heptane mixture using ethylene glycol containing deep eutectic solvents

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Abstract—Deep eutectic solvents (DESs) were synthesized and used to separate toluene from n-heptane. DES3 and DES4 were synthesized using choline chloride, urea, and ethylene glycol with a molar ratio of 1 : 2 : 1 and methyltriphenylphosphonium bromide and ethylene glycol with a 1 : 3 ratio, respectively. While dynamic viscosity of DES2 ranged from 575.9 to 73.8 over temperatures 293.2 to 323.2 K, respectively, that of DES3 ranged from 219.5 to 39.44 [mPa·s]. The viscosity of both DES3 and DES4 follows the Arrhenius equation with respect to temperature from 293.2 to 323.2 K. The liquid-liquid equilibrium (LLE) of the pseudoternary system of toluene, n-heptane, and DES3 were performed at temperature of 303.2 K at ambient pressure. Another LLE of the pseudoternary system of toluene, n-heptane, and DES4 were obtained over a temperature range of 298.2–313.2 K with a 10 K interval at atmospheric pressure. The experimental LLE data were correlated using the non-random two-liquid (NRTL) model. DESs were not detected in the raffinate phase, and as a result no further separation process for DES was necessary in the toluene separation process. The values of selectivity in the presence of DES 4 changed in a range from 24.4 to 147.5, however, those in the presence of DES3 from 4.1 to 18.7 at 313.2 K. The values of selectivity of toluene with DES applied in this study were far higher than those with other conventional solvents.

Keywords: Deep Eutectic Solvent, Viscosity, Distribution Coefficient, Liquid-liquid Equilibrium, Selectivity

INTRODUCTION

Extractive distillation and extraction are currently applied to separate aromatics from mixtures containing aliphatic hydrocarbons. Conventional solvents applied in those processes include sulfolane, N-formylmorpholine, and N-methylpyrrolidone, but they are toxic, volatile and/or flammable [1]. Furthermore, they dissolve in the raffinate phase when aromatics are extracted from aromatics/aliphatics mixtures, which makes the recovery of solvents difficult and energy consuming [2]. This has opened a door towards applying environmentally friendly solvents, such as ionic liquids. While ionic liquids have served as a promising solvent in aromatic recovery, the main drawback of ionic liquids is their higher viscosity compared to organic solvents used in aromatic extraction [3]. In addition, the extensive usage of ionic liquids was hindered by high cost due to a complicated synthesis scheme and toxicity [1].

Since Abbott et al. [4] reported synthesis of deep eutectic solvents (DESs), there have been many papers published in different areas [5–7]. Ionic liquids and DESs share many common traits, including low flammability, negligible vapor pressure, and task-specific solvents. DESs also much more environmentally friendly properties, including nontoxicity, and are inexpensive and easier to synthesize, because most hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs) come from nature [8].

Hosseini et al. [9] reported distribution coefficient of toluene and

selectivity in the presence of choline chloride based DESs. The highest distribution coefficient and selectivity was 0.355 and 47.373, respectively, at 303.2 K and 85 kPa. Lee and Park [10] applied choline chloride based DESs to separate toluene from a mixture containing n-heptane. They reported that the highest distribution coefficient and selectivity was 0.07 and 106.2, respectively, at 313.2 K and atmospheric pressure. Interestingly, DES was not detected in the raffinate phase and a negligible amount of n-heptane was found in the extract phase; thus, no further separation unit was required for DES and direct separation in the extract phase was possible [10]. It is noteworthy that the addition of third compound in DES synthesis results in a decrease in viscosity compared to the viscosity of DES synthesized by choline chloride as an HBA and urea as an HBD. Tetrabutylphosphonium bromide based DESs were applied to toluene separation by Kareem et al. [11] The highest distribution coefficient and selectivity was 0.901 and 15.381, respectively, at 313.2 K and 101.3 kPa. DES has not been found in raffinate phase after the experiments, which can be interpreted as the interaction between the HBA and HBD having trapped the ethylene glycol in the extract phase [11].

In this study, ethylene glycol-based DESs were synthesized for use as an extracting agent in toluene separation from mixtures containing n-heptane. Choline chloride and methyltriphenylphosphonium bromide were chosen as HBAs and two different DESs were used to determine toluene, n-heptane, and DES pseudoternary liquid-liquid equilibria (LLE) at 303.2 K. and ambient pressure. The effect of temperature on the distribution coefficient of toluene and selectivity in the presence of methyltriphenylphosphonium bromide-based DES was also investigated by varying the temperature from

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Table 1. Chemicals used in this study

Compound (CAS Number)	Supplier	Purity (wt%)
Toluene (108-88-3)	Sigma-Aldrich	≥99.5%
n-Heptane (142-82-5)	Sigma-Aldrich	≥99%
Methyltriphenylphosphonium bromide (1779-49-3)	Sigma-Aldrich	≥98%
Choline chloride (67-48-1)	Sigma-Aldrich	≥99%
Ethylene glycol (107-21-1)	Sigma-Aldrich	≥99%
Urea (57-13-6)	Sigma-Aldrich	≥99.5%
DMSO-d ₆ (2206-27-1)	Sigma-Aldrich	99.9 atom%D
Deutrochloroform (865-49-6)	Sigma-Aldrich	99.8 atom%D

293.2 to 313.2 K with an interval of 10 K. In addition, the viscosity of DESs was reported at several different temperatures. Both the LLE and viscosity experimental data were correlated with the non-random two-liquid (NRTL) model and the Arrhenius equation, respectively.

EXPERIMENTAL

1. Chemicals and Preparation of the DESs

Toluene, n-heptane, methyltriphenylphosphonium bromide, choline chloride, ethylene glycol, urea, deuterated chloroform (CDCl₃), and dimethyl sulfoxide-d₆ (DMSO-d₆) were purchased from Sigma-Aldrich, as shown in Table 1, and used without further purification. The DES was prepared by using HBA and HBD with a fixed mole ratio at 353.2 K for a few hours. An analytical balance (Shimadzu ATX 224, Japan) with an accuracy of $\pm 1 \times 10^{-1}$ mg was used to measure the mass of chemicals used. DES1 was prepared with choline chloride and urea with a mole ratio of 1 : 2. To investigate the effect of usage of additional HBDs on dynamic viscosity, glycol and ethylene glycol were added in DES1, resulting in DES2 and DES3, respectively. DES2 was synthesized using choline chloride, urea, and glycol with a mole ratio of 1 : 2 : 1 while DES3 was synthesized using choline chloride, urea, and ethylene glycol with the same mole ratio. DES4 was prepared with methyltriphenylphosphonium bromide and ethylene glycol at a mole ratio of 1 : 3. A Karl-Fisher titrator (Model V20, Mettler Toledo Inc.) was used to determine the water content in DESs, which was analyzed to be less than 0.5 wt%. Dimethyl sulfoxide-d₆ and CDCl₃ were used as solvents for DES3 and DES4 in NMR analysis, respectively.

2. Viscosity Measurement

The dynamic viscosity of the DESs prepared was measured using an Anton Paar Lovis 2000 with an accuracy of 0.5%. A steel ball of 1.5 mm diameter and 7.689 g/cm³ and a capillary Lovis of 1.8 mm diameter were used in the viscosity estimation from temperature of 293.2 K to 323.2 K with 5 K increment at ambient pressure. The uncertainty in the viscosity measurement was less than 0.7%.

3. Experimental Method

Specified amount of DES was measured using an analytical balance in a 50 cm³ beaker containing toluene and n-heptane to prepare several mixtures. They were added into a temperature controlled glass vessel under vigorous mixing for a few hours and held for several hours to obtain equilibrium. A ¹H NMR (JNM-LAMDA, 300 MHz, Jeol, Inc.) spectrometer was used to quantitatively analyze each compound in both phases, as reported elsewhere [5,10,

12]. To estimate the level of uncertainty, u_i of the mole fraction of each component (i) in each phase, we prepared vials of known composition of each compound five times and verified $u(x_i^I)=0.009$ and $u(x_i^{II})=0.016$, where superscripts I and II denote the raffinate phase and extract phase, respectively.

The LLE data were experimentally carried out at 293.2, 303.2 and 313.2 K and ambient pressure using the tie-line method. The presence of DESs in the raffinate phase was considered negligible because no DESs were detected. A two-methyl peak in heptane in both the raffinate and extract phases appearing at 0.9 ppm was used for quantitative analysis. Similarly, the methyl peak in toluene appearing at 2.4 was used to determine the amount of toluene in each phase. When DES3 was used in the LLE experiment, four protons in urea appearing at 5.8 were used for a quantitative analysis of the lower phase. When DES4 was used as an extractive agent, three protons in methyltriphenylphosphonium bromide appearing at 3.1 were used to measure the amount of DESs in the extract phase.

RESULTS AND DISCUSSION

1. Viscosity Measurement

It is well known that the effect of viscosity has a huge impact on mass transfer as well as the chemical reaction. Decreasing the vis-

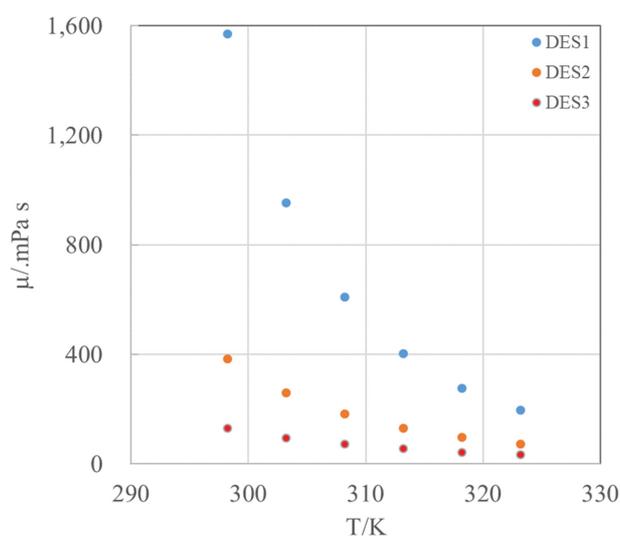


Fig. 1. Dynamic viscosities of DESs at different temperatures. Data for DES1 were from Ref. [14] and those for DES2 and DES3 from this study.

Table 2. Experimentally determined dynamic viscosity (μ [mPa·s]) of DESs at different temperature

DES	HBA	HBD1	HBD2	Molar ratio	T[K]							Ref.
					293.2	298.2	303.2	308.2	313.2	318.2	323.2	
DES1	Choline chloride	Urea	-	1 : 2	-	1571	953.7	608.4	403.2	277.2	195.9	14
DES2	Choline chloride	Urea	Glycerol	1 : 2 : 1	575.9	384.8	261.0	182.5	131.8	97.0	73.8	This study
DES3	Choline chloride	Urea	Ethylene glycol	1 : 2 : 1	219.5	155.4	113.08	81.14	64.2	50.02	39.44	This study
DES4	MTPPBr	Ethylene glycol	-	1 : 3	149.85	110.52	82.47	66.19	53.79	41.94	36.12	13

cosity of DES significantly improved carbon dioxide absorption capacity [13]. For example, Lee and Park [10] reported that the usage of additional chemicals in DES synthesis resulted not only in a decrease of the viscosity but also the time to reach phase equilibrium as well as the degree of mixing. Unfortunately, they did not report viscosity data quantitatively. Therefore, in this study the experimental data of the viscosity of a DES in the presence of an additional chemical that served as a thinner to the viscosity were included. Specifically, DES2 and DES3 were synthesized in the presence of glycerol and ethylene glycol, respectively, on the basis of DES1 (choline chloride and urea with a mole ratio of 1 : 3). While the viscosity for DES1 at 298.2 K was 1571.0, that for DES2 and DES3 was 384.8 and 155.4 mPa·s, respectively. The viscosity was dramatically decreased in the presence of the thinner, glycerol and ethylene glycol, as shown in Fig. 1 and Table 2.

The temperature dependency on viscosity is described by the Arrhenius equation, shown in Eq. (1).

$$\mu = \mu_0 e^{\frac{E_\mu}{RT}} \quad (1)$$

where μ [mPa·s] is the dynamic viscosity, μ_0 is the pre-exponential constant, E_μ [kJ/mol] is the activation energy, R is the gas constant, and T is the absolute temperature. Table 3 shows that both DES2 and DES3 follow the Arrhenius equation well.

2. Experimental LLE Data

The LLE experimental data of toluene (1), n-heptane (2), and DES3 (3) pseudoternary system were measured at ambient pressure and 303.2 K. LLE data for the pseudoternary system of toluene (1), n-heptane (2), and DES4 (3) were also obtained, at 293.2, 303.2, and 313.2 K, to investigate the effect of temperature on distribution coefficient (D_i) and selectivity (S) of toluene.

Table 3. Parameters in the Arrhenius equation for temperature dependence of viscosity

DES	μ_0 [mPa·s]	E_μ [kJ/mol]	R^2
DES2	1.26756E-07	54.121	0.9985
DES3	2.01679E-06	44.618	0.9984

The distribution coefficient for each component i and the selectivity of toluene were defined by Eqs. (2) and (3), respectively.

$$D_i = \frac{x_i^{II}}{x_i^I} \quad (2)$$

$$S = \frac{D_1}{D_2} \quad (3)$$

where x_i^I and x_i^{II} are the mole fraction of each component i in the raffinate phase (I) and that in the extract phase (II), respectively, and the subscripts 1 and 2 refer to toluene and n-heptane, respectively.

Table 4 shows the experimentally obtained mole fractions of each phase in the pseudoternary system of toluene, n-heptane, and DES3. The values of D_1 ranged from 0.15 to 0.31 and those of S ranged from 4.1 to 18.7. While the values of D_1 were similar to those with sulfolane, those of S were slightly lower than those with sulfolane [2]. When DES3 was replaced by DES4, a significant change of the values of S was observed. Specifically, the value of S in the presence of DES4 was 147.5, whereas that in the presence of DES3 was 18.7 at 303.2 K. One possible reason for this intriguing result might be that the interaction between toluene and methyltriphenylphosphonium bromide in DES4 is much higher than that between methyltriphenylphosphonium bromide and n-heptane, resulting in a lower

Table 4. Experimental data of the toluene (1)+n-heptane (2)+DES3 (3) at 303.2 K and atmospheric pressure, toluene distribution coefficient (D_1) and selectivity (S)

T/K	Raffinate phase		Extract phase				
	x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_3^{II}	D_1	S
303.2	0.327	0.673	0.050	0.006	0.945	0.15	18.7
	0.075	0.925	0.015	0.010	0.975	0.20	17.5
	0.166	0.834	0.033	0.016	0.952	0.20	10.3
	0.632	0.368	0.141	0.010	0.849	0.22	7.9
	0.811	0.189	0.212	0.008	0.780	0.26	5.9
	0.716	0.284	0.181	0.017	0.802	0.25	4.2
	0.921	0.080	0.288	0.006	0.706	0.31	4.1

The standard uncertainties are $u(x_1^I)=0.009$ and $u(x_1^{II})=0.016$. The relative standard uncertainty of the distribution ratio is $u(D_1)=0.2$. The relative standard uncertainty of the distribution ratio is $u(S)=0.6$.

Table 5. Experimental data of the toluene (1)+n-heptane (2)+DES 4 (3) at three temperatures and atmospheric pressure, toluene distribution coefficient (D_1) and selectivity (S)

T/K	Raffinate phase		Extract phase			D_1	S
	x_1^I	x_2^I	x_1^{II}	x_2^{II}	x_3^{II}		
293.2	0.288	0.712	0.103	0.001	0.896	0.36	254.6
	0.441	0.559	0.125	0.001	0.874	0.28	158.4
	0.763	0.237	0.254	0.003	0.743	0.33	26.3
	0.544	0.456	0.165	0.006	0.829	0.30	23.1
	0.652	0.348	0.210	0.006	0.784	0.32	18.7
	0.882	0.118	0.274	0.007	0.719	0.31	5.2
303.2	0.544	0.456	0.176	0.001	0.823	0.32	147.5
	0.654	0.346	0.231	0.001	0.769	0.35	122.2
	0.764	0.236	0.243	0.001	0.756	0.32	75.1
	0.212	0.788	0.073	0.004	0.923	0.34	67.8
	0.840	0.160	0.275	0.002	0.723	0.33	26.2
	0.141	0.859	0.036	0.009	0.955	0.26	24.4
313.2	0.150	0.850	0.058	0.002	0.940	0.39	164.3
	0.291	0.709	0.108	0.002	0.890	0.37	131.6
	0.217	0.783	0.085	0.003	0.912	0.39	102.2
	0.441	0.559	0.150	0.003	0.847	0.34	63.4
	0.360	0.640	0.140	0.004	0.856	0.39	62.2
	0.657	0.343	0.231	0.004	0.765	0.35	30.1
	0.766	0.234	0.247	0.005	0.748	0.32	15.1
	0.885	0.115	0.294	0.006	0.700	0.33	6.4

The standard uncertainties are $u(x_i^I)=0.009$ and $u(x_i^{II})=0.016$. The relative standard uncertainty of the distribution ratio is $u(D_1)=0.2$. The relative standard uncertainty of the distribution ratio is $u(S)=0.6$.

Table 6. Comparison of toluene distribution ratio (D_1) and selectivity (S) for the toluene (1) in the presence of different solvents

Solvent	T	D_1	S	Refs.
Sulfolane	313.15	0.41-0.54	2.1-43.8	2
[TEMA][MeSO ₄]	298.15	0.29-0.665	8.4-43.4	12
[C ₆ (MIM) ₂][(HSO ₄) ₂]	303.15	0.303-0.800	6.466-91.797	15
[EtIM][NTf ₂]	303.2	0.61-0.70	5.1-26.7	16
MTPPBr : EG (1 : 4)	308.15	0.23-0.29	12.60-∞	17
MTPPBr : Gly (1 : 4)	308.15	0.14-0.22	1.2-∞	17
DES2	313.2	0.01-0.07	0.6-106.2	10
DES3	303.2	0.15-0.31	4.1-18.7	This study
DES4	303.2	0.26-0.34	24.4-147.5	This study

[TEMA][MeSO₄]: Tris(2-hydroxyethyl)methylammonium methylsulfate, [C₆(MIM)₂][(HSO₄)₂]: bis-(3-methyl-1-imidazole)-hexylene hydrogen sulphate, [EtIM][NTf₂]: ethylimidazolium bis(trifluoromethylsulfonyl)imide

value of D_2 in the presence of DES4. However, the effect of temperature on both D_1 and S appears to be insignificant because there were no significant changes of those values by varying the temperature from 293.2 to 313.2 K, as shown in Table 5. The effect of temperature on selectivity is insignificant.

As shown in Table 6, in general, the values of D_1 were similar for almost all solvents applied within the range of about 1.2 with a few outliers. However, the values of S in the presence of DESs were higher than those in the presence of ionic liquids. For example, while the highest value of S in tris(2-hydroxyethyl)methylam-

monium methylsulfate was 43.4, that in DES4 was 147.5. Although the changes of cations as well as anions in the ionic liquid resulted in some degree of changes on selectivity, the observed changes were almost negligible. However, the changes on the HBA in DESs appear to be significant because the values of S in the methyltriphenylphosphonium bromide based DES were higher than those in the choline chloride based DES. One possible reason for this would be that the interaction between toluene and phosphonium in molecular level is higher than that of toluene and choline chloride. Furthermore, the choice of HBD appears to be playing a role in de-

termining the selectivity. Naik et al. [17] reported that an ethylene glycol based DES yielded higher values of selectivity than a glycerol based DES. This may be attributed to the difference in the viscosity.

The Otherman-Tobias correlation, as shown in Eq. (4), was used to carry out a consistency test of the experimental LLE data.

$$\ln\left(\frac{1-w_2^I}{w_2^I}\right) = a + b \ln\left(\frac{1-w_3^{II}}{w_3^{II}}\right) \quad (4)$$

where a and b are the fitting parameters and w_2^I and w_3^{II} are the weight fraction of n-heptane in the raffinate phase and that of DESs in the extract phase, respectively. Table 7 shows the parameters of the Otherman-Tobias correlations.

3. Data Correlation

The liquid-liquid equilibrium for a pseudoternary system is defined by Eq. (5):

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (5)$$

where γ_i is the activity coefficient of each component in the pseudoternary system. The NRTL equation [18] was used to correlate the experimentally measured LLE data. The activity coefficient for

each component in the pseudoternary system for the NRTL model is given by Eq. (6).

$$\ln \gamma_i = \frac{\sum_{j=1}^n x_j \tau_{ij} G_{ij}}{\sum_{k=1}^n G_{ki} x_k} + \sum_{j=1}^n \frac{x_j G_{ij}}{\sum_{k=1}^n G_{ki} x_k} \left(\tau_{ij} - \frac{\sum_{m=1}^n x_m \tau_{mj} G_{mj}}{\sum_{k=1}^n G_{ki} x_k} \right) \quad (6)$$

where,

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

$$\tau_{ij} = \frac{g_{ij} - g_{ji}}{RT} \quad (8)$$

In this study α was set equal to 0.2. The binary interaction parameters for the NRTL correlation were carried out by minimizing the objective function (O.F.) shown in Eq. (9).

$$\text{O.F.} = \min \sum_{i=1}^c \sum_{j=1}^t \sum_{k=1}^p [(x_{ij}^{\text{exp}} - x_{ij}^{\text{cal}})^2]^{1/k} \quad (9)$$

where $i, j, k, c, t, p, \text{exp}$, and cal are each component, tie-line, phase, number of chemical components, number of tie-lines, number of phases, and experimental and calculated equilibrium data, respectively. The root mean square deviation (RMSD) was defined to test the accuracy of the correlation and is defined in Eq. (10).

Table 7. Parameters of the Otherman-Tobias correlation and the regression coefficients

System	Temperature	a	b	R ²
Toluene+n-heptane+DES3	303.2 K	0.8474	0.9602	0.9802
Toluene+n-heptane+DES4	293.2 K	-3.0217	0.4519	0.9401
Toluene+n-heptane+DES4	303.2 K	-3.0636	0.6035	0.9528
Toluene+n-heptane+DES4	313.2 K	-2.9828	0.4962	0.9510

Table 8. NRTL binary interaction parameters and RMSD for toluene (1), n-heptane (2), and DES3 (3) or DES4 (3) system

Toluene (1)+n-heptane (2)+DES3 (3) at T=303.2 K				
i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)	α	RMSD
1-2	5,248.8	-3,041.9	0.2	0.079
1-3	3,658.1	3,159.3		
2-3	13,997.2	71,221.6		
Toluene (1)+n-heptane (2)+DES4 (3) at T=293.2 K				
i-j	Dg_{ij} (J/mol)	Dg_{ji} (J/mol)	α	RMSD
1-2	17,587.4	6,149.9	0.2	0.032
1-3	52,625.9	14,068.6		
2-3	194,197.7	93,330.4		
Toluene (1)+n-heptane (2)+DES4 (3) at T=303.2 K				
i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)	α	RMSD
1-2	14,695.6	-56.9	0.2	0.077
1-3	14,405.6	55,148.2		
2-3	95,618.6	20,948.6		
Toluene (1)+n-heptane (2)+DES4 (3) at T=313.2 K				
i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)	α	RMSD
1-2	14,716.4	22,931.1	0.2	0.049
1-3	7,786.6	35,212.9		
2-3	58,827.6	85,323.7		

$$\text{RMSD} = \sqrt{\frac{\sum_{i=1}^c \sum_{j=1}^t \sum_{k=1}^2 [(x_{ij}^{\text{exp}} - x_{ij}^{\text{cal}})^2]^k}{6t}} \quad (10)$$

The values of RMSD are small enough to confirm that a good experimental correlation with NRTL was obtained, as shown in Table 8.

CONCLUSIONS

Two DESs were synthesized to separate toluene from n-heptane. DES3 was synthesized using choline chloride, urea, and ethylene glycol with a mole ratio of 1 : 2 : 1. The reason ethylene glycol was added to the choline chloride and urea based DES (DES1) was to decrease the viscosity of the DES used for aromatic compound separation. DES4 was prepared using methyltriphenylphosphonium bromide and ethylene glycol with a mole ratio of 1 : 3. Both DES2 and DES3 behave like the Arrhenius equation with respect to temperature ranging from 293.2 to 323.2 K. The addition of ethylene glycol to decrease the viscosity of DES1 was much more significant compared to the addition of glycerol. This viscosity difference between ethylene glycol added DES (DES3) and glycol added DES (DES2) may originate from the viscosity of pristine chemicals of ethylene glycol and glycerol. The addition of lower viscosity value chemicals would thus serve as a better thinner than higher viscosity compounds.

Liquid-liquid equilibrium data for toluene, n-heptane, and DES3 were experimentally determined at 303.2 K and ambient pressure. The values of the distribution coefficient of toluene with DES3 were similar to those with sulfolane as a solvent. Additional pseudoternary data for toluene, n-heptane, and DES4 were carried out at three temperatures, 293.2, 303.2, and 313.2 K and atmospheric pressure. The effect of temperature on the distribution coefficient and the selectivity of toluene was insignificant. However, the usage of DES3 and DES4 appears to be quite promising in terms of cost saving in toluene separation because no DESs were detected in the raffinate phase under all conditions, and as a result no further separation unit was required.

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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

Separation of toluene from a toluene/n-heptane mixture using ethylene glycol containing deep eutectic solvents

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Table S1. The melting point of DESs synthesized

DES	HBA	HBD1	HBD2	Molar ratio	T _m [K]	Ref.
DES1	Choline chloride	Urea	-	1 : 2	285	S1
DES2	Choline chloride	Urea	Glycerol	1 : 2 : 1	<273 ^a	This study
DES3	Choline chloride	Urea	Ethylene glycol	1 : 2 : 1	<273 ^a	This study
DES4	Methyltriphenylphosphonium bromide	Ethylene glycol	-	1 : 3	226.75	S2

^aThe melting point of the DES are below 273 K.



Fig. S1. Pure DESs synthesized at room temperature.

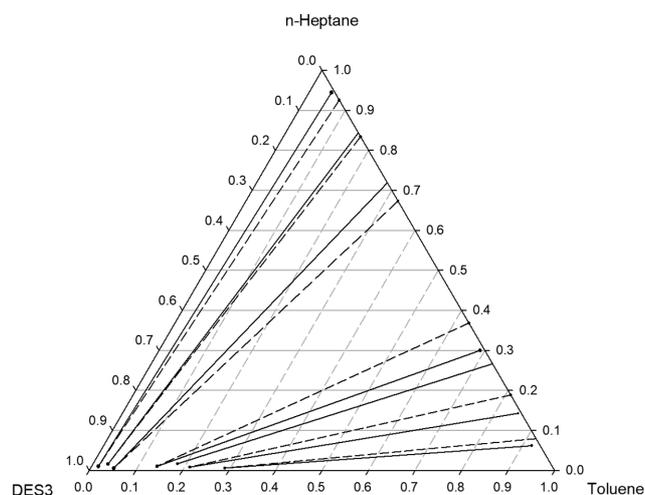


Fig. S2. Pseudoternary diagram for toluene, n-heptane, and DES3 at 303.2 K. Dashed lines represent experimental tie-lines and solid lines represent correlated data.

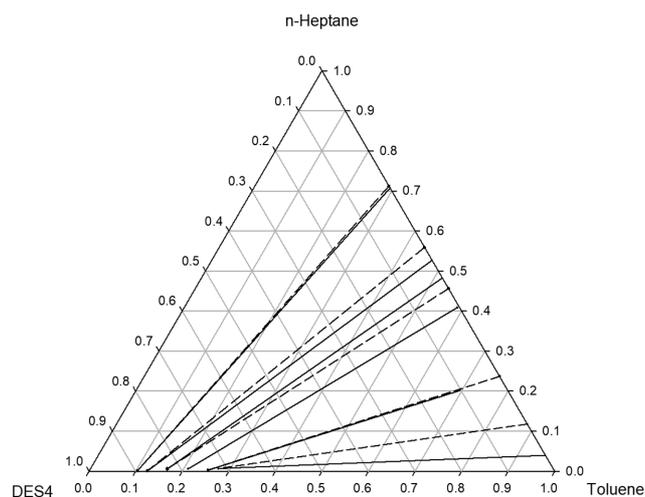


Fig. S3. Pseudoternary diagram for toluene, n-heptane, and DES4 at 293.2 K. Dashed lines represent experimental tie-lines and solid lines represent correlated data.

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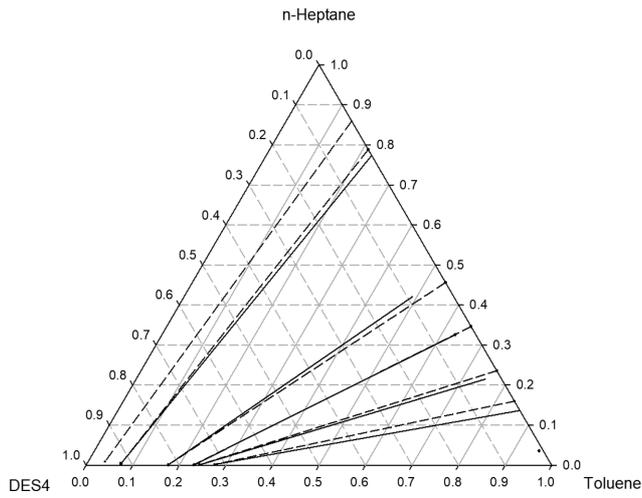


Fig. S4. Pseudoternary diagram for toluene, n-heptane, and DES4 at 303.2 K. Dashed lines represent experimental tie-lines and solid lines represent correlated data.

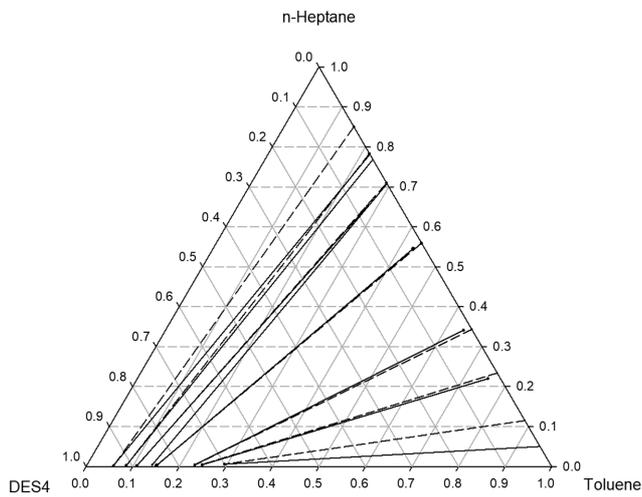


Fig. S5. Pseudoternary diagram for toluene, n-heptane, and DES4 at 313.2 K. Dashed lines represent experimental tie-lines and solid lines represent correlated data.