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Usage of a deep eutectic solvent based on three compounds for toluene separation

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Abstract−The separation of toluene from a mixture composed of toluene and heptane was carried out in the presence of a deep eutectic solvent (DES). The DES used in this study was synthesized using choline chloride, urea and glycerol with mole ratio of 1 : 2 : 1. The liquid-liquid equilibria (LLE) of the ternary system of toluene, heptane, and DES were determined at atmospheric pressure and three temperatures of 298.2-313.2 K with an interval of 10 K. The distribution coefficients and selectivities of toluene were reported. Only a small amount of heptane was detected in the extract phase, resulting in high value of selectivity. The experimental LLE data were reasonably well correlated using non-random two-liquid (NRTL) model. The *ab initio* results revealed that the interactions between the DES and toluene are stronger than those between DES and heptane, which may be a reasonable explanation for the high value of selectivity in this ternary system.

Keywords: Deep Eutectic Solvent, Ab Initio Calculation, Liquid-liquid Equilibrium, Selectivity, Interaction Energy

INTRODUCTION

In addition to use as a solvent, toluene has served as a raw chemical for trinitrotoluene and the production of other widely used industrial chemicals. The market value of toluene is high, with its sale generating about $24 billion in 2013 [1]. Solvent extraction has been the primary toluene separation process among many other processes, including azeotropic distillation and extractive distillation. However, there is still need for a suitable separation technology for mixture containing less than 20 wt% toluene [2].

In general, sulfolane has been commonly used as an extractive solvent in the aforementioned processes. While providing several advantages over other solvents, it is volatile and highly soluble in raffinate phase, causing solvent loss and the need for an additional separation unit. Numerous studies on toluene extraction in the presence of an ionic liquid (IL) have been reported. ILs have many outstanding physical properties, such as almost negligible vapor pressure and adjustable solvating properties by varying either the anions or cations. Further, a combination of different cations and anions may yield an optimum physical property to the application area. However, high cost due to a complicated synthesis and purification requirements [3] and potential environmental toxicity and poor biodegradability [4] have motivated a search for alternative green solvents with the desired characteristics of low cost and environmental friendliness, including deep eutectic solvents (DESs).

Since the term “DES” was coined by Abbott et al. [5], many different types of DESs [6] have been synthesized using one or more hydrogen bond acceptors (HBAs) and one or more hydrogen bond donors (HBDs). They have been applied in many areas, including extraction [7], reaction media [8], and nanotechnology [9]. On the basis of superior physical properties, such as, low or negligible vapor pressure, non-flammability, and a wide liquid range, DESs are attractive for toluene separation from heptane containing mixtures. In addition, almost all DES raw chemicals come from nature, and accordingly they are of reasonable cost and environmentally friendly. The most commonly and widely utilized DES is synthesized from choline chloride and urea.

Many researchers have applied DESs for separating aromatics from aliphatic containing hydrocarbon mixtures [10-12]. However, the rationale behind the interesting experimental results has been obscure. Although a conductor-like screening model for real solvents (COSMO-RS) appeared to be a successful tool to predict extraction performance, the results were limited in qualitative terms [3]. Meanwhile, the interaction between DESs and aromatic compound at a molecular level may yield information [13] as to why certain compounds have better affinity to toluene in a quantitative manner.

In this study, we chose heptane and toluene as a model compound as aliphatic and aromatic compounds. A DES synthesized from choline chloride, urea, and glycerol with a mole ratio of 1 : 2 : 1 was used to extract toluene at three different temperatures of 293.2, 303.2 and 313.2 K to investigate the effect of both additional HBD (glycerol) in the DES and temperature. The experimental data were correlated with the non-random two-liquid (NRTL) model. Further, the *ab initio* method was applied to illuminate the primary reason why the DES has a stronger affinity with toluene than heptane.

EXPERIMENTAL SECTION

1. Chemicals and DES Preparation

Toluene (≥99.5 wt%), heptane (99 wt%), urea (≥98 wt%), glycerol (≥99.5 wt%), dimethyl sulfoxide-d6 (DMSO-d6, 99.96%) and choline chloride (≥98 wt%) were purchased from Sigma-Aldrich and used as received. Two moles of urea, one mole of choline chloride,

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and one mole of glycerol were measured using the Shimadzu ATX 224 analytical balance (accuracy of ±0.1 mg) and initially mixed in a round flask at 350 K, maintained using a silicon oil bath, resulting in DES1. The ^{1}H NMR (JNM-LAMDA, 300 MHz, Jeol, Inc.) spectrometer was used to verify the synthesized DES1.

^{1}H NMR: CH_3, 9H, 3.4; α-CH_2, 2H, 3.8; β-CH_2, 2H, 4.4; OH (in choline chloride), 1H, 5.50; NH_2, 8H, broad, 6.24; OH (in glycerol); CH_3 (in glycerol)

2. LLE Determination

The typical LLE experimental setup and procedure was applied. The experimental setup consists of a jacketed glass vessel, a thermostat, a water circulator, and a magnetic stirrer. The temperature of the glass vessel was controlled by a circulating water bath with an accuracy of ±0.1 K. The liquid mixture was vigorously stirred in the glass vessel for three hours and kept eight hours to reach equilibrium.

The LLE data were experimentally obtained at 293.2, 303.2 and 313.2 K and atmospheric pressure using the tie-line method [14]. Both top and bottom layers were quantitatively analyzed to determine how much toluene was distributed in each phase by using an NMR spectrometer, as performed by Naik et al. [10]. While the methyl peak in toluene, the two-methyl peak in heptane, and the five-methylene peak in heptane appearing at 2.4, 0.9, and 1.2 ppm, respectively, were used for the quantitative analysis, the eight-proton peak in urea, and the two-proton peak in beta methylene in choline chloride appearing at 4.5 and 3.8, respectively, was used for the DES1 analysis. The peaks of the two chemical species, urea and glycerol, in DES1 overlapped each other and could not be used for the quantitative analysis.

RESULTS AND DISCUSSION

1. Experimental LLE Data

The LLE experimental data of the ternary system were determined at three temperatures, 293.2, 303.2, and 313.2 K, and atmospheric pressure. The mole fractions of each layer were determined and are shown in Table 1. The distribution coefficient (D) for toluene and the separation factor (S) were estimated to determine the capability of DES1 for toluene separation from heptane containing mixture using equations below:

$$D=\frac{\chi_1^{II}}{\chi_1^{I}} \tag{1}$$

$$S=\frac{\chi_1^{II}}{\chi_1^{I}}\Big/\frac{\chi_2^{II}}{\chi_2^{I}} \tag{2}$$

where superscripts I and II denote the raffinate and extract phase, respectively, and the subscripts 1 and 2 represent toluene and heptane, respectively. As shown in Table 1, the effect of temperature on both the distribution coefficient and the separation factor was insignificant with a range from 293.2 K to 313.2 K.

The value of D was as low as 0.0146 at 313.2 K, however, no extractive solvent, DES1, was detected in the raffinate phase, as reported by other researchers [2,3]. Consequently, it is not necessary to install an additional separation unit to recover DES1 in an actual continuous process. In addition to these advantages of using DES1 in aromatic separation, there was a quite low mole fraction of heptane, leading to high value of S. The low value of D could be a trade-off with the absence of need for a further purification unit for DES1 reuse. The usage of DES would allow much more economically feasible and environmentally friendly toluene separation from hydrocarbon mixtures.

Table 1. Experimental tie lines of the toluene (1)+n-heptane (2)+DES1 (3) at three temperatures and atmospheric pressure, distribution coefficient (D) of toluene and selectivity (S)

	Raffinate phase (I)			Extract phase (II)				
T(K)	χ_1^I	χ_2^I	χ_3^I	χ_1^{II}	χ_2^{II}	χ_3^{II}	D	S
293.2	0.356	0.644	0	0.001	0.003	0.995	0.00	0.6
	0.468	0.532	0	0.012	0.000	0.988	0.03	-
	0.600	0.400	0	0.028	0.000	0.972	0.05	-
	0.655	0.345	0	0.011	0.014	0.975	0.02	0.4
	0.742	0.258	0	0.035	0.000	0.965	0.05	-
	0.829	0.171	0	0.077	0.007	0.916	0.09	2.3
	0.945	0.055	0	0.158	0.000	0.842	0.17	-
303.2	0.359	0.641	0	0.001	0.000	0.999	0.00	-
	0.434	0.566	0	0.003	0.000	0.997	0.01	-
	0.467	0.533	0	0.003	0.000	0.997	0.01	-
	0.637	0.363	0	0.010	0.000	0.990	0.02	-
	0.816	0.184	0	0.023	0.000	0.977	0.03	-
	0.831	0.169	0	0.031	0.000	0.968	0.04	26.5
313.2	0.295	0.705	0	0.002	0.001	0.996	0.01	4.0
	0.343	0.657	0	0.001	0.004	0.995	0.00	0.6
	0.350	0.650	0	0.013	0.008	0.979	0.04	2.8
	0.437	0.563	0	0.005	0.000	0.994	0.01	20.4
	0.554	0.446	0	0.031	0.008	0.960	0.06	3.0
	0.666	0.334	0	0.010	0.000	0.990	0.01	-
	0.710	0.290	0	0.011	0.003	0.985	0.02	1.4
	0.831	0.169	0	0.021	0.000	0.979	0.02	-
	0.952	0.048	0	0.064	0.000	0.936	0.07	106.2

Uncertainties of temperature and mole fraction are 0.1 K and 0.003, respectively

2. Data Correlation

The LLE experimental data were correlated using the NRTL equation developed by Renon and Prausnitz [15]. We treated DES1 comprised of three chemicals as a single solvent in data correlation. The activity coefficient, g_i, for any component in the ternary system for the NRTL model is given by Eq. (3-1).

$$\ln\gamma_i=\frac{\sum_{j=1}^{n}\chi_j\tau_{ji}G_{ji}}{\sum_{k=1}^{n}G_{ki}\chi_k}+\sum_{j=1}^{n}\frac{\chi_j G_{ij}}{\sum_{k=1}^{n}G_{ki}\chi_k}\left(\tau_{ij}-\frac{\sum_{m=1}^{n}\chi_m\tau_{mj}G_{mj}}{\sum_{k=1}^{n}G_{ki}\chi_k}\right) \tag{3-1}$$

where,

$$G_{ij}=\exp(-\alpha_{ij}\tau_{ij})\quad G_{ji}=\exp(-\alpha_{ij}\tau_{ji}) \tag{3-2}$$

$$\tau_{ij}=\frac{g_{ij}-g_{jj}}{RT}=\frac{\Delta g_{ij}}{RT}=\frac{b_{ij}}{T}\quad \alpha_{ij}=\alpha_{ji} \tag{3-3}$$

In this study α was set to 0.3 according to the literature [15]. The binary interaction parameters for the NRTL correlation were obtained by minimizing the objective function (O.F.) shown in Eq. (4).

$$\mathrm{O.F.}=\min\sum_{j=1}^{t}\sum_{i=1}^{c}\{[(\chi_{ij}^{exp}-\chi_{ij}^{cal})^2]^{I}+[(\chi_{ij}^{exp}-\chi_{ij}^{cal})^2]^{II}\} \tag{4}$$

where i, j, t, c, exp, and cal are the each component, tie-line, number of tie-lines, number of components, experimental and calculated equilibrium data, respectively, The root mean square deviation (RMSD) was defined as below:

$$\mathrm{RMSD}=\sqrt{\frac{\Sigma_{j=1}^{t}\Sigma_{i=1}^{c}\{[(\chi_{ij}^{exp}-\chi_{ij}^{cal})^2]^{I}+[(\chi_{ij}^{exp}-\chi_{ij}^{cal})^2]^{II}\}}{6t}} \tag{5}$$

As can be seen in Table 2 and Fig. 1, the values of RMSD were small enough to confirm that a good experimental correlation with NRTL was obtained.

Table 2. NRTL binary interaction parameters and RMSD for the toluene (1), n-heptane (2), and DES1 (3) system at 293.2 K, 303.2 K and 313.2 K

		293.2 K		
i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)$_i$	α	RMSD
1-2	−2699.3	−72.4357		
1-3	10758	5071.3	0.3	0.030
2-3	12559	11185		
		303.2 K		
i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)$_i$	α	RMSD
1-2	873.8667	−140.0735		
1-3	6204.3	5348.5	0.3	0.105
2-3	9209.2	4465.7		
		313.2 K		
i-j	Δg_{ij} (J/mol)	Δg_{ji} (J/mol)$_i$	α	RMSD
1-2	3779.7	−261.9		
1-3	9213.1	698.03	0.3	0.087
2-3	13869	14954		

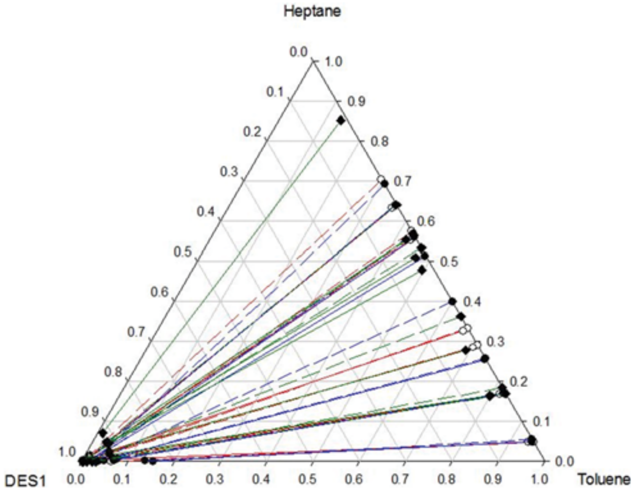


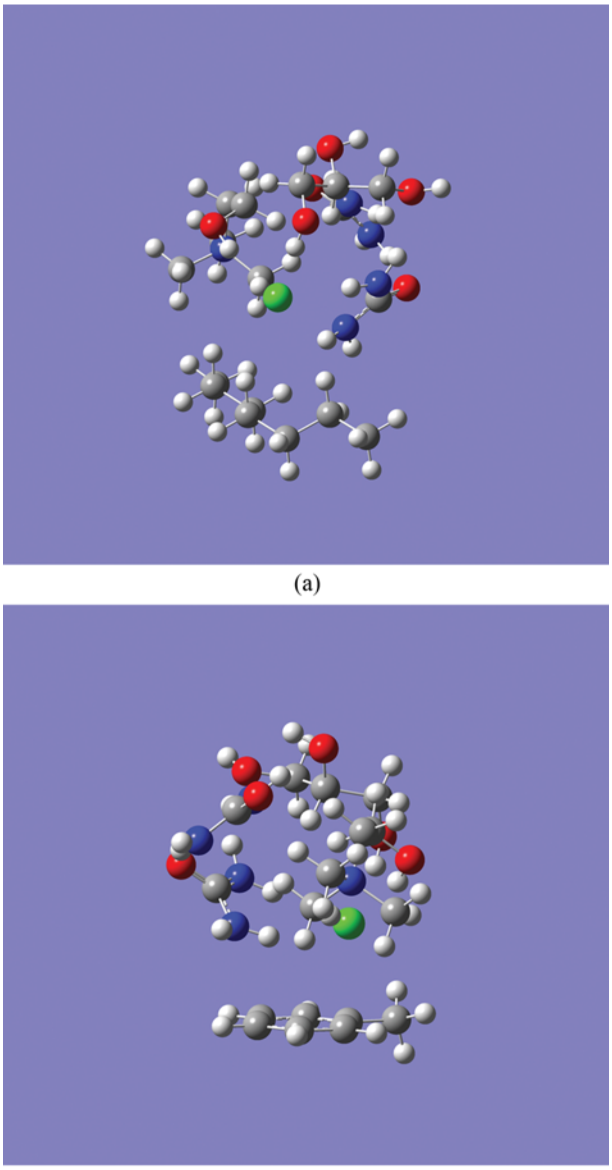
Fig. 1. Ternary diagram for toluene, heptane and DES1 at 293.2 K (blue), 303.2 K (green) and 313.2 K (red); experimental closed (solid), correlated open (dotted).

3. *Ab initio* Approach

The *ab initio* quantum chemistry method was applied to determine why DES1 composed of three chemicals has a higher affinity to toluene than to heptane, using Gaussian 09W [16]. Once the optimized geometries were obtained at B3LYP/6-31+G(d,p) with gd2 correction [17], the interaction energy was calculated using Eq. (6)

$$\Delta E=E_{cluster}-\sum E_i \tag{6}$$

where ΔE is the interaction energy, $E_{cluster}$ is the energy of the cluster, and E_i is the energy of a pure substance in an optimized geometry (see Fig. 2). DES1 compound was considered as a single compound in interaction energy estimation. The basis set superposition error (BSSE) [18] was applied to correct the interaction energy.


(a)

(b)

Fig. 2. Optimized structures of (a) DES1…heptane (b) DES1…toluene.

Table 3. Interaction energies (kcal/mol) of the DES and heptane and those of the DES and toluene using the B3LYP/6-31+G(d,p) with gd2 correction

System	ΔE[a]	ΔE[b]
DES0…heptane	−8.6	−8.0
DES0…toluene	−11.6	−10.6
DES1…heptane	−7.7	−7.0
DES1…toluene	−12.4	−11.3

DES0=choline chloride : urea=1 : 2 (mole ratio)

DES1=choline chloride : urea : glycerol=1 : 2 : 1 (mole ratio)

[a] Interaction energy

[b] Basis set superposition error (BSSE) corrected binding energy

To investigate the effect of additional HBD in DES, DES0 composed of choline chloride and urea with a mole ratio of one to two was selected in the evaluation of interaction energy between DES and hydrocarbons.

The interaction energy between DES0 and toluene was higher than that of DES0 and heptane, as shown in Table 3. The magnitude of interaction energy between DES1 and toluene was higher than that between DES0 and toluene. One possible explanation is that the addition of glycerol allowed a stronger interaction with HBA in DES 1, resulting in a stronger interaction between DES1 and toluene. As Sun et al. explained [19], regarding the interaction energies of the cation and anion in DES, the addition of a complexing agent reduces the interaction energy between the cations and anions of the salt, and there is an increase in the interaction energy between DES1 and toluene.

CONCLUSIONS

DES composed of choline chloride, urea and glycerol was applied to selectively extract toluene from toluene and heptane mixture. DES was not detected in the raffinate phase and a negligible amount of heptane was found in extract phase, and thus no further separation unit was required for DES and direct separation in extract phase was possible. Temperature did not have a significant effect on the distribution coefficient within the temperature range of 298.2 K to 313.2 K. The LLE experimental data correlated well with the NRTL model. *Ab initio* calculations were also carried out to quantitatively evaluate the interaction between DES and toluene and that between DES and heptane, using the Gaussian 09W package. The quantum chemical calculation results suggest that the DES has a stronger interaction with toluene than with heptane. This suggests that the interaction between an extractive solvent and an aromatic compound may be an important factor in aromatic compound separation in mixture including aliphatic hydrocarbons.

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