

Liquid-liquid equilibria of toluene + n-heptane + {1-benzyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide or 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide}

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Abstract—Both 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BzMeIM][NTf₂], and 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide, [BzPY][NTf₂], were used to separate toluene from heptane through liquid-liquid equilibria (LLE). The LLE of two ternary systems of toluene, n-heptane, and [BzMeIM][NTf₂] and [BzPY][NTf₂], were experimentally determined at temperature of 293.2 K and 0.1 MPa. The LLE experiments were also performed at 303.2 and 313.2 K to investigate the effect of temperature on toluene recovery. The distribution ratio of toluene and the selectivity in these two ternary systems were calculated and compared with different ternary mixtures. The LLE measured data were well correlated with nonrandom two-liquid (NRTL).

Keywords: Ionic Liquid, Toluene, n-Heptane, Selectivity, Liquid-liquid Equilibria

INTRODUCTION

Toluene has served as a raw chemical for the production of extensively used industrial chemicals. The conventional processes for the toluene separation are liquid extraction, extractive distillation, and azeotropic distillation. There are typical solvents such as sulfolane, N-methyl pyrrolidone and ethylene glycol that can be used for the extraction process [1]. Those solvents, however, are not only volatile and toxic but also hard to recover [2]. Ionic liquids (ILs) are considered desired candidates for an environmentally friendly alternative because they are nonvolatile, nontoxic, and convenient to recover for reuse as an extracting agent in extraction process.

ILs composed of bulky cations and anions have been utilized in many application areas, such as reaction [3], adsorption [4], and separation [5] on the basis of their adjustable physical properties by varying cations and anions depending on the target application. Many anions have been implemented in IL synthesis including nitrate [6], ethylsulfate (ESO₄) [7,8] and bis(trifluoromethylsulfonyl)imide (NTf₂) [2,5,9]. Gonzalez et al. [7,8] used ESO₄-based ILs to selectively separate aromatics from aliphatic hydrocarbons. They claimed that selectivity values for ESO₄-based ILs were higher than those for other ILs. However, Canales and Brennecke [10] reported that NTf₂-based ILs were the best anion in aromatic separation process in terms of selectivity.

In aromatic separation three primary cations are used: imidazolium (IM), pyridinium (PY), and tetraalkylammonium (TA). The usage of a PY-based IL yielded good aromatic separation results in terms of distribution ratio and selectivity [2]. Arce et al. [9] applied TA-based IL containing a hydroxyethyl group to yield higher selec-

tivity in a certain range of global compositions of toluene. The most commonly used cation, IM, has been employed by many research groups to demonstrate that the functional group on the cation plays a role on selectivity as well as the distribution ratio [11-14].

Zhang et al. [11] applied N-benzylmethylimidazolium bis(trifluoromethylsulfonyl)imide, [BzMeIM][NTf₂], to separate toluene from n-heptane, including mixture at 298.2 K to 318.2 K. They used gas chromatography analysis with an internal standard method to determine the distribution ratio of 1.2 and selectivity of toluene of 25.77 at 298.2 K. The quantum chemical calculation supported that [BzMeIM][NTf₂] had stronger interaction with aromatics than that with alkanes, resulting in higher distribution ratio and selectivity.

The effects of cation, anion, and alkyl chain length in the cation in ILs on aromatic compound separation have been reviewed [10, 17,18]. Specifically, the effect of alkyl chain length in aliphatic substituted cation containing ILs on the distribution ratio and selectivity is well understood. As the alkyl chain length increased from methyl to butyl in IM cation and NTf₂ anion based ILs, the distribution ratio and selectivity of aromatic compound was decreased because as the alkyl chain length increased, the electron donation from the alkyl group to the cation increased, as Hossain et al. [15] reported. When the alkyl group is substituted on both IM and PY cations, PY cation based ILs have slightly higher selectivities and aromatic capacities [15]. While the effect of aliphatic alkyl chain length in cation on the aromatic compound separation has been investigated by many researchers, the effect of benzyl ring on different cations, PY and IM, has not been reported.

In this study, NTf₂ anion-based ILs were used to selectively extract toluene from a mixture containing heptane by varying the cations from benzyl IM (BzIM) to benzyl PY (BzPY) to investigate the effect of cations on aromatic separation at 293.2 K, 303.2 K, and 313.2 K, and atmospheric pressure. The LLE data obtained experimentally were correlated with an NRTL model.

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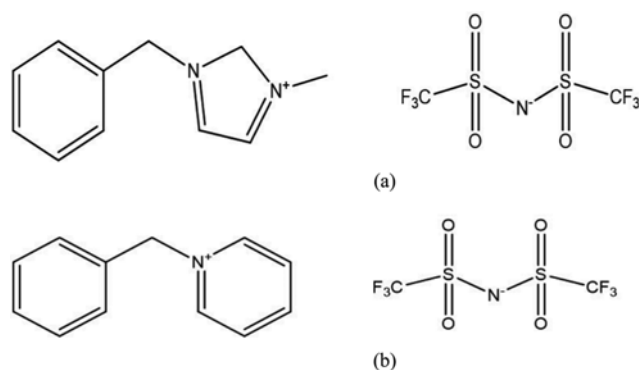


Fig. 1. Chemical structures of (a) 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BzMeIm][NTf₂]. (b) 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide [BzPy][NTf₂].

EXPERIMENTAL SECTION

1. Chemicals

Toluene (≥ 99.7 wt%), n-heptane (99 wt%), and chloroform-d (99.96 atom% D) were purchased from Sigma-Aldrich (Suwon, S. Korea). Both 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (>98 wt%) ([BzMeIm][NTf₂]) and 1-benzylpyridinium bis(trifluoromethylsulfonyl)imide (>98 wt%) ([BzPy][NTf₂]) were bought from C-tri (Chuncheon, S. Korea). Fig. 1 shows the chemical structure of both [BzMeIm][NTf₂] and [BzPy][NTf₂]. A Karl-Fisher titrator (Model V20, Mettler Toledo Inc.) was used to determine water content in ILs, which was analyzed to be less than 0.2 wt%. All chemicals were used as received. The structure of the ILs used in this study was verified by nuclear magnetic resonance (NMR) spectrometer (Figs. S1-1, S1-2, S2-1, and S2-2 in Supporting Information).

2. Experimental Procedure and Analysis

A ternary mixture was prepared at different molar concentrations in a jacketed glass vessel using a Shimadzu ATX 224 analytical balance (accuracy of ± 0.1 mg). The temperature of the glass vessel was maintained using a Lab. Companion (Daejeon, S. Korea) circulator (Model No. RW-0525G) with an accuracy of ± 0.1 K at 293.2 K. The liquid solution was mixed well in the glass vessel for four hours and kept for more than four hours to accomplish equilibrium. A similar step was taken by varying the temperature to 303.2 and 313.2 K at atmospheric pressure to investigate the effect of temperature on aromatic extraction.

Both the upper and lower layers were quantitatively analyzed using a ¹H NMR (JNM-LAMDA, 300 MHz, Jeol, Inc.) spectrometer, as performed by Seddon and coworkers [9]. In the case of toluene, n-heptane, and [BzMeIm][NTf₂] ternary LLE, the upper layer composition was determined using the methyl peak appearing at 2.4 ppm in toluene, the two-methyl peak appearing at 0.8 ppm, and the five-methyl peak appearing at 1.2 ppm in n-heptane. While no [BzMeIm][NTf₂] peaks were detected from the upper layer, peaks of [BzMeIm][NTf₂] from the lower layer were detected. The methyl peak as well as the methylene peak in the imidazolium ring appeared at 3.9 and 5.1 ppm, respectively. These two peaks were used to determine the amount of [BzMeIm][NTf₂] in the lower layer.

No [BzPy][NTf₂] peaks were detected from the upper layer in

Table 1. Experimental tie lines of the toluene (1)+n-heptane (2)+[BzMeIm][NTf₂] (3) at three temperatures and atmospheric pressure, distribution ratio (D₁) and selectivity (S)

T=293.2 K							
Hydrocarbon-rich (I)		IL-rich (II)					
x ₁	x ₂	x ₁	x ₂	x ₃	D ₁	D ₂	S
0.150	0.850	0.144	0.029	0.826	0.962	0.034	27.9
0.227	0.773	0.253	0.032	0.715	1.118	0.041	27.4
0.048	0.952	0.054	0.040	0.907	1.117	0.042	26.6
0.098	0.902	0.100	0.042	0.858	1.019	0.046	22.1
0.574	0.426	0.517	0.031	0.452	0.902	0.073	12.4
0.624	0.376	0.575	0.033	0.392	0.922	0.087	10.5
0.506	0.494	0.456	0.046	0.499	0.901	0.092	9.8
0.331	0.669	0.305	0.066	0.629	0.922	0.098	9.4
0.705	0.295	0.598	0.029	0.373	0.848	0.097	8.7
0.762	0.238	0.647	0.027	0.326	0.849	0.115	7.4
0.837	0.163	0.721	0.023	0.256	0.860	0.142	6.1
T=303.2 K							
Hydrocarbon-rich (I)		IL-rich (II)					
x ₁	x ₂	x ₁	x ₂	x ₃	D ₁	D ₂	S
0.150	0.850	0.167	0.040	0.794	1.116	0.046	24.0
0.049	0.951	0.067	0.054	0.879	1.362	0.057	23.9
0.115	0.885	0.135	0.048	0.818	1.168	0.054	21.7
0.335	0.665	0.326	0.032	0.642	0.972	0.048	20.1
0.099	0.901	0.119	0.057	0.825	1.206	0.063	19.2
0.225	0.775	0.265	0.049	0.686	1.179	0.063	18.6
0.573	0.427	0.515	0.037	0.448	0.898	0.087	10.3
0.624	0.376	0.588	0.037	0.375	0.942	0.099	9.5
0.705	0.295	0.616	0.035	0.349	0.874	0.119	7.4
0.761	0.239	0.680	0.033	0.287	0.893	0.139	6.4
0.835	0.165	0.718	0.027	0.255	0.860	0.163	5.3
T=313.2 K							
Hydrocarbon-rich (I)		IL-rich (II)					
x ₁	x ₂	x ₁	x ₂	x ₃	D ₁	D ₂	S
0.099	0.901	0.101	0.038	0.861	1.013	0.043	23.8
0.048	0.952	0.043	0.038	0.920	0.895	0.039	22.7
0.138	0.862	0.147	0.048	0.805	1.071	0.055	19.4
0.225	0.775	0.205	0.039	0.756	0.908	0.051	18.0
0.114	0.886	0.116	0.068	0.816	1.015	0.077	13.2
0.331	0.669	0.286	0.045	0.669	0.865	0.067	13.0
0.518	0.482	0.402	0.033	0.565	0.777	0.069	11.3
0.574	0.426	0.503	0.039	0.458	0.877	0.091	9.7
0.652	0.348	0.567	0.040	0.393	0.870	0.115	7.6
0.763	0.237	0.571	0.029	0.400	0.748	0.124	6.1
0.837	0.163	0.706	0.028	0.267	0.843	0.170	5.0

Standard uncertainties u are $u(x)=0.003$ and $u(T)=0.1$ K

toluene, n-heptane, and [BzPy][NTf₂] ternary system, as in the case of ternary including [BzMeIm][NTf₂]. Toluene and n-heptane were hence quantitatively analyzed with the same NMR peaks as used in the case of the ternary system containing [BzPy][NTf₂]. The

methylene peak, two Hs in the position of C9 and C10 in benzyl ring, and two Hs in the position of C2 and C6 in the pyridinium ring appeared at 5.7, 7.9, and 8.7 ppm, respectively. These three peaks were used to analyze the amount of [BzPY][NTf₂] in the lower layer. The uncertainty was determined by comparing the experimental compositions of five samples with known compositions to calculated ones. The maximum estimated error was ± 0.003 in mole fraction.

RESULTS AND DISCUSSION

At atmospheric pressure and temperature from 293.2 K to 313.2

Table 2. Experimental tie lines of the toluene (1)+n-heptane (2)+[BzPY][NTf₂] (3) at three temperatures and atmospheric pressure, distribution ratio (D_1) and selectivity (S)

T=293.2 K							
Hydrocarbon-rich (I)		IL-rich (II)			D_1	D_2	S
x_1	x_2	x_1	x_2	x_3			
0.058	0.942	0.052	0.012	0.936	0.906	0.012	74.2
0.239	0.761	0.183	0.019	0.797	0.768	0.025	30.1
0.390	0.610	0.308	0.019	0.673	0.788	0.032	24.8
0.289	0.711	0.226	0.054	0.720	0.784	0.075	10.4
0.684	0.316	0.490	0.025	0.485	0.717	0.079	9.1
0.752	0.248	0.629	0.027	0.345	0.836	0.109	7.7
0.541	0.459	0.425	0.056	0.519	0.785	0.122	6.4
0.922	0.078	0.792	0.017	0.191	0.860	0.212	4.1
T=303.2 K							
Hydrocarbon-rich (I)		IL-rich (II)			D_1	D_2	S
x_1	x_2	x_1	x_2	x_3			
0.056	0.944	0.054	0.017	0.929	0.963	0.018	53.4
0.292	0.708	0.211	0.022	0.767	0.721	0.031	23.1
0.511	0.489	0.378	0.025	0.597	0.739	0.051	14.6
0.617	0.383	0.489	0.025	0.486	0.793	0.065	12.1
0.390	0.610	0.284	0.047	0.669	0.729	0.077	9.4
0.684	0.316	0.552	0.030	0.418	0.806	0.094	8.5
0.825	0.175	0.661	0.023	0.316	0.801	0.132	6.0
0.926	0.074	0.772	0.015	0.213	0.834	0.195	4.3
0.928	0.072	0.788	0.015	0.198	0.849	0.204	4.2
T=313.2 K							
Hydrocarbon-rich (I)		IL-rich (II)			D_1	D_2	S
x_1	x_2	x_1	x_2	x_3			
0.182	0.818	0.192	0.019	0.788	1.057	0.024	44.6
0.293	0.707	0.249	0.031	0.719	0.852	0.044	19.2
0.610	0.390	0.458	0.016	0.526	0.750	0.041	18.3
0.242	0.758	0.208	0.037	0.755	0.860	0.049	17.5
0.684	0.316	0.524	0.030	0.445	0.766	0.096	8.0
0.383	0.617	0.314	0.075	0.612	0.818	0.121	6.8
0.820	0.180	0.661	0.026	0.313	0.807	0.142	5.7
0.973	0.027	0.879	0.005	0.116	0.904	0.172	5.3
0.928	0.072	0.775	0.015	0.210	0.835	0.209	4.0

Standard uncertainties u are $u(x)=0.003$ and $u(T)=0.1$ K

K with intervals of 5 K, the LLE data of two ternary systems of toluene, n-heptane and [BzMeIM][NTf₂] or [BzPY][NTf₂] were experimentally determined. No ILs were detected in the upper layer for both ILs containing ternary LLE, which would be a huge benefit for application of ILs to aromatic recovery, as other researchers have argued [6-14,19]. The experimental results for toluene (1), n-heptane (2), [BzMeIM][NTf₂] (3) and those for toluene (1), n-heptane (2), [BzPY][NTf₂] (3) are shown in Table 1 and Table 2, respectively. The distribution ratio, D_1 , for toluene and the selectivity, S , were calculated using Eqs. (1) and (2), respectively.

$$D_1 = \frac{x_1^{II}}{x_1^I} \quad (1)$$

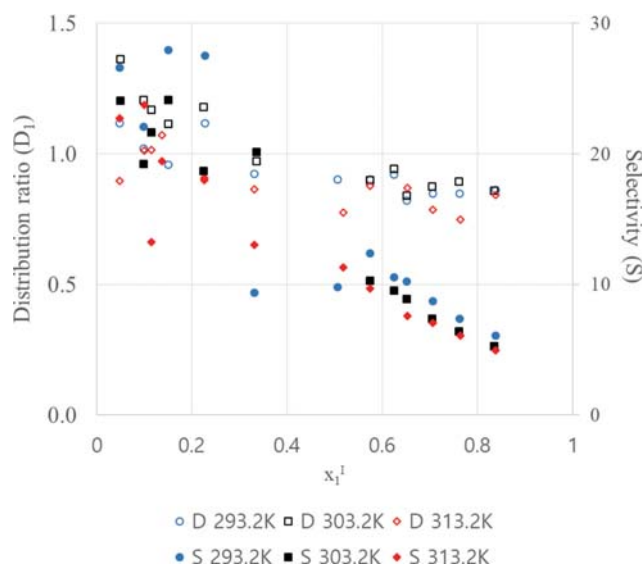


Fig. 2. Distribution ratio (D_1) and selectivity (S) as a function of toluene mole fraction in the upper layer in ternary system of toluene (1)+n-heptane (2)+[BzMeIM][NTf₂] (3).

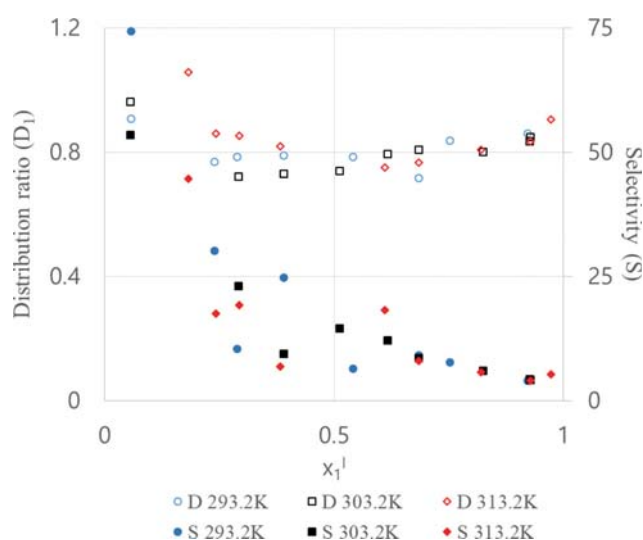


Fig. 3. Distribution ratio (D_1) and selectivity (S) as a function of toluene mole fraction in the upper layer in ternary system of toluene (1)+n-heptane (2)+[BzPY][NTf₂] (3).

$$S = \frac{x_1^{\text{II}}/x_2^{\text{II}}}{x_1^{\text{I}}/x_2^{\text{I}}} \quad (2)$$

where x is the mole fraction, the superscripts I and II denote the upper (hydrocarbon-rich) and lower (IL-rich) phase, respectively, and the subscripts 1 and 2 indicate toluene and n-heptane, respectively. As shown in Figs. 2 and 3, the effects of temperature on both the distribution ratio and the selectivity were insignificant over temperatures ranging from 293.2 K to 313.2 K.

1. Experimental LLE Data of Toluene, n-Heptane, and [BzMeIM][NTf₂]

Fig. 2 shows that the distribution ratios and selectivities of toluene depended on the mole fraction of toluene in the upper layer. In particular, the values of D_1 for the mixture containing less than 20 mole% toluene were greater than 1 for almost all cases at the three temperatures. For example, the value of D_1 for the mixture containing as little as 0.049 toluene in the upper layer was 1.362 at 303.2 K. This result indicates that [BzMeIM][NTf₂] would be viable for the recovery of toluene from the hydrocarbon mixture containing less toluene, because a higher distribution ratio resulted in a much more compatible feed to solvent ratio in aromatic recovery processes.

The value of S should be greater than 1 in the extraction process because higher selectivity values yield stronger extraction capability. The selectivities under a lower toluene molar concentration in the upper layer were higher than 20 except for a few outliers, as shown in Fig. 2. However, as the toluene mole fraction in the upper layer increased, the selectivity decreased, which is not uncommon for other ternary systems of toluene, n-heptane, and ILs [15]. Similar results to data reported in the literature [11] were obtained. At 303.2 K the values of D_1 and S reported in the literature and this study were 1.016, 22.7 and 1.36, 24.1, respectively. While Zhang et al. [11] reported LLE experimental data at various compositions at 298.2 K and data at one composition at four temperatures of 303.2 K, 308.2 K, 313.2 K, and 318.2 K, our data included various compositions at three temperatures of 293.2 K, 303.2 K, and 313.2 K. The combination of these two data sets covers the LLE of toluene, n-heptane, and [BzMeIM][NTf₂] at various compositions and temperatures.

The benzyl ring functionalized imidazolium-based IL, [BzMeIM][NTf₂], yielded similar values of D_1 and S compared to those for the imidazolium-based ILs including a di-substituted or tri-substituted methyl group. In those cases, [NTf₂] was chosen as a counterpart anion. The values of D_1 and S for the case of [BzMeIM][NTf₂] were 1.21 and 25.8, whereas those for the case of [PDMIM][NTf₂] were 1.142 and 29.7, as shown in Table 3.

2. Experimental LLE Data of Toluene, n-Heptane, and [BzPY][NTf₂]

As shown in Fig. 3, the D_1 values ranged from 0.7 to 1.0 over the toluene concentrations of the upper layer. While these D_1 values are less than those of toluene, n-heptane, and [BzMeIM][NTf₂] ternary system, they are still higher than those of toluene, n-heptane, and sulfolane ternary system [1]. ILs of both [BzMeIM][NTf₂] and [BzPY][NTf₂] hence could be a better extractive agent than sulfolane in terms of the distribution ratio.

The values of D_1 in the presence of [BzPY][NTf₂] were lower

Table 3. Comparison of distribution ratio and selectivity for the toluene (1) in the presence of different IL solvents

IL	$x_1^{I^B}$	T/K	D_1	S	Refs	
[EtMeIM][NTf ₂] ^a	0.104	298.15	0.81	24.24	2	
[PDMIM][NTf ₂] ^b	0.026	298.2	1.142	29.7	20	
[BzViIM][NTf ₂] ^c	0.064	313.2	1.109	13.9	11	
[EtMePY][NTf ₂] ^d	0.080	298.15	0.92	13.07	2	
[4EtMePY][NTf ₂] ^e	0.0276	313.2	1.29	38.3	21	
[BzMeIM][NTf ₂]	0.064	298.2	1.210	25.8	11	
	0.063	303.2	1.016	22.7	11	
	0.065	313.2	0.877	15.8	11	
	0.048	293.2	1.117	26.6	This study	
	0.049	303.2	1.362	24.1	This study	
	0.048	313.2	0.895	22.7	This study	
	[BzPY][NTf ₂]	0.058	293.2	0.906	74.3	This study
		0.056	303.2	0.963	53.4	This study
		0.182	313.2	1.057	44.6	This study

^aMole fraction of toluene in the upper layer

^a[EtMeIM][NTf₂]: 1-Ethyl-2-methylimidazolium bis(trifluoromethylsulfonfyl)imide

^b[PDMIM][NTf₂]: 1-Propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonfyl)imide

^c[BzViIM][NTf₂]: N-benzyl-N-vinylimidazolium bis(trifluoromethylsulfonfyl)imide

^d[EtMePY][NTf₂]: 1-Ethyl-3-methylpyridinium bis(trifluoromethylsulfonfyl)imide

^e[4EtMePY][NTf₂]: 4-Methyl-N-ethylpyridinium bis(trifluoromethylsulfonfyl)imide

than those in the presence of [BzMeIM][NTf₂] and sulfolane. As an example, D_1 of 0.963 was obtained at 303.2 K and 0.056 mole fraction of toluene in the upper phase. In the case of alkyl group functionalized IM and PY cations, the value of D_1 for alkyl group functionalized PY was higher than that for alkyl group functionalized IM at low concentration of toluene in the upper layer. While the value of D_1 for the case of [EtMePY][NTf₂] was 0.92, that for the case of [EtMeIM][NTf₂] was 0.81 (see Table 3). According to Corderi et al. [2], the pyridinium ring is formed by five atoms of carbon and one of nitrogen, and the imidazolium ring by three atoms of carbon and two of nitrogen; the IL with imidazolium cation has lower aromaticity than the IL with pyridinium cation. So it is expected a higher interaction between the toluene and the pyridinium ring of the IL, resulting in a higher value of D_1 . However, the benzyl ring functionalized pyridinium-based IL, [BzPY][NTf₂], resulted in a lower value of D_1 (0.963) than that (1.362) for the benzyl ring functionalized imidazolium based IL, [BzMeIM][NTf₂] at 303.2 K. Although the reason for this intriguing result is unknown, it is obvious that the presence of pi-pi interactions between benzyl ring in the both pyridinium and imidazolium cation and toluene plays a role on the interaction between toluene and ILs.

On the contrary, the value of S (74.3) for [BzPY][NTf₂] was much higher than that (26.6) for [BzMeIM][NTf₂] at low concentration of toluene in the upper layer. Furthermore, the value of S for [BzPY][NTf₂] was higher than that reported in literature for other ILs.

Table 4. NRTL binary interaction parameters for the toluene (1), n-heptane (2), and [BzMeIM][NTf₂] (3) and those for toluene (1), n-heptane (2), and [BzPY][NTf₂] (3) system at 293.2, 303.2, and 313.2 K

Binary parameter	a_{ij}	a_{ji}	b_{ij} (K)	b_{ji} (K)	α_{ij}
Toluene+n-heptane (IM)	15.7757	13.8847	-6875.7	-2729.3	-0.1044
Toluene+[BzMeIM][NTf ₂]	4.4238	16.1993	-3138.97	-3406.88	-0.0877
n-Heptane+[BzMeIM][NTf ₂]	1.4877	-0.6674	216.79	-588.36	-0.4967
Toluene+n-heptane (PY)	1.2832	-1.5894	57.499	-76.90	0.3
Toluene+[BzPY][NTf ₂]	-1.2482	-1.9542	193.06	332.07	-2.2999
n-Heptane+[BzPY][NTf ₂]	1.9243	-0.7106	140.51	-431.16	-0.4482

a: NRTL model parameter in Aspen Plus

b: NRTL model parameter in Aspen Plus (K)

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_m G_{ij}}{\sum_k x_k G_{ki}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{ki}} \right)$$

where: $G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$ $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$ [23]**Table 5.** Values of RMSD for the toluene (1), n-heptane (2), and [BzMeIM][NTf₂] (3) and those for toluene (1), n-heptane (2), and [BzPY][NTf₂] (3) system

Ternary system	Temperature (K)	RMSD
Toluene (1), n-heptane (2), and [BzMeIM][NTf ₂] (3)	293.2	0.0229
	303.2	0.0187
	313.2	0.0306
Toluene (1), n-heptane (2), and [BzPY][NTf ₂] (3)	293.2	0.0490
	303.2	0.0484
	313.2	0.0549

Therefore, the usage of [BzPY][NTf₂] as an extractive agent for toluene recovery from the mixture containing heptane would be attractive, in particular, in cases where there is a lower mole fraction of toluene. Although both [BzMeIM][NTf₂] and [BzPY][NTf₂] ILs contain the same benzyl-functionalized cation, the values of D_1 and S values were quite different. One possible explanation would be that the presence of benzyl ring on pyridinium cation is quite different from that on imidazolium cation in terms of interaction between toluene and those ILs.

3. Data Correlation and Verification

The NRTL equation developed by Renon and Prausnitz [22] was used to correlate the LLE data. All interaction parameters determined by the NRTL model are given in Table 4. The root mean square deviation (RMSD) was defined as

$$\text{RMSD} = \sqrt{\frac{\sum_{j=1}^t \sum_{i=1}^c \{ [(x_{ij}^{\text{exp}} - x_{ij}^{\text{cal}})^2]^I + [(x_{ij}^{\text{exp}} - x_{ij}^{\text{cal}})^2]^{\text{II}} \}}{6t}} \quad (3)$$

where i and j represented as component and tie lines, respectively; c and t as number of components and tie liens, respectively. The values of RMSD are small enough to confirm that a good experimental correlation with NRTL was obtained, as can be seen in Table 5.

The Othmer-Tobias method, delineated in Eq. (4), was applied to validate the reliability of the LLE experimental data.

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

Table 6. Fitting parameters (a and b) of the Othmer-Tobias correlation and regression coefficients (R²)

System	T/K	a	b	R ²
Toluene+n-heptane + [BzMeIM][NTf ₂]	293.2	-1.609	0.739	0.991
	303.2	-1.511	0.702	0.993
	313.2	-1.748	0.691	0.988
Toluene+n-heptane + [BzPY][NTf ₂]	293.2	-1.986	0.710	0.982
	303.2	-1.922	0.717	0.986
	313.2	-1.873	0.663	0.987

where w_1^{II} and w_2^{I} are the mass fraction of IL in the lower layer and that of n-heptane in the upper layer, respectively, and a and b are the fitting parameters. Table 6 shows that the values of regression coefficient, R^2 , are close to unity, representing a high degree of quality of the LLE experimental data.

CONCLUSIONS

Toluene+n-heptane+{[BzMeIM][NTf₂] or [BzPY][NTf₂]} LLE data were experimentally measured at 293.2 K, 303.2 K, and 313.2 K and 0.1 MPa. The values of the distribution ratio of toluene and the selectivities in both systems were either very close to unity or higher than unity and higher than 20 over a wide range of toluene mole fraction in the raffinate phase. These results indicate benzyl functionalized cation-based ILs hold promise to replace sulfolane widely used as an extractive agent in aromatic recovery processes. Despite that both [BzMeIM][NTf₂] and [BzPY][NTf₂] ILs contain a benzyl-functional group in the cation, [BzPY][NTf₂] yielded much higher selectivity. One possible reason for this intriguing result may be that pyridinium cations are more aromatic than imidazolium cations, as Kim and coworkers claimed [15]. The NRTL model, which was used to correlate the LLE experimental data, showed a high degree of correlation.

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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

Liquid-liquid equilibria of toluene+n-heptane+{1-benzyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide or 1-benzyl-pyridinium bis(trifluoromethylsulfonyl)imide}

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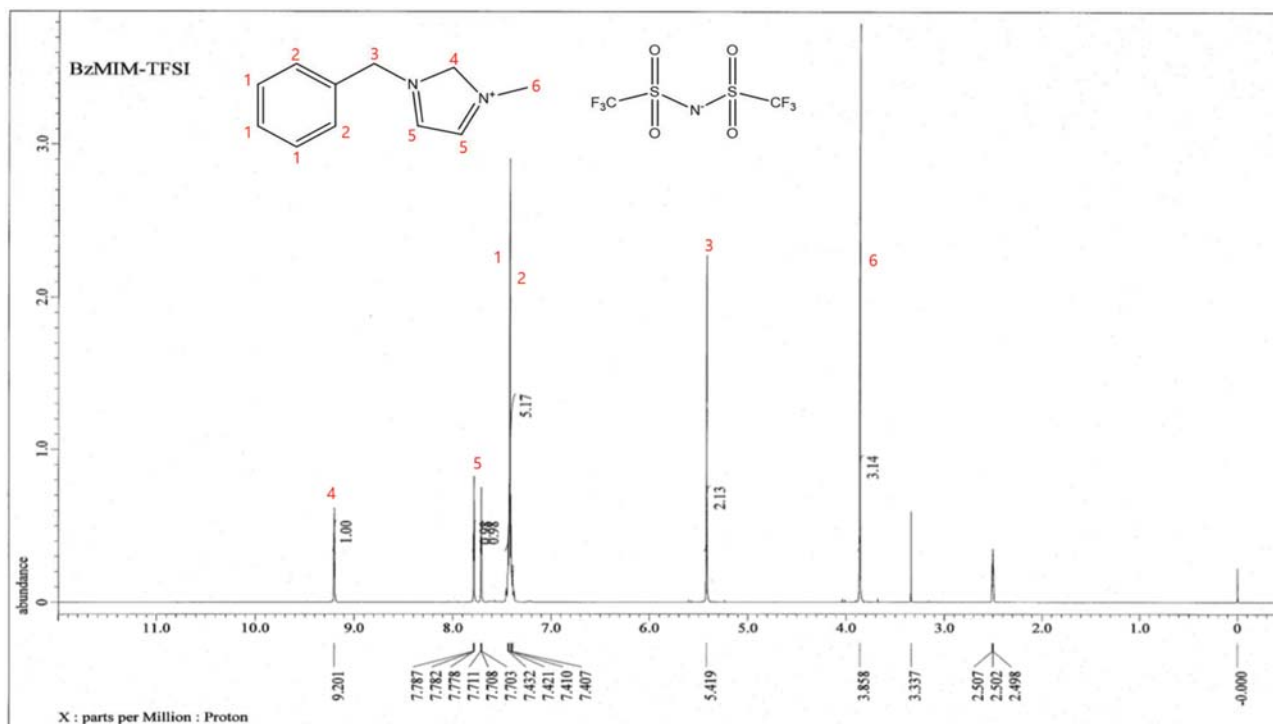


Fig. S1-1. ¹H NMR spectroscopy of pure [BzMeIM][NTf₂].

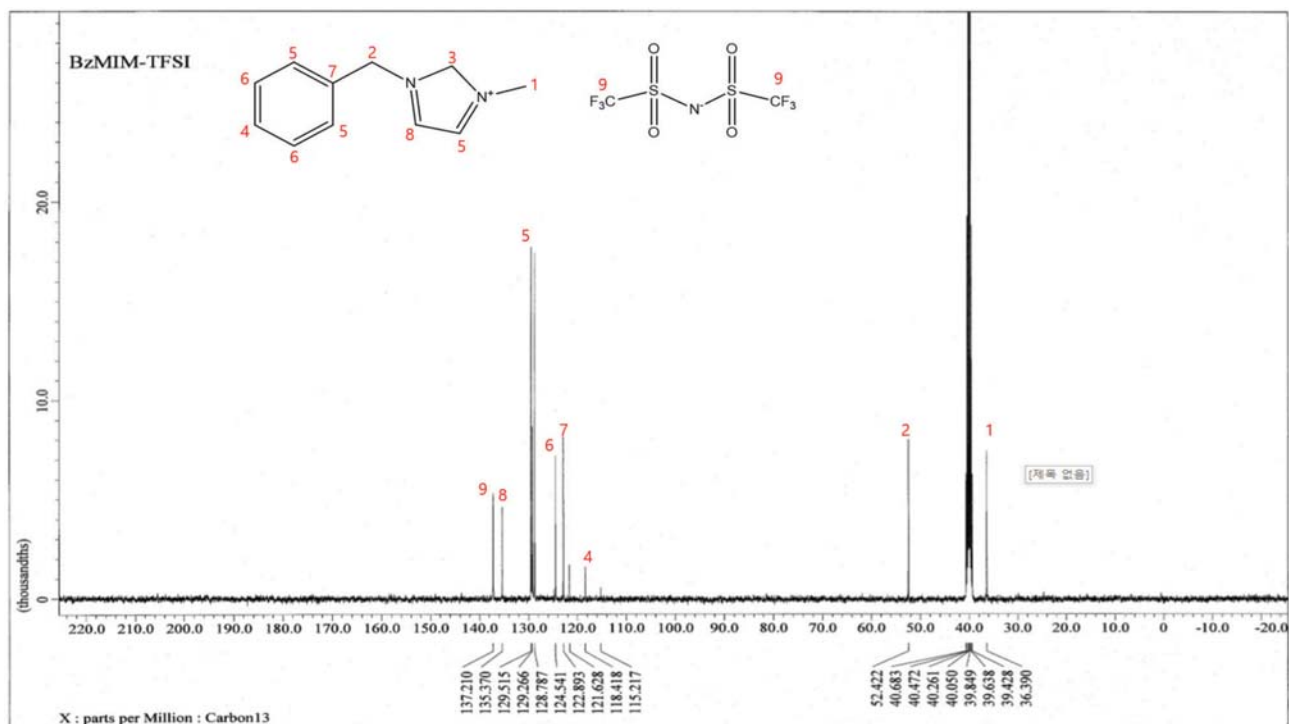


Fig. S1-2. ^{13}C -NMR spectroscopy of pure $[\text{BzMeIM}][\text{NTf}_2]$.

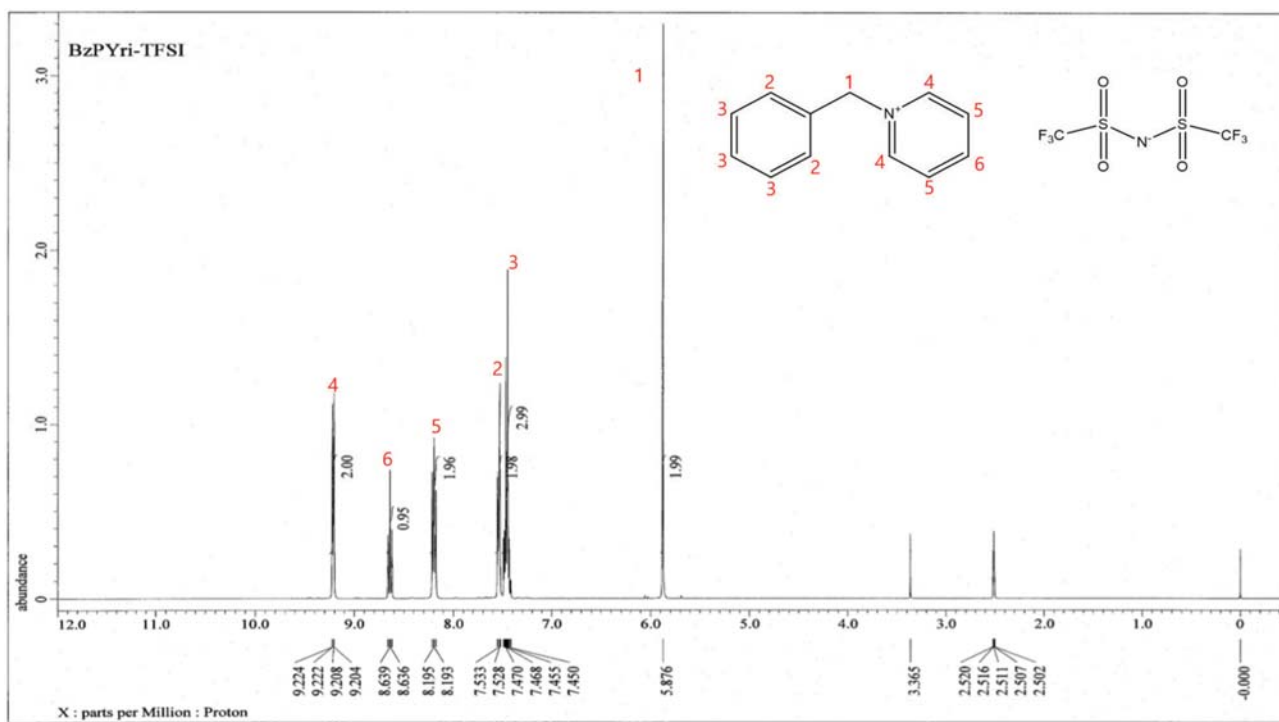


Fig. S2-1. ^1H NMR spectroscopy of pure $[\text{BzPY}][\text{NTf}_2]$.

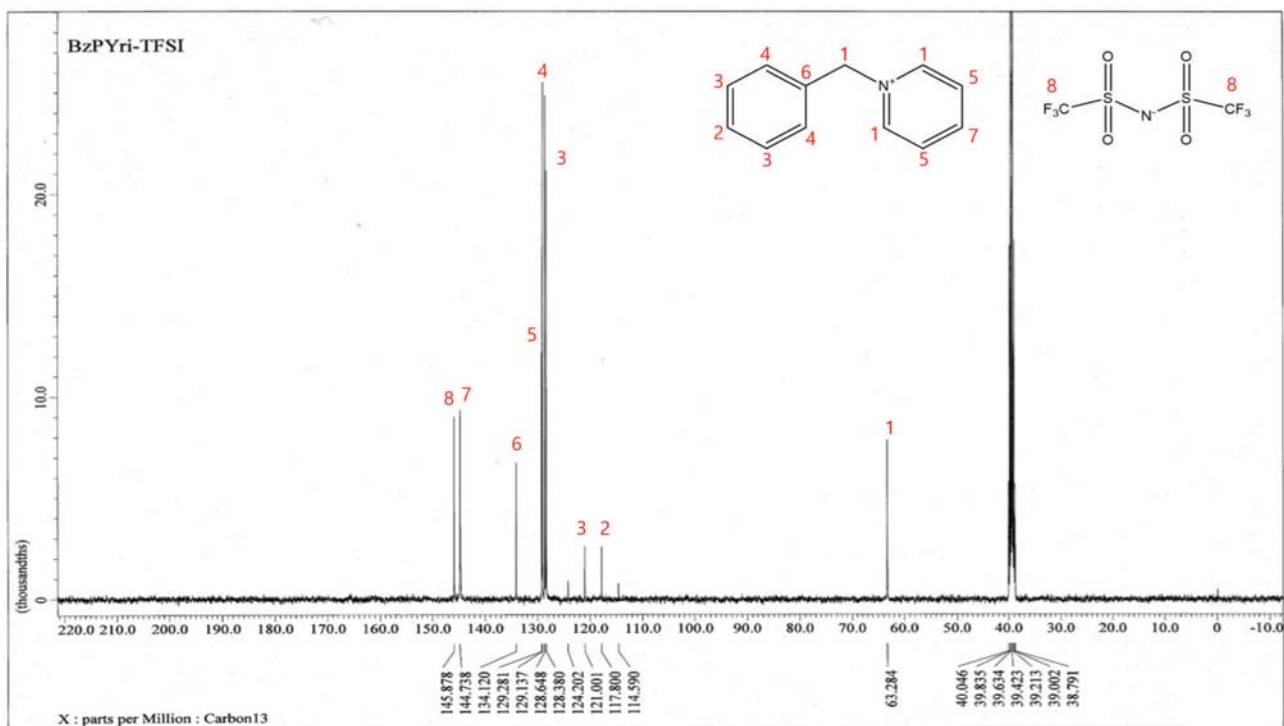


Fig. S2-2. ^{13}C NMR spectroscopy of pure $[\text{BzPY}][\text{NTf}_2]$.

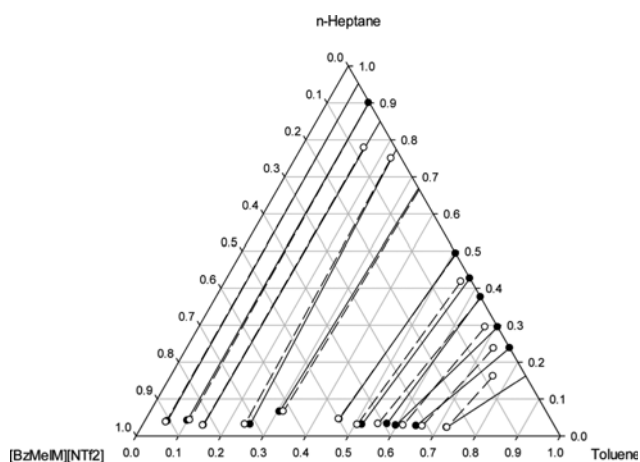


Fig. S3-1. Experimental LLE data for the ternary system: Toluene (1)+n-heptane (2)+ $[\text{BzMeIM}][\text{NTf}_2]$ (3) at temperature of 293.2 K and pressure of 0.1 MPa (solid lines: experimental tie lines; dashed lines: calculated tie lines).

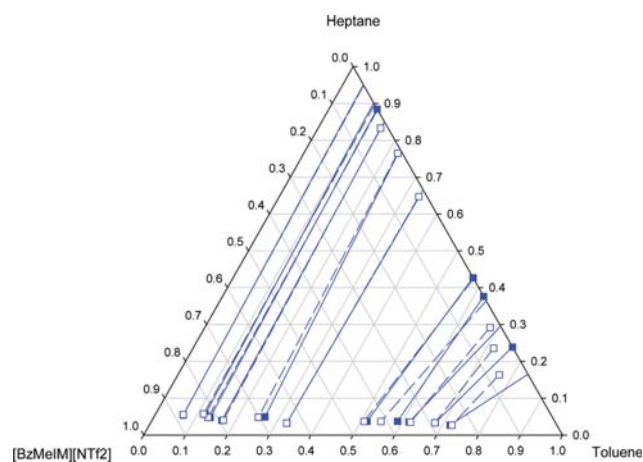


Fig. S3-2. Experimental LLE data for the ternary system: Toluene (1)+n-heptane (2)+ $[\text{BzMeIM}][\text{NTf}_2]$ (3) at temperature of 303.2 K and pressure of 0.1 MPa (solid lines: experimental tie lines; dashed lines: calculated tie lines).

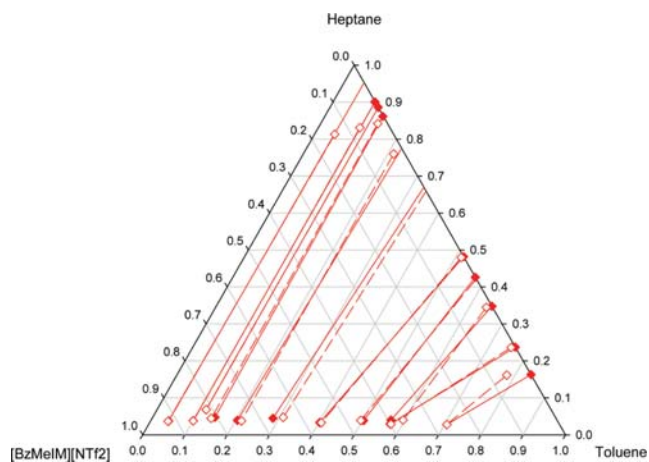


Fig. S3-3. Experimental LLE data for the ternary system: Toluene (1)+n-heptane (2)+[BzMeIM][NTf₂] (3) at temperature of 313.2 K and pressure of 0.1 MPa (solid lines: experimental tie lines; dashed lines: calculated tie lines).

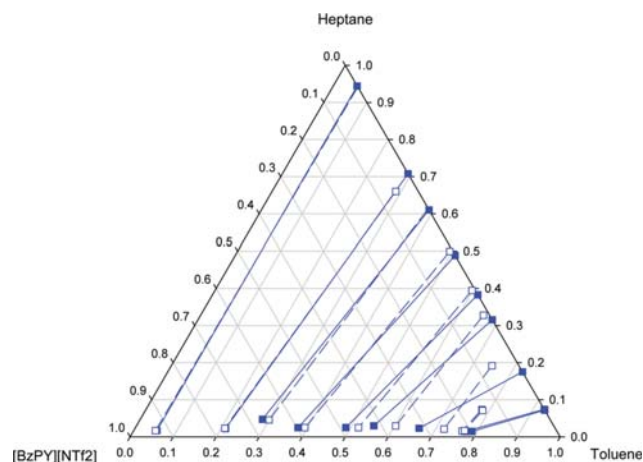


Fig. S4-2. Experimental LLE data for the ternary system: Toluene (1)+n-heptane (2)+[BzPY][NTf₂] (3) at temperature of 303.2 K and pressure of 0.1 MPa (solid lines: experimental tie lines; dashed lines: calculated tie lines).

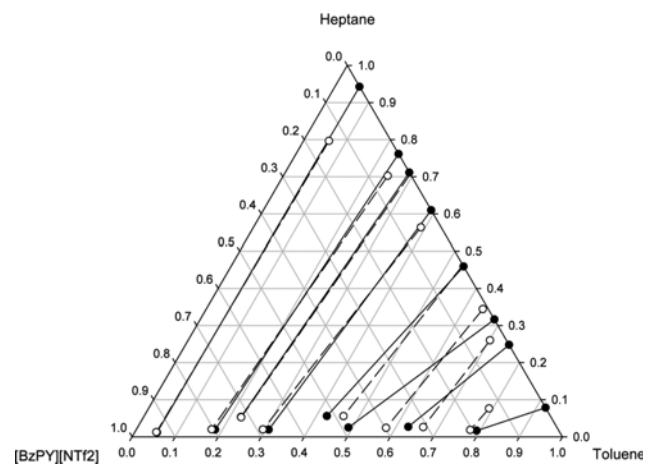


Fig. S4-1. Experimental LLE data for the ternary system: Toluene (1)+n-heptane (2)+[BzPY][NTf₂] (3) at temperature of 293.2 K and pressure of 0.1 MPa (solid lines: experimental tie lines; dashed lines: calculated tie lines).

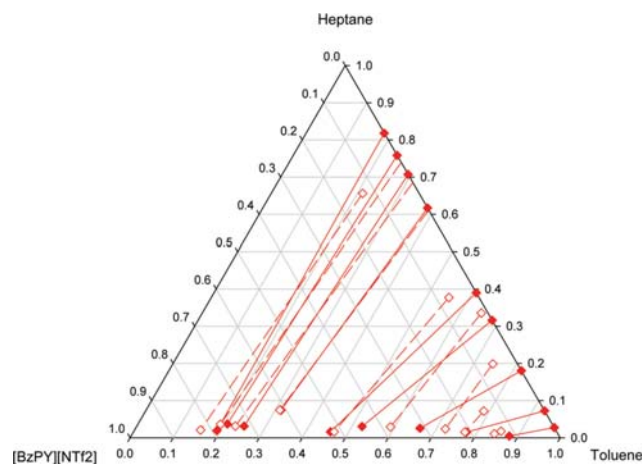


Fig. S4-3. Experimental LLE data for the ternary system: Toluene (1)+n-heptane (2)+[BzPY][NTf₂] (3) at temperature of 313.2 K and pressure of 0.1 MPa (solid lines: experimental tie lines; dashed lines: calculated tie lines).