

Experimental study on liquid – liquid equilibria of ionic liquids + alkane + ethyl benzene or *p*-xylene at 298.15 K

Babak Mokhtarani ^{a,*}, Javad Musavi ^b, Mehdi Parvini ^b, Ali Sharifi ^a, Mojtaba Mirzaei ^a

^a Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

^b Department of Chemical Engineering, 35196-45399 Semnan University, Semnan, Iran



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ABSTRACT

New experimental data for the ternary systems of 1-butyl 3-methylimidazolium nitrate ([Bmim][NO₃]) or 1-methyl 3-octylimidazolium nitrate ([Omim][NO₃]) + alkane (hexane or heptane or octane) + aromatic (ethyl benzene or *p*-xylene) at 298.15 K and atmospheric pressure are reported. The aromatic selectivity and distribution coefficient are calculated from experimental data. The effect of alkyl chain length of ionic liquids as well as alkane on the aromatic selectivity is studied. The selectivity values for the studied systems with [Bmim][NO₃] is more than [Omim][NO₃]. The reliability of the experimental data is tested with the Othmer-Tobias and Hand equations. The NRTL thermodynamic model was successfully used to correlate the experimental data.

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1. Introduction

Ionic liquids (ILs) may be replaced on classical solvent for separation processes especially liquid extraction, because these solvents have negligible vapor pressure, low melting point, and high solubility for polar and nonpolar substances [1]. Separation of aromatic compounds from alkane is a difficult process in petrochemical industry since these compounds have close boiling points and forms different azeotropes. Liquid extraction is the common process for mixtures with aromatic content in the range of 20–65 wt% and extractive distillation is suitable for 65–90 wt% of aromatics [2]. For mixtures with aromatic content more than 90 wt % azeotropic distillation is superior [2]. Sulfolane [3], *N*-methylpyrrolidone (NMP) [4], *N*-formylmorpholine (NFM) [5], ethylene glycols [6] and propylene carbonate [7] are conventional solvents for these processes but they are toxic, volatile and flammable. ILs can be used as an entrainer to facilitate the separation of azeotropic mixtures [8]. The recovery of solvent can be performed very easily in liquid extraction due to negligible vapor pressure of ILs. In recent years, numerous researches were published regarding to the potential of ILs for separation of aromatic compounds from alkane [9–22]. Liquid – liquid equilibrium (LLE) data may be assisted in

order to evaluate the potential of ILs for these processes. This work is the continuation of our previous research on the extraction of aromatic compounds from alkane using ILs [18,19,21]. The extraction of benzene and toluene from alkanes with ILs were studied in our previous researches [19,21], here the extractions of larger molecular weight aromatic (ethyl benzene or *p*-xylene) from hexane, heptane or octane with ILs at 298.15 K are investigated. The studied ILs are 1-butyl 3-methylimidazolium nitrate [Bmim][NO₃] and 1-methyl 3-octylimidazolium nitrate [Omim][NO₃]. These ILs are selected because the nitrate based ILs are halogen-free and therefore more environmental friendly than other ILs [23]. The LLE data for the ternary systems of ILs + aromatic + alkane are determined and the selectivity (*S*) and the distribution coefficient ratio (β) are calculated. The NRTL activity coefficient model is used to correlate the experimental data [24].

2. Experiments

2.1. Chemicals

The chemicals, suppliers and the purities are represented in Table 1.

All chemicals were dried over molecular sieves and kept under argon gas to avoid moisture. The ILs used in this research were

* Corresponding author.

E-mail address: mokhtaranib@ccerci.ac.ir (B. Mokhtarani).

Table 1

Suppliers and purities of chemicals in this research.

| Chemical name | Supplier | Mass fraction purity | Purity method analysis |
|--------------------------|--------------------|----------------------|--|
| Hexane | Merck | >0.99 | GC |
| Heptane | Merck | >0.99 | GC |
| Octane | Merck | >0.99 | GC |
| Ethyl benzene | Merck | >0.99 | GC |
| p-xylene | Merck | >0.99 | GC |
| [Bmim][NO ₃] | Synthesized in lab | >0.99 | NMR, Karl Fischer titration and potentiometric titration |

synthesized in laboratory. The procedures for preparation of ILs are similar to our previous works [25,26]. The purities of ILs are determined by nuclear magnetic resonance (NMR) spectroscopy. The ILs are subjected into vacuum for 24 h at 343.15 K in order to remove impurities and moisture. The moisture content of ILs are determined using Karl Fischer coulometer 684. The water mass fractions of ILs were less than 1×10^{-3} . Since, [Bmim][NO₃] and [Omim][NO₃] are prepared from [Bmim][Cl] and [Omim][Cl] respectively, the concentration of chloride anion should be measured. The mass fraction of chloride ion is determined by the potentiometric titration method and is less than 1×10^{-4} [25,26].

2.2. Apparatus and procedure

The detail descriptions of the experimental procedure are similar to our previous works [19,21]. Ternary mixtures of ethyl benzene or p-xylene + hexane, heptane or octane + ILs were weighed by a laboratory balance (OHAUS, Adventurer AV264C) with the precision of $\pm 10^{-4}$ g. The ternary mixtures were mixed with a shaker (IKA HS-260) for 180 min at 300 rpm.

The ternary mixtures formed a two phase systems and inserted into a Julabo, FP50 model water bath at 298.15 K for 12 h. This time is enough to reach the both phase in equilibrium. The water bath controls the temperature of mixtures with the precision of ± 0.1 K. The two phase systems were separated and their compositions were analyzed. The analysis of the phases was performed using a GC (Varian, cp 3800, FID detector, capillary column, Chrompack, 30 m \times 0.25 mm \times 1.2 μ m). The NMR analysis indicated no ILs existed in top phase and all ILs reside in bottom phase. The samples of the bottom phase are diluted with acetone in order to avoid phase splitting. As GC cannot detect the ILs a liner injector is applied to collect the ILs. The experimental uncertainties for composition analysis for alkane and IL rich phase are less than $\pm 3.10^{-3}$ and $\pm 1.10^{-3}$ in mole fraction, respectively.

The ILs are recovered from the mixture of alkane and aromatic after the experiments. Due to negligible vapor pressure of ILs, the mixture of alkane and aromatic is separated from IL in rotary evaporator (buchi model R-210). The rotary evaporator is connected to a vacuum pump at 400 mbar and 343 K. At this temperature most of the alkane and aromatic are vaporized. The vaporization process is continued for 6 h. In order to increase the purity of IL and eliminate the impurities, the IL is inserted into a water bath and reduces its pressure near to vacuum at 363 K. A nitrogen trap is inserted between the pipe of IL and vacuum pump (Edward model). This trap condenses the impurities and prevents to reach the vacuum pump and destroy it. The vacuum pump process is performed for 12 h. After this time the amount of water of purified IL is measured. The purified IL is injected to the GC, in order to detect the impurities peak.

3. Result and discussion

LLE data for ternary systems of [Bmim][NO₃] (1) + hexane, heptane or octane (2) + ethyl benzene or p-xylene (3) and [Omim][NO₃] (1) + hexane, heptane or octane (2) + ethyl benzene or p-xylene (3) at 298.15 K and atmospheric pressure are measured and

Table 2

Experimental LLE data in mole fraction for ternary systems of [Bmim][NO₃] (1) + alkane (2) + aromatic (3) at 298.15 K and calculated solute distribution coefficient (β) and selectivity (S).

| S | β | IL rich phase ^b | | Alkane rich phase ^a | |
|--|---------|----------------------------|------------|--------------------------------|---------|
| | | x_3^{II} | x_2^{II} | x_3^I | x_2^I |
| [Bmim][NO ₃] (1) + hexane (2) + ethyl benzene (3) | | | | | |
| 22.424 | 0.17 | 0.023 | 0.007 | 0.135 | 0.865 |
| 22.639 | 0.17 | 0.027 | 0.006 | 0.159 | 0.841 |
| 13.342 | 0.15 | 0.042 | 0.008 | 0.280 | 0.720 |
| 12.889 | 0.15 | 0.051 | 0.008 | 0.336 | 0.664 |
| 8.749 | 0.14 | 0.061 | 0.009 | 0.435 | 0.565 |
| 7.521 | 0.15 | 0.079 | 0.009 | 0.527 | 0.473 |
| 5.967 | 0.16 | 0.102 | 0.010 | 0.632 | 0.368 |
| 4.672 | 0.17 | 0.125 | 0.009 | 0.746 | 0.254 |
| 4.959 | 0.17 | 0.135 | 0.007 | 0.795 | 0.205 |
| [Bmim][NO ₃] (1) + heptane (2) + ethyl benzene (3) | | | | | |
| 39.847 | 0.25 | 0.038 | 0.005 | 0.153 | 0.847 |
| 40.200 | 0.25 | 0.043 | 0.005 | 0.173 | 0.827 |
| 17.658 | 0.17 | 0.053 | 0.007 | 0.309 | 0.691 |
| 19.892 | 0.16 | 0.059 | 0.005 | 0.367 | 0.633 |
| 10.934 | 0.14 | 0.065 | 0.006 | 0.479 | 0.521 |
| 10.335 | 0.14 | 0.079 | 0.006 | 0.569 | 0.431 |
| 7.527 | 0.14 | 0.092 | 0.007 | 0.641 | 0.359 |
| 5.890 | 0.15 | 0.117 | 0.006 | 0.775 | 0.225 |
| [Bmim][NO ₃] (1) + octane (2) + ethyl benzene (3) | | | | | |
| 39.182 | 0.19 | 0.031 | 0.004 | 0.167 | 0.833 |
| 40.139 | 0.19 | 0.037 | 0.004 | 0.196 | 0.804 |
| 25.781 | 0.16 | 0.055 | 0.004 | 0.337 | 0.663 |
| 27.358 | 0.16 | 0.063 | 0.004 | 0.396 | 0.604 |
| 19.435 | 0.15 | 0.075 | 0.004 | 0.500 | 0.500 |
| 14.922 | 0.16 | 0.082 | 0.005 | 0.507 | 0.493 |
| 15.966 | 0.15 | 0.091 | 0.004 | 0.593 | 0.407 |
| 9.618 | 0.15 | 0.102 | 0.005 | 0.672 | 0.328 |
| [Bmim][NO ₃] (1) + hexane (2) + p-xylene (3) | | | | | |
| 28.205 | 0.13 | 0.018 | 0.004 | 0.135 | 0.865 |
| 27.638 | 0.13 | 0.021 | 0.004 | 0.162 | 0.838 |
| 17.133 | 0.11 | 0.032 | 0.005 | 0.282 | 0.718 |
| 17.885 | 0.11 | 0.039 | 0.004 | 0.339 | 0.661 |
| 11.656 | 0.11 | 0.047 | 0.005 | 0.441 | 0.559 |
| 9.719 | 0.11 | 0.061 | 0.005 | 0.537 | 0.463 |
| 8.463 | 0.11 | 0.069 | 0.005 | 0.611 | 0.389 |
| 6.561 | 0.12 | 0.093 | 0.005 | 0.754 | 0.246 |
| 5.982 | 0.13 | 0.101 | 0.004 | 0.796 | 0.204 |
| [Bmim][NO ₃] (1) + heptane (2) + p-xylene (3) | | | | | |
| 32.891 | 0.16 | 0.024 | 0.004 | 0.153 | 0.847 |
| 32.253 | 0.17 | 0.029 | 0.004 | 0.176 | 0.824 |
| 22.003 | 0.17 | 0.051 | 0.005 | 0.308 | 0.692 |
| 18.899 | 0.17 | 0.062 | 0.006 | 0.366 | 0.634 |
| 14.378 | 0.17 | 0.079 | 0.006 | 0.464 | 0.536 |
| 14.008 | 0.18 | 0.085 | 0.007 | 0.471 | 0.529 |
| 11.244 | 0.18 | 0.099 | 0.007 | 0.550 | 0.450 |
| 8.054 | 0.20 | 0.127 | 0.009 | 0.644 | 0.356 |
| [Bmim][NO ₃] (1) + octane (2) + p-xylene (3) | | | | | |
| 36.401 | 0.21 | 0.036 | 0.005 | 0.172 | 0.828 |
| 36.910 | 0.21 | 0.040 | 0.005 | 0.192 | 0.808 |
| 20.881 | 0.18 | 0.060 | 0.006 | 0.335 | 0.665 |
| 20.684 | 0.18 | 0.072 | 0.005 | 0.392 | 0.608 |
| 16.237 | 0.18 | 0.088 | 0.006 | 0.483 | 0.517 |
| 14.869 | 0.18 | 0.092 | 0.006 | 0.502 | 0.498 |
| 12.520 | 0.19 | 0.112 | 0.006 | 0.584 | 0.416 |
| 11.070 | 0.21 | 0.139 | 0.006 | 0.664 | 0.336 |
| 8.408 | 0.22 | 0.174 | 0.006 | 0.790 | 0.210 |

^a Exp uncertainty = ± 0.003 .^b Exp uncertainty = ± 0.001 .

Table 3

Experimental LLE data in mole fraction for ternary systems [Omim][NO₃] (1) + alkane (2) + aromatic (3) at 298.15 K and calculated solute distribution coefficient (β) and selectivity (S).

| S | β | IL rich phase ^b | | Alkane rich phase ^a | |
|--|---------|----------------------------|------------|--------------------------------|---------|
| | | x_3^{II} | x_2^{II} | x_3^I | x_2^I |
| [Omim][NO ₃] (1) + hexane (2) + ethyl benzene (3) | | | | | |
| 4.814 | 0.62 | 0.080 | 0.112 | 0.129 | 0.871 |
| 4.904 | 0.61 | 0.092 | 0.105 | 0.151 | 0.849 |
| 3.362 | 0.62 | 0.160 | 0.136 | 0.260 | 0.740 |
| 3.718 | 0.68 | 0.226 | 0.122 | 0.333 | 0.667 |
| 3.633 | 0.68 | 0.259 | 0.117 | 0.378 | 0.622 |
| 3.003 | 0.70 | 0.283 | 0.139 | 0.404 | 0.596 |
| 3.021 | 0.70 | 0.329 | 0.123 | 0.470 | 0.530 |
| 2.471 | 0.74 | 0.420 | 0.131 | 0.564 | 0.436 |
| 2.402 | 0.81 | 0.525 | 0.120 | 0.645 | 0.355 |
| 2.296 | 0.83 | 0.593 | 0.102 | 0.717 | 0.283 |
| [Omim][NO ₃] (1) + heptane (2) + ethyl benzene (3) | | | | | |
| 6.176 | 0.65 | 0.091 | 0.091 | 0.139 | 0.861 |
| 6.395 | 0.64 | 0.100 | 0.084 | 0.156 | 0.844 |
| 4.865 | 0.57 | 0.168 | 0.082 | 0.296 | 0.704 |
| 5.131 | 0.53 | 0.182 | 0.068 | 0.341 | 0.659 |
| 4.124 | 0.50 | 0.216 | 0.069 | 0.432 | 0.568 |
| 4.056 | 0.50 | 0.227 | 0.067 | 0.455 | 0.545 |
| 3.497 | 0.47 | 0.256 | 0.063 | 0.538 | 0.462 |
| 3.024 | 0.50 | 0.310 | 0.063 | 0.621 | 0.379 |
| 2.521 | 0.50 | 0.376 | 0.050 | 0.750 | 0.250 |
| 2.326 | 0.51 | 0.414 | 0.043 | 0.805 | 0.195 |
| [Omim][NO ₃] (1) + octane (2) + ethyl benzene (3) | | | | | |
| 7.454 | 0.68 | 0.110 | 0.076 | 0.163 | 0.837 |
| 7.744 | 0.69 | 0.115 | 0.075 | 0.166 | 0.834 |
| 6.202 | 0.59 | 0.180 | 0.066 | 0.304 | 0.696 |
| 6.407 | 0.55 | 0.198 | 0.055 | 0.358 | 0.642 |
| 5.245 | 0.52 | 0.237 | 0.054 | 0.457 | 0.543 |
| 5.016 | 0.53 | 0.254 | 0.055 | 0.479 | 0.521 |
| 4.632 | 0.49 | 0.275 | 0.047 | 0.557 | 0.443 |
| 4.332 | 0.49 | 0.314 | 0.040 | 0.645 | 0.355 |
| 3.276 | 0.49 | 0.377 | 0.034 | 0.772 | 0.228 |
| 3.193 | 0.49 | 0.400 | 0.027 | 0.820 | 0.180 |
| [Omim][NO ₃] (1) + hexane (2) + p-xylene (3) | | | | | |
| 5.194 | 0.35 | 0.046 | 0.058 | 0.133 | 0.867 |
| 5.338 | 0.38 | 0.055 | 0.061 | 0.145 | 0.855 |
| 3.644 | 0.42 | 0.115 | 0.083 | 0.274 | 0.726 |
| 3.651 | 0.43 | 0.136 | 0.079 | 0.320 | 0.680 |
| 3.046 | 0.45 | 0.184 | 0.087 | 0.411 | 0.589 |
| 3.047 | 0.47 | 0.199 | 0.089 | 0.423 | 0.577 |
| 2.903 | 0.48 | 0.236 | 0.083 | 0.496 | 0.504 |
| 2.555 | 0.51 | 0.301 | 0.082 | 0.589 | 0.411 |
| 2.235 | 0.56 | 0.397 | 0.074 | 0.705 | 0.295 |
| 1.698 | 0.63 | 0.486 | 0.083 | 0.775 | 0.225 |
| [Omim][NO ₃] (1) + heptane (2) + p-xylene (3) | | | | | |
| 5.050 | 0.34 | 0.052 | 0.058 | 0.152 | 0.848 |
| 5.441 | 0.36 | 0.062 | 0.054 | 0.174 | 0.826 |
| 4.259 | 0.42 | 0.124 | 0.068 | 0.300 | 0.700 |
| 4.363 | 0.43 | 0.150 | 0.065 | 0.347 | 0.653 |
| 4.219 | 0.45 | 0.196 | 0.060 | 0.436 | 0.564 |
| 4.031 | 0.46 | 0.210 | 0.062 | 0.455 | 0.545 |
| 3.689 | 0.51 | 0.269 | 0.066 | 0.526 | 0.474 |
| 3.328 | 0.54 | 0.330 | 0.062 | 0.615 | 0.385 |
| 2.830 | 0.58 | 0.424 | 0.055 | 0.730 | 0.270 |
| [Omim][NO ₃] (1) + octane (2) + p-xylene (3) | | | | | |
| 6.446 | 0.57 | 0.087 | 0.074 | 0.154 | 0.846 |
| 6.667 | 0.56 | 0.099 | 0.069 | 0.177 | 0.823 |
| 5.274 | 0.51 | 0.161 | 0.065 | 0.319 | 0.681 |
| 5.341 | 0.47 | 0.174 | 0.056 | 0.370 | 0.630 |
| 4.827 | 0.46 | 0.213 | 0.051 | 0.465 | 0.535 |
| 4.753 | 0.46 | 0.222 | 0.050 | 0.483 | 0.517 |
| 4.190 | 0.46 | 0.259 | 0.048 | 0.565 | 0.435 |
| 3.696 | 0.48 | 0.309 | 0.045 | 0.648 | 0.352 |
| 3.543 | 0.49 | 0.378 | 0.032 | 0.770 | 0.230 |
| 3.087 | 0.51 | 0.415 | 0.030 | 0.816 | 0.184 |

^a Exp uncertainty = ±0.003.

^b Exp uncertainty = ±0.001.

reported in Tables 2 and 3. From the experimental data, the solute distribution coefficient (β) and selectivity (S) are calculated.

$$S = \frac{x_3^H x_2^I}{x_3^I x_2^H} \quad (1)$$

$$\beta = \frac{x_2^H}{x_3^I} \quad (2)$$

where x_2 and x_3 are the mole fraction of alkane and aromatic, respectively and superscript I and II denote the alkane and IL rich phase, respectively. According to these Tables, the selectivity values for both ILs are increasing with enlargement of the alkane.

As the Tables are shown, the selectivity of aromatic hydrocarbons is decrease with increase the alkyl chain length of ILs. This parameter is reduced with increasing the mole fraction of alkane for both type of ILs.

Table 4

The correlated binary interaction parameters (Δg) for NRTL model and the root mean square deviation (rmsd) for experimental ternary systems of IL + alkane + aromatic.

| Component i-j | NRTL parameter | | rmsd |
|--|------------------------------------|------------------------------------|------|
| | $\Delta g_{ij}/\text{kJ mol}^{-1}$ | $\Delta g_{ji}/\text{kJ mol}^{-1}$ | |
| [Bmim][NO ₃] (1) + hexane (2) + Ethyl benzene (3) | | | |
| 1-2 | 21.301 | -3.706 | |
| 1-3 | 7.498 | 2.715 | 0.20 |
| 2-3 | 3.373 | 18.001 | |
| [Bmim][NO ₃] (1) + heptane (2) + Ethyl benzene (3) | | | |
| 1-2 | 21.681 | -3.783 | |
| 1-3 | 8.328 | 2.129 | 0.27 |
| 2-3 | 5.343 | 17.906 | |
| [Bmim][NO ₃] (1) + octane (2) + Ethyl benzene (3) | | | |
| 1-2 | 23.284 | -4.142 | |
| 1-3 | 7.287 | 2.948 | 0.17 |
| 2-3 | 3.650 | 17.763 | |
| [Omim][NO ₃] (1) + hexane (2) + Ethyl benzene (3) | | | |
| 1-2 | 5.279 | 3.084 | |
| 1-3 | 8.389 | 4.909 | 0.47 |
| 2-3 | 0.564 | 1.586 | |
| [Omim][NO ₃] (1) + heptane (2) + Ethyl benzene (3) | | | |
| 1-2 | 5.960 | 2.369 | |
| 1-3 | 3.860 | 7.394 | 0.64 |
| 2-3 | 4.244 | 17.949 | |
| [Omim][NO ₃] (1) + octane (2) + Ethyl benzene (3) | | | |
| 1-2 | 5.706 | 2.623 | |
| 1-3 | 3.092 | 8.352 | 0.47 |
| 2-3 | 3.459 | 19.669 | |
| [Bmim][NO ₃] (1) + hexane (2) + p-xylene (3) | | | |
| 1-2 | 24.258 | -4.387 | |
| 1-3 | 8.503 | 1.909 | 0.28 |
| 2-3 | 3.426 | 18.613 | |
| [Bmim][NO ₃] (1) + heptane (2) + p-xylene (3) | | | |
| 1-2 | 23.123 | -4.159 | |
| 1-3 | 5.733 | 4.301 | 0.46 |
| 2-3 | 1.922 | 18.715 | |
| [Bmim][NO ₃] (1) + octane (2) + p-xylene (3) | | | |
| 1-2 | 23.526 | -4.210 | |
| 1-3 | 6.311 | 3.752 | 0.21 |
| 2-3 | 3.329 | 18.808 | |
| [Omim][NO ₃] (1) + hexane (2) + p-xylene (3) | | | |
| 1-2 | 3.579 | 4.565 | |
| 1-3 | 3.049 | 16.667 | 0.44 |
| 2-3 | 3.136 | 23.389 | |
| [Omim][NO ₃] (1) + heptane (2) + p-xylene (3) | | | |
| 1-2 | 5.741 | 2.484 | |
| 1-3 | 5.733 | 18.866 | 0.58 |
| 2-3 | 5.273 | 19.021 | |
| [Omim][NO ₃] (1) + octane (2) + p-xylene (3) | | | |
| 1-2 | 4.151 | 4.312 | |
| 1-3 | 2.344 | 15.328 | |
| 2-3 | 2.733 | 24.301 | 0.26 |

The ethyl benzene distribution coefficient for [Bmim][NO₃] is less than [Omim][NO₃] that means more [Bmim][NO₃] as a solvent should be used. In other words, the required amount of [Omim][NO₃] for separation process is less than [Bmim][NO₃], however, by reusing the ILs this problem is not serious.

In order to check the selectivity of different types of aromatic hydrocarbon in these ILs, the selectivity of aromatic hydrocarbons

against the mole fraction of aromatic hydrocarbons in the alkane rich phase for the [Bmim][NO₃] (1) + hexane(2) + aromatic (3) at 298.15 K are compared with our previous work [19,21] in Fig. 1S. The selectivity decreases when the mole fraction of aromatic hydrocarbons in the alkane rich phase increases. The selectivity of benzene is the largest and decrease with increase of the side chain of aromatic hydrocarbons rings ($S_{\text{benzene}} > S_{\text{Stoluene}} > S_{p\text{-xylene}} > S_{\text{ethyl}}$

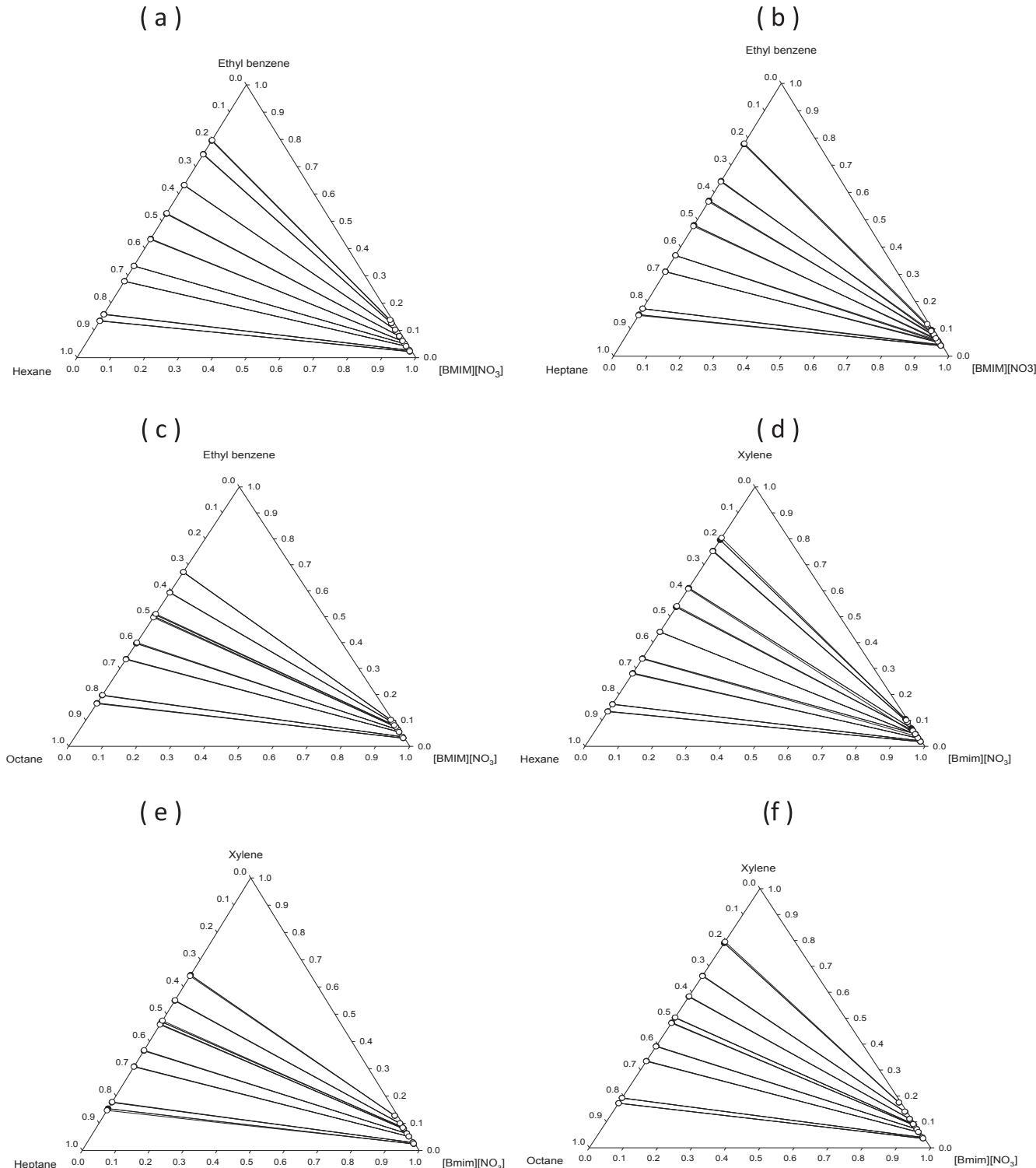


Fig. 1. Experimental and calculated LLE of the ternary systems [Bmim][NO₃] (1) + alkane (2) + ethyl benzene or *p*-xylene (3) at 298.15 K solid lines indicate the experimental data and dashed line indicate the NRTL correlation.

benzene). Similar behavior are observed with other alkane (heptane and octane) and [Omim][NO₃].

4. Data correlation

The NRTL model [24] was applied to correlate the experimental data for the studied ternary systems. The algorithm of calculation is similar to our previous work [19,21] and the non-randomness factor (α) was set to 0.3. The binary interaction parameter, Δg_{ij} , were estimated from experimental data by minimizing the following objective function:

$$F = \sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}}}{x_{ijk}^{\text{exp}}} \right)^2 \quad (3)$$

Where m is the number of tie lines, n is the number of component, k is the number of phases, and superscripts of exp and cal referred to experimental and calculated mole fraction values, respectively. The correlated interaction parameters, Δg_{ij} as well as the root mean square deviation for the studied systems are reported in Table 4.

$$\text{rmsd} = \left[\frac{\sum_i^m \sum_j^{n-1} \sum_k^2 \left(\frac{x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}}}{x_{ijk}^{\text{exp}}} \right)^2}{6m} \right]^{1/2} \times 100 \quad (4)$$

Where m is the number of the tie line.

The rmsd for all the studied systems are less than 0.7 that means the NRTL model can correlate the experimental data with a good accuracy. Moreover, the experimental tie lines data for the [Bmim][NO₃] (1) + alkane (2) + ethyl benzene or *p*-xylene (3) at 298.15 K are compared with the correlated in Fig. 1. As the figure is shown, the NRTL model correlates satisfactorily the experimental data. Similar agreement are observed for the ternary systems with [Omim][NO₃] and are shown in Fig. 2S.

5. Conclusion

New experimental data for extraction of ethyl benzene and *p*-xylene from hexane or heptane or octane with [Bmim][NO₃] or [Omim][NO₃] are determined at 298.15 K and atmospheric pressure. The selectivity and solute distribution coefficients are calculated and compared with the mixture containing other types of aromatic hydrocarbons. The experimental data indicated the effect of alkyl chain length of IL on selectivity of aromatic hydrocarbon is great and this parameter increases with enlargement the alkyl chain length of alkane. However the solute distribution coefficient is reduced with increasing the alkyl chain length of IL. Therefore, ILs with shorter alkyl chain length ([Bmim][NO₃]) is more favorable than ILs with larger alkyl chain length ([Omim][NO₃]) for extraction of ethyl benzene and *p*-xylene from alkane. Similar results were observed for extraction of other types of aromatic (benzene and toluene) from alkane. In general, low molecular weight aromatic hydrocarbons show higher selectivities than larger aromatic hydrocarbons and can be extracted more easily from alkanes. It is concluded that [Bmim][NO₃] can be used to separate different types of aromatic hydrocarbon (benzene, toluene, ethyl benzene and *p*-xylene) from alkane (hexane, heptane and octane) and the best results are obtained for systems containing benzene.

List of symbols

a The Othmer-Tobias or Hand parameters

| | |
|---------------|--------------------------------------|
| b | The Othmer-Tobias or Hand parameters |
| F | Objective function |
| k | Number of phases |
| m | Number of the tie lines |
| n | Number of the components |
| rmsd | Root mean square deviation |
| S | Selectivity |
| T | Temperature |
| x_i | mole fraction of component i |

Greek letters

| | |
|-----------------|---------------------------------|
| α | Non-randomness parameter |
| β | Solute distribution coefficient |
| Δg_{ij} | Energy parameter |

Subscripts and superscripts

| | |
|---------------|---------------------------|
| $1, 2, i, j$ | Components 1, 2, i, and j |
| I | Alkane rich phase |
| II | IL rich phase |
| cal. | Calculated values |
| exp. | Experimental values |

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.fluid.2015.08.031>.

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