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

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ABSTRACT

New experimental data for the ternary systems of 1-butyl 3- methylimidazolium nitrate ([Bmim][NO_3]) or 1-methyl 3-octylimidazolium nitrate ([Omim][NO_3]) + 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][NO_3] is more than [Omim][NO_3]. 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.

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][NO_3] and 1-methyl 3-octylimidazolium nitrate [Omim][NO_3]. 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

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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][NO_3] and [Omim][NO_3] 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 × 0.25 mm × 1.2 μm). 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][NO_3] (1) + hexane, heptane or octane (2) + ethyl benzene or *p*-xylene (3) and [Omim][NO_3] (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][NO_3] (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.