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# Solubilities of Benzene, Toluene, and Xylene Isomers in 1-Butyl-3-methylimidazolium Tetrafluoroborate

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The mass fraction solubilities of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in 1-buty-3-methylimidazolium tetrafluoroborate ([BMIM][$BF_4$]) ionic liquid in the temperature range from (298.21 to 353.15) K and the mass fraction solubility of [BMIM][$BF_4$] in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in the temperature range from (298.47 to 353.45) K have been measured using a cloud-point method. Measured solubility values $S$ were correlated as a function of temperature by a second-order polynomial. The calculated solubility values $100S$ of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in [BMIM][$BF_4$] at 320 K are 0.0995, 0.1361, 0.1425, 0.0883, and 0.1238, respectively. The calculated solubility values $100S$ of the ionic liquid in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene at 320 K are 0.1935, 0.2027, 0.2506, 0.1492, and 0.1654, respectively. The overall uncertainty was estimated to be about 4 % at 310 K for the first half of the work and decreased with increasing temperature and was estimated in a similar way to be 3.5 % for the second half of the work.

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## Introduction

The continuing search for the new generation of solvents for catalysis, synthesis, and thermal storage is constantly revealing new substances with both useful and environmentally benign properties in chemical processes.[1] Some ionic liquids (ILs) are salts based on a substituted imidazolium cation and an inorganic anion such as a halide, $[AlCl_4]^-$, $[BF_4]^-$, or $[PF_6]^-$ and are often liquids at room temperature. Room-temperature ILs may be of use in green chemistry because they may create a cleaner and more sustainable chemistry. They are an important topic that has received more and more attention in recent years. One of the applications is as environmentally friendly solvents for a range of synthetic and catalytic processes.[2−4]

It could be possible to replace water with [BMIM][$BF_4$] + water as a liquid-phase reaction medium in the synthesis of terephthalic acid from the oxidation of *p*-xylene to lower the reaction pressure at an equivalent temperature.

To aid in the development of ionic liquids for reactions and separations, the solubilities of a number of ionic liquids in aromatic hydrocarbons (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) and liquid−liquid phase equilibria have been reported.[5] The solubilities of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in [BMIM][$BF_4$] are not available in the literature.

## Experimental Section

***Materials.*** Benzene (AR 99.5 %), toluene (AR 99.5 %), *o*-xylene (AR 98.5 %), *m*-xylene (AR 98.5 %), and *p*-xylene (AR 99.5 %) were all purchased from Beijing Chemical Factory. These chemicals were distilled one more time before the solubility measurement. The chemicals used for the preparation of ionic liquid [BMIM][$BF_4$] were purchased from Beijing Chemical Factory and are of analytical grade. They were used without further purification.

***Preparation of [BMIM][$BF_4$].*** The synthesis and characterization of [BMIM][$BF_4$] was reported[6] in 1996. In this work, a different method of synthesis was adopted. 1-Butyl-3-methylimidazolium bromide was synthesized first. Butylbromide (1.1 mol) was added dropwise into 1-methylimidazole (1 mol) with agitation at 343 K, and the reaction mixture was refluxed for 24 h and then cooled to room temperature. The mixture was rinsed with ethyl acetate four times and separated with a funnel. The remaining ethyl acetate was removed by rotary evaporation, and then the solution was dried under high vacuum at (343 to 353) K for at least 6 h to obtain 1-butyl-3-methylimidazolium bromide ([BMIM][Br]) in very high yield (99 %).

Second, the tetrafluoroborate salt was prepared by metathesis reactions from the corresponding bromide. [BMIM][Br] (0.1 mol) was dissolved in acetonitrile (50 mL), and ammonium tertrafluorobarate (0.11 mol) was added. The mixture was refluxed for at least 24 h. When it was cooled to room temperature, the $NH_4Br$ precipitate was removed by filtration. The filtration process was conducted once more at reduced temperature to remove the remaining precipitate, and the residual acetonitrile was further removed by rotary evaporation to get crude 1-butyl-3-methylimidazolium tetrafluorobarate. The crude [BMIM][$BF_4$] was dissolved in dichloromethane (50 mL) and cooled below 278 K, and the solution was rinsed with 30 mL of deionized water at the same temperature five times until the aqueous phase did not form any precipitate with a 0.1 mol·L$^{-1}$ $AgNO_3$ solution. The dichloromethane solvent was removed by rotary evaporation, and [BMIM][$BF_4$] was dried under high vacuum from 323 to 333 K for at least 6 h.

The water content of the [BMIM][$BF_4$] product was determined to be about 200 ppm by Karl Fischer titration.

The chemical shifts in the $^1$H NMR spectrum ($D_2O$) appear as follows: $\delta$ 8.575 [s, 1H, H(2)], 7.390 [s, 1H, H(4)], 7.350 [s, 1H, H(5)], 4.133 [t, 2H, $NCH_2$], 3.817[s, 3H, $NCH_3$], 1.809 [m, 2H, $NCH_2CH_2$], 1.295 [m, 2H, $NCH_2CH_2CH_2$], and 0.853 [t, 3H, $CH_3$]. The $^{13}$ C NMR spectrum ($D_2O$) contains the following peaks: 138.625 [C(2)], 126.155 [C(4)], 124.861 [C(5)], 51.931 [$NCH_2$], 38.233 [$NCH_3$], 33.980 [$NCH_2CH_2$], 21.445 [$NCH_2CH_2CH_2$], and 15.288 [$CH_3$].

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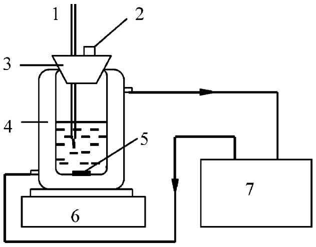

**Figure 1.** Setup of the solubility measurement: 1, glass mercury thermometer; 2, sampling opening; 3, rubber plug; 4, glass sleeve; 5, magnetic stirring rod; 6, magnetic stirrer; 7, thermostat.

***Apparatus and Procedure.*** A jacketed equilibrium cell with a working volume of 100 mL immersed in a circulating water bath with a thermostat (type 50l, Shanghai Laboratory Instrument Works Co. Ltd.) with a precision of ± 0.05 K as described by Chen et al.[7] (shown in Figure 1), an analytical balance (type TG328B, Shanghai Balance Instrument Works Co.) with an uncertainty of ± 0.1 mg, a magnetic stirrer, and a calibrated thermometer with precision of 0.1 K were used in the experiment. The equilibrium cell was sealed to prevent the evaporation of solvent or solute during the experiment.

***Solubility Measurement.*** The solubilities were measured on the basis of a cloud-point method. For the measurement of the mass fraction solubility $S$ of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in the ionic liquid at each selected temperature, the amount of solute dissolved was determined by a gravimetric method. With a known mass of ionic liquid at a constant temperature, continuous stirring was applied, and the solute was added through a titrimeter (syringe type, 3 mm in diameter) until the solution became slightly turbid by careful observation. A 100 mL Erlenmeyer flask half filled with the solute and with the syringe inserted was weighed before and after the titration operation, and the difference was taken. The charging inlet was sealed with a rubber plug to prevent the solute from evaporating. The equilibrium temperature was taken from the calibrated thermometer that was inserted into the solution. The method of the solubility measurement of the ionic liquid in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene is similar to that described above. All of the measurements reported in this article were repeated three times at each temperature, and the average value was taken. The solubility of benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene in the [BMIM][$BF_4$] ionic liquid and the solubility of [BMIM][$BF_4$] in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in the temperature range from (298 to 353) K are listed in Tables 1 and 2. Figure 2 is the plot of the solubility of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in the ionic liquid versus temperature, and Figure 3 is the plot of the solubility of the ionic liquid in the same aromatic hydrocarbons versus temperature. The amount of solvent used for each measurement was around 80 g.

**Table 1. Measured Mass Fraction Solubilities of Benzene, Toluene, *o*-Xylene, *m*-Xylene, and *p*-Xylene in [BMIM][$BF_4$]**

| | | 100$S$ | | | | 100$S$ | |
|---|---|---|---|---|---|---|---|
| compd | $T$/K | exptl | $\sigma$ | compd | $T$/K | exptl | $\sigma$ |
| benzene | 298.21 | 0.0230 | 0.0030 | *m*-xylene | 298.65 | 0.0390 | 0.0023 |
| | 308.33 | 0.0576 | | | 313.15 | 0.0696 | |
| | 313.62 | 0.0765 | | | 317.95 | 0.0806 | |
| | 318.77 | 0.0969 | | | 323.15 | 0.0959 | |
| | 323.20 | 0.1199 | | | 333.15 | 0.1210 | |
| | 333.58 | 0.1555 | | | 343.15 | 0.1431 | |
| | 343.53 | 0.1873 | | | 353.15 | 0.1750 | |
| toluene | 298.55 | 0.0376 | 0.0028 | *p*-xylene | 298.28 | 0.0262 | 0.0029 |
| | 303.15 | 0.0597 | | | 303.05 | 0.0484 | |
| | 308.35 | 0.0907 | | | 308.10 | 0.0717 | |
| | 312.95 | 0.1036 | | | 313.19 | 0.0925 | |
| | 318.15 | 0.1295 | | | 318.01 | 0.1159 | |
| | 323.05 | 0.1489 | | | 323.55 | 0.1352 | |
| | 333.15 | 0.1774 | | | 333.19 | 0.1600 | |
| | 343.15 | 0.1980 | | | 343.02 | 0.1848 | |
| | 353.15 | 0.2200 | | | 352.01 | 0.2110 | |
| *o*-xylene | 298.63 | 0.0246 | 0.0023 | | | | |
| | 303.20 | 0.0508 | | | | | |
| | 307.96 | 0.0785 | | | | | |
| | 313.65 | 0.1120 | | | | | |
| | 319.66 | 0.1465 | | | | | |
| | 324.20 | 0.1695 | | | | | |
| | 334.15 | 0.2190 | | | | | |
| | 343.51 | 0.2546 | | | | | |
| | 352.33 | 0.2960 | | | | | |

**Table 2. Measured Mass Fraction Solubilities of the [BMIM][$BF_4$] in Benzene, Toluene, *o*-Xylene, *m*-Xylene, and *p*-Xylene**

| | | 100$S$ | | | | 100$S$ | |
|---|---|---|---|---|---|---|---|
| compd | $T$/K | exptl | $\sigma$ | compd | $T$/K | exptl | $\sigma$ |
| benzene | 298.47 | 0.0471 | 0.0036 | *m*-xylene | 302.20 | 0.0405 | 0.0030 |
| | 302.97 | 0.0766 | | | 311.67 | 0.0864 | |
| | 308.23 | 0.1098 | | | 321.68 | 0.1439 | |
| | 313.35 | 0.1428 | | | 326.05 | 0.1662 | |
| | 318.35 | 0.1741 | | | 335.66 | 0.2184 | |
| | 323.28 | 0.1967 | | | 341.41 | 0.2553 | |
| | 333.82 | 0.2314 | | | 352.49 | 0.3114 | |
| | 343.96 | 0.2731 | | *p*-xylene | 301.63 | 0.0520 | 0.0034 |
| toluene | 301.47 | 0.0763 | 0.0037 | | 308.25 | 0.0968 | |
| | 308.20 | 0.1231 | | | 313.93 | 0.1361 | |
| | 318.18 | 0.1820 | | | 318.35 | 0.1683 | |
| | 326.19 | 0.2287 | | | 325.45 | 0.2041 | |
| | 333.22 | 0.2735 | | | 333.53 | 0.2433 | |
| | 343.18 | 0.3150 | | | 342.87 | 0.2808 | |
| | 353.41 | 0.3753 | | | 353.65 | 0.3289 | |
| *o*-xylene | 298.57 | 0.0803 | 0.0024 | | | | |
| | 303.18 | 0.1203 | | | | | |
| | 311.61 | 0.1802 | | | | | |
| | 322.83 | 0.2527 | | | | | |
| | 333.19 | 0.3156 | | | | | |
| | 344.40 | 0.3769 | | | | | |
| | 353.35 | 0.4281 | | | | | |

The overall uncertainty in the solubility measurement depends on the purity of the solvent and solute, the precision of the calibrated thermometer, the precision of the electronic digital balance, and the mass increment of the solute added. For the solubility measurement of benzene, *o*-xylene, *m*-xylene, and *p*-xylene in [BMIM][$BF_4$], one drop of liquid from the titrimeter was 0.0050 g, and the uncertainty was estimated to be about 10 % for benzene, *o*-xylene, and *p*-xylene and about 7 % for toluene and *m*-xylene at 298 K. The overall uncertainty was about 4 % at 310 K and improved further at higher temperatures because of the nature of the method adopted. For the solubility measurement of [BMIM][$BF_4$] in the same aromatic hydrocarbons, one drop of liquid from the titrimeter was 0.0070 g, and the uncertainty was about 9 % for benzene, *m*-xylene, and *p*-xylene and about 5 % for toluene and *o*-xylene at 298 K. The overall uncertainty was about 3.5 % at 310 K and improved further at higher temperatures for the same reason.

## Data Correlation

The mass fraction solubility $S$ of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in the ionic liquid and the solubility of the ionic liquid in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene were all correlated as a function of temperature by the following form of a second-order polynomial:

$$100S = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 \qquad (1)$$

Parameters $a$, $b$, and $c$ correlated for the different systems are listed in Table 3. The standard deviation $\sigma$ of the experimental data from the smoothed results based on eq 1 are

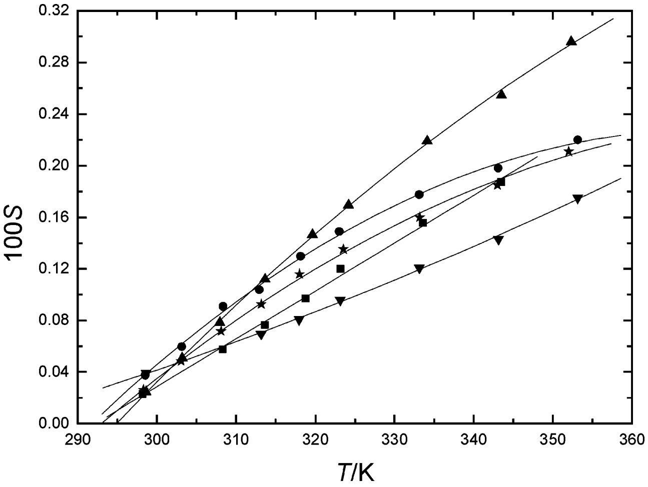

**Figure 2.** Mass fraction solubility of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in [BMIM][BF$_4$]. Measured solubility of ■, benzene; ●, toluene; ▲, *o*-xylene; ▼, *m*-xylene; and ★, *p*-xylene in [BMIM][BF$_4$]; −, calculated according to eq 1.

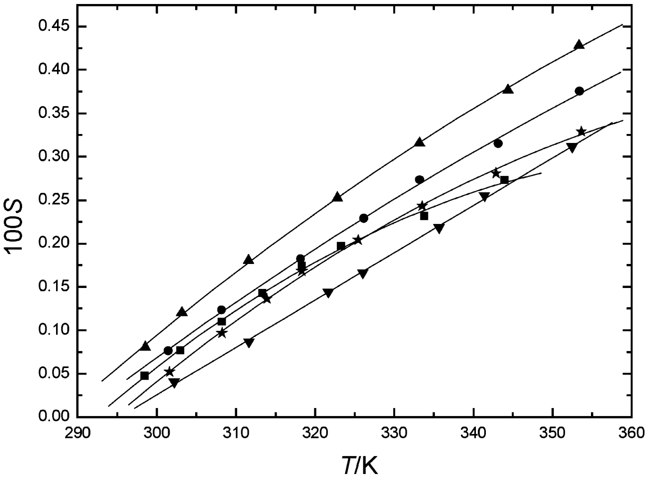

**Figure 3.** Mass fraction solubility of [BMIM][BF$_4$] in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene. Measured solubility of [BMIM][BF$_4$] in ■, benzene; ●, toluene; ▲, *o*-xylene; ▼, *m*-xylene; and ★, *p*-xylene; −, calculated according to eq 1.

**Table 3. Parameters in Equation 1 for Each System**

| system | *a* | *b* | $c \times 10^5$ |
|---|---|---|---|
| benzene + IL | −1.0845 | 0.0037 | 0 |
| toluene + IL | −4.9102 | 0.0278 | −3.7595 |
| *o*-xylene + IL | −3.8696 | 0.0198 | −2.2694 |
| *m*-xylene + IL | 0.0723 | −0.0023 | 0.7344 |
| *p*-xylene + IL | −3.969 | 0.0219 | −2.8469 |
| IL + benzene | −6.5892 | 0.0373 | −5.0325 |
| IL + toluene | −3.4220 | 0.0167 | −1.6790 |
| IL + *o*-xylene | −4.2909 | 0.0218 | −2.3774 |
| IL + *m*-xylene | −1.6108 | 0.0055 | 0 |
| IL + *p*-xylene | −5.5795 | 0.0301 | −3.7960 |

listed in Tables 1 and 2. The standard deviation of the experimental data from smoothed data is expressed as

$$\sigma = \sqrt{\frac{\Sigma\,(S_i^{\mathrm{rd}} - S_i^{\mathrm{calcd}})^2}{N - 1}} \qquad (2)$$

The experimental data and the smoothed results are shown in Figure 2 and Figure 3.

where superscripts rd and calcd stand for experimental and calculated values, respectively, and *N* stands for the total number of experimental data points. The standard deviations of the correlated solubility of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in [BMIM][BF$_4$] are 0.0030, 0.0028, 0.0023, 0.0023, and 0.0029, respectively. The standard deviations of the correlated solubility of the ionic liquid in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene are 0.0036, 0.0037, 0.0024, 0.0030, and 0.0034, respectively.

## Results and Discussion

Within the temperature range of the measurements, the solubilities of benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene in the [BMIM][BF$_4$] ionic liquid increased with increasing temperature, but the tendency of each varied to a certain extent. The intersolubility of *o*-xylene with [BMIM][BF$_4$] was considerably higher than that of the rest of the compounds, especially at elevated temperatures because it had a greater slope of increase. The increase rate of solubility of benzene and toluene with temperature slowed a little with increasing temperature compared with that of xylenes. Among the three xylene isomers, *o*-xylene showed a relatively higher solubility in the ionized liquid. One of the possible reasons might be the difference in the induced dipole moment related to molecular structure. At the same time, the solubility of [BMIM][BF$_4$] in benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene was much higher than that of the aromatic hydrocarbons in the ionic liquid at the same temperature. For example, the solubility (100*S*) of [BMIM][BF$_4$] in *o*-xylene increased from 0.0803 at 298.57 K to 0.4281 at 353.35 K, whereas that of *o*-xylene in [BMIM][BF$_4$] increased from 0.0246 at 298.63 K to 0.2960 at 352.33 K. Because of the nature of the measurement method, solubility values at lower temperatures were less reliable than those at higher temperatures.

The formation of liquid clathrates of organic salts with halide-containing anions when in contact with aromatic hydrocarbons[8] explained one of the reasons that aromatic hydrocarbons are soluble in tetrafluoroborate ionic liquid as reported in this work whereas this ionic liquid is completely miscible with water.

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