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# Experimental Liquid−Liquid Equilibria of 1-Alkyl-3-methylimidazolium Hexafluorophosphate with 1-Alcohols

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Liquid−liquid equilibria were measured for nine binary systems containing 1-alkyl-3-methylimidazolium hexafluorophosphates with alcohols in the following temperature ranges: BMIM $PF_6$ with 1-propanol or 1-butanol or 1-pentanol and HMIM $PF_6$ with 1-butanol or 1-pentanol from (278.15 to 343.15) K; HMIM $PF_6$ with 1-propanol from (278.15 to 328.15) K; and OMIM $PF_6$ with 1-propanol or 1-butanol or 1-pentanol from (278.15 to 307.15) K, (278.15 to 323.15) K, and (278.15 to 333.15) K, respectively. The equation results were satisfactorily correlated by the NRTL and UNIQUAC models.

## Introduction

In the last years, ionic liquids (ILs) have had increasing attention as possible replacement solvents for volatile organic compounds and the development of a sustainable green chemistry. Liquid−liquid equilibria data are essential for a proper understanding of extraction processes. The analysis of the composition of the two phases in equilibrium supplies considerable information about mass balance and mass transfer calculations in the design and optimization of separation processes. In this paper, we have chosen the most extensively investigated cation in ILs, that is, 1-alkyl-3-methylimidazolium and hexafluorophosphate ($PF_6^-$) as the anion. The interest of these ILs based on the $PF_6^-$ anion has weakened over the past few years due to the concerns that they can degrade in the presence of water[1] and at high temperatures[2] leading to the formation of HF. Consequently, the application of the hexafluorophosphate ILs is restricted to those applications under water-free conditions and moderate temperatures.

In this paper, liquid−liquid equilibria (LLE) of several ILs with an increasing alkyl chain of the cation ($C_n$MIM from $n$ = 4 to 6 to 8) with three different alkanols were carried out. The binary liquid−liquid equilibria have been measured from (278.15 to 343.15) K for BMIM $PF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate) with 1-propanol or 1-butanol or 1-pentanol and HMIM $PF_6$ (1-hexyl-3-methylimidazolium hexafluorophosphate) with 1-butanol or 1-pentanol; from (278.15 to 328.15) K for HMIM $PF_6$ with 1-propanol; and from (278.15 to 307.15) K, (278.15 to 323.15) K, and (278.15 to 333.15) K for OMIM $PF_6$ (1-methyl-3-octylimidazolium hexafluorophosphate) with 1-propanol or 1-butanol or 1-pentanol, respectively. This work is a continuation of our research[3−6] in the knowledge of the separation processes of these new solvents with different organic chemicals. Likewise, the obtained LLE data were correlated by applying the NRTL[7] and UNIQUAC[8] equations.

## Experimental Section

***Chemicals.*** The chemicals were supplied by Sigma Aldrich for 1-propanol (99.9 % mass fraction), by Merck for 1-butanol (99.8 % mass fraction), and by Sigma Aldrich for 1-pentanol (99.0 % mass fraction). Chromatographic tests of the solvents showed purities that fulfilled purchaser specifications. Immediately prior to their use, the alcohols were degassed ultrasonically, dried over freshly activated molecular sieves (type 4 Å, supplied by Aldrich) for several weeks, and kept in an inert argon atmosphere as soon as the bottles were opened. The ILs were supplied by Green Solutions Chemicals S. L. with a certified purity higher than 98 % mass fraction. To reduce the water content to negligible values (mass fraction lower than 0.03 %, determined using a 756 Karl Fisher coulometer), a vacuum ($2 \cdot 10^{-1}$ Pa) was applied to the ILs for several days, always before their use, and submitted to NMR and positive FABMS (FISONS VG AUTOSPEC mass spectrometer) to ensure their purity. The ILs were kept in bottles under an inert gas. Figure 1 shows the RMIM $PF_6$ structure, where R is the alkyl chain of butyl, hexyl, and octyl, respectively. The density and the refractive index of the chemicals together with recent literature[9−16] values are presented in Table 1.

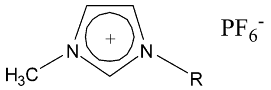

**Figure 1.** Schematic structure of RMIM $PF_6$ where R is the alkane alkyl chain.

**Table 1. Comparison of Density $\rho$ and Refractive Index $n_D$ with Literature Data for Pure Components at 298.15 K**

| | $\rho$/g·cm$^{-3}$ | | $n_D$ | |
|---|---|---|---|---|
| component | exptl | lit. | exptl | lit. |
| 1-propanol | 0.7996 | 0.79962[a] | 1.38305 | 1.3830[a] |
| 1-butanol | 0.8056 | 0.80576[a] | 1.39726 | 1.3973[a] |
| 1-pentanol | 0.8108 | 0.81083[a] | 1.40797 | 1.4080[a] |
| BMIM $PF_6$ | 1.3673 | 1.36745[b]<br>1.36612[c] | 1.40937 | 1.40925[g] |
| HMIM $PF_6$ | 1.2937 | 1.2935[d] | 1.41787 | na[i] |
| OMIM $PF_6$ | 1.2357 | 1.23684[e]<br>1.2245[f] | 1.42302 | 1.423[h] |

[a] Ref 9. [b] Ref 10. [c] Ref 11. [d] Ref 12. [e] Ref 13. [f] Ref 14. [g] Ref 15. [h] Ref 16. [i] na (not available).

***Experimental Procedure.*** A calibration curve was made by measuring the density of the samples with known composition. The samples were prepared by filling glass vials with the IL

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**Table 2. Experimental Liquid−Liquid Equilibria for the Binary Mixtures C$_n$MIM PF$_6$ (1) + 1-Alcohols (2)**

| $T$/K | $x_1$ (IL - poor phase) | $x_1$ (IL - rich phase) | $T$/K | $x_1$ (IL - poor phase) | $x_1$ (IL - rich phase) |
|---|---|---|---|---|---|
| BMIM PF$_6$ (1) + 1-Propanol (2) | | | | | |
| 278.15 | 0.0004 | 0.7864 | 313.15 | 0.0015 | 0.6033 |
| 283.15 | 0.0005 | 0.7667 | 318.15 | 0.0018 | 0.5760 |
| 288.15 | 0.0006 | 0.7437 | 323.15 | 0.0024 | 0.5497 |
| 293.15 | 0.0007 | 0.7198 | 328.15 | 0.0032 | 0.5303 |
| 298.15 | 0.0008 | 0.6946 | 333.15 | 0.0049 | 0.5085 |
| 303.15 | 0.0010 | 0.6664 | 338.15 | 0.0090 | 0.4842 |
| 308.15 | 0.0012 | 0.6380 | 343.15 | 0.0101 | 0.4706 |
| BMIM PF$_6$ (1) + 1-Butanol (2) | | | | | |
| 278.15 | 0.0003 | 0.8730 | 313.15 | 0.0010 | 0.7597 |
| 283.15 | 0.0004 | 0.8610 | 318.15 | 0.0013 | 0.7387 |
| 288.15 | 0.0004 | 0.8465 | 323.15 | 0.0016 | 0.7164 |
| 293.15 | 0.0005 | 0.8299 | 328.15 | 0.0020 | 0.7069 |
| 298.15 | 0.0007 | 0.8124 | 333.15 | 0.0025 | 0.6980 |
| 303.15 | 0.0008 | 0.7932 | 338.15 | 0.0032 | 0.6893 |
| 308.15 | 0.0009 | 0.7718 | 343.15 | 0.0040 | 0.6785 |
| BMIM PF$_6$ (1) + 1-Pentanol (2) | | | | | |
| 278.15 | 0.0007 | 0.9193 | 313.15 | 0.0013 | 0.8379 |
| 283.15 | 0.0007 | 0.9157 | 318.15 | 0.0015 | 0.8212 |
| 288.15 | 0.0007 | 0.9066 | 323.15 | 0.0018 | 0.8044 |
| 293.15 | 0.0007 | 0.8960 | 328.15 | 0.0021 | 0.7872 |
| 298.15 | 0.0008 | 0.8832 | 333.15 | 0.0025 | 0.7695 |
| 303.15 | 0.0009 | 0.8714 | 338.15 | 0.0030 | 0.7584 |
| 308.15 | 0.0010 | 0.8568 | 343.15 | 0.0035 | 0.7470 |
| HMIM PF$_6$ (1) + 1-Propanol (2) | | | | | |
| 278.15 | 0.0018 | 0.6973 | 308.15 | 0.0078 | 0.5072 |
| 283.15 | 0.0022 | 0.6674 | 313.15 | 0.0106 | 0.4646 |
| 288.15 | 0.0027 | 0.6365 | 318.15 | 0.0175 | 0.4346 |
| 293.15 | 0.0035 | 0.6023 | 323.15 | 0.0482 | 0.4120 |
| 298.15 | 0.0044 | 0.5691 | 328.15 | 0.0785 | 0.3819 |
| 303.15 | 0.0057 | 0.5331 | | | |
| HMIM PF$_6$ (1) + 1-Butanol (2) | | | | | |
| 278.15 | 0.0009 | 0.7691 | 313.15 | 0.0043 | 0.5864 |
| 283.15 | 0.0012 | 0.7501 | 318.15 | 0.0056 | 0.5576 |
| 288.15 | 0.0015 | 0.7255 | 323.15 | 0.0073 | 0.5314 |
| 293.15 | 0.0018 | 0.6991 | 328.15 | 0.0101 | 0.5017 |
| 298.15 | 0.0021 | 0.6706 | 333.15 | 0.0169 | 0.4824 |
| 303.15 | 0.0026 | 0.6401 | 338.15 | 0.0275 | 0.4581 |
| 308.15 | 0.0034 | 0.6128 | 343.15 | 0.0407 | 0.4298 |
| HMIM PF$_6$ (1) + 1-Pentanol (2) | | | | | |
| 278.15 | 0.0010 | 0.8402 | 313.15 | 0.0019 | 0.6963 |
| 283.15 | 0.0010 | 0.8261 | 318.15 | 0.0026 | 0.6779 |
| 288.15 | 0.0010 | 0.8130 | 323.15 | 0.0029 | 0.6555 |
| 293.15 | 0.0010 | 0.7931 | 328.15 | 0.0036 | 0.6326 |
| 298.15 | 0.0013 | 0.7708 | 333.15 | 0.0046 | 0.6079 |
| 303.15 | 0.0014 | 0.7474 | 338.15 | 0.0057 | 0.5858 |
| 308.15 | 0.0016 | 0.7233 | 343.15 | 0.0091 | 0.5654 |
| OMIM PF$_6$ (1) + 1-Propanol (2) | | | | | |
| 278.15 | 0.0024 | 0.4646 | 298.15 | 0.0088 | 0.2910 |
| 283.15 | 0.0030 | 0.4278 | 303.15 | 0.0151 | 0.2335 |
| 288.15 | 0.0040 | 0.3870 | 305.15 | 0.0171 | 0.2026 |
| 293.15 | 0.0058 | 0.3422 | 307.15 | 0.0269 | 0.1566 |
| OMIM PF$_6$ (1) + 1-Butanol (2) | | | | | |
| 278.15 | 0.0013 | 0.6184 | 303.15 | 0.0040 | 0.4395 |
| 283.15 | 0.0014 | 0.5903 | 308.15 | 0.0055 | 0.3963 |
| 288.15 | 0.0018 | 0.5549 | 313.15 | 0.0082 | 0.3390 |
| 293.15 | 0.0022 | 0.5202 | 318.15 | 0.0138 | 0.2924 |
| 298.15 | 0.0030 | 0.4820 | 323.15 | 0.0284 | 0.2341 |
| OMIM PF$_6$ (1) + 1-Pentanol (2) | | | | | |
| 278.15 | 0.0004 | 0.7551 | 308.15 | 0.0027 | 0.5370 |
| 283.15 | 0.0006 | 0.7158 | 313.15 | 0.0034 | 0.5001 |
| 288.15 | 0.0008 | 0.6787 | 318.15 | 0.0048 | 0.4523 |
| 293.15 | 0.0012 | 0.6384 | 323.15 | 0.0068 | 0.4175 |
| 298.15 | 0.0016 | 0.6068 | 328.15 | 0.0106 | 0.3807 |
| 303.15 | 0.0022 | 0.5730 | 333.15 | 0.0290 | 0.3482 |

and the organic compound. Vials are closed with screw caps to ensure a secure seal and to prevent humidity. The sample was taken from the vial with a syringe through a silicone septum and was immediately put into the apparatus. The mass of the chemicals was determined using a Mettler AX-205 Delta Range balance with a precision of $\pm 10^{-5}$ g. The estimated uncertainty of the composition of the mixtures was $\pm 10^{-4}$ in mole fraction.

The density of the pure liquids and the binary mixtures was measured with an Anton Paar DSA-48 digital vibrating tube densimeter. The uncertainty in the measurement of the samples

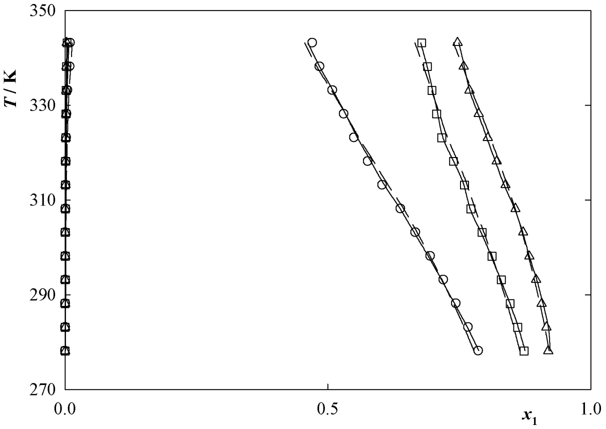

**Figure 2.** Liquid−liquid phase diagram vs mole fraction of BMIM PF$_6$ (1) + 1-alcohols (2): ○, 1-propanol; □, 1-butanol; △, 1-pentanol. Experimental tie-lines and correlated NRTL (solid line) and UNIQUAC (dashed line) curves.

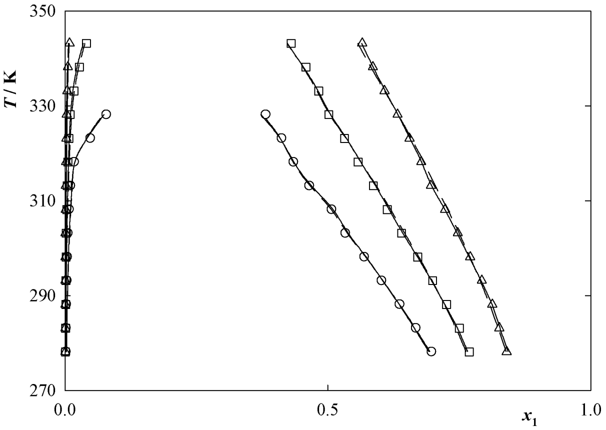

**Figure 3.** Liquid−liquid phase diagram vs mole fraction of HMIM PF$_6$ (1) + 1-alcohols (2): ○, 1-propanol; □, 1-butanol; △, 1-pentanol. Experimental tie-lines and correlated NRTL (solid line) and UNIQUAC (dashed line) curves.

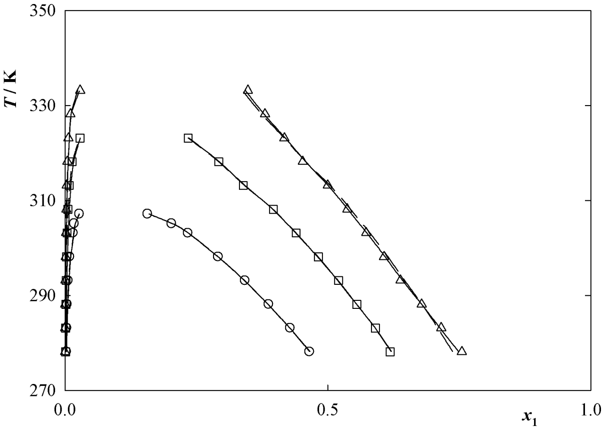

**Figure 4.** Liquid−liquid phase diagram vs mole fraction of OMIM PF$_6$ (1) + 1-alcohols (2): ○, 1-propanol; □, 1-butanol; △, 1-pentanol. Experimental tie-lines and correlated NRTL (solid line) and UNIQUAC (dashed line) curves.

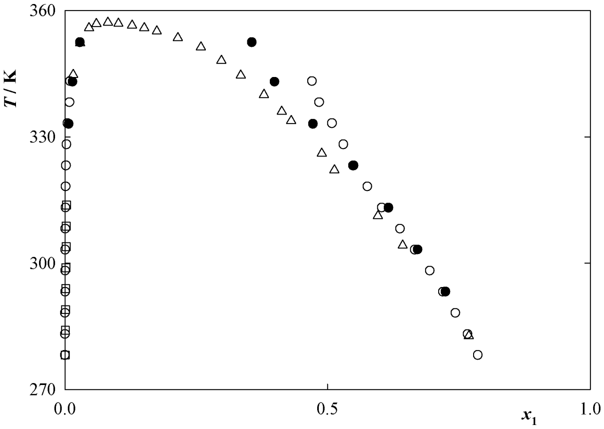

**Figure 5.** Liquid−liquid phase diagram vs mole fraction of BMIM PF$_6$ (1) + 1-propanol (2): ○, this work; ●, cloud-point measurement, Sahandzhieva et al.;[17] □, UV measurement, Sahandzhieva et al.;[17] △, Marsh et al.[18]

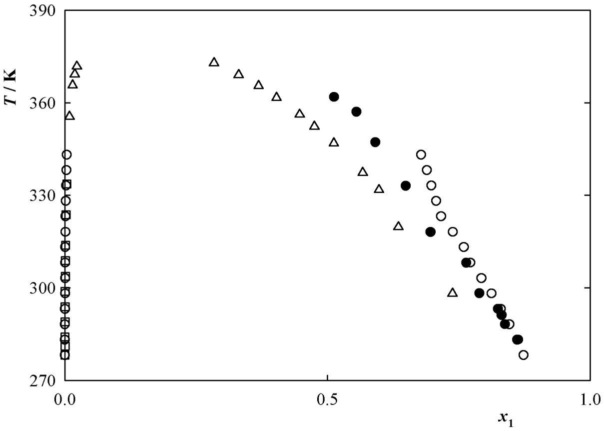

**Figure 6.** Liquid−liquid phase diagram vs mole fraction of BMIM PF$_6$ (1) + 1-butanol (2): ○, this work; ●, cloud-point measurement, Sahandzhieva et al.;[17] □, UV measurement, Sahandzhieva et al.;[17] △, Wu et al.[19]

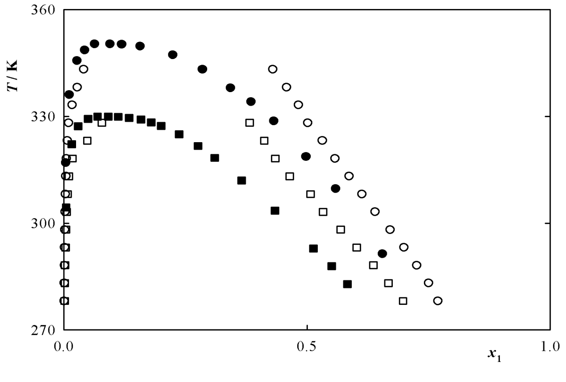

**Figure 7.** Liquid−liquid phase diagram vs mole fraction of HMIM PF$_6$ (1) + 1-propanol (2): □, this work; ■, Marsh et al.[18] HMIM PF$_6$ (1) + 1-butanol (2): ○, this work; ●, Wu et al.[19]

is ± 2·10$^{-4}$ g·cm$^{-3}$. The apparatus was calibrated by measuring the density of Millipore quality water and ambient air according to instructions. To determine the composition of the coexisting phase, the density of the samples was determined at 343.15 K.

Tie-line data determinations were performed in a jacketed glass vessel containing a magnetic stirrer connected to a temperature-controlled circulating bath (controlled to ± 0.01 K). The vessel was closed to moisture and was flushed with dry argon. The temperature was measured with a Pt-100 resistance temperature probe, which was introduced in the mixture and connected to a F200 ASL digital thermometer with an accuracy of ± 0.01 K. The uncertainty of the whole temperature measurements in the systems was estimated to be ± 0.05 K. The measurements were started with the addition of 100 mL of an immiscible binary mixture of known composition; the temperature was adjusted; and the mixture was stirred vigorously during 1 h and left to settle for 3 h. Samples were

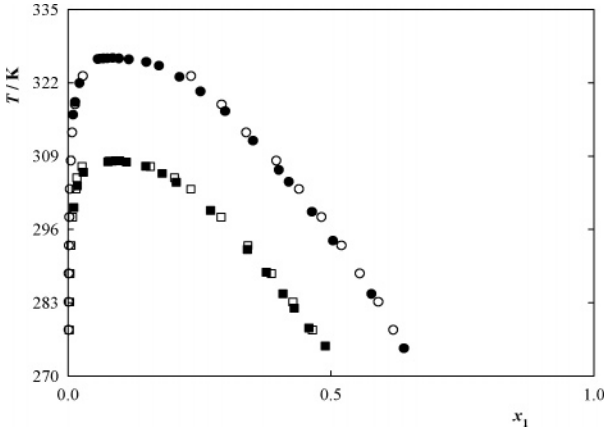

**Figure 8.** Liquid−liquid phase diagram vs mole fraction of OMIM $PF_6$ (1) + 1-propanol (2): □, this work; ■, Marsh et al.[18] OMIM $PF_6$ (1) + 1-butanol (2): ○, this work; ●, Wu et al.[19]

taken by a syringe from the upper and lower layers. A series of binary LLE measurements were made at different temperatures. Phase compositions were determined measuring the density of the samples. The uncertainty of the phase composition is estimated to be ± 0.0005 in mole fraction. The LLE for the binary systems were determined until 343.15 K to prevent hydrolysis.

## Results and Discussion

LLE for the binary mixtures were determined experimentally from (278.15 to 343.15) K for BMIM $PF_6$ with 1-propanol or 1-butanol or 1-pentanol and HMIM $PF_6$ with 1-butanol or 1-pentanol; from (278.15 to 328.15) K for HMIM $PF_6$ with 1-propanol; and from (278.15 to 307.15) K, (278.15 to 323.15) K, and (278.15 to 333.15) K for OMIM $PF_6$ with 1-propanol or 1-butanol or 1-pentanol, respectively. The results are shown in Table 2. Experimental phase diagrams of LLE investigated are shown in Figures 2 to 4. A comparison with the literature[17−19] data was made in Figures 5 to 8. In general terms, the literature LLE data and this work agree with the studied binary systems.

***Liquid−Liquid Equilibria Correlation.*** In this work, the NRTL and UNIQUAC equations with temperature-dependent interaction parameters are used to correlate the experimental binary LLE data. For the NRTL model, the third randomness parameter α was optimized, and their values are reported in Table 3. The volume $R_k$ and surface area $Q_k$ parameters of the UNIQUAC equation were obtained from the literature.[20]

In these equations, the adjustable parameter was defined as a linear temperature dependence, described as follows for NRTL and UNIQUAC, respectively

$$\Delta g_{ij} = a_{ij} + b_{ij}T/\text{K} \text{ and } \Delta u_{ij} = a_{ij} + b_{ij}T/\text{K} \qquad (1)$$

The SOLVER function in Microsoft EXCEL was used to adjust the parameters so that the objective function was minimized, providing the set of temperature-dependent adjustable parameters for the binary systems. The objective function (OF) is defined as follows

$$\text{OF} = \sum_{i=1}^{2} (x_i^{l,\text{exptl}} - x_i^{l,\text{calcd}})^2 \qquad (2)$$

where $x$ is the mole fraction and the subscripts $i$ and $l$ provide a designation for the component and the phase, respectively.

The fitting parameters of these equations are presented in Table 3. The standard deviation of the mole fraction and the temperature dependence of the correlative parameters are listed in Table 3. These deviations were calculated applying the following expression for the binary mixtures

$$\sigma = \left( \sum_{i=1}^{2} \left( \frac{x_i^{l,\text{exptl}} - x_i^{l,\text{calcd}}}{x_i^{l,\text{exptl}}} \right)^2 \right)^{0.5} \qquad (3)$$

where $x$ is the mole fraction and the subscripts $i$ and $l$ provide a designation for the component and the phase, respectively.

A view of the standard deviation between the experimental data and those obtained from their correlation by the NRTL and UNIQUAC equations indicates a good fit. In general terms, the worst correlation results were obtained for BMIM $PF_6$ with the alcohols, probably because the variation of the BMIM $PF_6$ composition in the IL rich phase is slighter than in the other ILs where the difference in size of the components is higher.

## Conclusions

LLE of the binary mixtures involving $C_n$MIM $PF_6$ with 1-propanol or 1-butanol or 1-pentanol were determined experimentally at several temperatures and from (278.15 to 343.15)

**Table 3. Fitting Parameters and Root Mean Square Deviation of the LLE Data**

| system | $a_{12}$ / $J \cdot mol^{-1}$ | $a_{21}$ / $J \cdot mol^{-1}$ | $b_{12}$ / $J \cdot mol^{-1} \cdot K^{-1}$ | $b_{21}$ / $J \cdot mol^{-1} \cdot K^{-1}$ | α | σ |
|---|---|---|---|---|---|---|
| | | | NRTL | | | |
| BMIM $PF_6$ (1) + 1-propanol (2) | 24999 | 20999 | −74.60 | −20.09 | 0.32 | 0.557 |
| BMIM $PF_6$ (1) + 1-butanol (2) | 24999 | 20999 | −62.00 | −20.56 | 0.36 | 1.443 |
| BMIM $PF_6$ (1) + 1-pentanol (2) | 24999 | 20999 | −55.02 | −23.57 | 0.39 | 2.498 |
| HMIM $PF_6$ (1) + 1-propanol (2) | 24999 | 20999 | −77.31 | −34.81 | 0.37 | 1.437 |
| HMIM $PF_6$ (1) + 1-butanol (2) | 24999 | 20999 | −73.40 | −29.53 | 0.36 | 1.197 |
| HMIM $PF_6$ (1) + 1-pentanol (2) | 24999 | 20999 | −68.56 | −25.05 | 0.36 | 0.850 |
| OMIM $PF_6$ (1) + 1-propanol (2) | 24999 | 20999 | −91.60 | −29.61 | 0.31 | 0.763 |
| OMIM $PF_6$ (1) + 1-butanol (2) | 24999 | 20999 | −85.75 | −28.16 | 0.31 | 1.507 |
| OMIM $PF_6$ (1) + 1-pentanol (2) | 24999 | 20999 | −83.72 | −21.84 | 0.27 | 1.323 |
| | | | UNIQUAC | | | |
| BMIM $PF_6$ (1) + 1-propanol (2) | −1651.0 | −1851.1 | 18.92 | 8.684 | | 2.185 |
| BMIM $PF_6$ (1) + 1- butanol (2) | −1448.6 | −1512.9 | 17.22 | 7.728 | | 2.532 |
| BMIM $PF_6$ (1) + 1-pentanol (2) | −1651.0 | −1851.1 | 18.35 | 8.327 | | 2.025 |
| HMIM $PF_6$ (1) + 1-propanol (2) | −1526.0 | −1691.1 | 14.92 | 11.01 | | 1.573 |
| HMIM $PF_6$ (1) + 1-butanol (2) | −1408.5 | −1430.0 | 17.02 | 8.317 | | 1.378 |
| HMIM $PF_6$ (1) + 1-pentanol (2) | −1651.0 | −1851.1 | 17.30 | 8.624 | | 2.334 |
| OMIM $PF_6$ (1) + 1-propanol (2) | −1525.9 | −1691.0 | 20.75 | 8.699 | | 0.463 |
| OMIM $PF_6$ (1) + 1-butanol (2) | −1536.7 | −1686.7 | 21.56 | 7.950 | | 1.063 |
| OMIM $PF_6$ (1) + 1-pentanol (2) | −1583.0 | −1615.2 | 21.56 | 7.496 | | 1.254 |

K for BMIM $PF_6$ with the three alcohols. HMIM $PF_6$ with 1-butanol or 1-pentanol and the rest of the binary LLE were measured until the miscibility point. The immiscibility area of the binary systems decreases with an increase in the IL alkyl chain length. Taking into account this effect, it is possible to consider that greater interactions with the alcohols were observed for OMIM $PF_6$ than for BMIM $PF_6$. This fact is due to the interactions between the nitrogen of the imidazole ring and the oxygen of the alcohol group. The interactions are greater for $n = 8$ because the free electronic pair of the nitrogen is able to form interactions with solvents when the alkyl chain of the ring is long.

In this study, it is observed that the upper critical solution temperature (UCST) increases as the alcohol alkyl chain is increased. The same behavior is observed for the different ILs; that is, the UCST increases regularly if the alkyl chain on the imidazolium ring is increased, as was observed in recent papers.[21,22]

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