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Mutual Solubility of Alkyl Imidazolium Hexafluorophosphate Ionic Liquids and Water

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Mutual solubilities of water and the ionic liquids (ILs) 1-butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium hexafluorophosphate, and 1-octyl-3-methylimidazolium hexafluorophosphate were measured between (278.15 and 364.15) K at atmospheric pressure. The temperature dependence of the solubilities of ILs in water and water in ILs have calculated from experimental data. The proposed correlations showed a relative maximum deviation from the experimental mole fraction data of 4.7 %. The liquid−liquid equilibrium data were correlated by the nonrandom two-liquid (NRTL) equation, and the average root-mean-square deviation of the mole fractions for the three ionic liquid + water mixtures is 0.0025.

Introduction

Ionic liquids (ILs) have been used widely in catalytic reactions, synthesis, and the other branches of chemistry in recent years.[1] Particularly, hydrophobic ILs can be applied as catalysts[2] and solid supported solutions.[3] It is important to estimate the properties of their mixtures with other solutes since ILs are becoming the solution of large-scale application. Mutual solubilities of ILs and water are essential for the design and development of separation processes and are also important in evaluating the environmental impact of the ILs. ILs are known as "green" solvents, but their hazard to the environment is not very clear. The knowledge of ILs and water mutual solubilities can provide a way to evaluate their effect on the ecosystem.

Despite the importance of the knowledge of the mutual solubilities of ILs and water, only few publications reporting measurements are available,[4−14] and most data were measured under a single temperature. The only systematic study of the mutual solubilities between alkyl imidazolium hexafluorophosphate ILs and water from (288.15 to 318.15) K has been accomplished by Freire et al.[4] The experimental solubility results measured in this work are compared with the available literature data in Figure 2. It can be seen that most of the relative deviations are within 10 %, which is different from the conclusion as described by Freire et al.[4] in which the relative deviation calculated from the same literature data[11] is almost 100 %. This may be due to some calculated uncertainties in their study. The large differences emerge in the water-rich side, which is about 30 %, probably due to the accuracy in the measurements of very low solubilities. According to the method used in literature, there are some drawbacks. UV spectroscopy cannot be used to determine low IL concentrations. If a Karl Fisher titration is used to determine the IL content in water, it may lead to significant errors. Thermogravimetry and mass spectroscopy are time-consuming. Therefore, the cloud-point method was chosen to determine the solubility of ILs in water in this work.

All literature data were obtained under room temperature, which is far from industry operating temperature. It is not accurate to extrapolate the solubilities of ILs in water using correlation equations when the error of experiment results is not small. The measurement of mutual solubilities at high temperature is necessary for the good of application. In this work, the mutual solubilites between water and 1-butyl-3-methyl-imidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$), and 1-octyl-3-methyl-imidazolium hexafluorophosphate ($[C_8mim][PF_6]$) from (278.15 to 364.15) K had been measured at atmospheric pressure.

Experimental Section

Materials. Deionized and freshly distilled water was prepared in the laboratory. The ILs 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6mim][PF_6]$), and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim][PF_6]$) are supplied by Shanghai Cheng Jie Chemical Co., Ltd. with a purity of 99.5 %. The chemical shifts for the ^1H NMR spectrum (parts per million, C_3D_6O) appear as follows: $[C_4mim][PF_6]$, δ: 8.93 (s, 1H, CH−N), 7.73−7.67 (d, 2H, CH═CH−N), 4.36−4.33 (t, 2H, CH_2Me), 4.04 (s, 3H, CH_3N), 1.94−1.91 (t, 2H, CH_2N), 1.41−1.36 (m, 2H, CH_2), 0.96−0.93 (t, 3H, CH_2CH_3); $[C_6mim][PF_6]$, δ: 9.07 (s, 1H, CH−N), 7.73−7.66 (d, 2H, CH═CH−N), 4.16−4.12 (t, 2H, CH_2Me), 3.84 (s, 3H, CH_3N), 1.79−1.74 (t, 2H, CH_2N), 1.26−1.22 (m, 6H, $(CH_2)_3$), 0.87−0.84 (t, 3H, CH_2CH_3); $[C_8mim][PF_6]$, δ: 9.07 (s, 1H, CH−N), 7.74−7.67 (d, 2H, CH═CH−N), 4.15−4.12 (t, 2H, CH_2Me), 3.84 (s, 3H, CH_3N), 1.80−1.76 (t, 2H, CH_2N), 1.26−1.23 (m, 10H, $(CH_{2)5})$, 0.86−0.84 (t, 3H, CH_2CH_3).

Experimental Procedure. Liquid−liquid equilibrium experiments were carried out in a constant water bath (type 50 L, made from Shanghai Laboratory Instrument Works Co., Ltd.). Temperature of the bath during the experiment was measured independently using a thermometer (0.1 K). For the measurements of the solubilities of water in the ILs, the IL and the water were mixed in a jacketed equilibrium cell, stirred for 3 h, and analyzed after 48 h of stabilization. Samples from each

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Table 1. Experimental Mole Fraction Solubility of Water in ILs, x_w, and ILs in Water, x_{IL}, as a Function of Temperature

	[bmim][PF$_6$]	[hmim][PF$_6$]	[omim] [PF$_6$]		[bmim][PF$_6$]		[hmim][PF$_6$]		[omim] [PF$_6$]
T/K	x_w	x_w	x_w	T/K	$10^3\ x_{IL}$	T/K	$10^4\ x_{IL}$	T/K	$10^4\ x_{IL}$
278.15	0.193	0.153	0.118	278.75	0.90	286.45	3.26	285.85	0.94
283.15	0.204	0.167	0.129	283.55	1.02	296.65	4.10	293.95	1.16
288.15	0.224	0.175	0.143	289.55	1.08	302.65	4.48	299.05	1.28
293.15	0.234	0.199	0.151	295.95	1.26	307.85	5.03	307.35	1.54
298.15	0.255	0.210	0.173	302.25	1.46	312.95	5.45	311.35	1.69
303.15	0.280	0.238	0.189	310.35	1.71	319.35	6.60	318.15	1.97
308.15	0.295	0.251	0.211	314.95	1.95	326.35	7.34	324.75	2.16
313.15	0.312	0.275	0.233	319.65	2.18	331.75	8.52	328.15	2.39
318.15	0.337	0.303	0.253	326.65	2.44	336.15	9.19	331.15	2.57
323.15	0.363	0.322	0.275	333.25	2.90	340.25	10.5	338.85	3.04
328.15	0.396	0.349	0.299	338.35	3.39	345.85	11.3	343.35	3.45
333.15	0.423	0.386	0.317	344.35	3.71	350.75	12.8	348.45	3.83
338.15	0.464	0.408	0.350	350.85	4.44	355.25	14.4	353.75	4.45
343.15	0.492	0.435	0.371	357.35	5.32	359.95	15.7	358.55	5.05
348.15	0.525	0.463	0.405	362.15	6.28	363.05	18.0	364.55	5.74
353.15	0.574	0.492	0.424						

phase were drawn using a syringe. The amount of water in the ILs was determined using an Karl Fischer titrator (moisture meter CA-21, Mitsubishi Chemical Analytech). A sample size of 0.5 g was used for each analysis. The temperature of the syringe was higher than the sample to prevent phase split in the syringe and erroneous results. Sampling was performed three times for every measurement, and the relative deviation is under 0.1 %. The average experimental results are displayed in Table 1.

The solubilities of ILs in the water were determined by cloud-point measurement. The method used in our previous experiment[15] was improved to avoid error caused by evaporating water and multiple operations. The ILs and water were gravimetrically prepared using an analytical high precision balance (± 0.01 mg) and placed in a jacketed glass vessel carefully. The vessel was sealed to prevent water evaporating; this procedure was repeated when the IL mole fraction changed.

The cloud points were usually determined with visual detection of the solution turbidity; it is simple but difficult to gain a convincing result. Many optical systems were used to make the experimental result accurate. One system consists of a laser emitter as the light source and a photodiode as the light sensor. In this apparatus, the cloud point was determined by detecting the laser signal intensity accompanied by the turbidity degree.[16,17] The other system consists of a focus light emitter as the light source, and the cloud point was determined by detecting the laser signal intensity accompanied by a charge coupled device (CCD) camera.[18] The focus light emitter as the light source and a photodiode as the light sensor were used in this experiment. The optical system is located in the center of the liquid phase (as shown in Figure 1). The cloud point is detected by measuring the intensity of scattered light, at an angle of 90° with respect to the direction of the focus light beam. This system provides a calibrated electrical voltage proportional to the intensity of the scattered light. The appearance of the cloud point can be determined by the change of electrical voltage displayed on the liquid crystal box. The rate of temperature change near the cloud point was no more than 10 K·h^{-1}. The overall accuracy in the determination of the cloud-point temperatures is estimated to be ± 0.1 K.

The overall uncertainty in the measurement depends on the purity of the solvent and solute and the precision of thermometer and balance. The purity of ILs was higher than 99.5 %. The temperature was measured by a thermometer with an uncertainty of ± 0.1 K. The ILs and water were gravimetrically prepared using an analytical high precision balance (± 0.01 mg). The average relative uncertainty in the mole fraction of the mixtures was estimated to be less than ± 0.001.

This method is different from the titration method for obtaining the cloud-point data at a constant temperature as reported in our previous work.[15] In the titration method, the uncertainty depends on the mass increment of the solute added. As reported in our previous paper,[15] 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 relative uncertainty was estimated to be about 10 % at 298 K, to be about 4 % at 310 K, and improved further at higher temperature because of the nature of the method adopted. The uncertainty was significantly reduced in this work.

Results and Discussion

Temperature Dependence of Mutual Solubility. The mutual solubilities between ILs and water were measured in the temperature range between (278.15 and 364.15) K and at atmospheric pressure. It can be assumed that the molar enthalpy of solution of water in each IL can be considered temperature-independent, and eq 1 can be thus used to correlate the experimental solubility data

$$\ln x_w = A + \frac{B}{(T/\mathrm{K})} \qquad (1)$$

where x_w is the mole fraction solubility of the water in IL, T is the temperature, and A and B are correlation parameters. The

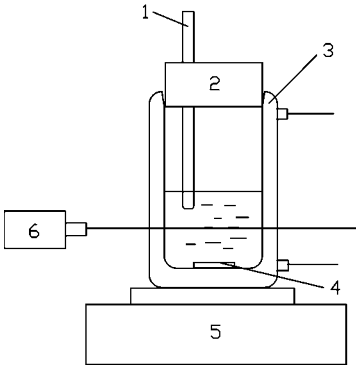

Figure 1. Liquid−liquid phase equilibrium cell: 1, glass mercury thermometer; 2, rubber plug; 3, glass sleeve; 4, magnetic stirring rod; 5, magnetic stirrer; 6, focus light emitter; 7, photodiode.

Table 2. Correlation Parameters for the Mole Fraction Solubility of Water in ILs and ILs in Water as a Function of Temperature Using Equations 1 and 2, Respectively

IL	A	B	C	D	E
[bmim][PF$_6$]	3.43	−1424.5	−173.649	5918.594	25.8314
[hmim][PF$_6$]	3.74	−1569.8	−142.551	4515.882	20.9944
[omim][PF$_6$]	4.05	−1725.9	−145.498	4504.152	21.3073

correlation constants obtained from the fitting for the water solubility are presented in Table 2. The relative deviation calculated by $\sigma_x = (x_{\text{exp}} - x_{\text{cal}})/x_{\text{exp}}$, the average relative deviation, is 1.82 %. A maximum relative deviation from the experimental mole fraction data of 4.7 % was observed.

Equation 2 can be thus used to correlate the experimental solubility data of ILs in water

$$\ln x_{\text{IL}} = C + \frac{D}{(T/\text{K})} + E\ln(T/\text{K}) \tag{2}$$

where x_{IL} is the mole fraction solubility of the IL in water, T is the temperature, and C, D, and E are correlation parameters. The correlation constants obtained from the fitting for the IL solubility are presented in Table 2. The average relative deviation is 1.84 %. A maximum relative deviation from the experimental mole fraction data of 4.4 % was observed. It is noticed that the relative deviations are sensitive to the parameter E. The value of this parameter changes a little, which will cause a larger error.

Modeling. The experimental results of all IL−water systems with liquid−liquid phase behavior were correlated using the binary parameters nonrandom two-liquid (NRTL) equation.[23] The temperature-dependent model adjustable parameters $[g_{12} - g_{22} = a_{12} + b_{12}(T/\text{K}) + c_{12}(T/\text{K})^2]$ and $[g_{21} - g_{11} = a_{21} + b_{21}(T/\text{K}) + c_{21}(T/\text{K})^2]$ were found by minimization of the objective function:[18]

$$F = \sum_{i}^{n}[(\ln x_1\gamma_1 - \ln x_1^*\gamma_1^*)^2 + (\ln x_2\gamma_2 - \ln x_2^*\gamma_2^*)^2] \tag{3}$$

where n is the number of experimental points. The root-mean-square deviation of mole fraction was defined as follows:

$$\sigma_x = \left(\frac{\sum_{i=1}^{n}(x_{\text{exptl}} - x_{\text{calcd}})_i^2}{n-1}\right)^{1/2} \tag{4}$$

The NRTL parameters and the corresponding standard deviations are reported in Table 3. For the systems presented in this work, the average root mean-square deviation, σ_x, is 0.0025. The results of the correlations are plotted in Figure 3. The NRTL nonrandomness parameter was set to a value of $\alpha_{12} = 0.3$.

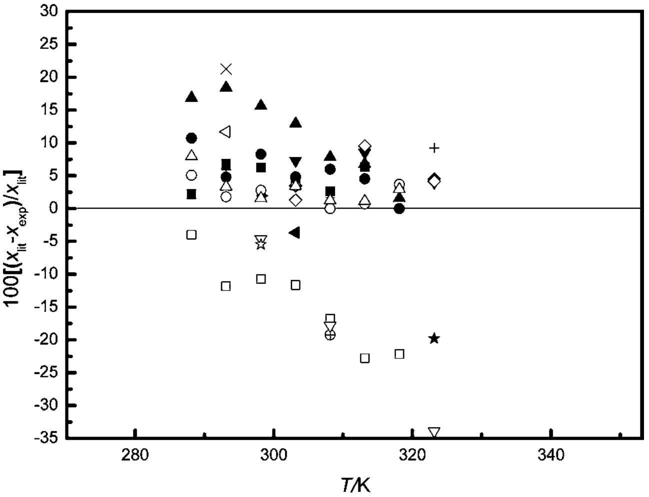

Figure 2. Relative deviations between the experimental mole fraction solubility of water in ILs and ILs in water (empty symbols) obtained in this work (x_{exp}) and those reported in the literature (x_{lit}) as a function of temperature: ■, [bmim][PF$_6$];[4] ▼, [bmim][PF$_6$];[6] ◆, [bmim][PF$_6$];[7] +, [bmim][PF$_6$];[5] ★, [bmim][PF$_6$];[10] ⊕, [bmim][PF$_6$];[11] solid left-pointing triangle, [bmim][PF$_6$];[8] solid right-pointing triangle, [bmim][PF$_6$];[9] ●, [hmim][PF$_6$];[4] —, [hmim][PF$_6$];[12] ▲, [omim][PF$_6$];[4] |, [omim][PF$_6$];[13] ×, [omim][PF$_6$];[12] ◊, [bmim][PF$_6$];[6] □, [bmim][PF$_6$];[4] ▽, [bmim][PF$_6$];[5] ☆, [bmim][PF$_6$];[9] empty left triangular, [bmim][PF$_6$];[14] ○, [hmim][PF$_6$];[4] △, [omim][PF$_6$].[4]

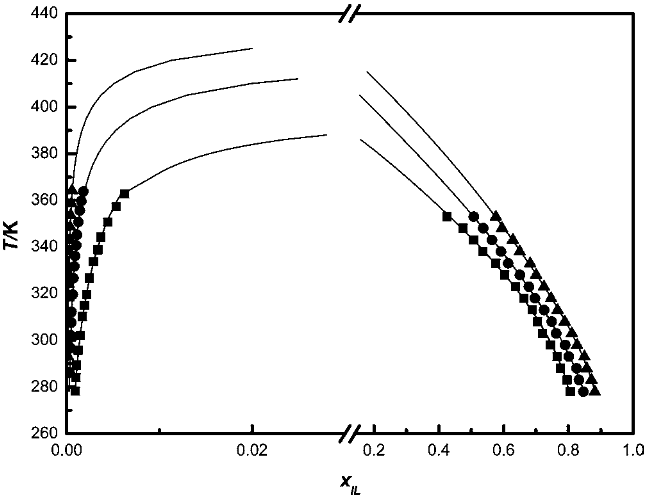

Figure 3. Liquid−liquid phase diagram for water and ILs, experimental data obtained in this work: ■, [bmim][PF$_6$]; ●, [hmim][PF$_6$]; ▲, [omim][PF$_6$]; —, NRTL equation.

Discussion. The experimental solubility results measured here are compared with the available literature data[4−14] in Figure 2. The solubility of water in ILs were determined by a Karl Fischer

Table 3. Correlation of the LLE Data by Means of the NRTL Equation: Parameters $[g_{12} - g_{22} = a_{12} + b_{12}(T/\text{K}) + c_{12}(T/\text{K})^2]$ and $[g_{21} - g_{11} = a_{21} + b_{21}(T/\text{K}) + c_{21}(T/\text{K})^2]$, the Nonrandom Parameter, $\alpha_{12} = 0.3$, and the Mole Fraction Deviations, σ_x

	NRTL parameters						
	$g_{12} - g_{22}$ (J·mol^{-1})			$g_{21} - g_{11}$ (J·mol^{-1})			
	a_{12}	b_{12}	c_{12}	a_{21}	b_{21}	c_{21}	
system	J·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	J·mol^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-2}	σ_x
[bmim][PF$_6$]	25755.5	−94.3315	0.1872	3067.1	−32713.9	277.6	0.0032
[hmim][PF$_6$]	18625.7	−34.1710	0.0929	−22962.1	222.4	−0.4479	0.0024
[omim][PF$_6$]	13041.8	22.5608	−0.0047	−28713.9	262.6	−0.5031	0.0019

Table 4. Mole Fraction Solubility of Water in Hydrophobic ILs at 303.15 K

ILs			ILs		
cations	anions	x_w	cations	anions	x_w
[emmim]	[Tf$_2$N]	0.26[a]	[C$_4$mim]	[C(CN)$_3$]	0.86[b]
[pmmim]	[Tf$_2$N]	0.24[a]	[bmim]	[PF$_6$]	0.28[d]
[C$_3$mpy]	[Tf$_2$N]	0.26[b]	[hmim]	[PF$_6$]	0.24[d]
[C$_3$mpyr]	[Tf$_2$N]	0.25[b]	[omim]	[PF$_6$]	0.19[d]
[C$_4$mpyr]	[Tf$_2$N]	0.23[b]	[C$_4$C$_1$mim]	[PF$_6$]	0.22[b]
[C$_3$mpip]	[Tf$_2$N]	0.23[b]	[C$_3$O$_1$mim]	[PF$_6$]	0.59[e]
[C$_2$mim]	[Tf$_2$N]	0.31[c]	[C$_7$O$_3$mim]	[PF$_6$]	0.86[e]
[C$_3$mim]	[Tf$_2$N]	0.29[c]			
[C$_4$mim]	[Tf$_2$N]	0.27[c]			
[C$_5$mim]	[Tf$_2$N]	0.23[c]			
[C$_6$mim]	[Tf$_2$N]	0.22[c]			
[C$_7$mim]	[Tf$_2$N]	0.21[c]			
[C$_8$mim]	[Tf$_2$N]	0.19[c]			

[a] Obtained from ref 8. [b] Ref 4. [c] Ref 22. [d] This work. [e] Ref 7.

coulometer[4,6,10−13] and the cloud-point method,[7,8] and the solubility of ILs in water were determined by UV spectroscopy,[4−6,9,11] the cloud-point method,[7,8] thermogravimetric analysis (TGA) method,[6] and potentiometry with ion-selective electrodes (ISE).[14] According to the accuracy in the measurements of low solubilities in the water-rich side, there are large differences among different authors; the largest relative deviation is about 30 % between data of ours and from Anthony et al.[5] The smallest relative deviation is about 1.3 % between data of ours and from Wong et al.[6] which are double-checked by the TGA method and UV spectroscopy. On the other side, the relative deviations are smaller among different authors in the IL-rich side which can be related to the larger mole fraction solubilities. The mutual solubilities between the investigated imidazolium hexafluorophosphate ILs and water were reported in the temperature range between (288.15 and 318.15) K by Freire et al.[4] The average relative deviation between our data and the data obtained from Freire et al.[4] was about 7 %.

The experimental solubility data measured and the respective standard deviations are presented in Table 1. It can be observed that for all of the studied ILs the solubility of water increases with the temperature. The hexafluorophosphate-based ILs are known as “hydrophobic”, but from the water solubility results, it can be seen as “hygroscopic”; particularly, the mole fraction of water in [bmim][PF$_6$] was 0.574 at 353.15 K. The mole fraction solubility of ILs in water is in an order of 10^{-3}, so the water-rich phase can be considered as a pure phase with the dissolved IL at infinite dilution. All mutual solubilities of the investigated ILs and water decrease with the increase of the cation alkyl chain length, and this is due to the “hydrophobic” property of long alkyl chain.

The experimental results obtained in this work and the reported solubilities of water in other hydrophobic ILs are listed in Table 4. It shows that the hydrophobic tendency increase with alkyl chain for the same anion. The solubility of ILs and water is affected by the following factors: the interactions of ILs and water, anion molecular volume, and entropy. The interactions of ILs and water are dependent on the relative cation−anion interaction strength which is determined by mass spectrometry.[4] The relative strength of the cation−anion interaction decreases as the alkyl side chain length increases in the order [C$_8$mim] < [C$_6$mim] < [C$_4$mim] for imidazolium-based cation [BF$_4$] and [Tf$_2$N] ILs. The higher the relative cation−anion interaction strength is, the higher the interactions with water and therefore the higher solubilities will be. There is an increase in the hydrophobic tendency due to the anion following the order [C(CN)$_3$] < [PF$_6$] < [Tf$_2$N], and it does not follow the relative interaction between cation and anion observed in the mass spectrometry studies.[4] The van der Waals volume for the anion [PF$_6$],[19] [C(CN)$_3$],[24] and [Tf$_2$N][25] has been calculated as 68 Å^3, 123 Å^3, and 230 Å^3, respectively. It can be established that the hydrophobic tendency increases as the van der Waals volume of anion increases, which will cause the cation−anion interaction to decrease. The smaller molecular volume results in a higher charge density, which leads to higher cation−anion interaction.[19] It should be noticed that the interaction determined by mass spectrometry does not reflect the real charge distribution of molecules in solution.

It is observed that the hydrophobic tendency increases because of the cation family from [C$_n$mim] < [C$_n$mpy] < [C$_n$mpyr] < [C$_n$mpip] for the anion [Tf$_2$N]. Structural modifications in the imidazolium cation could also improve water miscibilities, such as when a carbonyl[7] or hydroxyl group is induced. The hydrophilic tendency increases because of the cation from [C$_8$mim] < [C$_4$C$_1$mim] < [C$_6$mim] < [C$_4$mim] < [C$_3$O$_1$mim] < [C$_7$O$_3$mim] when the anion is [PF$_6$]. It may caused by the increase of H-bond strength when the carbonyl or hydroxyl group is induced. The cosolvent effect could play an important role in increasing the miscibility of IL.[21] Sometimes, the increase of cation alkyl chain length leads to the lower solubility of ILs in alcohol.[20] It may caused by the decrease of H-bond strength in alcohol as compared with water.

Conclusions

The mutual solubilities between water and [bmim][PF$_6$], [hmim][PF$_6$], and [omim][PF$_6$] from (278.15 to 364.15) K have been measured at atmospheric pressure. Solubilities of ILs in water are much smaller than the solubility of water in these ILs; this should be considered in industrial design according to the large solubility of water in these so-called “hydrophobic” ILs.

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