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### A New Class of Solvents for CCC: The Room Temperature Ionic Liquids

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## A New Class of Solvents for CCC: The Room Temperature Ionic Liquids

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### ABSTRACT

Room temperature ionic liquids (RTILs) are salts with melting point close or below room temperature. Changing the nature of the anion or the cation produces a new salt that may or may not be a RTIL. The physico chemical properties of RTILs are briefly reviewed. The partitioning of 38 aromatic derivatives with acid, base, or neutral functionalities was studied between the biphasic liquid system 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIM PF<sub>6</sub>) and water. It was found that the viscosity of pure RTILs is too high for direct use as a liquid phase in countercurrent chromatography (CCC). The addition of a third solvent was needed to decrease viscosity. The ternary phase diagrams of BMIM PF<sub>6</sub>-water and acetonitrile, methanol, ethanol, 1-propanol, and 2-propanol are presented

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in mass and mole percentages. The organic solvent-RTIL-water systems form two liquid phases with a viscosity low enough to allow CCC operation which was not done, due to the low amount of RTIL prepared.

*Key Words:* Ionic liquid; Room temperature molten salt; Solvent; Ternary phase diagram.

## INTRODUCTION

Ethyl ammonium nitrate was a salt investigated in 1914 as a possible explosive alternative to nitroglycerine.<sup>[1]</sup> Indeed, this salt has a melting point as low as 12°C. It was the first room temperature ionic liquid (RTIL) which can be defined as a salt, with a melting point lower than 30°C. Molten salts were used for years as high temperature solvents in inorganic chemistry.<sup>[2]</sup> Room temperature ionic liquids can be used to perform organic chemistry. They are possible candidates as “green” solvents due to their extremely low volatility.<sup>[3]</sup> They are extensively studied as nonaqueous polar solvents with unique electrochemical and spectroscopic properties.<sup>[4-6]</sup>

Ionic liquids look like classical viscous organic liquids. They are actually molten salts made of ions free to move within the liquid volume. There is a big difference between a classical solvent with molecules and molecular interactions and ionic liquids made of ions with strong electrostatic interactions. Typically, RTILs consist of bulky nitrogen- or phosphorous-containing organic cations and large organic or inorganic anions.<sup>[1]</sup>

Organic cations such as *N*-alkylpyridinium and 1-alkyl-3-methylimidazolium are combined with inorganic anions such as Cl<sup>-</sup>, Cl<sup>-</sup>/AlCl<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and/or BF<sub>4</sub><sup>-</sup>. Less common anions in RTILs include organic anions such as the simple trifluoroacetate, pentafluoropropanate, *bis*(trifluoro-methanesulfonyl) imide(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, and trifluoromethanesulfonate or triflate (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>). The combination of such cations and anions can lead to a large number of ionic liquids that provide considerable flexibility in the selection of the most suitable pair for a specific chemical application.

However, it is not possible to predict the melting point of a particular salt by just looking at its cation and anion. Table 1 lists some physicochemical data for several salts, all formed by associating the 1-butyl-3-methyl imidazolium (BMIM) cation with different anions. It can be seen, that BMIM Cl<sup>-</sup> is not a RTIL since its melting point is 65°C. Also, there is a 74°C difference in melting points between BMIM PF<sub>6</sub> and BMIM BF<sub>4</sub>.

The main physicochemical properties of RTILs are: (i) under an inert atmosphere, they remain liquid over a temperature range 200–300°C; (ii) they have practically no vapor pressure;<sup>[6]</sup> (iii) they are reported to have a wide



**Table 1.** Physicochemical properties of BMIM salts.

Anion	Melting point (°C)	$d$ (g/cm <sup>3</sup> )	$n_D$	Viscosity cP (20°C)	Conductivity (S/m)
BF <sub>4</sub> <sup>-</sup>	-82 (g)	1.17	1.429	233	0.17
PF <sub>6</sub> <sup>-</sup>	-8	1.36	1.411	312	0.14
Cl <sup>-</sup>	65	1.10 <sup>a</sup>	Solid	Solid	Solid
CF <sub>3</sub> COO <sup>-</sup>	~-40 (g)	1.21	1.449	73	0.32
CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	16	1.29	1.438	90	0.37
(CF <sub>3</sub> SO <sub>2</sub> )N <sup>-</sup>	-4	1.43	1.427	52	0.39
C <sub>3</sub> F <sub>7</sub> COO <sup>-</sup>	~-40 (g)	1.33	1.414	182	0.10
C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub> <sup>-</sup>	20	1.47	1.405	373	0.045

Note:  $n_D$ , Refractive index at 20°C; (g), glass transition, approximate value at  $\pm 10^\circ\text{C}$ ; Data from Refs.<sup>[1,4-8]</sup>.

<sup>a</sup>In the supercooled liquid state at 25°C.

window of electrochemical stability, good electrical conductivity, high ionic mobility, and excellent chemical stabilities.<sup>[7,8]</sup>

The most interesting physicochemical property of RTILs is their extremely low vapor pressure, due to the very strong electrostatic interaction between the ions that cannot exist in gas state at room temperature. Room temperature ionic liquids are used in chemistry for purposes such as:<sup>[9]</sup> (i) non-volatile solvents in organic synthesis, catalyzed reactions, electrochemistry, and spectroscopy; (ii) non-molecular environment (any solute dissolved in a RTIL is surrounded by ions); and (iii) room temperature chemistry. The very low vapor pressure of RTILs makes them possible candidates in analytical chemistry for gas chromatography stationary phases,<sup>[10]</sup> and for matrixes in matrix-assisted laser desorption/ionization mass spectrometry (MALDI) experiments.<sup>[11]</sup>

It is important to evaluate them as possible mobile, as well as, stationary phases in countercurrent chromatography (CCC). Countercurrent chromatography uses a liquid as the support-free stationary phase.<sup>[12]</sup> The mobile phase is also a liquid. Thus, the unique properties of RTILs could be used in CCC.

In this work, the general properties of RTILs are briefly summarized. The partitioning of 38 substituted aromatic compounds between the RTIL 1-butyl-3-methyl imidazolium hexafluorophosphate (BMIM PF<sub>6</sub>) and water and, also heptane, is presented and ternary phase diagrams of water—BMIM PF<sub>6</sub> and acetonitrile and short chain alcohols, are given as a preliminary evaluation of the capability of a particular ionic liquid for use in CCC. Unfortunately, it was not possible, at the moment, to synthesize enough RTIL to be able to test it in a CCC machine.

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## EXPERIMENTAL

## Chemicals

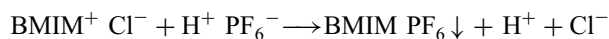
1-Chlorobutane, hexafluorophosphoric acid, trifluoroacetic acid, and 1-methylimidazole were purchased from Aldrich (Milwaukee, WI). The aromatic test solutes were from Aldrich, Sigma (L'Isles d'Abeau Chesnes, France), and Fluka Chemical Co. (Ronkonkoma, NY). Methanol (HPLC grade), ethyl acetate, and hydrochloric acid were from Fisher (St. Louis, MO). Water was freshly deionized and distilled before use. Reagents were buffered with hydrochloric acid 1 M to pH 2, with 0.01 M sodium hydrogenophosphate to pH 5.1, or adjusting the pH of a 0.01 M ammonium acetate solution to 10 with a 2 M NaOH solution. Hexafluorophosphoric and trifluoroacetic acids are corrosive and toxic chemicals. They must be handled with care.

## Ionic Liquid Synthesis

To date, a major problem in the use of ionic liquids is that they are not commercially available at a decent price. They must be synthesized. 1-butyl-3-methyl imidazolium hexafluorophosphate was synthesized according to the procedure described by Bonhôte et al.<sup>[13]</sup> First, BMIM Cl is synthesized according to the chemical addition reaction between butyl chloride and methyl-imidazole:



BMIM-Cl is purified by ethyl acetate washing and recrystallization. Next, BMIM-PF<sub>6</sub> (mw 284) is obtained by metathesis (exchange of anions) of the chloride ion of BMIM-Cl using hexafluorophosphoric acid:



The full experimental procedure has recently been described elsewhere.<sup>[14]</sup> Practically, batches of 200 g of BMIM Cl were prepared and purified without any problems. Two hundred grams of solid BMIM Cl (~1.15 mole) were dissolved in 100 mL water and slowly reacted in a 1-L Teflon<sup>®</sup> beaker at room temperature with 200 mL HPF<sub>6</sub>, since this acid can attack glass. Two phases form. The lower layer is the water saturated BMIM PF<sub>6</sub> compound. This metathesis reaction should be performed under the hood with proper

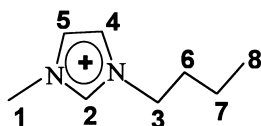




protective equipment and extreme care. The commercial 60% aqueous HPF<sub>6</sub> solution is extremely corrosive (6.7 M concentration). It was obtained from Aldrich in 500 mL Teflon bottles. Table 2 lists the physicochemical data of the BMIM-PF<sub>6</sub> ionic liquid that we synthesized. When we tried to dry the compound by heating in an open vessel, it started to decompose around 170°C emitting HF fumes that attacked the glass container. Under inert atmosphere, BMIM-PF<sub>6</sub> is stable up to 300°C.<sup>[1,6]</sup> Our compound was dried at 110°C in air for 24 hours. It was not fully anhydrous, since its viscosity was only about 30 cP when it was reported to be 312 cP.<sup>[4]</sup> No further effort was done to dehydrate our product more, since ionic liquid–water solute distribution studies were the goal of the work.

**Table 2.** Physicochemical properties of BMIM PF<sub>6</sub>.

Parameter	Value
Molecular weight	284 g mol <sup>-1</sup>
Density	1.362 g cm <sup>-3</sup>
Solubility in water	18 g/L or 63 mM or 0.13% v/v or 0.00113 mole fraction
Water content at saturation	19 g/L or 1.05 M or 1.8% v/v or 0.21 mole fraction
Max UV absorbance	210 nm
Absorptivity	
@ 197 nm	2.58 × 10 <sup>5</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
@ 200 nm	2.83 × 10 <sup>5</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
@ 210 nm	4.08 × 10 <sup>5</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
@ 220 nm	2.65 × 10 <sup>5</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
@ 230 nm	0.36 × 10 <sup>5</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
@ 240 nm	0.06 × 10 <sup>5</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
@ 254 nm	3 × 10 <sup>2</sup> a.u.m <sup>-1</sup> M <sup>-1</sup>
Thermal stability	Start to decompose in air at 180°C
<sup>1</sup> H-NMR spectrum (in CDCl <sub>3</sub> ) <sup>a</sup>	δCH <sub>3</sub> (1): 3H, single 3.962 ppm δH (2): 1H, single 8.649 ppm δCH <sub>2</sub> (3): 2H, triplet 4.181 ppm δH (4): 1H, single 7.321 ppm δH (5): 1H, single 7.231 ppm δCH <sub>2</sub> (6): 2H, quint. 1.857 ppm δCH <sub>2</sub> (7): 2H, sext. 1.367 ppm δCH <sub>3</sub> (8): 3H, triplet 0.982 ppm



<sup>a</sup>Proton assigned following Bonhôte and Grätzel numbering, Ref.<sup>[13]</sup> ppm relative to TMS.





### Protocol

#### Distribution Coefficients Measurement

The water/BMIM-PF<sub>6</sub> distribution coefficients were determined as follows. A known amount of the solute under investigation was dissolved in water (concentration range: 0.1–0.5 g/L). Three milliliter of the solution was added to 3 mL of BMIM-PF<sub>6</sub> in a 10 mL cylindrical vial and placed on a vortex for 10 min. Then, the vial stood at room temperature for an hour and vortexed again for 10 min. After centrifugation, the solute concentration in both phases was determined using HPLC peak areas. For very hydrophobic solutes, the heptane/ionic liquid distribution coefficients were determined following the same procedure, replacing water by heptane.

The HPLC system was a Shimadzu apparatus with a LC6A pump, a SPD-6A UV detector, and a CR-601 integrator. A 125 mm × 4.6 mm i.d. C18 column (Astec, Whippany, NJ) was used with methanol–water mobile phases. The detector was set at 254 nm, a wavelength not absorbed by the BMIM-PF<sub>6</sub> ionic liquid. Twenty microliters of the aqueous phase were injected for analysis. Prior to injection, the viscous ionic liquid phase was diluted with an equal amount of methanol.

#### Phase Diagrams

The phase diagrams were prepared by weighting the liquid components and simple visual observation of the mixtures after 5 min standing at room temperature. As many titrations as needed to find the biphasic boundaries and to draw the mass ternary phase diagram were performed using, alternatively, one of the three solvent constituents. After mixing the desired amounts of the three components, the test tube was vortexed for 10 min and observed after 5 min. If transparent, the mixture was declared monophasic. The molar ternary phase diagrams were calculated using the liquid molecular weights: BMIM PF<sub>6</sub>: 284 g/mol, water: 18 g/mol, acetonitrile: 41 g/mol, methanol: 32 g/mol, ethanol: 46 g/mol, and propanol isomers: 60 g/mol. The orthogonal representation described by Foucault<sup>[15]</sup> was used in Excel (Microsoft) spreadsheets. In this representation, the amount of ionic liquid is listed in the *X* column and the amount of organic solvent is listed in the *Y* column. The percentage amount of water should be calculated as (100 – *X* – *Y*). Pure water corresponds to the right angle of the diagram. Pure organic solvent and pure BMIM-PF<sub>6</sub> ionic liquid are the top and right corner of the diagram, respectively. These diagrams were prepared for the CCC chromatographer at room temperature (21°C ± 1°C). They are indicative only, and not accurate enough to be used in physico chemical studies.





## RESULTS AND DISCUSSION

## Solute Partitioning in Ionic Liquid/Solvent Systems

1-Butyl-3-methyl imidazolium hexafluorophosphate forms a biphasic liquid system with water, as well as, with heptane. The partitioning of a set of substituted aromatic compounds was studied with these two biphasic systems. Table 3 lists the distribution constants,  $K_D$  ionic liquid/water and  $K_D$  ionic liquid/heptane, obtained along with the octanol/water distribution coefficients,  $P_{\text{oct/water}}$ , and the dissociation constants of the compounds.

## Ionic Liquid–Water Partitioning

Since most of the compounds selected are ionizable, they have apparent distribution constants that depend on their ionization state, i.e., on the aqueous phase pH. The measurements were done at three different pH values. The complete set of results and the fitting procedure have already been reported.<sup>[14]</sup>

The last column of Table 3 lists  $\Delta \log K_D$ , the difference between the ionic liquid/water and the octanol/water distribution constant for the same compound. A clear trend can be observed: aromatic compounds with an acid character (carboxylic acid group present) have more affinity for the octanol phase than for the BMIM PF<sub>6</sub> ionic liquid phase (negative values for  $\Delta \log K_D$ ). Conversely, aromatic compounds with a basic amino group substituent have more affinity for the BMIM PF<sub>6</sub> ionic liquid phase than for the octanol phase (positive values for  $\Delta \log K_D$ ). It can be seen that when both constituents are present (aminobenzoic acids), a partial compensation is observed with a small positive value for  $\Delta \log K_D$ . For non-ionizable compounds (e.g. benzene, toluene or benzamide), the  $\Delta \log K_D$  value is very small.

The full solvent properties of the ionic liquid BMIM PF<sub>6</sub> were studied using the Abraham approach.<sup>[14,16]</sup> It was established, that this ionic liquid has a lower basicity than octanol with a polarity comparable to ethanol. It forms two phases with both very polar solvents, such as water or dimethylsulfoxide, and apolar solvent, such as heptane or chloroform. Triphasic systems can be obtained easily, as illustrated by Fig. 1. The ionic liquid phase can be sandwiched between a polar and an apolar liquid phase (Fig. 1 left) or it can be the bottom phase (Fig. 1 right).

## Ionic Liquid–Heptane Partitioning

The BMIM PF<sub>6</sub>–heptane distribution constants,  $K_D$  ionic liquid/heptane, are also listed in Table 3 for compounds that allowed the measurement. When the







**Table 3.** Distribution coefficients of substituted aromatic compounds between BMIM PF<sub>6</sub> and water,  $K_D$  ionic liquid/water or heptane,  $K_D$  ionic liquid/heptane.

Compound	fw	p <i>K</i> <sub>o1</sub>	$K_D$ ionic liquid/water	$K_D$ ionic liquid heptane	$P_{\text{octanol water}}$	$\Delta \log K_D^a$
Ascorbic acid	176.1	4.17	0.008		0.014	-0.24
3-Aminophenol	109.1	3.5	4.1		1.6	0.41
2-Amino benzamide	136.1	3	7.1		2.2	0.51
2-Amino benzoic acid	137.1	2.5	22	240	16	0.14
3-Amino benzoic acid	137.1	3.3	6.6		4.5	0.17
4-Amino benzoic acid	137.1	2.8	12		6.8	0.25
Aniline	93.1	5.2	37	36	8	0.67
Benzamide	121.1	n.i.	4.8	120	4.4	0.03
Benzene	78	n.i.	140	0.64	130	0.03
Benzoic acid	122.1	4.5	53	41	74	-0.14
4-Bromoaniline	172	4	200	43	180	0.05
2-Bromobenzoic acid	201.1	2.84	21	85	160	-0.88
1-Bromo-2-nitrobenzene	202	n.i.	430	9.1	330	0.11
4-Bromophenol	173.1	9	87	130	430	-0.69
Caffeic acid <sup>b</sup>	180.1	4.5	2		14	-0.84
2-Chlorobenzoic acid	156.6	4.1	15	94	110	-0.86
3-Chlorophenol	128.6	8.8	103	76	320	-0.49
2,3-Diaminotoluene	122.1	3.4	13	120	5	0.41
2,3-Dihydroxybenzoic acid	154.1	3.5	2.2		16	-0.86
2,5-Dihydroxybenzoic acid	154.1	3	1		55	-1.74
3,4-Dihydroxybenzoic acid	154.1	4.48	0.57		7.2	-1.10





## New Class of Solvents for CCC

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3,5-Dinitrobenzoic acid	212.1	3.9	38	35	0.04
Ferulic acid <sup>e</sup>	194.1	4.5	14	32	-0.36
2-Fluorophenol	112.1	9	25	51	-0.31
Glutathione <sup>d</sup>	307.3	2.12	0.12	4.0E-06	4.5
4-Hydroxybenzoic acid	138.1	4.48	2.3	38	-1.22
<i>N</i> -Acetyl cysteine	163.2	1.8	0.7	0.22	0.50
3-Nitrobenzoic acid	167.1	4.1	22	68	-0.49
2-Nitrophenol	139.1	5.7	110	60	0.26
Phenol	94.1	10	16	29	-0.26
1,3-Phenylenediamine	108.1	3.2	6.2	0.47	1.12
Phthalic acid	166.1	2.89	1.1	5.4	-0.69
Pyrocatechol	110.1	9.85	7	7.6	-0.03
Theaflavine <sup>e</sup>	564.5	8.5	1	3	-0.48
Toluene	92	n.i.	240	540	-0.35
4-Toluic acid	136.1	5.2	20	190	-0.98
4-Tolidine	107.1	4.8	35	25	0.15
Trolox <sup>f</sup>	250.3	4	3	250	-1.92

Note: Accuracy: 8%, n.i., nonionizable compound. The octanol-water partition coefficients were obtained from <http://esc-plaza.syrres.com/interkow/kowdemo.htm>.

<sup>a</sup> $\Delta \log K_D = \log K_{D \text{ ionic liquid/water}} - \log P_{\text{oct/water}}$ .

<sup>b</sup>3-(3,4-Dihydroxyphenyl)-2-propenoic acid.

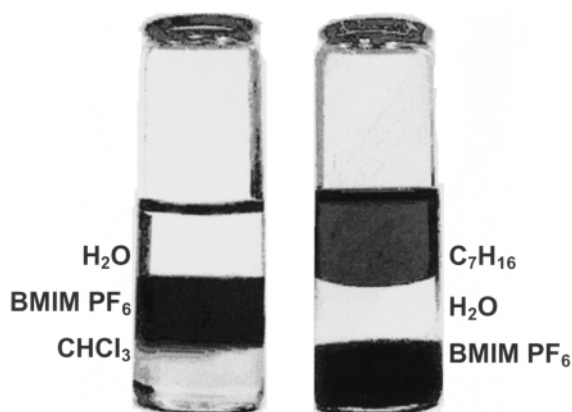
<sup>c</sup>2-Hydroxy-3-methoxycinnamic acid.

<sup>d</sup>*N*-(*N*-*L*-γ-Glutamyl-*L*-cysteinyl)glycine.

<sup>e</sup>1,8-bis[(2*R*,3*R*)-3,4-di-hydro-3,5,7-trihydroxy-2*H*-1-benzopyran-2-yl]-3,4,6-trihydroxy-5*H*-benzocyclohepten-5-one.

<sup>f</sup>6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid.





**Figure 1.** Three liquid phase systems obtained with BMIM PF<sub>6</sub>-water and chloroform (left) or heptane (right). Iodine (I<sub>2</sub>) was added to color the ionic liquid and organic phases.

data is missing (e.g. ascorbic acid, amino phenol), it means that the compound has a heptane solubility so low that it cannot be seen using the HPLC method.

The distribution constants obtained confirm that, obviously, the BMIM-PF<sub>6</sub> liquid phase has a polarity higher than that of heptane. The methanol/heptane distribution constant of benzene and toluene were 0.95 and 0.76,<sup>[17]</sup> comparing well with the  $K_D$  ionic liquid/heptane values of 0.64 and 0.38, respectively (Table 3). The polarity of BMIM PF<sub>6</sub> is close to that of a short chain water soluble alcohol.

The heptane/water distribution constants of benzamide, benzene, and toluene, three non ionizable compounds, were found to be 20, 200, and 550. Table 3 shows that the corresponding  $K_D$  ionic liquid/water/ $K_D$  ionic liquid/heptane ratio are 25, 220, and 630, respectively. The two constants should be theoretically identical. The distribution constants obtained experimentally are between 10 and 20% lower than the ratio of the constants obtained with the ionic liquid phase for the same compounds. This may be due to a difference in the ionic liquid phase water content. Indeed, in the ionic liquid/heptane partitioning study, the ionic liquid phase was not saturated by water. It was obviously the case in the ionic liquid/water partitioning experiments. It was found that the water content of the ionic liquid also had a dramatic effect on its viscosity.<sup>[4-6]</sup>





## Distribution Constant and Solute Retention in Countercurrent Chromatography

The basic retention equation in CCC is:<sup>[12,15,18]</sup>

$$V_R = V_M + K_{D \text{ stat/mobile}} V_S$$

in which, the subscripts *R*, *M*, and *S* stand for retention, mobile, and stationary phase volumes.  $K_{D \text{ stat/mobile}}$  is the solute distribution constant between the stationary and the mobile phase. The resolution factor, *Rs*, measures the quality of the separation between two adjacent compounds in a chromatogram. Its expression is:<sup>[12,15,18]</sup>

$$Rs = \frac{0.25\sqrt{N}(K_{D2} - K_{D1})}{V_M/V_S + K_D}$$

$\sqrt{N}$  is the square root of the column efficiency (peak sharpness).  $K_{D1}$ ,  $K_{D2}$ , and  $K_D$  are, respectively, the distribution constants of Solute 1, Solute 2, and the average value  $(K_{D1} + K_{D2})/2$ .

When the BMIM PF<sub>6</sub> liquid phase is used as the stationary phase in a CCC machine with water as the mobile phase, baseline separation of many solutes listed in Table 3 will be possible. The lower  $K_D$  values were 0.008, 0.12, and 0.57, obtained with ascorbic acid, glutathione, and 3,4-dihydroxybenzoic acid, respectively (Table 3). The higher  $K_D$  values were 430 and 240 for 1-bromo-2-nitrobenzene and toluene, respectively. The problem is the BMIM PF<sub>6</sub> high viscosity that precludes its use in a CCC machine. The dry ionic liquid has a viscosity of 312 cP (centipoises) or Pas (Pascal second) at 20°C (tooth paste consistency). Any molecule dissolved in the ionic liquid decreases its viscosity. The water saturated BMIM PF<sub>6</sub> phase contains about 1.8% v/v water (Table 2). It is much less viscous<sup>[14]</sup> (resembling ethylene glycol ~30 cP), but still too viscous, for easy CCC use (desired viscosity ~10 cP or lower, also depending on the machine tubing bore).

### Ternary Phase Diagrams with 1-Butyl-3-Methyl Imidazolium Hexafluorophosphate

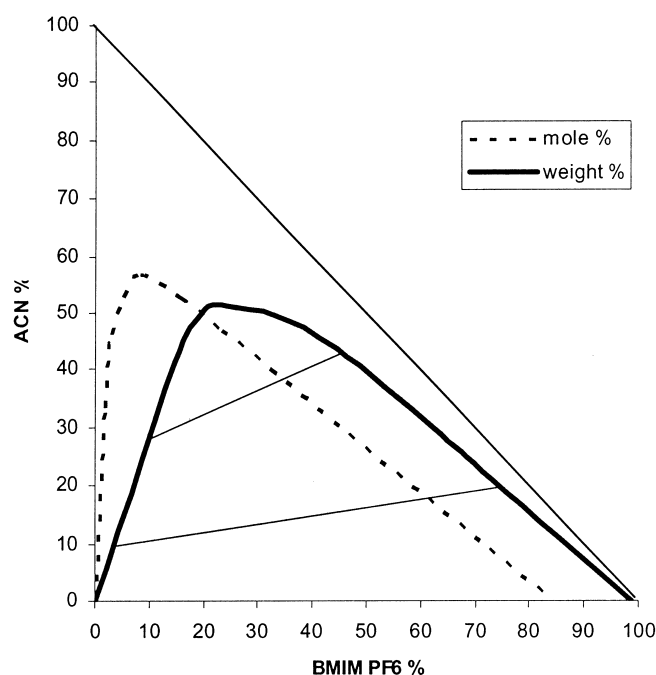
The mass ternary phase diagrams of BMIM PF<sub>6</sub> with water and short chain alcohol and acetonitrile were determined by simple visual examination.





## 1-Butyl-3-Methyl Imidazolium Hexafluorophosphate–Water–Acetonitrile System

Figure 2 shows the phase diagram with acetonitrile, a dipolar aprotic solvent. The thick line corresponds to the mass percentage boundary of the biphasic domain that occupies a large area in the bottom of the diagram. If there is more than 51% in mass of acetonitrile, BMIM PF<sub>6</sub> and water are miscible and form a clear solution. It was observed that in the biphasic area the volumes of the two phases had similar sizes. It seemed that the water-rich lower phase had a volume lower than the volume of added water. This means, that the amount of water going in the organic phase after equilibrium was not equally compensated by acetonitrile going in the aqueous phase (tie lines tilted to the left as indicated in Fig. 2). Since no density and/or phase composition determinations were done, the two tie-lines indicated in Fig. 2 should not be taken as references.



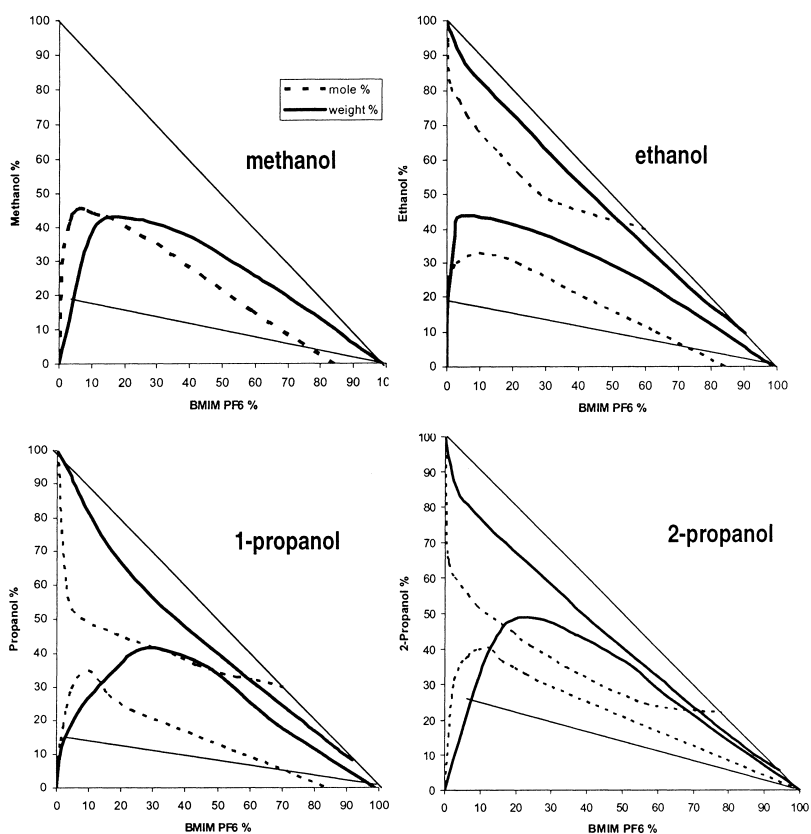
**Figure 2.** The BMIM PF<sub>6</sub>–water ternary phase diagram with acetonitrile (ACN). The thick line corresponds to mass percentages (experimental values); the dotted line corresponds to mole percentages (calculated). The tie-lines were not accurately determined, they only indicate a trend.



The ionic liquid partitioned well in the two liquid phases in which both had low viscosity. The ACN–water–BMIM PF<sub>6</sub> ternary system could be used in a CCC machine.

1-Butyl-3-Methyl Imidazolium Hexafluorophosphate–Water–Alcohol System

Figure 3 shows the four ternary diagrams obtained with the four first short chain alcohols.



**Figure 3.** The BMIM PF<sub>6</sub>–water ternary phase diagram with short chain alcohols. The thick line corresponds to mass percentages (experimental values); the dotted line corresponds to mole percentages (calculated). The tie-lines were not accurately determined, they only indicate a trend. The upper right biphasic zones in ethanol and propanols diagrams may have a high inaccuracy (ionic liquid not fully dried).

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### Methanol

The methanol phase diagram looks like the acetonitrile phase diagram. Two liquid phases exist for mixtures containing less than 44 mass percent methanol. The big difference is in the liquid phase compositions. The ionic liquid does not partition well in the two phases. It stays concentrated in the lower phase (tie lines tilted to the right, Fig. 3). Once again, the phase compositions were not determined. The tie-lines indicated in the figures should not be taken as references. During the titration experiments, it was striking to see the lower ionic liquid rich phase shrink to become a small drop at the end of the experiment, just before full dissolution when enough methanol was added.

### Ethanol

The big difference between ethanol and methanol is that BMIM-PF<sub>6</sub> is not fully soluble in pure ethanol. A small amount of water (5% in mass or 20% in mole fraction) is needed to obtain a clear solution. This produces a biphasic area in the upper right part of the ternary diagram (Fig. 3). In this upper area, the two liquid phases are an upper ethanol-rich organic phase and a lower ionic liquid-rich phase. The ionic liquid seems to partition significantly in the ethanol-rich upper phase. It should be pointed out, that the delineation of this upper biphasic area depends greatly on the water content of the ionic liquid used. The trace amounts of water remaining in our product likely induced an error in the upper line position (both in mass and even more in mole representation).

The lower part of the phase diagram shows a second biphasic area, similar to the one observed with methanol. In this area, the two liquid phases are an upper ethanol-water phase containing low amounts of ionic liquid and a lower ionic liquid-rich phase.

### Propanols

The propanol phase diagrams are similar to the ethanol ones. 1-Butyl-3-methyl imidazolium hexafluorophosphate is not fully soluble in pure alcohols. Two biphasic areas exist in the diagram. The propanol-rich biphasic area grows in size. Fifteen to 19 mass percent of water (more than 40% in mole fraction) is needed to solubilize the ionic liquid. The monophasic area in between becomes very thin. In the lower biphasic area, the lower liquid phase is also the ionic liquid-rich phase.





## CONCLUSION

Ionic liquids are new solvents with original properties. The study of the partitioning of aromatic solutes between water, heptane, and BMIM PF<sub>6</sub> demonstrated the solvent capability of this ionic liquid. Unfortunately, ionic liquids cannot be used directly in CCC because their viscosity is too high at room temperature. The viscosity is dramatically reduced by dissolving molecules in the ionic liquid. It seems that the acetonitrile–water–BMIM PF<sub>6</sub> ternary liquid system will produce interesting biphasic systems for CCC separations. The ternary systems with short chain alcohols will also be usable; especially the alcohol-rich biphasic systems, since it was found that the polarity of the ionic liquids could be compared to that of ethanol. If the alcohol-rich phase and the ionic liquid phase have similar polarities, the solutes will partition well between the two phases (distribution constants close to unity) producing fast chromatograms. No experiments were done with a CCC machine because ionic liquids are not easily available in large amounts, they should be synthesized. Such experiments will be done soon.

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