

Electrochemically-Induced Reactions of Hexafluorophosphate Anions with Water in Negative Ion Electrospray Mass Spectrometry of Undiluted Ionic Liquids

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The influence of water on the observed gas-phase population of negative ions in electrospray mass spectrometry was studied for the *undiluted* ionic liquid 1,3-butyl-methyl-imidazolium hexafluorophosphate (BMIM⁺PF₆⁻). During the electrospray process, electrolytic reduction of water enhances the production of tetrafluorophosphate (F₄PO₃⁻), which undergoes further reactions to produce difluorophosphate (F₂PO₂⁻) anions. These anions are observed in addition to the pre-existing hexafluorophosphate anion. The apparent substitution of two fluorine atoms with one oxygen is attributed to a series of reactions initiated by hydrolysis of hexafluorophosphate. This hydrolysis reaction was enhanced by the addition of hydroxide, formed via the hydrolysis of water or through the addition of ammonium hydroxide. The formation of F_xPO_y⁻ was studied as a function of the electrospray current and solution flow rate. The mass spectral response shows a quantitative logarithmic relationship between ΣF_xPO_y⁻ signal intensities (adjusted for mole equivalents of H₂O required) and the amount of water present, against which the water content could be rapidly assessed. Results were found to be comparable to Karl Fischer titration data. (J Am Soc Mass Spectrom 2006, 17, 939–944)
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Composed entirely of organic cations and inorganic complex anions, room temperature ionic liquids (ILs) have attracted tremendous attention as novel solvents. The most commonly investigated cations are *N*, *N*-dialkylimidazolium, *N*-alkylpyridinium, and tetra-alkyl-ammonium. Common anions are tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), bis[(trifluoromethyl)sulfonate]amide (TF₂N⁻), and trifluoroethanoate (CF₃CO₂⁻). These salts display unique properties in addition to being liquid at room-temperature. These include negligible vapor pressure, wide electrochemical windows, and high ionic conductivity. As an alternative to aqueous or organic solvents, ILs are thought to hold much promise for green chemistry applications. As a new solvent system, ILs are being investigated in a variety of applications such as polymer synthesis [1–3], catalytic processes [4, 5], electrochemical reactions [6], liquid-liquid extractions [7], and

as a vacuum compatible matrix for matrix-assisted laser desorption/ionization [8–13].

Impurities and their effects on the properties of the ILs have been the subject of several studies [6, 14–16]. Because ILs often absorb water, the effect of water on electrochemical properties has been studied [6, 14]. Research on the solubility of water in ILs is very important, particularly when the ILs are used with water sensitive materials and reactions. Depending on the choice of anions, water solubility varies [14]. For example, ILs composed of PF₆⁻ anions are not water-miscible, yet Cl⁻ based ILs are water-miscible. Despite the immiscibility of PF₆⁻ based ILs, water is often absorbed at concentrations as high as 16% (wt/wt) [14]. Studies of water-contaminated 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM⁺PF₆⁻) ionic liquids suggest that the water/IL system is not homogenous but is instead a “nano-structured”, bi-phasic solution [6]. The presence of water in such water-immiscible ILs was found to affect electrochemical characteristics and increase ion diffusion rates [6, 14–16].

Electrospray mass spectrometry (ES-MS) has been widely used to transfer ions from the liquid phase into the gas-phase for MS analysis. It has extended the range

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of MS applications to high polarity, high mass, and highly labile molecules. Alfassi et al. developed a method using ES-MS to quantify the hydrophobic IL solubilities in water [17]. Acceptable ES-MS detection of minor analyte species, such as $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-triphos})\text{Cl}]^+$, within an IL matrix has been performed following a $10^5:1$ dilution with methanol [18]. Similarly, negative ion ES-MS has proven useful for the detection of negative species such as the anionic catalyst $[\text{Ru}(\text{CO})_2\text{I}_2]^-$ and Cl^- [18]. ES-MS analysis of tetrabutylammonium ions and neutral ferrocene ions in neat (undiluted) ILs has been investigated and was found to have sensitivity for these dissolved analytes comparable to the diluted ILs [19, 20]. The nonvolatile nature of ILs has not proven to be a limitation in the generation of these ions via electrospray.

In our laboratory, negative ion ES-MS of undiluted $\text{BMIM}^+\text{PF}_6^-$ ILs is observed to generate water-related product anions from PF_6^- with the general formula F_xPO_y^- (i.e., F_4PO^- and F_2PO_2^-). This chemistry is thought to be driven by electrochemical processes within the ES emitter. The study of this chemistry is presented here, and the correlation between water content and F_xPO_y^- response is characterized.

Experimental

1,3-butyl-methyl-imidazolium hexafluorophosphate ($\text{BMIM}^+\text{PF}_6^-$) and 1,3-ethyl-methyl-imidazolium tetrafluoroborate ($\text{EMIM}^+\text{BF}_4^-$) (Sigma-Aldrich, St. Louis, MO), were vacuum-dried for 48 h and stored in a nitrogen filled desiccator. Biphasic water/ $\text{BMIM}^+\text{PF}_6^-$ mixtures formed when deionized water ($>18\text{M}\Omega\cdot\text{cm}$, MilliQ, Billerica, MA) was spiked into the ILs. Homogenous solutions were obtained by ultra-sonication for 20 min. Water concentrations reported in this study were calculated as follows. Karl Fischer titration (Brinkmann KF-652, Herisan, Switzerland) was used to establish the residual percent water in samples that were vacuum dried. If water was spiked into a sample, the weight of additional water was summed with that from the Karl Fischer determined "blank" to calculate the total water content.

Electrospray mass spectra were obtained with a Thermo Electron PolarisQ ion-trap mass spectrometer (Austin, TX) modified with the addition of a Thermo Electron Deca electrospray ion source. The ion optical system between the ion source and the mass analyzer is composed of two ion guides and an ion gating lens. The ion gating lens is a disk electrode with a 0.8 mm orifice that is positioned between quadrupole and octopole ion guides. Both ion guides operate at the same rf frequency, rf amplitude, and dc floating voltage, and are driven by a custom-built RF power supply [21]. The relative ion current was measured at the ion transfer tube by an electrometer (Orteck 710, Oak Ridge, TN). It should be noted that the high voltage emitter was operated without an upstream grounding point. Due to the high conductivity of ILs, (about 1000 times larger

than conventional volatile solvents), grounding the injection line through the insertion of an ammeter decreased the spray voltage at the emitter tip, and disrupted the electrospray process.

An Oxford dual track syringe pump (AH55-2122, Holliston, MA) was used to continuously inject samples from a 250 μL syringe (Hamilton, Reno, NV) at a constant flow rate of 0.3 $\mu\text{L}/\text{min}$ unless otherwise noted. A 1 m PEEK tube with 125 μm internal diameter (i.d.) connected the syringe and the emitter. The 125 μm i.d. tubing was used to maintain a low backpressure for the viscous ILs. For the same purpose, PEEK unions (No. P-742, Upchurch Scientific, Oak Harbor, WA) with 250 μm i.d. were used. A 6 cm long stainless steel emitter with 100 μm i.d. and 500 μm o.d. was used in conjunction with a stainless steel union to which the spray voltage was applied. A Tennelec/Oxford dual-polarity 0–5 kV power supply (TC950A, Oak Ridge, TN) was used to provide the negative 3–5 kV emitter potential.

Results and Discussion

To perform the initial characterization of electrospray mass spectrometry of undiluted ion liquids containing water, $\text{BMIM}^+\text{PF}_6^-$ was spiked with 0 to 6% (wt/wt) of water, and conventional Karl Fischer titration was used to measure the water content. The samples were then studied by negative ion ES-MS as a function of voltage, flow rate, and water content.

Mass Spectral Characterization

It is known that electrochemical processes at the emitter surface can influence the abundance and identity of gas-phase ions in ES-MS [22, 23], with the degree of redox chemistry occurring being a function of both reaction time at the emitter surface and the spray current. To explore this, the emitter voltage was increased to increase spray current and the flow rate was reduced to increase redox efficiency to determine their effect of these parameters on gas-phase ion abundances of F_xPO_y^- .

Negative ion electrospray mass spectra of $\text{BMIM}^+\text{PF}_6^-$ containing 0.24% H_2O are shown in Figure 1 for different emitter voltages. Injection flow rate was held constant at 0.3 $\mu\text{L}/\text{min}$. Operating at a threshold voltage for ion production (3.0 kV in Figure 1a), only pre-formed PF_6^- ions are observed. The relative ion current (i_{RC}) measured at the transfer tube was 0.31 μA . When the spray voltage was increased to 3.7 kV and 5.0 kV (Figure 1b and c), the i_{RC} increased to 0.90 and 2.02 μA , respectively, with a corresponding increase in F_xPO_y^- anion intensities increased and a decrease in PF_6^- intensity. Anions F_4PO^- and F_2PO_2^- are the primary product ions observed along with HPO_3^- and other less abundant ions whose identity could not be confirmed.

The effect of current on product ion distribution is not surprising because the electrospray ionization

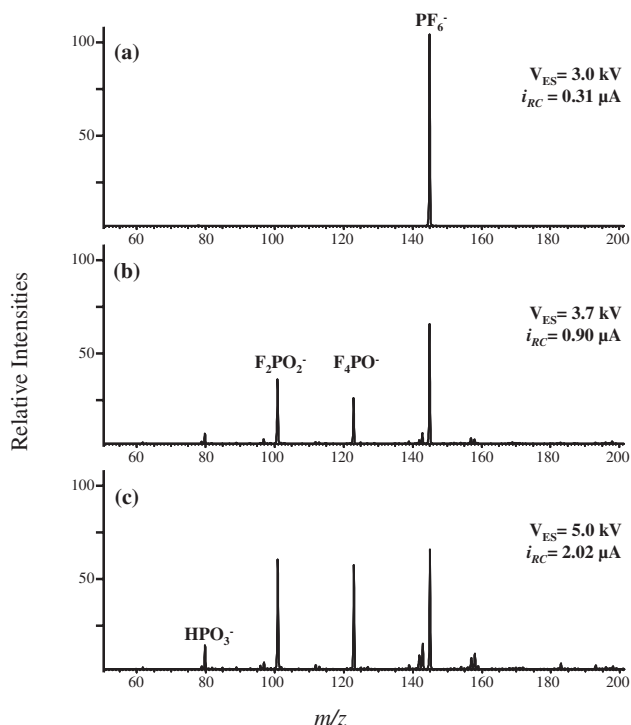
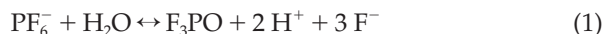


Figure 1. Negative ion ES-MS of $\text{BMIM}^+\text{PF}_6^-$ at (a) 3.0 kV, (b) 3.7 kV, and (c) 5.0 kV, each normalized to (a). Water content and flow rate were held constant at 0.24% (wt/wt) and 0.3 $\mu\text{l}/\text{min}$, respectively.

process is a controlled-current electrolytic process [22, 23]. Increases in emitter potential affect the magnitude of the redox current at the emitter surface. The extent of the reaction, and therefore F_xPO_y^- abundances, increases with the magnitude of ES current. As will be shown later, higher spray voltage V_{ES} (resulting in higher emitter current) can be used to improve the sensitivity of water concentration determination.

Studies have shown that tetrafluorophosphate (F_4PO^-), difluorophosphate (F_2PO_2^-), and metaphosphate (HPO_3^-) complex ions can be formed in battery cells from reactions initiated by the hydrolysis reaction of PF_6^- [24–28]. The reactions are not simple consecutive processes. The decomposition of PF_6^- starts with the formation of F_3PO through the reaction of PF_6^- with H_2O ,



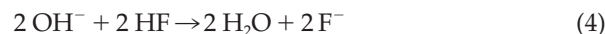
and F_3PO readily adds F^- to form the F_4PO^- anion [25]:



Electrolytic hydrolysis of water during the electrospray process produces hydroxide ions as shown,



which neutralize the hydrofluoric acid produced in reaction (1),



assisting the decomposition of PF_6^- according to Le Chatelier's principle. The net reaction of the PF_6^- with water [reactions (1) to (4)] is



The role of hydroxide ions in the hydrolysis reactions was tested by ES-MS analysis of $\text{BMIM}^+\text{PF}_6^-$ samples that were spiked with water and ammonium hydroxide. Figure 2 shows the mass spectrometric response to varying concentrations of OH^- . Water content (2.03% wt/wt) and the electrospray voltage (3.7 kV) were held constant. The spectrum shown in Figure 2a was obtained before the addition of hydroxide ions. PF_6^- is the dominant species and a relatively small fraction of fluorophosphates was transformed to F_xPO_y^- . As the concentration of OH^- was increased [up to 0.16% (wt/wt)], F_xPO_y^- products became more abundant with the dominant species in mass spectra being F_2PO_2^- at the highest hydroxide concentration.

Difluorophosphate anion formation has been observed by others who reported that F_4PO^- anion undergoes the exothermic disproportionation reaction ($\Delta H = -76 \text{ kcal} \cdot \text{mol}^{-1}$) [24, 25],

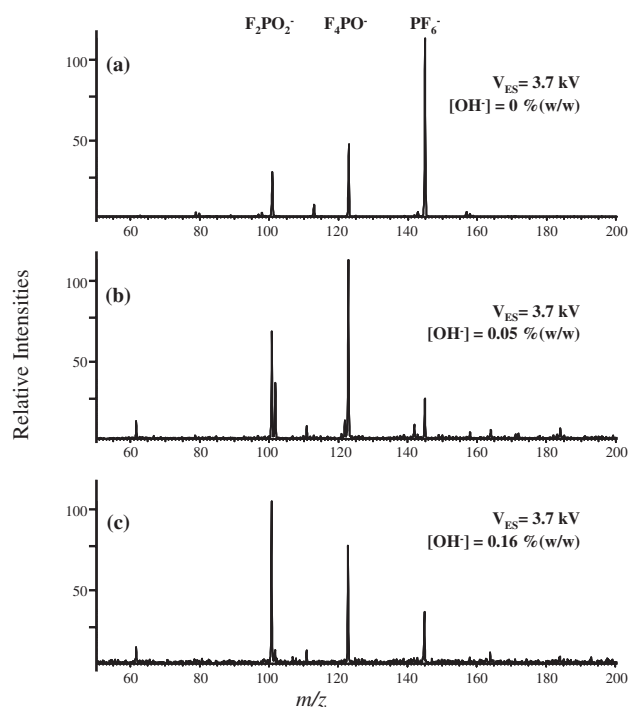


Figure 2. Negative ion ES-MS of $\text{BMIM}^+\text{PF}_6^-$ spiked with NH_4OH with $[\text{OH}^-]$ at (a) 0% (wt/wt), (b) 0.05% (wt/wt), and (c) 0.16% (wt/wt), each normalized to (a). Water content, electrospray voltage, and flow rate were held constant at 2.03% (wt/wt), 3.7 kV, and 0.3 $\mu\text{l}/\text{min}$, respectively.

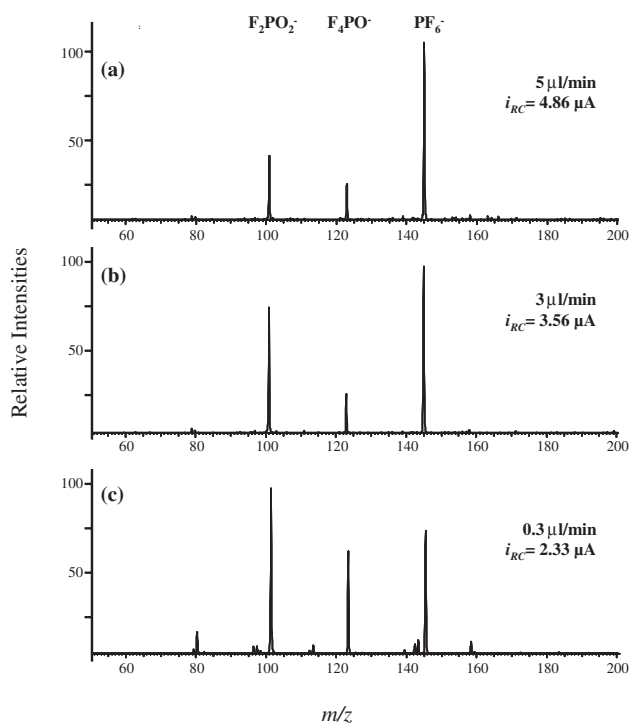


Figure 3. Negative ion ES-MS of $\text{BMIM}^+\text{PF}_6^-$ at various flow rates, (a) $5 \mu\text{l}/\text{min}$, (b) $3 \mu\text{l}/\text{min}$, and (c) $0.3 \mu\text{l}/\text{min}$, each normalized to (a). Water content and electro spray voltage were held constant at 3.43% (wt/wt) and 5.0 kV, respectively.

As the concentration of F_4PO^- increases, reaction (6) becomes kinetically favored. The amount of F_4PO^- anions decreases due to the disproportion reaction, and the abundance of F_2PO_2^- increases. Other negative ions of low abundance (e.g., PO_3^- , HPO_3^- , H_2PO_4^- in Figures 1, 2, 3, and 4) were also observed in ES-MS, but their origin and role in PF_6^- reactions cannot be confirmed due to their low abundance and poor correlation with experimental variables.

The mass spectra shown in Figure 3 demonstrate the effect of solution flow rate on multifluorophosphate anion formation. $\text{BMIM}^+\text{PF}_6^-$ solution was injected through the emitter at flow rates of 0.3, 3, and $5 \mu\text{l}/\text{min}$ with a constant emitter voltage of 5.0 kV. The degree of PF_6^- hydrolysis is inversely proportional to flow rate. This is consistent with an electrochemically-induced reaction at the electro spray emitter that proceeds as a function of the interaction time of water at emitter surface. The reduction in i_{RC} primarily reflects the lowered mass throughput at low flow rates because i_{RC} reflects the oxidation current for all ions arriving at the ion transfer line (including PF_6^-) and is not a direct indication of the hydrolysis process alone. More IL and water mass is supplied at the higher flow rate, but the formation of hydrolysis products was low, presumably due to diffusion rate limitations.

Effect of Water Content on F_xPO_y^- Response

Karl Fischer titration results indicated that the “pure” vacuum-dried $\text{BMIM}^+\text{PF}_6^-$ retains 0.24% (wt/wt) resid-

ual water, demonstrating the difficulty in removing water from even water-immiscible ionic liquids. Incrementally increasing the electro spray voltage from 0 to 5 kV resulted in threshold voltages (V_T)—the voltage at which gas-phase ions are generated—that are proportional to water content. The lowest threshold value of spray voltage was 3.0 kV for the IL sample with the smallest amount of water. V_T increased with water content up to 3.3 kV for 1.4% water, reaching a plateau at 2%.

Figure 4 shows ES mass spectra of three $\text{BMIM}^+\text{PF}_6^-$ samples with different water contents electro sprayed at an emitter voltage of 5.0 kV and a flow rate of $0.3 \mu\text{l}/\text{min}$. The gas-phase abundances of the F_xPO_y^- ions relative to PF_6^- increase with water content. Since water content is directly related to the abundance of F_xPO_y^- ions, these can provide a convenient method to quantify the water content of undiluted ILs using electro spray mass spectrometry.

In Figure 5, two calibration curves are shown that were generated using emitter voltages of 3.6 kV ($R^2 = 0.96$) and 4.6 kV ($R^2 = 0.98$). The anions F_4PO^- and F_2PO_2^- were plotted as function of weight concentration of water and normalized to the total ion signal measured in each scan. A weighting factor of two was used for F_2PO_2^- to reflect the number of water equivalents involved in F_2PO_2^- production. These demonstrate an empirically-determined logarithmic relationship be-

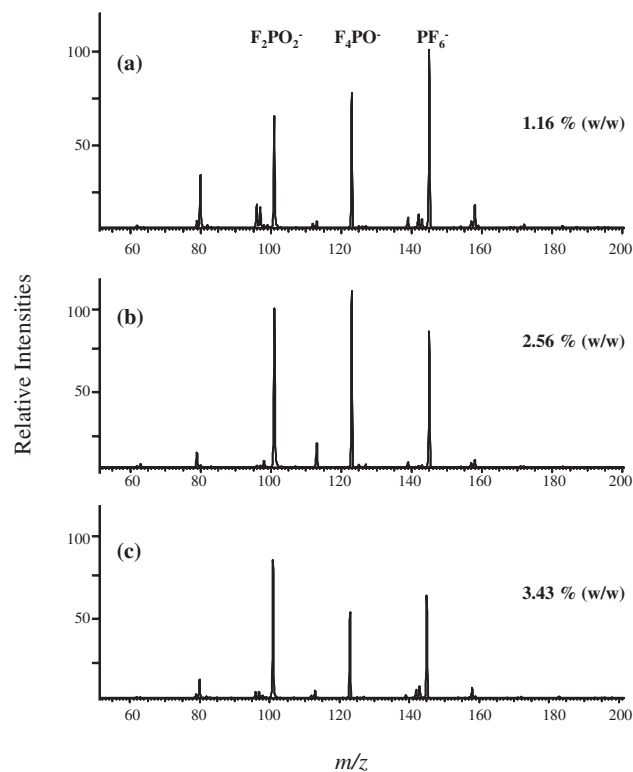


Figure 4. Negative ion ES-MS of $\text{BMIM}^+\text{PF}_6^-$ at various water contents, (a) 1.16% (wt/wt), (b) 2.56% (wt/wt), and (c) 3.43% (wt/wt), each normalized to (a). Flow rate and electro spray voltage were held constant at $0.3 \mu\text{l}/\text{min}$ and 5.0 kV, respectively.

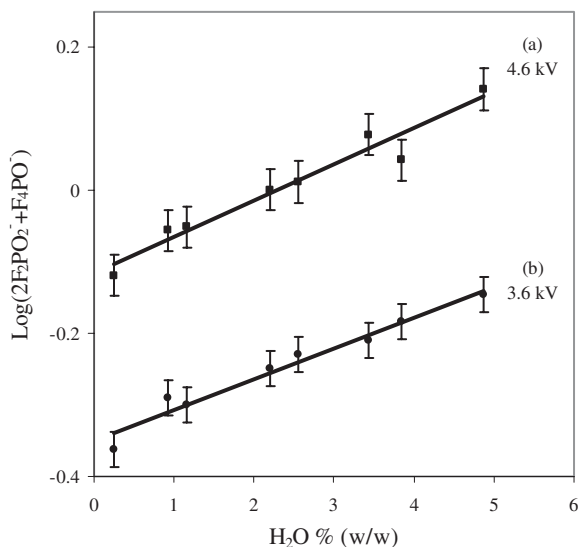


Figure 5. Relationship between extent of $\text{PF}_6^-/\text{H}_2\text{O}$ reaction and water content for $\text{BMIM}^+\text{PF}_6^-$ ES-MS at 3.6 kV and 4.6 kV and at flow rate of $0.3 \mu\text{l}/\text{min}$. The response of the fluorophosphates were weighted for mole equivalents of water required and the sum was normalized to the total ion current in each scan.

tween water content, as determined by Karl Fischer titration, and the sum ($\text{F}_4\text{PO}^- + 2\text{F}_2\text{PO}_2^-$) normalized to total ion current. The nonlinear relationship with respect to water content is thought to be due to the relative and unknown rates of the pseudo-first-order reaction in eq 5 and the second-order disproportionation reaction (eq 6). Because the reaction rate constants are not known, the use of summed intensities of the multifluorophosphate ions is thought to be more accurate and straightforward.

The results of three measurements of $\text{BMIM}^+\text{PF}_6^-$ were averaged for each calibrant solution, ranging from $\sim 0.24\%$ (wt/wt) to $\sim 6\%$ (wt/wt) water. Consistent with redox current considerations, analytical sensitivity was higher at the 4.6 kV emitter voltage. The slopes of two curves are 0.063 and 0.108, resulting in a 1.7-fold enhancement in sensitivity at the higher emitter voltage.

The unspiked vacuum-dried sample retained a water content of 0.24% (wt/wt). More vigorous cleaning procedures were not attempted. Because of the difficulty in removing the water residue from the IL, lower water concentrations could not be evaluated and the dynamic range of the measurement was limited. The dynamic range of the method is bounded by water-solubility at the upper concentration limit and sample dehydration methods at the lower concentration limit.

The response curve shown in Figure 5a (4.6 kV) was used to quantify water content in two $\text{BMIM}^+\text{PF}_6^-$ samples. After spiking, the resulting water contents were calculated to be 0.92% (wt/wt) and 1.16% (wt/wt). The results based on ES-MS measurements were 0.94% (wt/wt) and 1.23% (wt/wt) with relative standard deviations (RSD) of 7 and 12%, respectively. Karl

Fischer titration results for the same samples were 0.92% and 1.04% with RSD of 13 and 8%, respectively. The relative error of the measurement was less than 10%, and accuracy and precision are comparable to the conventional Karl Fischer titration results, suggesting that negative ion ES-MS can provide an approach for the direct determination of water content for ionic liquids containing the PF_6^- anion.

Conclusions

To most efficiently detect analytes or impurities within ionic liquids, electrochemical phenomenon favoring their formation must be considered. In the case of negative ion ES-MS of PF_6^- -based ILs, the reactions of water with PF_6^- results in the formation of multifluorophosphate (F_xPO_y^-) ions. The substitution reaction that follows from the hydrolysis reaction of water with PF_6^- to generate F_xPO_y^- species during the electrospray process is consistent with known electrochemical reactions, and parametric studies of flow rate and electrospray current support this conclusion.

The F_xPO_y^- products of the electrochemical reactions reported here provide an indicator of the water content in water-immiscible $\text{BMIM}^+\text{PF}_6^-$. The dependence on other residual solvents, dissolved contaminant species, and their concentrations on negative ion ES-MS will require further study, but the use of negative ion ES-MS for indirect measurement of water content in undiluted ILs can provide a rapid assessment of IL purity.

Initial studies indicate that similar product ions are obtained in ES-MS of $\text{EMIM}^+\text{BF}_4^-$. The electrochemically induced species F_2BO^- and BO_2^- were observed when neat BF_4^- based ILs were electrosprayed. The hydrolysis of BF_4^- is thought to occur in an analogous manner to PF_6^- and is a matter of ongoing chemical investigations.

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