Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids[†]

Mara G. Freire,[‡] Catarina M. S. S. Neves,[‡] Isabel M. Marrucho,[‡] João A. P. Coutinho,[‡] and Ana M. Fernandes*,[§]

CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal, and QOPNA, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

Controversy behind the postulation that ionic liquids (ILs) are entirely green materials emerged a few years ago. This statement is not always valid, and properties such as toxicity and chemical/thermal stability of ILs should be fully characterized to evaluate their potential use as green solvents. Therefore, in this work, the thermal and chemical decompositions of hexafluorophosphate- and tetrafluoroborate-based ILs in aqueous solutions were evaluated. The experimental conditions employed allowed the study of the possible decomposition of both anions, the effect of the cation side alkyl chain length, the influence of the pH of the aqueous solutions, as well as the temperature influence. Three experimental techniques were employed to fully characterize those anions' stability, electrospray mass spectrometry, nuclear magnetic resonance spectroscopy, and pH measurements of the equilibrium aqueous solutions. The results noticeably indicate that it is suitable to use aqueous solutions of hexafluorophosphate-based ILs at moderate temperatures while acidic conditions promote the anion hydrolysis, even at low temperatures. On the other hand, the tetrafluoroborate-based ILs are not water-stable compounds since they hydrolyze under all of the conditions tested and the hydrolysis extent is markedly dependent on the temperature.

Introduction

Room-temperature ionic liquids are a novel class of liquid salts that have engaged exponential attention in recent years, especially due to their negligible vapor pressures. Ionic liquids (ILs) appeared as environmentally friendly alternatives for the ordinary volatile organic solvents reducing the emissions into the atmosphere. Nevertheless, the ILs' classification as green solvents should also take into account their entire life cycle, in particular, their environmental fate, possible hazardous properties, potential toxicity issues, and thermal and chemical stability.

The most widely studied ILs are composed of bulky and asymmetrical nitrogen-containing cations (e.g., imidazole, pyrrole, piperidine, and pyridine) in combination with a large variety of anions, ranging from simple halides to more complex organic species. Imidazolium-based ILs with tetrafluoroborate and hexafluorophosphate anions have, so far, been the focus of numerous publications dealing with their physicochemical properties, phase equilibria, and direct application studies. Nonetheless, these fluorine-based anions have been the subject of extensive debates about their eventual decomposition into the toxic hydrofluoridric acid. In only a few of those publications, the possible occurrence of hydrolysis of these anions has been mentioned[1–6] or has been studied using different techniques, such as single-crystal X-ray diffraction[7] (which enabled the identification of the 1-butyl-3-methylimidazolium fluoride monohydrate complex, $[C_4mim]F \cdot H_2O$, formed during the preparation and drying of $[C_4mim][PF_6]$) or ^{31}P nuclear magnetic resonance, which indicated a conversion of $[PF_6]^-$ to $[PO_4]^{3-}$

at high concentrations of nitric acid (8 M).[8] Ionic chromatography[9] was also used to evaluate the influence of the solvent in the fluoride ion formation extent in solutions of $[C_4mim][BF_4]$ in water and in methanol/water and acetonitrile/water mixtures. The rate of hydrolysis was clearly lower for the acetonitrile/water mixture.[9] Moreover, when compared to $[C_4mim][BF_4]$, the hexafluorophosphate analogous hydrolysis occurs to an apparently much lower extent at room temperature and in aqueous solutions. The quantification of the fluoride ions generated during the hydrolysis of imidazolium-based ILs incorporating $[BF_4]^-$, $[PF_6]^-$, and $[SbF_6]^-$ as the counterions was performed over a 9 day period also by ionic chromatography.[10] The results[10] indicated that fluoride ions appeared in $[C_4mim][SbF_6]$ and $[C_4mim][BF_4]$ aqueous solutions, with the former producing the greatest amount of fluoride ion, but they did not appear for aqueous solutions of $[C_4mim][PF_6]$. Negative ion electrospray mass spectrometry[11] was used to study the influence of the electrospray current and solution flow rate on the formation of $[F_4PO]^-$ and $[F_2PO_2]^-$ for the undiluted $[C_4mim][PF_6]$. The authors[11] state that the formation of these ions is driven by electrochemical processes and depends on the electrospray emitter and on the IL water content.

Nonetheless, previously from the studies involving ILs,[7–11] it was already well-known that aqueous solutions of fluoroboric acid, HBF_4, are hydrolyzed depending on the dilution, temperature, and time they have been standing after preparation.[12] At room temperature and equilibrium conditions, the studies of Wamser[12] showed that 13.7% of the tetrafluoroborate anions present in an aqueous and acidic solution of HBF_4 had hydrolyzed to $[BF_3OH]^-$ and hydrogen fluoride. Additional hydrolysis reactions[13] produced rather ionic products such as $[BF_2(OH)_2]^-$, $[BF(OH)_3]^-$, and $[B(OH)_4]^-$, which have been identified by negative electrospray mass spectrometry in both 1 day and 3 month old aqueous solutions of $NaBF_4$ at pH 3.0.[13] Kinetic

‡ CICECO.

§ QOPNA.

* To whom correspondence should be addressed. E-mail: afernandes@ua.pt.

Hydrolysis of Tetrafluoroborate and Hexafluorophosphate

J. Phys. Chem. A, Vol. 114, No. 11, 2010 **3745**

TABLE 1: pH Experimental Values of the Aqueous-Rich Phases after Reaching Each of the Equilibration Conditions

equilibration conditions	[C$_4$mim][PF$_6$] + water (biphasic system)	[C$_4$mim][BF$_4$] + water (monophasic system)	[C$_8$mim][PF$_6$] + water (biphasic system)	[C$_8$mim][BF$_4$] + water (biphasic system)
24 h at 298 K	7.24	1.64	6.83	2.25
24 h at 318 K	7.43	1.60	5.93	2.19
24 h at 298 K; pH 3	5.04	1.42	3.94	2.45
24 h at 298 K; pH 12	10.30	3.55	11.35	4.36
30 min at 343 K	7.44	1.35	6.12	1.96
30 min at 373 K	6.34	1.14	4.86	1.65

studies on the hydrolysis of acidic solutions of sodium or potassium tetrafluoroborate, indicate that the rate of hydrolysis is first order in [BF$_4$]$^-$ and in H$^+$ in acidic conditions.[13] On the other hand, for the hexafluorophosphate anion, ^{19}F and ^{31}P nuclear magnetic resonance presented evidence for [F$_2$PO$_2$]$^-$ formation in the reaction of the palladium complex [Pd(η^3-2-Me-C$_3$H$_4$)](μ-Cl)]$_2$ with AgPF$_6$ in CH$_2$Cl$_2$.[14] Furthermore, using the same spectroscopic technique, significant amounts of [PO$_2$F$_2$]$^-$, [PO$_3$F]$^{2-}$, and HF in 1 M solutions of LiPF$_6$ in a 1:1 mixture of propylene carbonate/dimethyl carbonate and with 0.5% of added water to the former solution were also identified.[15] On the contrary, potentiometric determination of F$^-$ using a fluoride-ion-selective electrode showed that [PF$_6$]$^-$ ions produced from solutions of KPF$_6$ are stable in strongly alkaline (pH > 12) or strongly acidic (pH < 1) solutions.[16]

Although the tetrafluoroborate and hexafluorophosphate anion hydrolysis might not completely invalidate thermodynamic measurements on aqueous systems of these ILs, it will introduce new species into the samples, changing their composition and phase equilibrium and eventually preventing the application of thermodynamic correlations and approaches to the description of those data. To the best of our knowledge, the results presented hitherto concerning the hydrolytic decomposition of those anions do not provide systematic information on external factors, such as pH, temperature, and IL structure, which might control the hydrolysis extent. Therefore, the main goal of the present work is to contribute with a systematic study on the hypothetical hydrolysis of [BF$_4$]$^-$ and [PF$_6$]$^-$ of [C$_4$mim][BF$_4$], [C$_8$mim]-[BF$_4$], [C$_4$mim][PF$_6$], and [C$_8$mim][PF$_6$] in equilibrium with water, at extreme pH and temperatures, using electrospray ionization mass spectrometry and ^{1}H and ^{19}F nuclear magnetic resonance spectroscopy (NMR) for the identification of the hydrolysis products.

Experimental Section

Materials and Sample Preparation. The hydrolysis extent was studied with the ILs 1-butyl-3-methylimidazolium tetrafluoroborate, [C$_4$mim][BF$_4$], 1-methyl-3-octylimidazolium tetrafluoroborate, [C$_8$mim][BF$_4$], 1-butyl-3-methylimidazolium hexafluorophosphate, [C$_4$mim][PF$_6$], and 1-methyl-3-octylimidazolium hexafluorophosphate, [C$_8$mim][PF$_6$]. All of the ILs were acquired from Iolitec with mass fraction purities > 99% as doubly verified by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy. The water used was double distilled, passed by a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus. The pH of the aqueous solutions was adjusted with a HCl 37 w/w % solution from Riedel-de Haën or NaOH > 99 w/w % pure from Panreac. The buffers used for the pH meter calibration were buffer pH 4.00 and 7.00 from Riedel-de Haën. Approximately 2 mL of IL was added to 2 mL of pure water (or aqueous acidic or alkaline solutions, depending on the pH that is being evaluated) and left in equilibrium under the temperature and time required for the study. Note that for the pH influence study, the pH of each aqueous solution was

TABLE 2: Relative Abundance (%)^a of the Ions Identified in the ESI(−)-MS Spectra of the Aqueous-Rich Phase of [C$_4$mim][PF$_6$] and [C$_8$mim][PF$_6$]

IL	equilibrium conditions	m/z 51 [CH$_3$OH·F]$^-$	m/z 101 [F$_2$PO$_2$]$^-$	m/z 145 [PF$_6$]$^-$
[C$_4$mim][PF$_6$]	24 h at 298 K	0.41		100
	24 h at 318 K	<0.1		100
	24 h at 298 K; pH 3	0.34		100
	24 h at 298 K; pH 12	0.27		100
	30 min at 343 K	<0.1	<0.1	100
	30 min at 373 K	<0.1	<0.1	100
[C$_8$mim][PF$_6$]	24 h at 298 K	0.17		100
	24 h at 318 K	0.30		100
	24 h at 298 K; pH 3	0.1	1.37	100
	24 h at 298 K; pH 12	1.48		100
	30 min at 343 K		4.40	100
	30 min at 373 K	0.36	13.4	100

^{a} Relative to the base peak taken as 100%.

adjusted at pH 3 or 12 by the addition of HCl or NaOH, respectively, before the aqueous solution equilibration with the IL. The temperature was determined by means of a calibrated Pt100 (class 1/10) temperature sensor and maintained with an uncertainty of ±0.5 K using an oil or water bath.

pH Determination. The pH of each aqueous-rich phase after the equilibration conditions was determined with a pH meter, model HI9321, from Hanna Instruments.

Mass Spectrometry. Electrospray ionization mass spectra (ESI-MS) and tandem mass spectra (ESI-MS−MS) were acquired with a Micromass Quattro LC triple quadrupole mass spectrometer operating in the negative ion mode. Source and desolvation temperatures were 353 and 423 K, respectively. N$_2$ was used as the nebulization gas. The capillary voltage was 2600 V, and the cone voltage was 30 V. ESI-MS−MS spectra were acquired by selecting the precursor ion with the first quadrupole, performing collisions with argon at energies of 15 eV in the second quadrupole, followed by mass analysis of product ions in the third quadrupole. The IL solutions were introduced at a 10 μL·min^{-1} flow using methanol or methanol−water (1:1 v/v) as eluent solvents.

NMR Spectroscopy. The ^{1}H and ^{19}F NMR spectra were recorded using a Bruker Avance 300 at 300.13 and 282.38 MHz, respectively, using D$_2$O or CDCl$_3$ as solvents. Aliquots of the water and IL-rich phases were taken after each of the equilibration conditions and diluted in D$_2$O or CDCl$_3$, respectively.

Results and Discussion

The equilibration conditions used in the [BF$_4$]$^-$ and [PF$_6$]$^-$ hydrolysis extent study are indicated in Table 1 (together with the pH of each aqueous solution and the indication of the biphasic/monophasic nature of the system). The pH values indicate a general trend of prevalent acidic solutions for the [BF$_4$]-based ILs and near-neutral solutions for the [PF$_6$]-based ILs, with the exception of the aqueous solutions kept for 30 min at 373 K and 24 h at 298 K with pH 3. Although the pure ILs have a characteristic alkaline or acidic behavior depending
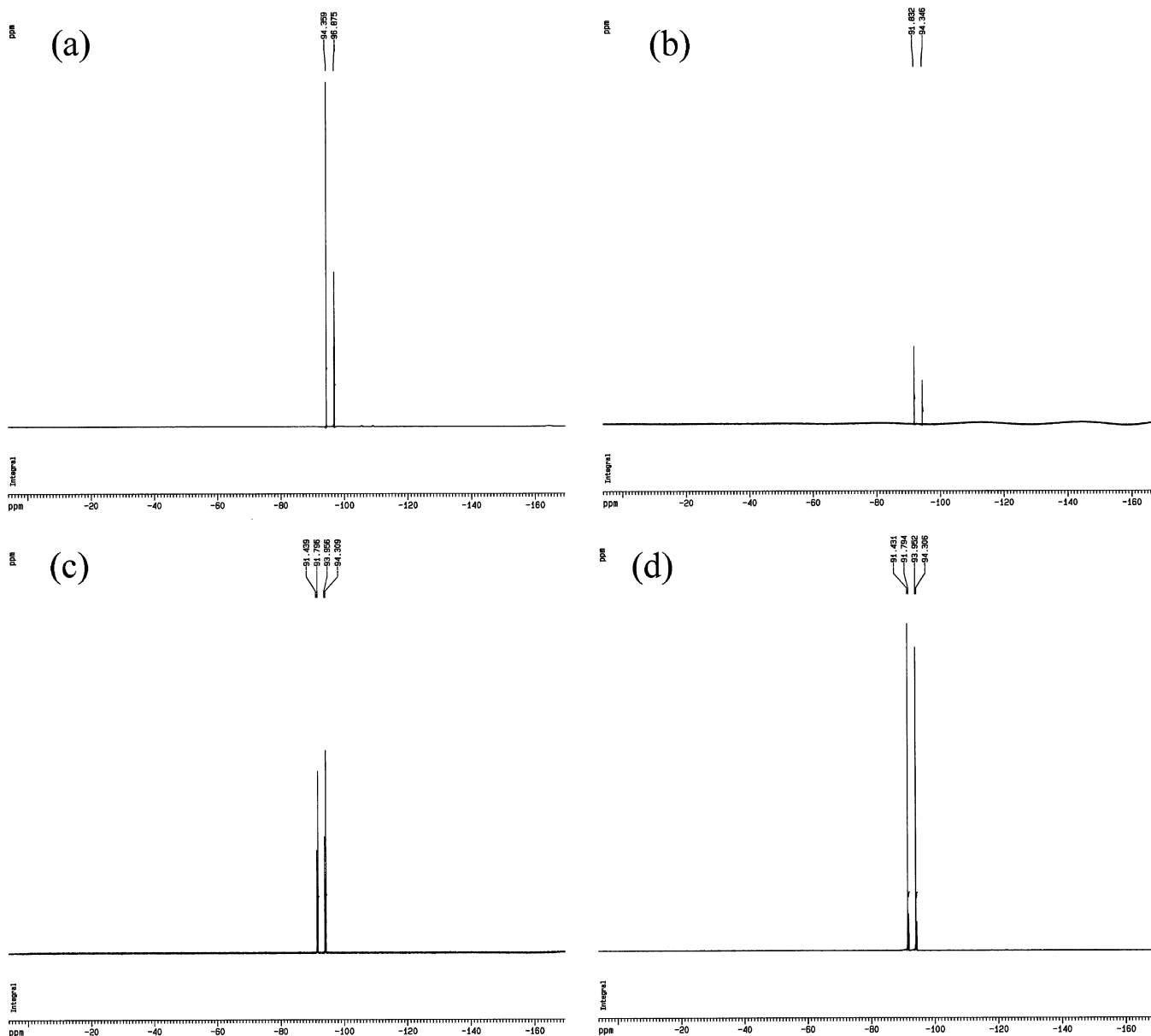
Figure 1. ^{19}F NMR chemical shift for pure $[C_8mim][PF_6]$ (a), in equilibrium with pure water for 24 h at 298 K (b), in equilibrium with an aqueous solution of pH 3 for 24 h at 298 K (c), and in equilibrium with pure water for 30 min at 373 K (d). Note that for (a), $CDCl_3$ was used as the solvent, while for (b), (c), and (d), D_2O was used as the solvent.

on the cations and anions, the acidic pH values observed may indicate, in a first and qualitative approach, the occurrence of hydrolysis and hydrofluoridric acid formation for the $[BF_4]$-based ILs. For the $[PF_6]$-based ILs, especially $[C_8mim][PF_6]$, the results also point to hydrolysis, only under acidic conditions and high temperatures.

To further investigate the products eventually formed in aqueous solutions of $[PF_6]$- and $[BF_4]$-based ILs, electrospray ionization mass spectrometry (ESI-MS) was used as the selected quantitative method, while ^{19}F and ^1H nuclear magnetic resonance spectroscopy (NMR) were further used to corroborate the ESI-MS results.

The ESI mass spectra in the negative mode of the pure ILs $[C_4mim][BF_4]$, $[C_8mim][BF_4]$, $[C_4mim][PF_6]$, and $[C_8mim][PF_6]$ diluted in methanol/water (1:1 v/v) show as a base peak the anions $[BF_4]^-$ or $[PF_6]^-$ and lower abundance peaks corresponding to the formation of aggregate ions of the general formula $[(cation)_m(anion)_{m+1}]^-$. In the positive ion mode, only the peaks corresponding to the clusters $[(cation)_{m+1}(anion)_m]^+$

and to $[C_4mim]^+$ and $[C_8mim]^+$ (base peaks) are observed. The ^{19}F and ^1H NMR spectra of the pure ILs show no other peaks besides the ones corresponding to the cation and anion structures. In addition, the ESI (positive and negative mode) and NMR spectra of the IL-rich phase do not show any peaks corresponding to decomposition products of the cation (or anion), pointing to the absence of hydrolysis in this phase or to the preferential migration of the hydrolysis products to the aqueous phase. On the other hand, ESI spectra, in the positive ion mode and ^1H NMR spectra of the aqueous-rich phase clearly indicate no decomposition of the imidazolium cation.

The analysis of the ESI-MS (Table 2) of the aqueous-rich phase of $[C_4mim][PF_6]$ submitted to different pHs (3 and 12) and several temperature conditions (298, 318, 343, and 373) K did not reveal any ions described in the literature[11,14,16] as the result of hydrolysis of the hexafluorophosphate anion, namely, m/z 123 ($[F_4PO]^-$) and m/z 101 ($[F_2PO_2]^-$). The fluoride anion per se was also absent in all of the spectra, although an ion at m/z 51 was observed for the samples of 24 h at 298 K, 24 h at

TABLE 3: Relative Abundance (%)^a of the Ions Identified in the ESI(−)-MS Spectra of an Aqueous Solution of [C$_4$mim][BF$_4$] and of the Aqueous-Rich Phase of [C$_8$mim][BF$_4$]

IL	equilibrium conditions	m/z 51 [CH$_3$OH·F]$^-$	m/z 87 [^{11}BF$_4$]$^-$	m/z 99^b [^{11}BF$_3$OCH$_3$]$^-$	m/z 111^b [^{11}BF$_2$(OCH$_3$)$_2$]$^-$
[C$_4$mim][BF$_4$]	24 h at 298 K	1.24	100	2.43	0.61
	24 h at 318 K	0.19	100	4.41	0.93
	24 h at 298 K; pH 3	0.69	100	1.96	0.50
	24 h at 298 K; pH 12	0.72	100	0.04	<0.1
	30 min at 343 K	0.22	100	3.49	0.64
	30 min at 373 K	0.55	100	1.83	0.56
[C$_8$mim][BF$_4$]	24 h at 298 K	2.17	100	5.10	1.76
	24 h at 318 K	3.41	100	12.16	3.31
	24 h at 298 K; pH 3	1.46	100	2.4	0.86
	24 h at 298 K; pH 12	3.16	100	0.27	0.14
	30 min at 343 K	1.71	100	17.71	4.65
	30 min at 373 K	1.13	100	25.61	6.68

^{a} Relative to the base peak taken as 100%. ^{b} Ions corresponding to ^{10}B were observed with an abundance corresponding to the isotopic pattern of boron.

SCHEME 1
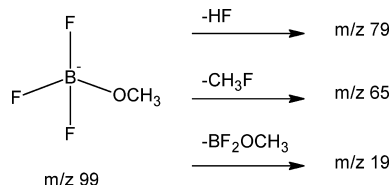
SCHEME 2
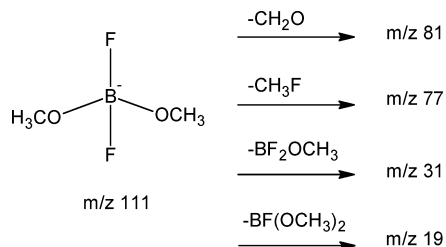
298 K and pH 3, and 24 h at 298 K and pH 12. Nevertheless, the m/z 51 peak's relative abundance never exceeds 0.4% of the base peak (m/z 145) and can thus be considered as negligible and baseline. The assignment of this ion to the adduct [CH$_3$OH·F]$^-$ was made by ESI-MS−MS, and its fragmentation upon collision with argon produced the expected fluoride anion (m/z 19). Replacing [C$_4$mim]$^+$ with [C$_8$mim]$^+$, the formation of the ion [F$_2$PO$_2$]$^-$ (m/z 101), previously reported[11,14,16] as one hydrolytic decomposition product of [PF$_6$]$^-$, was observed for the aqueous-rich phase samples in the following conditions: 24 h at 298 K and pH 3, 30 min at 343 K, and 30 min at 373 K. The analysis of the ^{19}F NMR chemical shift spectra of the aqueous solutions, listed in Table 2, agree with the mass spectrometry results, as illustrated in Figure 1, which presents the ^{19}F NMR chemical shift spectra of the pure [C$_8$mim][PF$_6$] (a), in equilibrium with pure water at 298 K for 24 h (b), in equilibrium with an aqueous solution at pH 3 and 298 K for 24 h (c), and in equilibrium with pure water for 30 min at 373 K (d). The ^{19}F NMR typical doublets of the [PF$_6$]$^-$ octahedral structure (Figure 1a) emerge into two pairs of doublets at acidic pH (Figure 1c) and high temperature (Figure 1d).

The behavior toward hydrolysis of the [C$_4$mim][PF$_6$] and [C$_8$mim][PF$_6$] just discussed points to an effect of the alkyl chain length on the extent of the anion hydrolysis. The results clearly indicate (and will be further corroborated by the results obtained for the [BF$_4$]-based ILs) that the longer the alkyl chain length, the larger the extent of the anion hydrolysis. This fact might be correlated with the cation−anion interaction strength. As the

cation alkyl chain length increases, the interaction energy between the anion and cation decreases, leaving the anion less protected and thus facilitating the hydrolysis in the presence of water.[17] Moreover, it is safe to assume that the hydrolytic decomposition of [PF$_6$]-based ILs is only present under acidic and high-temperature conditions. The product [F$_2$PO$_2$]$^-$ is not observed in the sample kept at 298 K for 24 h and has a relative abundance of 1.37% in the ESI-MS of the acidic (pH 3) sample of [C$_8$mim][PF$_6$] in equilibrium with water. In addition, the temperature increase shows 4.40% and 13.4% of [F$_2$PO$_2$]$^-$ for the samples kept at 343 and 373 K for 30 min, respectively.

Using equilibrium samples from our previous works[17,18] concerning water and IL mutual solubilities, 3 year old samples of [C$_4$mim][PF$_6$], [C$_6$mim][PF$_6$], and [C$_8$mim][PF$_6$] in equilibrium with pure water at room temperature were also analyzed by electrospray mass spectrometry (negative ion mode). The fluoride anion was absent in all spectra. The ion at m/z 51 assigned by MS/MS to [CH$_3$OH·F]$^-$ was observed for all of the samples evaluated, although with an abundance always lower than 0.4% of the base peak (which corresponds to [PF$_6$]$^-$). Hydrolysis of [PF$_6$]-based ILs at moderate temperatures can thus be considered negligible even for long time periods.

The assignment and relative intensities of the peaks observed in the mass spectra of an aqueous solution of [C$_4$mim][BF$_4$] and of the aqueous phase in equilibrium with [C$_8$mim][BF$_4$] are shown in Table 3. Ions m/z 99 and 111 contain boron, as shown by the characteristic isotopic pattern of boron in the mass spectra. ESI-MS−MS spectra of these ions afforded information on their fragmentation reactions, pointing to the presence of [BF$_3$OCH$_3$]$^-$ and [BF$_2$(OCH$_3$)$_2$]$^-$, Schemes 1 and 2, respectively.

Note that these ions are not observed in the mass spectra of the IL-rich phase of [C$_8$mim][BF$_4$], which excludes the hypothesis of ion generation induced by the electrospray process inside of the mass spectrometer. The formation of ions [BF$_3$OCH$_3$]$^-$ and [BF$_2$(OCH$_3$)$_2$]$^-$ can be explained by the addition of the methoxyl anion to boron trifluoride, preformed in the aqueous solution as a decomposition product of the tetrafluoroborate anion or by the replacement of the hydroxyl group in [BF$_3$OH]$^-$ and [BF$_2$(OH)$_2$]$^-$ by methoxyl. The source of methoxyl anions is the methanol, used as the solvent in the ESI-MS in the negative mode.

From the inspection of Table 3, it is evident that [BF$_4$]-based ILs undergo hydrolysis at all of the conditions used, even at moderate temperatures. Again, the effect of a longer alkyl chain of the cation on the extent of hydrolysis is expressed by the larger abundances of the hydrolysis resultant ions in the ESI-MS of [C$_8$mim][BF$_4$].
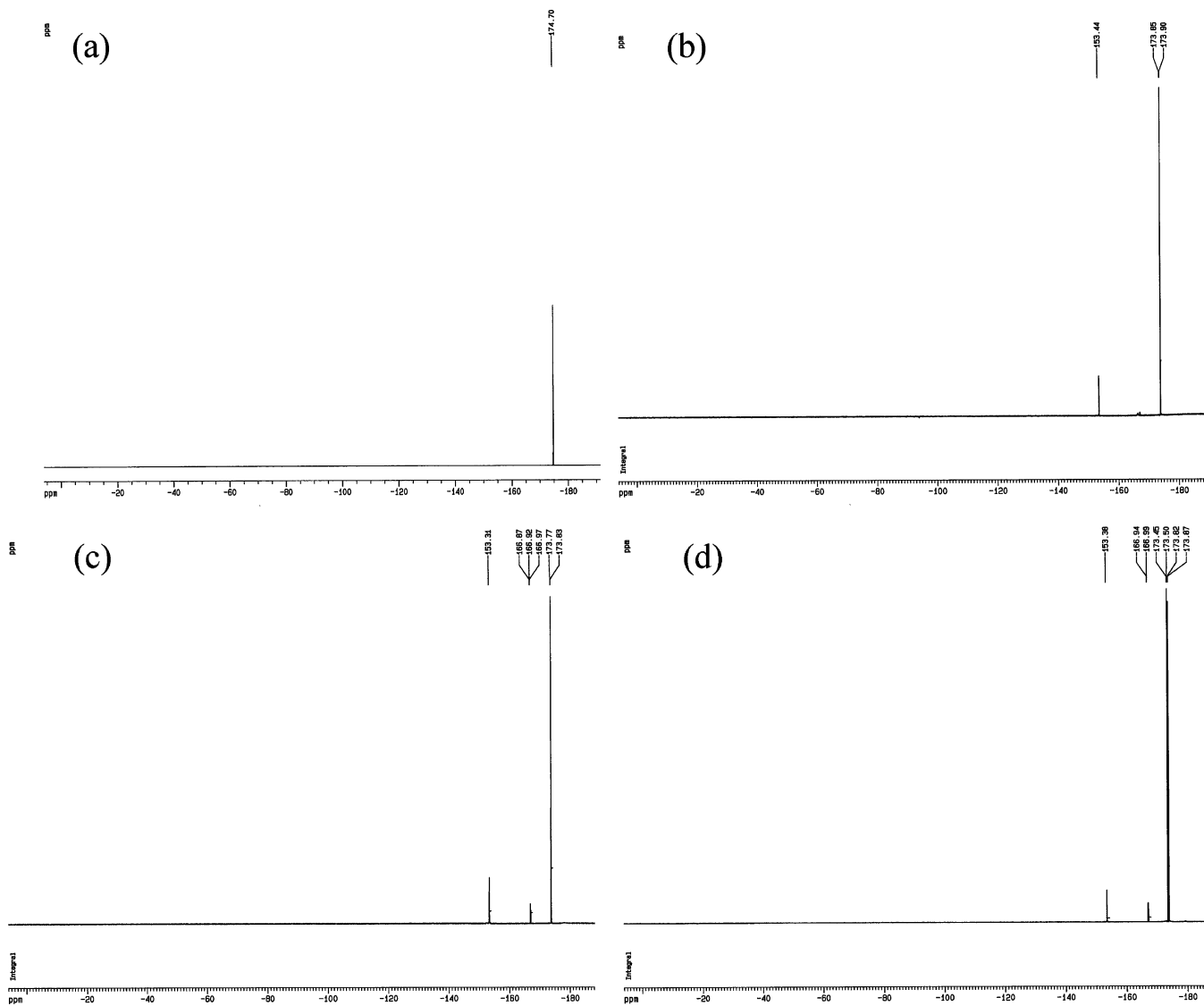
Figure 2. ^{19}F NMR chemical shift for pure [C$_8$mim][BF$_4$] (a), in equilibrium with pure water for 24 h at 298 K (b), in equilibrium with pure water for 24 h at 318 K (c), and in equilibrium with pure water for 30 min at 373 K (d). Note that for (a), CDCl$_3$ was used as the solvent, while for (b), (c), and (d), D$_2$O was used as the solvent.

The 1 and 3 year old samples of [C$_8$mim][BF$_4$] in equilibrium with water at room temperature were also analyzed by ESI-MS to complement this study. The abundances of ions m/z 99 and 111 largely increase over this time period, indicating that hydrolysis of [BF$_4$]-based ILs proceeds even at moderate temperatures. At 298 K, the ion m/z 99 abundance increases from 2.43 (24 h) to 14.1 (1 year old) and to 38.9% (3 year old). Under the same experimental conditions, the peak at m/z 111 increases from 0.61 (24 h) to 4.71 (1 year old) and to 6.70% (3 year old).

Figure 2 presents the ^{19}F NMR chemical shift spectra of the pure [C$_8$mim][BF$_4$] and of three samples of the same IL in equilibrium with water submitted to different temperatures (298, 318, and 373 K). The aqueous-rich phase samples' ^{19}F NMR spectra show, besides one peak due to the tetrahedral [BF$_4$]$^-$ ion, two extra peaks derived from hydrolysis and in full agreement with the mass spectrometry data.

Conclusions

ILs have been attracting a great deal of interest as solvents for a wide variety of chemical reactions and processes. Therefore, their hazardous impact, environmental toxicity, and chemical and thermal stability are issues that should be clarified before industrial applications. Thus, the hydrolysis of hexafluorophosphate- and tetrafluoroborate-based ILs was investigated under several experimental conditions of pH and temperature. The results obtained by electrospray ionization mass spectrometry, NMR spectroscopy, and pH measurements clearly indicate that hydrolysis is a process restricted to [PF$_6$]$^-$ and [BF$_4$]$^-$, while the imidazolium cation remains unchanged. The [PF$_6$]$^-$ was observed to be chemically and thermally stable at moderate experimental conditions, although decomposition becomes significant under acidic conditions (pH 3) or high temperatures (343 and 373 K). On the other hand, hydrolysis of [BF$_4$]$^-$ was observed under all of the experimental conditions used, even at room temperature. Furthermore, the hydrolysis extent was shown to increase for both anions with the cation side alkyl chain length due to a decrease of the cation−anion interaction strength that further facilitates the interaction of water molecules with the anion.

This work intends to be a contribution toward the specification of the adequate experimental conditions when dealing with aqueous solutions of hexafluorophosphate- and tetrafluoroborate-based ILs.

References and Notes

(1) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.

(2) Gubicza, L.; Nemestóthy, N.; Fráter, T.; Bélafi-Bakó, K. *Green. Chem.* **2003**, *5*, 236.

(3) Tseng, M.; Liang, Y.; Chu, Y. *Tetrahedron Lett.* **2005**, *46*, 6131.

(4) Nikitenko, S. I.; Berthon, C.; Moisy, P. C. R. *Chimie* **2007**, *10*, 1122.

(5) Archer, D. G.; Widegren, J. A.; Kirklin, D. R.; Magee, J. W. *J. Chem. Eng. Data* **2005**, *50*, 1484.

(6) Najdanovic-Visak, V.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Nunes da Ponte, M.; Guedes, H. J. R.; Seddon, K. R.; Szydlowski, J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701.

(7) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2003**, *5*, 361.

(8) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Griffin, S. T.; Rogers, R. D. *Ind. Eng. Chem. Res.* **2000**, *39*, 3596.

(9) Villagrán, C.; Deetlefs, M.; Pitner, W. R.; Hardacre, C. *Anal. Chem.* **2004**, *76*, 2118.

(10) Cho, C.-W.; Pham, T. P. T.; Jeon, Y.-C.; Yun, Y.-S. *Green Chem.* **2008**, *10*, 67.

(11) Lu, Y.; King, F. L.; Duckworth, D. C. *J. Am. Soc. Mass. Spectrom.* **2006**, *17*, 939.

(12) Wamser, C. A. *J. Am. Chem. Soc.* **1948**, *70*, 1209.

(13) Archer, D. G. *Inorg. Chem.* **1973**, *12*, 89.

(14) Fernández-Galán, R.; Manzano, B. R.; Otero, A.; Lanfranchi, M.; Pellinghelli, M. A. *Inorg. Chem.* **1994**, *33*, 2309.

(15) Ponikvar, M.; Zemva, B.; Liebman, J. F. *J. Fluorine Chem.* **2003**, *123*, 217.

(16) Plakhtnyk, A. V.; Ernst, L.; Schmutzler, R. *J. Fluorine Chem.* **2005**, *126*, 27.

(17) Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardas, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. *J. Phys. Chem. B* **2007**, *111*, 13082.

(18) Freire, M. G.; Carvalho, P. J.; Gardas, R. L.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. P. *J. Phys. Chem B* **2008**, *112*, 1604.

JP903292N