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Article

Stability of Divalent Europium in an Ionic Liquid: Spectroscopic Investigations in 1-Methyl-3-butylimidazolium Hexafluorophosphate

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In this work, devoted to 1-methyl-3-butylimidazolium hexafluorophosphate ionic liquid (BumimPF$_6$), the importance of the purity of the solvent for spectroscopic investigations is highlighted. Results from small angle X-ray scattering indicate that the pure solvent exhibits a local organization. Europium(II), which appears to be unusually stable in BumimPF$_6$, is characterized by spectroscopic techniques (absorption, luminescence). Solvation of Eu(II) in BumimPF$_6$ and complexation effects in the presence of the crown ether 15C5 solubilized in the ionic liquid are discussed.

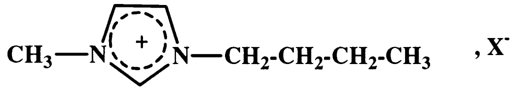
1. Introduction

The use of organic solvents in process operations leads to many problems, the main ones concerning their toxicity for both the process operator and the environment and their volatility and flammable nature, which are also of importance for their transport and storage.[1,2] Industrial processes, including nuclear waste management and nuclear fuel cycle processes, use organic phases that emit volatile organic compounds (VOCs) damaging the environment.

Recently, room temperature ionic liquids (RTILs) have emerged and are gaining academic and industrial attention in catalysis, separation processes, and electrochemistry due to their particular properties, especially with the emergence of the new *N*,*N*-dialkylimidazolium cation derivatives (Scheme 1).

Both the cationic and the anionic partners can be easily varied, so that these ionic liquid solvents can be designed for particular applications or for particular sets of properties.[3−5] Whatever the alkyl length or the counteranion structure, they display very low vapor pressure, and hence do not emit VOCs, and are easy to transport and to store. They are air and moisture stable and, as a consequence, usable for biphasic systems such as in liquid−liquid extraction. They are highly solvating for both ionic and molecular species, noncoordinating, conductive, and polar (equivalent to ethanol).[6−8] Their high thermal stability and their wide liquidus allow temperature variations to be used for process optimization.

Scheme 1



Moreover, RTILs may also appear as an interesting alternative to pyrochemical processes because they present properties similar to the ones obtained in high temperature molten salts[9] such as high solubilization capacities and large electrochemical windows but at room temperature.

From the very specific viewpoint of nuclear industry, in which the actual processes mainly rely on specific oxidation states (such as Pu(III)/Pu(IV)) and variable acidic conditions

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(for reviews on the subject, see refs 10−13), it is now understood that aqueous solutions in contact with the actual organic phases may not be the best system for partitioning actinides and lanthanides because water is a very good complexing agent that competes with other ligands even in the organic phase.[14,15] Two possible alternatives may be considered: (i) liquid−liquid extraction using water in contact with new solvents, in which complexation and solvation effects would be more favorable as compared to the present situation, and (ii) new solvents that could stabilize unusual oxidation states in order to avoid liquid−liquid extraction, that would be replaced by direct metal electrodeposition. Recently, it has been shown that some ionic liquids present an interesting stability under α and γ irradiation[16] and that the use of ionic liquids in actinide process flow sheets would significantly enhance the criticality safety of these processes.[17] Therefore, ionic liquids appear as promising media to investigate other routes than those used nowadays.

This work reports the first results on the spectroscopic characterization of pure 1-methyl-3-butylimidazolium hexafluorophosphate ($BumimPF_6$) and of europium(II) salts dissolved in this ionic liquid. $BumimPF_6$ was chosen because it is particularly air and moisture stable, is a good electrochemical conductor, has a moderate viscosity as compared to other RTILs, and is usable in biphasic separation.[5] In order to improve our knowledge of the physicochemical properties of actinides and lanthanides dissolved in ionic liquids, we focused on a spectroscopic characterization through absorption and luminescence spectroscopy. Synthesized $BumimPF_6$ and commercially available $BumimPF_6$ (Solvent Innovation, Köln, Germany) were compared in terms of purity and stability under laser irradiation. Results obtained show that, for spectroscopic purposes, $BumimPF_6$ must be purified until it is colorless. Spectroscopic data were obtained that allow the characterization of $BumimPF_6$ and of Eu(II) dissolved in it.

2. Materials, Chemicals, and Methods

2.1. Synthesis of $BumimPF_6$. The synthesis of $BumimPF_6$ is based on a method by Visser et al.[18] and is typically performed as described in the following: All chemicals were of the best reagent grades (Aldrich) and were used without further purification. All aqueous solutions were prepared with deionized water that was purified with a Millipore deionization system ($w = 18.3$ MΩ cm).

First Step: Synthesis of BumimCl. A three-necked round-bottomed flask under argon, equipped with a water refrigerant, is charged with 1 mol (82.11 g) of methylimidazole and 1 mol (92.57 g) of n-chlorobutane. The mixture is stirred under argon for 48 h at 70 °C, until a pale yellow viscous mixture is obtained. It is then transferred into a flask and stored at 3−5 °C under argon until the mixture precipitates quantitatively (≈12 h). White crystals are obtained which are washed several times with ethyl acetate and filtered each time on a Buchner apparatus. These white crystals are then transferred into a drybox containing phosphorus pentoxide under vacuum. A fine white powder of BumimCl is obtained with typical yields of ≈80%.

Second Step: Synthesis of $BumimPF_6$. BumimCl crystals (125 g, 0.71 mol) are dissolved in deionized water (360 mL), stirred, and cooled at 0 °C in an ice bath. Hexafluorophosphoric acid (1.1 equiv of a 40% aqueous solution, 192 g, 0.78 mol) is slowly added (30−45 min) under vigorous stirring. After addition, the mixture is allowed to come to room temperature and stirred for 2 h. Two phases are obtained, and the upper one (acidic aqueous phase) is decanted. The bottom phase ($BumimPF_6$) is washed several times with deionized water (10 × 350 mL), until neutrality of the upper aqueous phase is ensured and no chloride ions are found in the aqueous phase transferred from the $BumimPF_6$ phase (silver nitrate test in the aqueous phase). $BumimPF_6$, as a pale yellow viscous liquid, is transferred and stored in a drybox under vacuum containing phosphorus pentoxide. Typical yields of ≈80% were obtained. As our interest is to study $BumimPF_6$ in liquid−liquid extraction conditions versus an aqueous phase, we did not try to dry the ionic liquid more than described in this section.

$BumimPF_6$ was also purchased from Solvent Innovation (>98% purum) as a deep yellow viscous liquid. In order to avoid confusion, this chemical will be denoted as $BumimPF_6$-SI in the following.

2.2. Other Chemicals and Solutions with $BumimPF_6$ as a Solvent. Europium(II) iodide (Aldrich), NaI (Prolabo), KI (Prolabo), $K_2Cr_2O_7$ (Prolabo), and the two crown ethers 15C5 and 12C4 (Aldrich) were used as received.

2.3. Methods of Characterization. Elemental CHN microanalyses are performed by complete oxidation, and detection is performed by gas chromatography (Perkin-Elmer).

Chloride ions were analyzed by high performance ionic chromatography (HPIC) using a Dionex 4500i ion chromatograph equipped with a conductivity detection, an AG 12A guard column, an AS12A column, and an anion chemical suppressor AMMS. A CO_3^{2-}/HCO_3^- buffer (2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$) at 1 $mL\cdot min^{-1}$ was used as eluent, and 12.5 mM H_2SO_4 at 3−5 $mL\cdot min^{-1}$ as regenerant.

The water amount in $BumimPF_6$ is determined by the Karl Fischer technique using standard procedures. The apparatus is composed of a Metrohm 703TI Stand titrator and a Metrohm 756KF coulometer.

Absorption spectra in the range 190−900 nm are recorded on a Uvikon 930 (Kontron). In the case of highly absorbing samples (see later), quartz cuvettes of 2 mm path length are used. For other samples, 1 cm path length quartz cuvettes are used. The former spectra are normalized to a 1 cm path length for the sake of comparison. For pure solvents, the reference is an empty quartz cuvette, and for solutions, the reference is the pure solvent. Experiments are performed at a controlled temperature of 294 ± 1 K.

The XRD patterns (small-angle X-ray scattering, SAXS) are obtained with the liquid being filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu $K\alpha_1$ beam ($\lambda = 1.5405$ Å) is obtained using a Debye−Scherrer camera equipped with a

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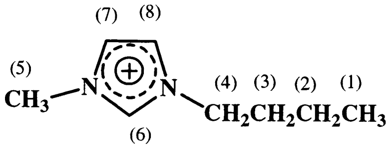
Table 1. ^{1}H and ^{13}C Chemical Shifts for $BumimPF_6$ in Acetone-d_6 Solvent from NMR Spectroscopy



	$\delta_1{}^{a}$	δ_2	δ_3	δ_4	δ_5	δ_6	$\delta_{7,8}$
^{1}H	0.9	1.4	1.8	4.3	4	8.89	7.6/7.7
^{13}C	12.6	19.2	31.89	49.5	35.63	136.37	122.37/123.71

[a] δ values in ppm relative to internal reference $SiMe_4$.

bent quartz monochromator and an electric oven. The diffraction patterns are registered with a gas curved counter (Inel CPS 120) associated with a data acquisition computer system; periodicities up to 60 Å can be measured, and the sample temperature is controlled within ±0.05 °C. Central diffusion experiments are carried out at room temperature with a small-angle X-ray scattering spectrometer Nanostar, developed by Bruker-Anton Paar. The sample is held in calibrated mica cells of 1 mm thickness to avoid multiple scattering. The Nanostar spectrometer operates with a pinhole collimator and a wire proportional gas detector. A monochromatic ($\lambda = 1.54$ Å) and almost parallel beam (divergence $= 0.03°$) is obtained through two Gobel crossed mirrors. The size of the incident beam on the sample is close to 300 μm. The sample–detector distance is set at 1 m (0.01 Å$^{-1} < q < 0.2$ Å^{-1}). The q resolutions are 0.003 Å^{-1}.

Emission spectra are recorded on a classical spectrofluorimeter (Photon Technology International) which does not allow time-resolved emission spectra. The time-resolved emission spectroscopy (TRES) apparatus is described in detail elsewhere.[19,20] Experiments are performed at a controlled temperature of 294 ± 1 K.

3. BumimPF$_6$ Characterization and Purification

3.1. General Characterization. A structural characterization of $BumimPF_6$ has been obtained by ^{1}H and ^{13}C NMR spectroscopy. Signals were attributed using the DEPT protocol. The major findings are reported in Table 1 and are in agreement with the expected cationic structure. It can be observed that the resonances of proton and carbon 6 suffer an important downfield shift ($\delta H_6 = 8.89$ ppm, $\delta C_6 = 136.37$ ppm), confirming the quaternary structure of the proximate ammonium atom and the strong sp^2 hybridization character of carbon 6. This effect also affects protons and carbons 4 and 5 ($\delta H_4 = 4.3$ ppm, $\delta C_4 = 49.5$ ppm, $\delta H_5 = 4$ ppm, $\delta C_5 = 35.63$ ppm) which are also relatively moved toward downfield shift.

Elemental analysis (C, H, N) is in agreement with the theoretical structure of $BumimPF_6$ (Table 2).

The water content in $BumimPF_6$ of various origin is reported in Table 2. As one of our final goals is to use ionic liquids in liquid–liquid extraction versus an aqueous phase, $BumimPF_6$ is not dried further after synthesis (Table 2). This also allows comparison with data from usual liquid–liquid extraction systems where the organic phase is not particularly dried either. From these results, two major points can be highlighted: (1) The purification procedure as described in section 3.2 eliminates about half of the water present. (2) The presence of water in $BumimPF_6$ cannot be neglected considering its solvation capabilities for ionic species, a point to be discussed in section 5.

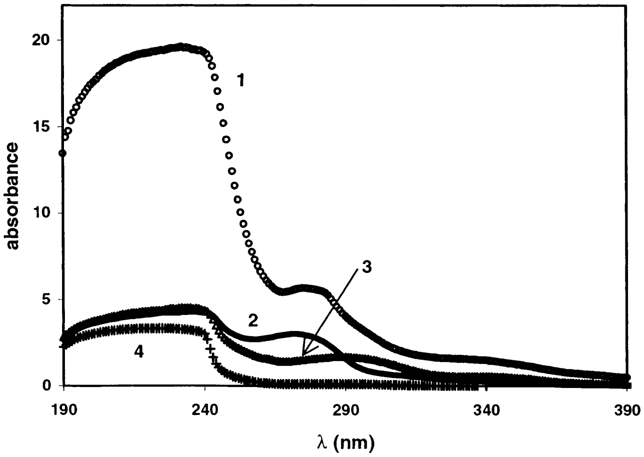


Figure 1. Absorption spectra of $BumimPF_6$ of various origin: (1) raw $BumimPF_6$-SI; (2) raw $BumimPF_6$, (Cl^-) = 46 ± 5 ppm; (3) purified $BumimPF_6$-SI; (4) purified $BumimPF_6$.

The large difference in color between the two ionic liquids (synthesized and commercial) indicates the presence of impurities in variable amounts. This seems to be a common feature of commercial products of this kind.[8] The presence of impurities is confirmed by high performance ionic chromatography (Table 2): $BumimPF_6$-SI (as received) contains large amounts of Cl^- and additional $SO_4{}^{2-}$, $PO_4{}^{3-}$, $NO_3{}^{-}$, and F^- ions, plus, at least, an additional anion which was not identified. In contrast, $BumimPF_6$ contains Cl^- as the only anionic impurity, in smaller amounts. Most probably, Cl^- anions come from the first synthesis step (see section 2.1). The chloride amount significantly differs from one synthesized batch to the other. These differences in impurity are also revealed in the absorption spectra (see Figure 1). The $BumimPF_6$-SI spectrum (2 mm path length cuvette required) shows a significant absorption up to the visible region.

3.2. Purification Procedures. Following the work of Cammarata and co-workers,[21] purification was attempted according to three different procedures: (i) alumina alone (aluminum oxide, anhydrous γ-alumina, Merck), (ii) activated charcoal alone (3 mm grain size), (iii) activated charcoal plus alumina. The impact of each procedure onto raw $BumimPF_6$ has been evaluated by absorption spectroscopy and by HPIC. The last procedure is very efficient and is thus described in detail: 100 mL of $BumimPF_6$ is mixed with 5 g of activated charcoal (3 mm grain size or 100 mesh give similar results) and stirred for 12 h. The resulting mixture is centrifuged (15 min, 6000 rpm), and the floating phase is transferred in a 4 cm height alumina column preequilibrated with $BumimPF_6$. A colorless liquid is obtained and stored in a drybox under vacuum containing P_2O_5. The yield of this purification procedure is very low (around

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Table 2. Characterization of $BumimPF_6$ of Different Origin (See Text)

	raw $BumimPF_6$	purified $BumimPF_6$	raw $BumimPF_6$-SI	purified $BumimPF_6$-SI
elemental anal. exptl[b] (calcd) (%)	C: 33.66 (33.81) H: 5.37 (5.32) N: 9.70 (9.86)			
HPIC (ppm)	Cl^-: from (46 ± 5) to 0.1[c]	Cl^-: <0.1	Cl^-: (80 ± 5) SO_4^{2-}, NO_3^-, PO_4^{3-}	Cl^-: (14 ± 1) SO_4^{2-}, NO_3^-, PO_4^{3-}
water content (ppm)	20000	9000	450	not determined
maximum time of irradiation (min)	17 ($Cl^- = 46$ ppm)	40	<8	<10

[a] HPIC measurements show that all samples contain F^- anions. [b] Average of two determinations. [c] Depending on the synthesized batch.

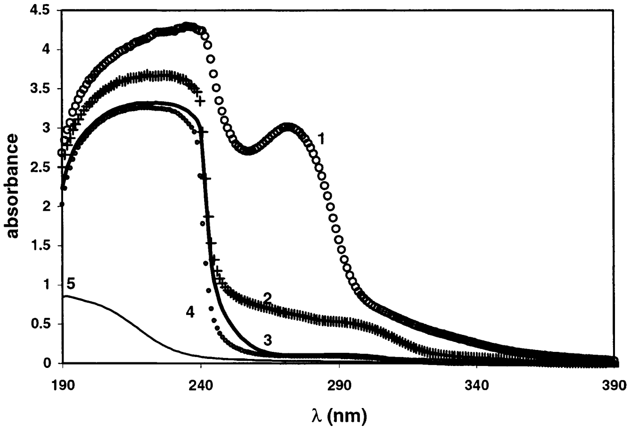

Figure 2. Absorption spectra: (1) (batch 1) raw $BumimPF_6$, (Cl^-) = 46 ± 5 ppm; (2) (batch 2) purified $BumimPF_6$ (starting from batch 1), (Cl^-) ≈ 0.1 ppm; (3) best purified $BumimPF_6$ (starting from batch 2); (4) $BumimCl^-$ in water (1 M); (5) HPF_6 in water (1 M).

50%), mainly because the activated charcoal retains part of the liquid.

With this purification procedure, some anionic impurities remain in the $BumimPF_6$-SI (see Table 2): this may be due to the high amounts of various anions present in the commercial product. After purification, the commercial product is a pale yellow liquid, for which 1 cm path length cuvettes are usable for spectrophotometry (see Figure 1).

As for anions, the purification specifically eliminates the chloride ions from the synthesized $BumimPF_6$ (Table 2), as has been checked with HPIC. Furthermore, by comparison of the various absorption spectra, it can be deduced that the purification procedures suppress the absorption band in the range 250−300 nm (Figure 2). The purification procedure has been tested for two aliquots of synthesized $BumimPF_6$, and the results appear to be reasonably reproducible in terms of absorption spectra. Starting from $BumimPF_6$ with a rather low amount of chloride ions (around the detection limit of HPIC, i.e., 0.1 ppm), the purification procedure leads to a further decrease of the absorbance in the 250−300 nm region (see Figure 2), which is attributed to an enhanced purification of the solvent. This improved purification cannot be followed by HPIC (below detection limit), and no attempts of quantification have been made by use of the absorption spectra. However, the decrease in the chloride concentration (as measured by HPIC), the change in color (from yellow to transparent by visual observation), and the change in the absorption spectrum are qualitatively correlated to the use of the purification procedure. Indeed, it is well-known that activated charcoal is of great efficiency for the fixation of aromatic or heteroaromatic rings (including VOCs) by developing electrostatic interactions, such as van der Waals bonds. Moreover, the presence of an absorption band in the range 200−300 nm is often characteristic of the appearance of vibrational levels arising from a modification of the electron density repartition in an aromatic or heteroaromatic ring. In the case of $BumimPF_6$, several hypotheses can be evoked to explain both the retention on activated charcoal and alumina column and the absorption band: (1) an oxidoreduction reaction on the five-membered ring, (2) an electrophilic addition on the ring, (3) a partial retrogradation of the addition of the butyl substituent. All these paths are known to be sensitive to the presence of chloride ions. Although there is no reason to assume that chloride ions are neither directly responsible for the color of the raw $BumimPF_6$ nor for the band in the 250−300 nm region, conversely, it is reasonable to assume that the presence of chloride ions, even in small amounts, has an indirect effect on these two aspects.

Therefore, it is our opinion that the purification procedure both eliminates chloride anions and some organic partners, which have not been studied further, chloride ions being mainly eliminated as a counteranion of the corresponding charged organic species.

As a whole, the absorption spectrum of purified $BumimPF_6$ as displayed in Figure 2 (batch 3) is considered to be the "true" absorption spectrum of the pure liquid. This spectrum is compared to the absorption spectra of 1-methyl-3-butylimidazolium, (introduced as its chloride salt) and PF_6^- (introduced as HPF_6) in water (Figure 2).

3.3. Influence of Impurities on Photostability. The stability of the solvents $BumimPF_6$ and $BumimPF_6$-SI (either raw or purified) toward laser irradiation has been investigated under the usual conditions of TRES.[19] This is necessary considering the non-negligible absorption of some of the solvents at $\lambda_{exc} = 266$ nm (Figure 1).

Photodegradation is conveniently followed by spectrophotometry.[22−24] An aliquot of the solvent is irradiated at $\lambda_{exc} = 266$ nm at a constant beam average power for fixed short time durations (i.e., 2 min on average), and an

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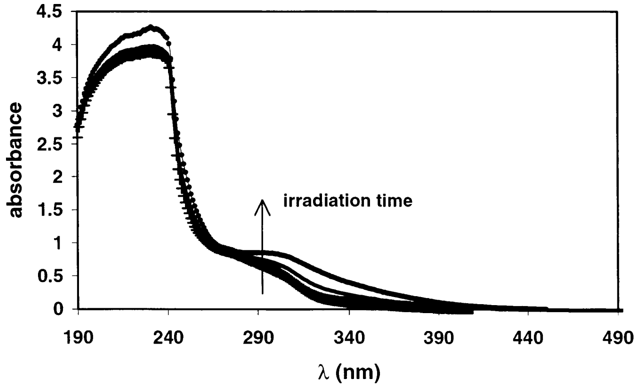

Figure 3. Absorption spectra of raw BumimPF$_6$ (with (Cl$^-$) ≈ 46 ppm) after various lengths of time of pulse laser irradiation. Average laser power 13 mW, repetition rate 10 Hz, $\lambda_{exc} = 266$ nm, $t_{irr} = 0$, 56, and 93 min.

absorption spectrum is recorded between each laser irradiation. Changes in the absorption spectrum monitor the photodegradation. Note that the samples were not shaken to enhance diffusion of the photodegradation products. Figure 3 presents a set of absorption spectra at increasing irradiation times for raw BumimPF$_6$ as a typical example. Assuming that photodegradation is a linear function of time (i.e., additive), a criteria has to be defined in order to set a limit to the irradiation duration below which the solvent is considered to be stable. It was decided that changes upon irradiation in the range 250−390 nm exceeding 0.1 in absorbance arbitrary units are indicative of photodegradation. On this basis, the duration for which the solvents are photostable have been determined and are reported in Table 2. Again, impurities have a large impact onto the photostability: Emission spectra by TRES can be conveniently obtained solely for purified BumimPF$_6$. In the case of raw BumimPF$_6$-SI, above $t = 8$ min, a brown region is observed around the laser beam impact in the liquid. This is considered to be incompatible with photostability. In this respect, purification enhances the photostability of BumimPF$_6$-SI. It is most probable that the impurities present in BumimPF$_6$-SI have an impact onto other physicochemical properties of this liquid as well, and caution should be paid to this problem.

4. BumimPF$_6$ Properties

4.1. First Investigation of the Structure of Pure BumimPF$_6$. Small angle X-ray scattering provides insight about the structural inhomogeneity of the medium. It is mainly used to measure crystalline and amorphous structures on the atomic scale. Figure 4 presents the results obtained by this technique for purified BumimPF$_6$. Two peaks at $2\theta = 20°$ and $2\theta \approx 14°$ are observed, together with their first harmonics, which correspond to two structures with specific dimensions of 6.3 and 4.4 Å. Peak deconvolution and measurement of the full width at half-maximum give the coherence distance which was estimated to be 15 Å for the 6.3 Å structure and should be of the same order of magnitude for the 4.4 Å structure. Complementary investigation with polarized light showed, however, that this solvent is not a liquid crystal (no birefringence observed). This is in line with previous studies on related ionic liquids, for which a liquid crystal behavior was observed for cationic side chains containing more than 14 carbons for a PF$_6^-$ counteranion.[25,26] Further experiments (central diffusion) showed that no aggregates are present in BumimPF$_6$ (data not shown): the liquid is purely monophasic, although it presents a local organization.

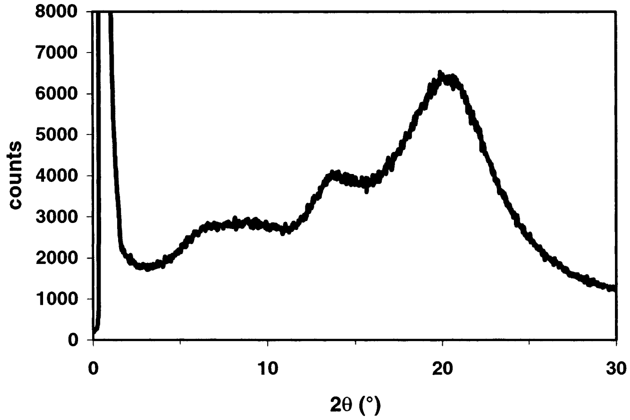

Figure 4. Small angle X-ray diffusion of BumimPF$_6$.

Law and Gannon[27,28] have investigated the molecular orientation at the surface of various ionic liquids, including BumimPF$_6$. In this liquid, they found that the surface is populated by both anions and cations, with no segregation, the cation ring being perpendicular to the surface. This is consistent with the hypothesis that the ions are associated as ion pairs in the liquid state. A study of the structure of 1-methylimidazolium with CF$_3$SO$_3^-$ or NO$_3^-$ [29] shows that the cations adopt a face to face orientation. In two previous works on solid 1-ethyl-3-methylimidazolium based ionic liquids, either with hexafluorophosphate[30] or NO$_3^-$ counteranions,[31] it was also shown that imidazolium cations are positioned in pairs, with a plane to plane separation of 4.5 Å. This value is not very different from the 4.4 Å value obtained in this work. It seems therefore reasonable to ascribe the 4.4 Å value observed in the liquid phase of BumimPF$_6$ to an interplanar distance between the imidazolium rings. Under this assumption, the coherence distance of 15 Å roughly corresponds to three repetitions of the pattern of parallel imidazolium rings. The presence of an alkyl chain involves a large parallel offset between the cations. Fuller et al.[30] found a centroid to centroid separation distance of 5.39 Å with 1-methyl-3-ethylimidazolium. Therefore, in the case of Bumim, we may attribute the 6.3 Å distance to this cation−cation separation.

4.2. Estimations of Some Solubilities. The solubilities of various salts in purified BumimPF$_6$ have been estimated by visual observation of the diffusion of HeNe laser light

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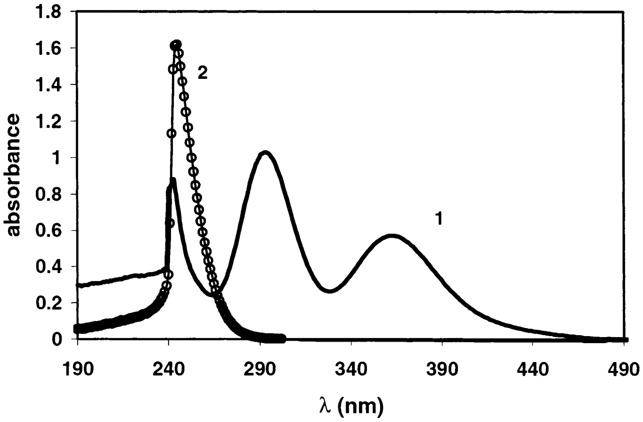

Figure 5. Absorption spectrum of (1) EuI_2 ($C = 10^{-4}$ M) in $BumimPF_6$ and (2) KI ($C = 2.4 \times 10^{-3}$ M) in $BumimPF_6$.

Table 3. Estimated Solubilities of Various Salts in Purified $BumimPF_6$

	EuI_2	NaI	KI	$K_2Cr_2O_7$
estimated solubility (M)	2×10^{-3}	$>1.1 \times 10^{-2}$	9×10^{-3}	9.5×10^{-3}

(see Table 3).[32] Salts that are not hygroscopic (such as EuI_2) could be easily dissolved in $BumimPF_6$.

5. Eu(II) Solutions in $BumimPF_6$: A Preliminary Study

5.1. UV−Vis Absorption Spectra. The absorption spectrum of Eu(II) iodide salt in $BumimPF_6$ at a concentration of 10^{-4} M is displayed in Figure 5. To our knowledge, this is the first report on the solubility of Eu(II) in ionic liquids. Some publications already deal with the dissolution of Cd(II), Sr(II), or Co(II).[18,33,34] In these studies, the metals are assumed to exist as doubly charged cations in solution (Sr^{2+} for example in ref 33), but it is not possible with the data of Figure 5 alone to determine whether Eu(II) is in a molecular form, such as EuI_2, or in an ionic form, such as Eu^{2+}. Therefore, the notation Eu(II) will be used in the following.

The peak at $\lambda = 240$ nm is ascribed to iodine, by comparison with the absorption spectra of NaI and KI in $BumimPF_6$ (see Figure 5 for KI). The two absorption maxima at 290 and 355 nm are thus ascribed to Eu(II). The molar absorption coefficient of Eu(II) in $BumimPF_6$ at $\lambda = 290$ nm is equal to $\epsilon = 10^4$ M^{-1} cm^{-1}, which is rather high per se and is approximatively 1 order of magnitude larger than the molar absorption coefficient of Eu^{2+} in water or in methanol.[35,36] The positions of the maxima are in line with what is known for Eu(II) or various Eu(II) crown ether complexes in methanol.[37] In methanol, the presence of two absorption bands for Eu(II) is attributed to the 5d level splitting due to the coordination properties of the surroundings (either methanol or a crown ether ligand).[37] For all crown ether complexes studied in methanol,[37] a red shift of the higher energy band and a blue shift of the lower energy band with respect to those of $EuCl_2$ in methanol are observed. In $BumimPF_6$, the two Eu(II) bands present a strong red shift as compared to the maxima ($\lambda = 248$ and 328 nm, from ref 37) of $EuCl_2$ in methanol. In $BumimPF_6$, Eu(II) is most probably solvated, but the exact nature of the first solvation sphere remains unclear.

5.2. Stability of Divalent Europium in $BumimPF_6$. Solutions of Eu(II) in $BumimPF_6$ appear to be perfectly stable, even without protecting them from natural light. It was attempted to oxidize Eu(II) into Eu(III) via three chemical methods, which all were unsuccessful: In a first trial, $K_2Cr_2O_7$ in excess was dissolved in a solution of Eu(II) in $BumimPF_6$. This salt has been chosen for its well-known oxidizing properties in water, but no changes in the absorption spectrum were observed even 18 h after the introduction of $K_2Cr_2O_7$. Actually, $Cr_2O_7^{2-}$ is a strong oxidizer in water at pH below 2, and the oxidizing/reducing couple requires the presence of H^+ ions: these chemical conditions are very different from those prevailing in $BumimPF_6$ solutions. As seen from Table 2, the $BumimPF_6$ used in this work contains a non-negligible amount of water, but this water is unlikely to be very acidic as the pH of a water phase in contact with $BumimPF_6$ is around pH = 6. In a second trial, a solution of Eu(II) in $BumimPF_6$ was stirred for 18 h with a large excess of $Ce(SO_4)_2$ (this salt does not dissolve significantly in $BumimPF_6$, but even a low solubility should be sufficient to obtain oxidation, the chemical equilibrium being then moved toward a low but continuous solubilization of $Ce(SO_4)_2$ to obey the mass action law): After stirring, the solution was cloudy, and centrifugation was of no help in this respect. Spectrophotometry could nevertheless be performed, and it was observed that the relative absorbance ratio of the three peaks ascribed to iodine and Eu(II) were not significantly modified as compared to a solution without $Ce(SO_4)_2$. It is therefore concluded that no oxidation of Eu(II) occurred. Finally, O_2 was bubbled through a solution of Eu(II) for 50 min, but again, no changes in the absorption spectrum could be detected. This is in line with the fact that O_2 is poorly soluble in $BumimPF_6$.[38]

Obviously, oxidation of Eu(II) is much more difficult in $BumimPF_6$ than in other solvents.[39] It has been noted previously that methanol should be carefully degassed to prevent oxidation of Eu(II) to Eu(III) and that Eu(II) polymers remain stable for a day or so.[39] In contrast, a Eu(II)/$BumimPF_6$ solution left in a container without special care is stable for months. This leads to the conclusion that solvation effects in $BumimPF_6$ are markedly different from what is known in an aqueous phase, as was discussed in a recent simulation study.[40] It can be hypothesized that water

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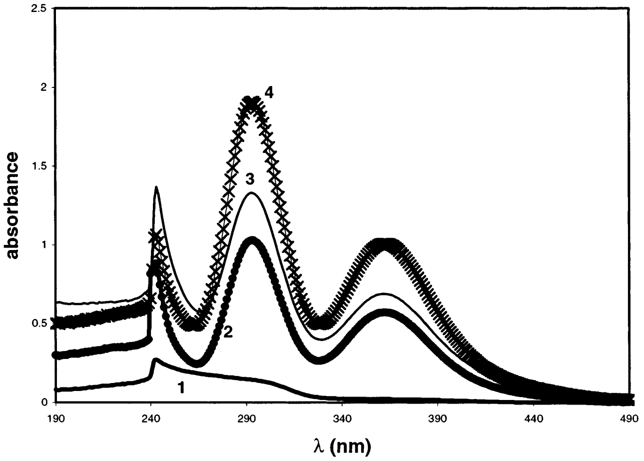

Figure 6. Absorption spectra in BumimPF_6: (1) 15C5 alone ($C = 5 \times 10^{-3}$ M); (2) EuI_2 alone ($C = 10^{-4}$ M); (3) EuI_2 ($C = 10^{-4}$ M) and 15C5 ($C = 3 \times 10^{-4}$ M); (4) EuI_2 ($C = 10^{-4}$ M) and 15C5 ($C = 5 \times 10^{-3}$ M).

does not significantly cluster around Eu(II) in BumimPF_6, otherwise Eu(II) would be readily oxidized to Eu(III). This offers interesting potential for the stabilization of uncommon oxidation numbers, either for synthesis or for liquid−liquid extraction, and requires in consequence extensive studies.

5.3. Evidence for Eu(II) Complexation in BumimPF_6. Considering the high stability of Eu(II) in BumimPF_6, it is interesting to examine the possibility of complexation of Eu(II). In a first attempt, the complexing abilities of two crown ethers (namely 15C5 and 12C4) were evaluated. These molecules have been chosen because the complexing ability of 15C5 toward Eu(II) in methanol has been already studied[37] and 12C4 was chosen for the sake of comparison.

Previous works have shown that various crown ethers are highly soluble in ionic liquids,[33] and while no attempt was made to determine the maximum solubilities, a concentration of 5×10^{-3} M of 15C5 (or 4×10^{-3} M of 12C4) dissolves readily in BumimPF_6. Figure 6 displays the absorption spectra of 15C5 and of 15C5 with Eu(II) in BumimPF_6 for a 3-fold and a 50-fold excess of crown ether. As can be seen, the 15C5 affects the Eu(II) absorption bands: although the positions of the two maxima and their relative ratio remain unchanged, a global increase of the molar absorption coefficient is observed. This situation is very different from that prevailing in methanol. Finally, the absorption band of iodide is not affected, neither in shape nor in intensity. In contrast, 12C4, even at concentration as high as 4×10^{-3} M (as compared to Eu(II) at 10^{-4} M), does not modify the Eu(II) spectrum (data not shown).

These results are strong indications that europium is complexed as Eu^{2+} by 15C5 in BumimPF_6 while 12C4 does not significantly complex Eu(II). The equilibrium reaction rate constant of 15C5 toward Eu(II) is not very large, because complexation is not fully achieved for a 15C5 to Eu(II) ratio of 3 (see Figure 6). The present data show that the determination of the value of the equilibrium reaction rate constant and the stoichiometry of the 15C5/Eu(II) system is a priori possible by use of spectrophotometry. Two possible reasons can be evoked to explain the presumably low complexation constant of the 15C5/Eu(II) system: (1) the viscosity of BumimPF_6 does not favor diffusion, and (2) the solvation shell of Eu(II) and of the complex may also play an important role.

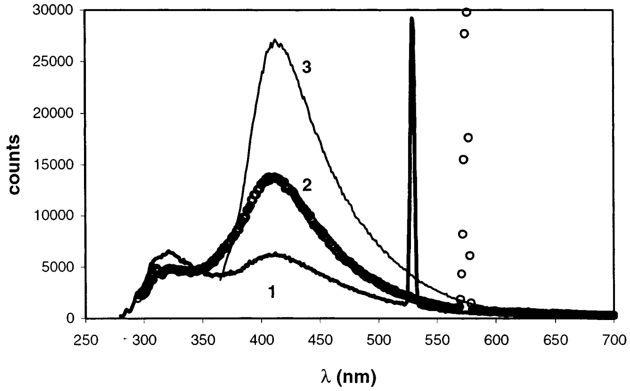

Figure 7. Emission spectra of purified BumimPF_6 at (1) $\lambda_{exc} = 266$ nm; (2) $\lambda_{exc} = 288$ nm; (3) $\lambda_{exc} = 355$ nm. The intense peaks at 532 and 576 nm correspond to the second harmonics of the excitation light.

5.4. First Investigation of the Eu(II) Luminescence Properties. Figure 7 displays the emission spectra of purified BumimPF_6 at excitation wavelengths of 266, 290, and 355 nm. The last two wavelengths correspond to the maxima of the Eu(II) absorption spectrum (see Figure 5), and $\lambda = 266$ nm corresponds to the fourth harmonic of the Nd:YAG laser of the TRES setup. Again, the emission spectrum of purified and raw BumimPF_6 differ significantly (data not shown). In the region where Eu(II) luminesces (typically from 400 to 550 nm),[37] the signal provided by the pure solvent is obviously non-negligible. These conditions are not the most favorable ones for a luminescence study, either by conventional spectrofluorimetry or TRES, but still allow for detection.

As a matter of fact, no luminescence was detected for a solution of EuI_2 in BumimPF_6 ($C = 10^{-4}$ M). Such an absence of luminescence is similar to what is observed for Eu^{2+} in water.[35] Previous studies have shown that complexation with crown ethers or cryptands strongly enhances the Eu^{2+} luminescence in methanol[37] and in water,[35] where Eu^{2+} encapsulated in a cryptand becomes luminescent. These results have been attributed to more or less efficient deactivation mechanisms due to the presence of OH bonds in the first solvation sphere of the excited Eu^{2+} ions: complexation is said to decrease the efficiency of these energy transfers, because the solvent molecules are not as close to Eu^{2+} in the complex as in the case of the free ion, thus allowing luminescence to be detected.[37] The luminescence enhancement of Eu^{3+} upon complexation in various solvents was interpreted along similar lines in refs 41 and 42 and was put in question, however, in ref 43. As is well-known, PF_6 based ionic liquids may contain water,[8] and the BumimPF_6 solutions studied in this work do so (see Table 2). Thus, water molecules might contribute to luminescence

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inhibition. On the other hand, it is not clear whether the solvation sphere of Eu(II) is constituted of H_2O or PF_6^- species.

In order to gain insight into this question, the Eu(II) luminescence in $BumimPF_6$ was examined in the presence of the 15C5 crown ether already studied. This crown ether has been chosen because it appears to be very efficient in promoting Eu^{2+} luminescence in methanol (luminescence increase of a factor of 700).[37] In order to observe Eu(II) luminescence, if any, a compromise has to be found between the amount of complexed Eu(II) and the amount of free 15C5, the luminescence of which is non-negligible. Despite the various experiments performed (different excitation wavelengths and 15C5/Eu(II) ratios) no significant luminescence ascribable to Eu(II) could be observed. No attempts were made with 12C4, as it does not complex Eu(II) (see section 5).

As no luminescence enhancement could be observed following the addition/complexation of 15C5, the aforementioned hypothesis of a deactivation mechanism via OH bonds only can be ruled out in the present case. The absence of luminescence should be therefore ascribed to global deactivation processes due to the solvent itself. In this respect, it has been shown that the CH and NH bonds of ligands have an important quenching effect onto Eu^{3+} luminescence in various solvents.[44] In $BumimPF_6$, it can be hypothesised that the first solvation sphere of Eu(II) is composed solely of PF_6^- anions. The deactivation mechanism thus might occur at rather long distances, possibly via the CH bonds of the Bumim cation, and should be considered as a bulk effect.

6. Conclusion

This work has highlighted the great importance of chloride purification for selected physicochemical properties of $BumimPF_6$. It should be understood that no reproducible and well-assessed results can be obtained with ionic liquids that are not perfectly characterized and, if possible, purified. In this respect, the purification procedure used in this work is very efficient. $BumimPF_6$ is an unusual liquid, as it presents a local order at short distances and as it stabilizes Eu(II), which has been characterized by absorption spectroscopy. Some insight into the solvation sphere of Eu(II) in $BumimPF_6$ could be obtained. The preliminary results on complexation offer promising perspective for the chemistry of Eu(II). Moreover, these results are also interesting in the field of nuclear waste reprocessing, considering that actual aqueous processes are mainly based on the oxidation states of the species involved. Ionic liquids, allowing the stabilization of unusual oxidation states, may lead to a fresh look on these processes.

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