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Etienne Jean, Didier Villemin, Laurent Lebrun. New ionic liquids with fluoruous anions for supported liquid membranes and characterization. *Journal of Fluorine Chemistry*, 2019, 227, pp.109365. 10.1016/j.jfluchem.2019.109365 . hal-02369622

**HAL Id: hal-02369622**

**<https://normandie-univ.hal.science/hal-02369622>**

Submitted on 21 Dec 2021

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## **New ionic liquids with fluorous anions for supported liquid membranes and characterization.**

Etienne Jean<sup>a,b</sup>, Didier Villemin<sup>a\*</sup>, Laurent Lebrun<sup>b</sup>

*a LCMT, UMR 6507 CNRS, ENSICAEN, Normandie Université*

*b PBS, UMR 6270, UR, Normandie Université*

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**Keywords:** Fluorous ionic liquids, Phosphate, Supported liquid membranes

### **Abstract:**

This article reports the synthesis and the characterization of novel fluorous ionic liquids with fluorous anions to be used as carrier for fluorous supported liquid membrane in view of future applications to the extraction of metal ions. Dialkylimidazolium perfluorodialkylphosphate with C8, C10 and C12 phosphate chains have been synthesized as ionic liquid. The different dialkylimidazolium cations were prepared by microwave technique. Finally, 1-butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorodecylphosphate) was found as the most appropriated ionic liquid for the considering application and was characterized with volumetric mass density, viscosity and thermal stability measures.

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\* Corresponding author. Tel: 33 2 31 45 28 40. Fax: 33 2 31 45 28 77.

E-mail address: [didier.villemin@ensicaen.fr](mailto:didier.villemin@ensicaen.fr) (D. Villemin).

## 1. Introduction

Ionic liquids were recently used to separate metal cations by various methods [1]. We are interested in the application of the ionic liquids as cations carriers with fluorinated supported liquid membranes. In fact, one of the major drawbacks of supported liquid membranes is the leakage of the carrier in aqueous media [2]. We sought to solve this problem by using ionic liquid with fluorinated anions. P. Bühlmann has used ion-exchanger perfluorinated membranes impregnated with phosphonium perfluorinated cations in ion-selective electrodes [3].

The support membrane used for the facilitated transport of metal cations in water is poly(vinylidene fluoride). The PVDF membrane being a hydrophobic fluorinated polymer, we sought to use the concept of fluorophilic and hydrophobic properties of the fluorinated compounds in order to improve the retention of ionic fluorinated liquids on membranes. In fact fluorinated compounds have a strong affinity for fluorophilic and hydrophobic fluorinated polymers in the presence of water. These properties were already used by Horvath *et al.* [4,5,8] and Curran *et al.* [6,7,8] in catalysis in the presence of water.

We have chosen to use imidazolium perfluorodialkylphosphate. The nature of exchangeable cation is not very important, ionic liquid based on imidazolium cation are the most common. The nature of anion is fundamental in the transport of metallic cations [9-12](coordination, transport, de-coordination), so we have chosen dialkylphosphate anion as conveying anion because they are well-known in hydrometallurgy, for example dibutylphosphate (DBP), dioctylphosphate (DOP) or di(2-ethylhexyl)phosphate (DEHPA) [13-15].

For the synthesis of the dialkylimidazolium di(perfluoroalkyl)phosphates (Figure 1), we carried out a synthesis via an ion exchange [16]. The two components of the ionic liquid: imidazoliums and new perfluorinated dialkylphosphates, have to be synthesized separately.

## 2. Results and discussion

### 2.1. Synthesis of dialkylimidazolium cations

At the beginning of this study, the dialkylimidazolium cations were synthesized by imidazole alkylation by classical thermal activation (Figure 2). The reaction performed in toluene under reflux ( $T = 110\text{ }^{\circ}\text{C}$ ) is effective, with yields varying from 69 to 76 % after 12 h.

We have also performed the alkylation under microwave conditions.

The results of dialkylimidazolium synthesis were summarised in Table 1 under microwave irradiation or thermal conditions. The microwave synthesis without solvent allowed increased yields in comparison to the classical thermal process and allowed to obtain a colourless ionic liquid in shorter times [17,18]. Moreover, no supplementary separation steps were necessary.

R	R'X	Yield (%)		Microwave conditions
		Thermal activation	Microwave	
CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub> Br	73	95	90 °C, 8 min
CH <sub>3</sub>	C <sub>6</sub> H <sub>13</sub> Br	71	94	100 °C, 8 min
CH <sub>3</sub>	C <sub>8</sub> H <sub>17</sub> Br	69	91	110 °C, 8 min
CH <sub>3</sub>	C <sub>10</sub> H <sub>21</sub> Br	70	95	130 °C, 10 min
C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub> Br	76	97	90 °C, 8 min
C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>13</sub> Br	74	96	100 °C, 8 min
C <sub>4</sub> H <sub>9</sub>	C <sub>8</sub> H <sub>17</sub> Br	73	96	110 °C, 8 min
C <sub>4</sub> H <sub>9</sub>	C <sub>10</sub> H <sub>21</sub> Br	72	95	130 °C, 10 min

**Table 1:** Solvent-free N-alkylation of 1-methylimidazole and 1-butylimidazole by n-bromoalkanes under thermal conditions and mono-mode microwave irradiation.

## 2.2 Synthesis of perfluorodialkylphosphate anions

A nonfluorinated spacer was used in order to preserve the reactivity of the alcohol group. A spacer arm of only one carbon could especially result in elimination reactions under basic conditions so a fluorinated alcohols with a two carbons spacer arm were chosen. These compounds obtained by oligomerisation of ethylene/tetrafluoroethylene are commercially available. In order to exploit the synthesized ionic liquid as carrier in membrane, it was necessary that ionic liquid was insoluble in water and soluble in organic solvent for the membrane impregnation. So, the choice of the chain length needs to find the true balance between hydrophobic and solvent solubility properties. Consequently, we have prepared and test perfluorinated phosphates with C<sub>8</sub>, C<sub>10</sub> and C<sub>12</sub> chain. However, only C<sub>10</sub> was found appropriated for the study and only the C<sub>10</sub> compound was described herein.

Perfluorinated dialkylphosphates were generally prepared from phosphoryl trichloride as surfactants [19,20] according Figure 3.

The process previously described in literature used organic or inorganic base and conducted to salt impurities. This way of synthesis was discarded because no efficient method was found to eliminate the salt impurities in the ionic liquid. For the synthesis of perfluorodialkylphosphate without salt we have first prepared a perfluorodialkylphosphite using the McCombie process [21] and in a second step, the oxidation of perfluorodialkylphosphite into perfluorodialkylphosphate (Figure 4).

### 2.3 Synthesis of ionic liquids

The synthesis of the ionic liquid was carried out without isolation of perfluorodialkylphosphate (see experimental part). The overall yields of the reactions are displayed in Table 2.

R	R'	Overall yield (%)
CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	10
C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	40
C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>13</sub>	47
C <sub>4</sub> H <sub>9</sub>	C <sub>8</sub> H <sub>17</sub>	54
C <sub>4</sub> H <sub>9</sub>	C <sub>10</sub> H <sub>21</sub>	70
CH <sub>3</sub>	C <sub>6</sub> H <sub>13</sub>	19
CH <sub>3</sub>	C <sub>8</sub> H <sub>17</sub>	21
CH <sub>3</sub>	C <sub>10</sub> H <sub>21</sub>	21

**Table 2.** Overall yields in ionic liquids with the di(1H,1H,2H,2H-perfluorodecyl)phosphate anion

The structures were confirmed by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR (see experimental part). For the further transport studies with membrane impregnated with ionic liquid we have selected 1-butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorodecylphosphate) due to the higher yield of synthesis.

### 2.4 Characterization of 1-butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorodecylphosphate)

With the aim of using this ionic liquid as carrier in a supported liquid membrane, the measure of its solubility in organic solvents became necessary. The ionic liquid must be soluble in an organic solvent and insoluble in water to prevent its leakage during the metal ions extraction experiments.

The volumetric mass density of the ionic liquid at room temperature was  $1.143 \pm 0.001 \text{ g.cm}^{-3}$ . The density value is higher than those of most common ionic liquids due to the perfluoroalkyl chains of the anion. The density of the most common ionic liquids is typically greater than water but usually decreases with the ions size [22].

First, we have performed an empirical qualitative study of solubility with common solvents: The same amount of ionic liquid and solvent ( $1\text{cm}^3/1\text{cm}^3$ ) were placed in a vial, stirred for 2 min at room temperature. The results are reported Table 3. The ionic liquid is not water soluble which is suitable for the use as carrier. However, it is soluble in ethanol, acetone and isopropanol that are water miscible and in chloroform that is partially miscible with water. None of these solvents can be used for membrane impregnation.

Solvent	Soluble	Insoluble
Diethyl ether		x
Pentane		x
Cyclohexane		x
Dodecane		x
Pentadecane		x
Dichloromethane		x
Ethanol	x	
Acetone	x	
Isopropanol	x	
Chloroform	x	
Water		x
Acetonitrile		x
Ethyl acetate		

**Table 3.** Empirical solubility study of 1-butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorodecylphosphate) determined by  $^{19}\text{F}$  NMR.

In order to predict the solubility of the ionic liquid in other non polar solvents, the Small hypothesis [23-25] was considered. It links the solubility parameter  $\delta$  (H) with the sum of molar attraction constants of each group in the molecule  $\Sigma G$  ( $\text{cal}^{1/2} \text{ mol}^{-1} \text{ cm}^{3/2}$ ), the volumetric mass density  $\rho$  and the molar mass  $M$  ( $\text{g.mol}^{-1}$ ) (Eq. 1).

$$\delta = \frac{\rho \times \sum G}{M} \quad \text{Eq. 1}$$

The ionic liquid solubility parameter was 7.7 H for  $[\text{C}_{10}\text{BIm}^+ \text{PFC}_{10}^-]$  (with  $G(\text{CF}_2)=150$ ,  $G(\text{CF}_3) =274$ ,  $G(\text{PO}_4)=500$ ,  $G(\text{CH}_2)=133$ ,  $G(\text{CH}_3)=214$ ,  $G(\text{CH}=\text{CH})=111$ , et  $G(\text{C}=\text{N})=410 \text{ cal}^{1/2} \text{ mol}^{-1} \text{ cm}^{3/2}$  et  $\rho = 1.143 \text{ g cm}^{-3}$ . Small [20] considers that a (macro) molecule is soluble in a solvent if their  $\delta$  are equal  $\pm 0.5$ . Thus, we could predict that the ionic liquid would be soluble in higher alkanes

such as dodecane ( $\delta = 7.65$  H) or pentadecane ( $\delta = 7.8$  H). This latter was chosen for its high boiling point. The ionic liquid exhibited total solubility in this solvent at concentration as high as 0.1M. It is generally considered that the solubility of ionic liquids in aqueous phase is highly controlled by the anion nature [26]. For example, butylmethyl imidazolium tetrafluoroborate is very soluble in water while butylmethyl imidazolium hexafluorophosphate is low soluble. However, the solubility of ionic liquid depends also with the nature of the cation. In fact, both ions influence the solubility because the size of the ions and the surface charge control the interactions with water and consequently the lipophilic character [27].

The values of ionic liquids viscosities are interesting to know for investigations of intermolecular interactions and calculation of fluid dynamics. The viscosity of the fluorod ionic liquid was 0.26 Pa.s (260 cP). This value is large compared to those of the most common liquid ionic due to the hindered 1-butyl-3-decylimidazolium cation and di(1H,1H,2H,2H-perfluorodecylphosphate) anion. Yu *et al.* have showed that the more the cation is large and asymmetric, more the ionic liquid is viscous [28]. On the other side, Pool *et al.* have highlighted the strong influence of the anion on viscosity of ionic liquids. Thus, low viscosity values ( $< 30$  cP) are related to small anions with a limited capability for hydrogen bonding [29].

The thermal stability of the liquid ionic was observed until 230°C, which is high due to the fluorous chains. A quick loss of mass was observed between 50 and 200 °C (about 30 %) with an inflexion point at 100 °C which corresponds to the vaporization of linked water molecules. After 230 °C, the loss of mass increased until total degradation at 400 °C. The studies on thermal decomposition of imidazoliums performed by Maton *et al* [30] and on fluorinated anions by Hanneman *et al.* [31] were used to predict the fragments formed during the degradation. However, TGA-MS technique used detects only fragments with m/z values lower than 200. The first ions due to the thermal degradation appeared from 200 °C. Their formation is explained by homolytic breaks of bonds which occur preferentially in  $\alpha$  position of heteroatoms or by rearrangement reactions according to the proposed mechanisms in Figure 5. The first fragmentation corresponds to the loss of the decyl chain of imidazolium ( $m/z = 140$ ). Around 320 °C, concomitant formation of imidazolium fragments ( $m / z = 68$ ) and unexpected imidazolium hydrofluoride ( $m/z = 88$ ) were observed. Perfluorobut-1-ene fragment ( $m/z$ ) = 200 was also detected. On the other hand, no formation of tetrafluoroethylene fragments was observed

( $m/z = 100$ ). The fragment corresponding to the butyl chain ( $m/z = 56$ ) was not found since its departure was required for the detection of the imidazolium group. As the degradation reactions only start at 200 °C, we can conclude that the fluorinated ionic liquid is suitable as carrier for supported liquid membranes.

### 3. Experimental

#### 3.1 Materials

The imidazolium bromides were synthesized using an Anton-Paar monowave 300 microwave reactor monitored by a computer.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker Advance 400 spectrometer at 400 MHz, 100 MHz, 167 MHz and 367 MHz, respectively. Chemical shifts ( $\delta$ ) are expressed in parts per million (ppm) and are referenced to the internal deuterated solvents with tetramethylsilane as the internal standard. Data are reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet). Coupling constants are expressed in Hertz (Hz).

The volumetric mass of the ionic liquid ( $\text{g cm}^{-3}$ ) was determined at 25 °C using a 5  $\text{cm}^3$  Blaubrand glass pycnometer (Brand). The measurements were repeated three times and averaged.

The viscosity of pure liquid ionic was measured using a Discovery Hybrid Rheometer (HR2 from TA Instrument) using a plan-cone geometry and a standard-size double concentric cylinder geometry. Flow experiments were performed between 0.01 and 1000  $\text{s}^{-1}$  at 25 °C. The oscillation procedures were carried out from 0.1 to 10 Hz for the frequency sweep. The linearity domain was checked using a stress sweep procedure at 1 Hz between 0.01 and 100 Pa at 25 °C.

The thermal stability of the ionic liquid was studied by thermal gravimetric analysis using a TA Instruments Q500 TGA. The measurements were performed on 8 mg mass sample at 10 °C  $\text{min}^{-1}$  from 25 to 580 °C, under nitrogen atmosphere (90  $\text{mL} \cdot \text{min}^{-1}$ ). Q500 TGA was coupled to a Pfeiffer Vacuum GSD 320 mass spectrometer in order to study the degradation products (detection range  $0 < m/z < 200$ ). Two detection modes were used, by multi-ions detection to detect the formed ions of known mass and by scanning detection to scan the  $m/z$  range to detect the unpredicted ions.



### 3.2 Chemicals

All reagents were used as received without further purification unless otherwise specified. N-butylimidazole, N-methylimidazole, 1H,1H,2H,2H-perfluorooctanol, 1H,1H,2H,2H-perfluorodecanol, 1H,1H,2H,2H-perfluorododecanol were purchased from Alfa Aesar, 1-bromobutane, 1-bromohexane, 1-bromooctane, 1-bromodecane were purchased from Sigma Aldrich. Phosphorus trichloride was purchased from Acros: its purity was controlled by  $^{31}\text{P}$  NMR and when needed it was purified by distillation ( $b_p = 76.1\text{ }^\circ\text{C}$ ). Hydrogen peroxide (30% w/v) was purchased from VWR.

### 3.3 Experimental procedures

#### 3.3.1 Synthesis of imidazolium bromides under thermal conditions

A mixture of 20 mmol of 1-alkylbromide and 20 mmol of 1-alkylimidazole in 30 mL of toluene was refluxed for 12 h under nitrogen. The obtained ionic liquids were washed with diethyl ether (3 x 20 mL). No further purification was needed. The ionic liquids were obtained as brown viscous oils (yield: 69 to 76 %).

#### 3.3.2 Synthesis of imidazolium bromides under microwave irradiations

A mixture of 20 mmol of 1-alkylimidazole and 20 mmol of alkylbromide were irradiated by microwave (2450 MHz) in a closed 30 mL glass reactor. The reaction mixture was stirred and heated at the chosen temperature for 8 or 10 min (Table 1). The crude was washed with diethyl ether (3 x 25 mL). No further purification was needed (yield: 91 to 97 %).

##### *1-Methyl-3-butylimidazolium bromide*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  10.27 (s, 1H); 7.60 (s, 1H), 7.47 (s, 1H), 4.28 (t,  $J=7.2$  Hz, 2H), 4.07 (s, 3H), 1.85 (quintet,  $J=7.6$  Hz), 1.32 (sextet,  $J=7.6$  Hz, 2H), 0.89 (t,  $J=7.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  137.0, 123.8, 122.3, 49.7, 36.65, 32.1, 19.4, 13.4.

##### *1-Methyl-3-hexylimidazolium bromide*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ): 10.00 (s, 1H), 7.53 (s, 1H), 7.37 (s, 1H), 4.07 (t,  $J=7.2$  Hz, 2H), 3.87 (s, 3H), 1.64 (m, 2H), 1.02 (m, 6H), 0.58 (t,  $J=7.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  136.7; 123.7; 122.1; 49.8; 36.48; 30.88; 30.0 ; 25.6; 22.10; 13.7 .

##### *1-Methyl-3-octylimidazolium bromide*

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  10.06 (s, 1H), 7.59 (s, 1H), 7.40 (s, 1H), 4.17 (t,  $J=7.2$  Hz, 2H), 3.99 (s, 3H), 1.76-1.77 (m, 2H), 1.09-1.17 (m, 10H), 0.70 (t,  $J=7.5$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  136.0, 123.1, 121.4, 49.2, 35.9, 30.7, 29.4, 28.1, 28.0, 25.3, 21.6, 13.2.

##### *1-Methyl-3-decylimidazolium bromide*

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 10.07 (s, 1H), 7.73 (s, 1H), 7.55 (s, 1H), 4.33 (t, *J*=7.2 Hz, 2H), 4.13 (s, 3H), 1.91 (m, 2H), 1.20-1.40 (m, 14H), 0.87 (t, *J*=7.6 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 136.4, 123.5, 121.8, 49.6, 36.3, 31.3, 29.8, 28.9, 28.9, 28.7, 28.5, 25.8, 22.1, 13.6.

*1,3-Dibutylimidazolium bromide*

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.86 (s, 1H), 7.86 (s, 1H), 7.51 (s, 1H), 4.94 (t, *J*=7.2 Hz, 4H), 2.01 (m, 4H), 1.29 (m, 4H), 0.90 (t, *J*=7.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 138.20, 124.6, 122.8, 51.5, 32.2, 20.5, 13.0.

*1-Butyl-3-hexylimidazolium bromide*

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ ppm = 10.09 (s, 1H); 7.75 (s, 1H); 7.57 (s, 1H); 4.21 (t, *J*=7.2 Hz, 2H); 4.19 (t, *J*=7.2 Hz, 2H); 4.13 (t, 2H, *J* = 7.0 Hz); 1.91-1.78 (m, 4H); 1.20-1.40 (m, 8H); 0.87 (t, 3H, *J* = 7.0 Hz); 0.78 (t, 3H, *J*=7.0 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): (δ ppm): 136.7; 123.7; 122.1; 49.8; 36.4; 30.80; 30.0; 25.6; 22.1; 13.

*1-Butyl-3-octylimidazolium bromide*

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.51 (s, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 4.21 (t, *J*=7.2 Hz, 2H), 4.19 (t, *J*=7.2 Hz, 2H), 1.83-1.75 (m, 4H), 1.35-1.18 (m, 10H), 0.88 (t, 3H), 0.80 (t, *J*=7.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 136.0, 123, 121.4, 49.2, 35.9, 30.7, 29.4, 28.1, 28.0, 25.3, 21.6, 13.2.

*1-Butyl-3-decylimidazolium bromide*

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 8.54 (s, 1H), 7.32 (s, 1H), 7.28 (s, 1H), 4.22 (t, *J*=7.2 Hz, 2H), 4.19 (t, *J*=7.2 Hz, 2H), 1.84-1.69 (m, 4H), 1.36-1.18 (m, 12H), 0.87 (t, 3H), 0.79 (t, *J*=7.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 136.4, 123.5, 121.8, 49.6, 36.3, 31.3, 29.8, 28.9, 28.9, 28.7, 28.5, 25.8, 22.1, 13.6.

### 3.3.3 Synthesis of 1,3 dialkylimidazolium di(perfluoroalkyl)phosphates

To a 1000 mL RB flask fitted with a magnetic stir bar, 10 mmol of the appropriate fluorinated alcohol were placed and heated above their melting point under Argon atmosphere. 3 mmol (0.41 g; 0.25 mL) of phosphorus trichloride were added dropwise over a period of 15 min. The mixture was heated at 90°C for 6 h. 9 mmol of cold (-18°C) H<sub>2</sub>O<sub>2</sub> (2.75 mL) were added followed by ultrapure water (30 mL). The pH was adjusted to pH 9 using KOH pellets. 3.3 equivalents of the 1,3-dialkylimidazolium bromide was then introduced in the reaction media. The mixture was stirred over night at 0 °C and then stirred for 8 h at room temperature. The organic phase was washed with ultrapure water (5 x 20 mL) and distilled using with Kugelrohr apparatus (120 °C / 10 mmHg). The undistilled product was obtained as incolor to light yellow viscous oils (yield: 10 to 70 %).

*1-Butyl-3-methylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.41 (s, 1H), 7.28 (s, 2H), 4.29 (t, *J* = 7.3 Hz, 2H),

4.06 (s, 3H), 3.99 (t,  $J = 6.1$  Hz, 4H), 3.90 (tt,  $J = 13.4, 6.1$  Hz, 4H), 1.87 (m, 2H), 1.39 (sextet, 7.5 Hz, 2H), 0.90 (t,  $J = 7.4$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -81.40 (t, 6F,  $J = 10.1$  Hz), -113.95 (t, 4F,  $J = 13.4$  Hz), -122.38 (s, 12F), -123.22 (s, 4F), -124.06 (s, 4F), -126.68 (d, 4F,  $J = 6.2$  Hz);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  -0.49.

*1-Hexyl-3-methylimidazolium di(1H,1H,2H,2H-perfluorodecyl)phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.41 (s, 1H), 7.28 (s, 2H), 4.29 (t,  $J = 7.3$  Hz, 2H), 4.06 (s, 3H), 3.99 (t,  $J = 6.4$  Hz, 2H), 3.90 (tt,  $J = 13.4; 6.1$  Hz, 4H), 2.40 (tt,  $J = 18.5, 6.1$  Hz, 4H), 1.31 – 1.19 (m, 6H), 0.96 (t,  $J = 7.4$  Hz, 2H), 0.90 (t,  $J = 7.4$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -81.73 (t, 6F,  $J = 10.1$  Hz), -113.44 (t, 4F,  $J = 13.7$  Hz), -121.69 (s, 12F), -122.71 (s, 4F), -123.68 (s, 4F), -126.09 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.50.

*1-Methyl-3-octylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

NMR  $^1\text{H}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  10.03 (s, 1H); 7.59 (s, 1H), 7.51 (s, 1H), 4.17 (t,  $J=6.8$  Hz, 2H), 3.99 (s, 3H), 3.84 (dt,  $J = 17.2, 6.3$  Hz, 4H), 2.40 (tt,  $J = 18.0, 6.3$  Hz, 4H) 1.76-1.77 (m, 2H); 1.09-1.17 (m, 10H); 0.70 (t,  $J=6.4$ Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.84 (t, 6F,  $J=10.2$  Hz), -112.50 (s, 12F), -113.56 ((t, 4F,  $J = 13.7$  Hz), 121.71 (s, 4F), -122.73 (s, 4F), -123.70 (s, 4F), -126.08 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.49.

*1-Decyl-3-methylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.12 (s, 1H); 7.67 (s, 1H); 7.28 (s, 1H) 4.25 (t,  $J=7.6$  Hz, 2H); 4.12 (s, 3H) 3.78 (t,  $J = 7.6$  Hz, 4H); 2.33 (tt,  $J=17.1; 7.6$  Hz, 4H) 1.73 (quintet, 6.8 Hz, 2H); 1.38 – 1.19 (m, 14H); 0.91 (t,  $J = 7.4$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.84 (t, 6F,  $J=11$  Hz), -112.45 (s, 4F), -113.53 (d, 12F), -121.77 (s, 4F), -122.78 (s, 4F), -123.75 (s, 4F), -126.15 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.50.

*1,3-Dibutylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.18 (s, 1H), 7.79 (s, 1H), 7.51 (s, 1H), 4.94 (t,  $J= 7.3$  Hz, 4H), 3.99 (t,  $J = 6.1$  Hz, 4H), 3.90 (tt,  $J = 13.0, 6.1$  Hz, 4H), 2.09 (m, 4H), 1.30 (m, 4H), 0.90 (t,  $J = 7.4$  Hz, 6H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.73 (t, 6F,  $J= 11$  Hz), -113.44 (m, 12F), -121.69 (s, 4F), -122.71 (s, 4F), -123.68 (s, 4F), -126.09 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.49.

*1-Butyl-3-hexylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.22 (s, 1H), 7.28 (s, 1H), 7.25 (s, 1H), 4.17 (m, 4H), 3.70 (t,  $J=6.9$  Hz, 4H), 2.28 (tt,  $J = 17.4$  Hz, 6.9 Hz, 4H), 1.78 – 1.54 (m, 4H), 1.39 – 0.89 (m, 8H), 0.93 (t,  $J = 7.4$  Hz, 3H), 0.77 (t,  $J = 6.7$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.83, -81.01 (m, 6F), -113.56 (s, 4F), -121.87 (s, 12F), -122.86 (s, 4F), -123.77 (s, 4F), -126.21(s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.51.

*1-Butyl-3-octylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.09 (s, 1H), 7.29 (s, 1H), 7.27 (s, 1H), 7.24 (s, 1H), 4.21 (m, 4H), 3.83 (t,  $J = 7.0$  Hz, 4H), 2.35 (tt,  $J = 18.8$  Hz, 7.0 Hz, 4H), 1.92 – 1.73 (m, 4H), 1.39 – 0.89 (m, 12H), 0.92 (t,  $J = 7.4$  Hz, 3H), 0.81 (t,  $J = 6.7$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.83, -81.01 (m, 6F), -113.84 (s, 4F), -122.04 (s, 12F), -123.05 (s, 4F), -123.93 (s, 4F), -126.30 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.48

*1-Butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorooctyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.59 (s, 1H); 7.14 (d,  $J = 1.0$  Hz, 2H); 4.16 (dt, 4H,

$J = 15.4, 7.1$  Hz); 3.70 (t,  $J = 7.1$  Hz, 3H), 2.62 – 2.26 (m, 4H), 1.86 (dq,  $J = 12.7, 7.6$  Hz, 4H), 1.45 – 1.10 (m, 16H), 0.95 (t,  $J = 7.4$  Hz, 3H), 0.85 (t,  $J = 6.8$  Hz, 3H),  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.87 (t, 6F,  $J = 10.2$  Hz), -113.59 (td, 4F,  $J = 14.5, 4.2$  Hz), -113.68 – -113.77 (m, 4F), -123.77, -123.85 (m, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.42.

*1-Butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorodecyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.98 (s, 1H), 7.27 (s, 1H), 7.25 (s, 1H); 4.25 (dt, 2H,  $J = 7.5, 7.5$  Hz), 3.86 (t, 4H,  $J = 6.8$  Hz), 2.33 (tt, 4H,  $J = 19.2, 6.8$  Hz), 1.91 – 1.75 (m, 4H), 1.38–1.13 (m, 16H), 0.91 (t, 3H,  $J = 7.2$  Hz), 0.82 (t, 3H,  $J = 7.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -81.43 (t, 6F,  $J=11.3$  Hz), -113.93 (s, 4F), -122.15 (s, 12F), -123.21 (s, 4F), -123.78 (s, 4F), -126.66 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.49.

*1-Butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorododecyl) phosphate*

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.24 (s, 1H), 7.24 (d,  $J = 1.75$  Hz, 2H), 4.11 (dt,  $J = 15.9, 7.9$  Hz, 4H), 3.70 (t,  $J=7.1$  Hz, 4H), 2.28 (tt,  $J = 18.0, 7.1$  Hz, 4H), 1.85 – 1.60 (m, 4H), 1.39 – 0.89 (m, 18H), 0.73 (t,  $J = 7.4$  Hz, 3H), 0.63 (t,  $J = 6.7$  Hz, 3H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -80.87 (t, 6F  $J = 9.8$  Hz), -113.58 (s, 4F), -121.85 (s, 20F), -122.83 (s, 4F), -123.80 (s, 4F), -126.24 (s, 4F);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.54.

## Conclusion

The aim of this work was to find appropriate ionic liquids as carrier for fluoruous supported liquid membrane in view of future application to the extraction of metal ions. For this application, it was necessary to have solubility in organic solvent for the membrane impregnation and hydrophobic properties to avoid the carrier leakage. To obtain this balance, ionic liquids with various chain lengths were synthesized: fluoruous phosphates with C8, C10 and C12 chains and imidazolium with various chain lengths. The 1-butyl-3-decylimidazolium di(1H,1H,2H,2H-perfluorodecylphosphate) was found as the most appropriated ionic liquid for the considering application and was characterized. The metal ions extraction experiments with these selected ionic liquids will be reported in the near future.

## Acknowledgements

The authors gratefully acknowledge the interregional program Centre Régional Universitaire Normand de Chimie (CRUNCh) for its financial support. The authors thank the Conseil Régional de Haute Normandie, France, for the PhD Grant awarded to Etienne Jean. The authors thanks Dr Nathalie Bar for the helpfull discussions.

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## Captions of the figures:

**Figure 1:** General formula of target ionic liquids.

**Figure 2:** Synthesis of dialkylimidazolium bromide.

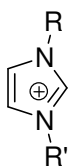
**Figure 3:** Perfluorinated dialkylphosphate synthetic pathway as proposed by Keiper *et al.* [4].

**Figure 4:** Synthesis of methylalkylimidazolium perfluorodialkylphosphate.

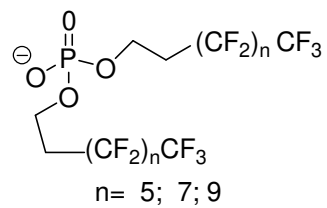
**Figure 5:** Fragmentation mechanisms of ionic liquid ions.



**Fig. 1** : *Jean et al.*

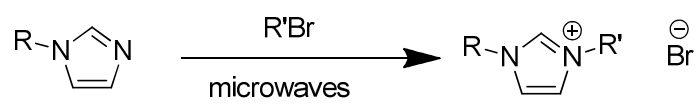


R: CH<sub>3</sub> ; C<sub>4</sub>H<sub>9</sub>  
R': C<sub>4</sub>H<sub>9</sub> ; C<sub>6</sub>H<sub>11</sub> ; C<sub>8</sub>H<sub>17</sub> ; C<sub>10</sub>H<sub>21</sub>



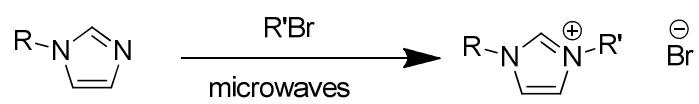
**Figure 2** : *Jean et al.*

E  
M  
B  
E  
D

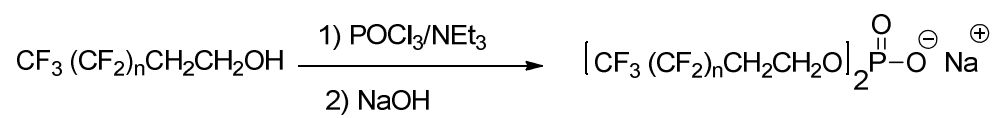


**Figure 2** : *Jean et al.*

E  
M  
B  
E  
D



**Figure 3** : *Jean et al.*



**Figure 4** : *Jean et al.*

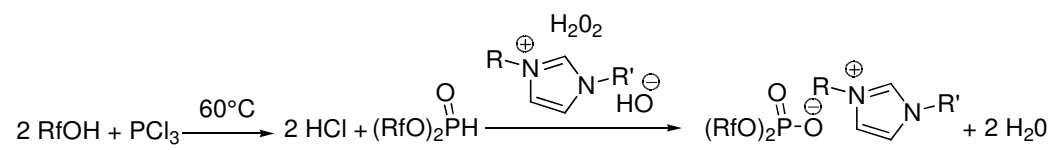
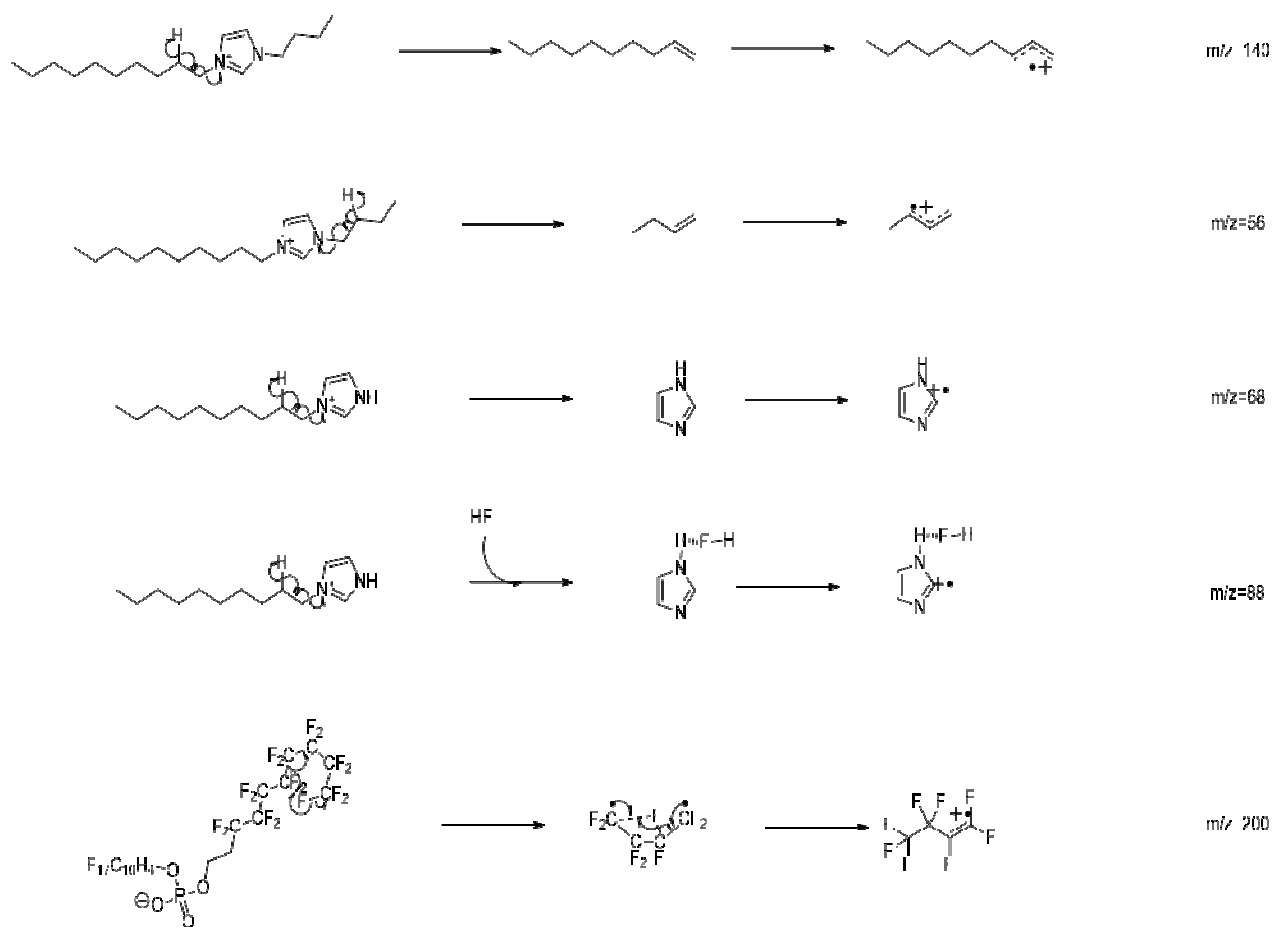
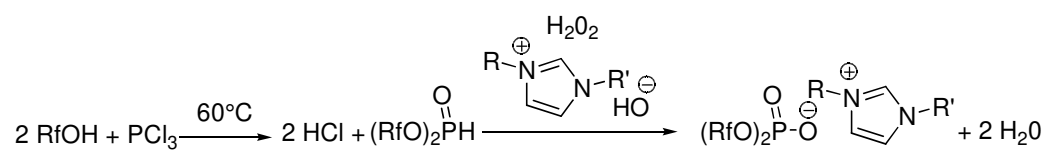


Figure 5 : Jean et al.



**Graphical abstract:**



Rf = CF<sub>3</sub>(CF<sub>2</sub>)<sub>7</sub>CH<sub>2</sub>CH<sub>2</sub>    R = C<sub>4</sub>H<sub>9</sub>    R' = C<sub>10</sub>H<sub>21</sub>  
was the most appropriate for membrane impregnation