Fluorinated Ionic Liquids: Properties and Applications

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Ⓢ *Supporting Information*

ABSTRACT: Ionic liquids have become a green media for engineering applications due to exceptional physicochemical properties, such as their practically nonvolatile nature, null flammability, low melting point, high ionic conductivity, and thermal and electrochemical stability. This work aimed to select the best fluorinated ionic liquids for the following applications: recovery/recycling of perfluorocarbon contaminants such as greenhouse perfluorocarbons gases and perfluoroalkyl acids of industrial effluents that are persistent, bioaccumulative, and toxic, and the partial or total replacement of inert perfluorocarbons in oxygen therapeutic emulsions by enhancing the emulsion stability and increasing the solubility of respiratory gas. With this dual goal in mind, thermodynamic and thermophysical properties of fluorinated ionic liquids (FILs) and their toxicity and biocompatibility are discussed so that the feasibility of the proposed applications can be evaluated. Herein, FILs are defined as ionic liquids with fluorinated chain lengths equal or greater than four carbon atoms. This paper provides a critical review of the experimental data for fluorinated ionic liquids available in the literature, and subsequently, with the aim of expanding knowledge of FILs, eight new fluorinated ionic liquids were selected for characterization. The attained results will clearly impact applications using polyfluorinated compounds.

KEYWORDS: *Fluorinated ionic liquids, Physical and thermal properties, Cytotoxicity, PFCs, Environmental protection, Greenhouse gases*
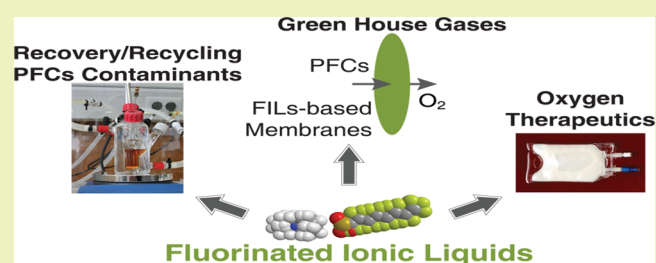
INTRODUCTION

Perfluorinated compounds (PFCs) display many exceptional physicochemical properties, and their industrial production has increased drastically in recent decades as a result of prevalent applications, such as surfactants, polymers, oxygen therapeutics, fire retardants, lubricants, and insecticides.[1,2] This class of compounds can be organized according to their properties. On the one hand, there are inert benign compounds, such as perfluorocarbons, that can be used in biomedical applications such as artificial blood substitutes.[3] On the other hand, environmental contaminants, such as greenhouse PFCs gases and perfluoroalkyl acids, have been found to be persistent and bioaccumulative in food chains and toxic to various species.[4,5]

The solvation in fully or partially fluorinated media is of particular interest in areas where PFCs find relevant applications, such as separation methods and fluorous phase organic synthesis, surfactants in supercritical solvents, substitutes for chlorinated solvents, environmental probes as dielectric solvents, and in uranium enrichment.[3] In biomedical applications, PFCs are used as in vivo gas carriers in liquid ventilation or artificial blood substitute formulations. The gasphylic behavior of fluorinated compounds in general is well known.[6,7]

Another class of compounds where the fluorination effect has been explored is that of ionic liquids (ILs). Although the number of publications on ILs has witnessed exponential growth, their chemical diversity has not been exhaustively explored. Anions such as bis(trifluoromethylsulfonyl)imide, hexafluorophosphate, or tetrafluoroborate anions have been frequently characterized and used for several purposes, but few works have dealt with the fluorinated ionic liquid (FILs) family, where fluorine chains of variable length are used in the cation or in the anion. The first article where FILs were described[8] illustrates the peculiar properties that these compounds can display.

It has been shown that for longer alkyl chain lengths ionic liquids exhibit structures in the liquid phase with the formation of apolar and polar nanodomains corresponding to the apolar part and charged polar part of the ionic liquid.[9] The formation of distinguishable hydrophobic and hydrophilic solvation fields has already been observed in the binary mixtures of small chain (up to three carbons) fluorinated alcohols and water and is due

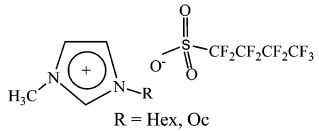**Table 1. Structure, Family, and Abbreviation of Fluorinated Ionic Liquids**
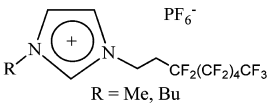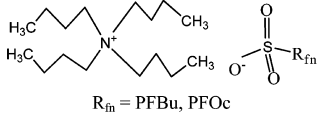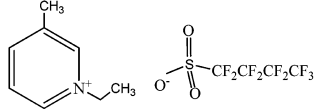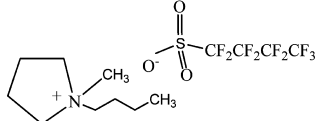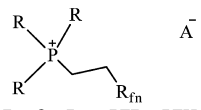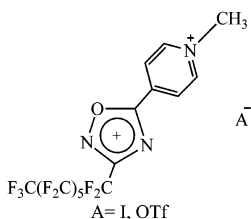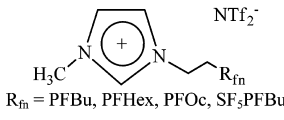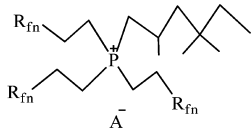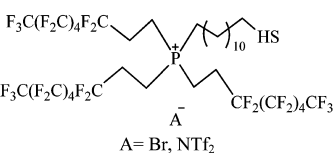
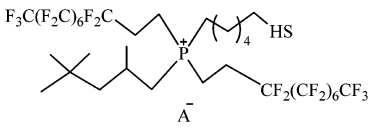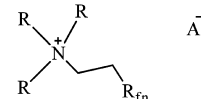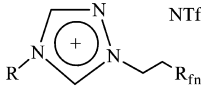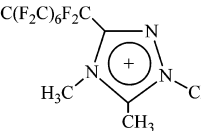| Structure	Family	Abbreviation	Reference	Remarks
R—N⊕N—CF₂(CF₂)₄CF₃, PF₆⁻, R = Me, Bu	Imidazolium ionic liquids containing perfluoroalkyl substituent with hexafluorophosphate anion	[(EtPFHex)RIm][PF₆]	This work	Melting Point (DSC) Decomposition Temperature (TGA) Cytotoxicity
Tetrabutylammonium cation, O=S(O⁻)(O)Rfn, Rfn = PFBu, PFOc	Tetrabutylammonium with perfluoroalkyl sulfonate anion	[NBu₄][RfnSO₃]	This work	Melting Point (DSC) Decomposition Temperature (TGA) Density (densimeter) Viscosity (viscometer) Refractive index (refractometer) Ionic conductivity (conductimeter) Cytotoxicity
1-Ethyl-3-methylpyridinium cation, O=S(O⁻)(O)CF₂CF₂CF₂CF₃	1-Ethyl-3-methylpyridinium perfluorobutanesulfonate	[EtMepy][(PFBu)SO₃]	This work	Melting Point (DSC) Decomposition Temperature (TGA) Density (densimeter) Viscosity (viscometer) Refractive index (refractometer) Ionic conductivity (conductimeter) Cytotoxicity
H₃C—N⊕N—R, O=S(O⁻)(O)CF₂CF₂CF₂CF₃, R = Hex, Oc	Imidazolium ionic liquids with perfluorobutanesulfonate anion	[RMeIm][(PFBu)SO₃]	This work	Melting Point (DSC) Decomposition Temperature (TGA) Density (densimeter) Viscosity (viscometer) Refractive index (refractometer) Ionic conductivity (conductimeter) Cytotoxicity
1-Butyl-1-methylpyrrolidinium cation, O=S(O⁻)(O)CF₂CF₂CF₂CF₃	1-Butyl-1-methylpyrrolidinium perfluorobutanesulfonate	[BuMepyr][(PFBu)SO₃]	This work	Melting Point (DSC) Decomposition Temperature (TGA) Cytotoxicity
R₃P⊕—Rfn, A⁻; R = Me, Bu, Oc; Rfn = PFBu, PFHex, PFDe; A= I, BF₄, PF₆, OTs, OTf	Phosphonium ionic liquids containing perfluoroalkyl substituent	[PR₃(EtRfn)][A]	23	Melting Point (DSC) Decomposition Temperature (TGA)
1-methylpyridinium oxadiazole, F₃C(F₂C)₅F₂C, A⁻	1,2,4-oxadiazolylpyridinium ionic liquids containing perfluoheptyl substituent	[(PFHep)1,2,4-oxadiazolMpy][A]	19	Melting Point (DSC)
H₃C—N⊕N—Rfn, NTf₂⁻, Rfn = PFBu, PFHex, PFOc, SF₅PFBu	Imidazolium ionic liquids containing perfluoroalkyl substituent with bis(trifluoromethylsulfonyl)imide anion	[(EtRfn)MeIm][NTf₂]	11 / 26 / 13 / 21	Density (pycnometer) / Density / Density (densimeter) Viscosity (viscometer) / Density (pycnometer) Ionic conductivity (conductimeter) Viscosity (rheometer)
Rfn—P⊕(triMePe)—Rfn, Rfn, A⁻; Rfn = PFHex, PFOc; A= I, BF₄, PF₆, NTf₂, OTs, OTf	Phosphonium ionic liquids containing tri-perfluoroalkyl and 2,4,4-trimethylpentyl substituents	[P(EtRfn)₃(triMePe)][A]	24	Melting Point (DSC) Decomposition Temperature (TGA)
F₃C(F₂C)₄F₂C—P⊕—(CH₂)₁₀HS, CF₂(CF₂)₄CF₃, A⁻; A= Br, NTf₂	Phosphonium ionic liquids containing tri-perfluoroalkyl and dodecanethiol substituents	[P(EtPFHex)₃(DocHS)][A]	24	Melting Point (DSC) Decomposition Temperature (TGA)

Table 1. continued
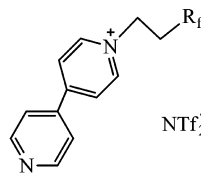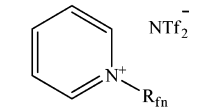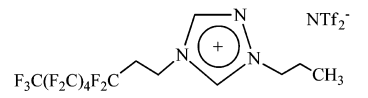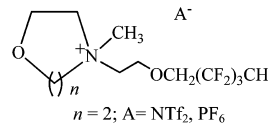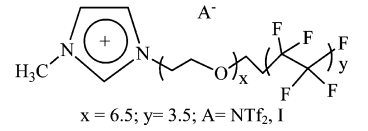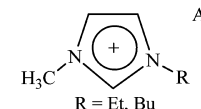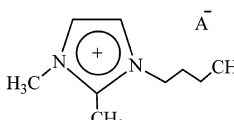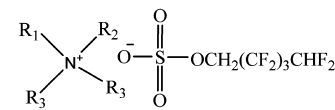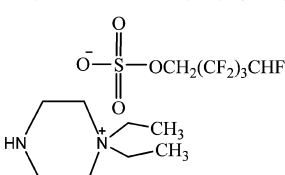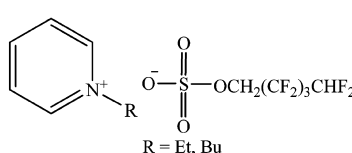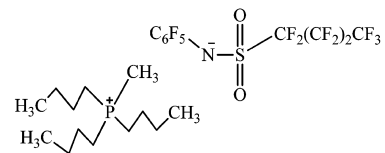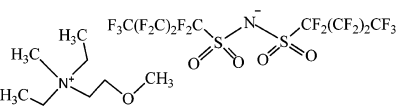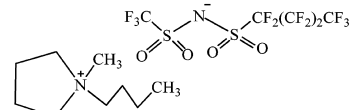
Structure	Family	Abbreviation	Reference	Remarks
F₃C(F₂C)₆F₂C ... P⁺ ... CF₂(CF₂)₆CF₃ ... A⁻ ... HS; A= Br, PF₆, NTf₂	Phosphonium ionic liquids containing bis-perfluoroalkyl, 2,4,4-trimethylpentyl and hexanethiol substituents	[P(EtPFOc)₂(HexHS)(triMePe)][A]	22	Melting Point (DSC) Decomposition Temperature (TGA)
R, R, N⁺, R, R_fn, A⁻; R = Bu, Oc; R_fn = PFBu, PFOc, PFDe; A= I, NTf₂, C₃F₇CO₂H	Ammonium ionic liquids containing perfluoroalkyl substituent	[NR₃(EtR_fn)][A]	26	Melting Point Decomposition Temperature Density (pycnometer)
R, N-N, +, N, R_fn, NTf₂⁻; R = Me, Bu, Hep, De; R_fn = PFBu, PFHex	Triazolium ionic liquids containing perfluoroalkyl substituent with bis(trifluoromethylsulfonyl)imide anion	[(EtR_fn)RTaz][NTf₂]	26	Melting Point Decomposition Temperature
F₃C(F₂C)₆F₂C, N-N, +, H₃C, N, CH₃, CH₃, A⁻; A= NTf₂, ClO₄, BF₄	Triazolium ionic liquids containing perfluoroalkyl substituent	[(PFOc)Me₃Taz][A]	26	Melting Point Decomposition Temperature
R_fn, N⁺, N, NTf₂⁻; R_fn = PFHex, PFOc	Bipyridinium ionic liquids containing perfluoroalkyl substituent with bis(trifluoromethylsulfonyl)imide anion	[(EtR_fn)bipy][NTf₂]	26	Melting Point
NTf₂⁻, N⁺, R_fn; R_fn = EtSF₅PFBu, EtPFHex	Pyridinium ionic liquids containing perfluoroalkyl substituent with bis(trifluoromethylsulfonyl)imide anion	[R_fnpy][NTf₂]	26	Melting Point Density
N-N, +, N, CH₃, NTf₂⁻, F₃C(F₂C)₄F₂C	1-Methyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)1,2,4-triazolium bis(trifluoromethylsulfonyl)imide	[(EtPFHex)PrTaz][NTf₂]	26	Melting Point (glass transition temperature)
O, N⁺, CH₃, OCH₂(CF₂)₃CHF₂, A⁻, n; n = 2; A= NTf₂, PF₆	Oxazolidinium ionic liquids containing perfluoroalkyl substituent	[EtOCH₂(CF₂)₃CHF₂Ox][A]	26	Melting Point Decomposition Temperature Density Viscosity
H₃C, N, +, N, A⁻, O, x, F, F, F, F, F, y; x = 6.5; y= 3.5; A= NTf₂, I	Imidazolium ionic liquids containing perfluoroalkyl PEG functionalized substituent	[(EtOEtR_fn)MeIm][A]	17	Melting Point (glass transition temperature, DSC) Decomposition Temperature (TGA) Ionic conductivity (impedance spectroscopy) Viscosity (viscometer)
H₃C, N, +, N, R, A⁻; R = Et, Bu; A= CHF₂(CF₂)₃CH₂SO₄, (PFPh)NSO₂(PFBu), CF₃CHFO(CF₂)₂SO₃, CF₃CF₂OCHFCF₂SO₃	Imidazolium ionic liquids with anion containing perfluoroalkyl functionalized substituent	[RMeIm][A]	25	Melting Point Viscosity Ionic conductivity
			18	Melting Point (DSC, glass transition temperature) Decomposition Temperature (DSC)
			20	Decomposition Temperature Density (densimeter)

Table 1. continued

Structure	Family	Abbreviation	Reference	Remarks
A= CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$, (PFPh)NSO$_2$(PFBu)	1-Butyl-2,3-dimethylimidazolium with anion containing perfluoroalkyl functionalized substituent	[BuMe$_2$Im][A]	25	Melting Point Viscosity Ionic conductivity
			18	Melting Point (DSC or capillary tubes) Decomposition Temperature (DSC)
R$_1$ = Me, Et, Bu; R$_2$ = Et, Bu, Oc; R$_3$ = Et, Bu	Ammonium ionic liquids with 2,2,3,3,4,4,5,5-octafluoropentanesulfate anion	[NR$_4$][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	Melting Point Viscosity Ionic conductivity
(structure)	Diethylpiperazinium 2,2,3,3,4,4,5,5-octafluoropentanesulfate	[Et$_2$pipz] [CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	Melting Point Viscosity Ionic conductivity
R = Et, Bu	Pyridinium ionic liquids with 2,2,3,3,4,4,5,5-octafluoropentanesulfate anion	[Rpy][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	Melting Point Viscosity Ionic conductivity
(structure)	Tributylmethylphosphonium 2,3,4,5,6-pentafluorophenyl-nonafluorobutylsulfonamide	[PBu$_3$Me] [(PFPh)NSO$_2$(PFBu)]	18	Melting Point (DSC, glass transition temperature) Decomposition Temperature (DSC)
(structure)	Diethylmethyl(2-methoxyethyl)ammonium bis(perfluorobutanesulfonyl)imide	[NEt$_2$Me(EtOMe)] [N(PFBuSO$_2$)$_2$]	27	Melting Point (DSC) Decomposition Temperature (TGA) Density (pycnometer) Viscosity (viscometer) Ionic conductivity (impedance method)
(structure)	1-Butyl-1-methylpyrrolidinium (perfluorobutanesulfonyl)(trifluoromethylsulfonyl)imide	[BuMepyr] [N(PFBuSO$_2$)(CF$_3$SO$_2$)]	16	Density (densimeter) Viscosity (rheometer) Ionic conductivity (conductimeter)

to the strong formation of fluorinated alcohol clusters and water clusters.[10] It is thus expected that the fluorinated alkyl chain present in FILs will also control the formation of fluorinated nanodomains easing the accommodation of fluorinated solutes (gases or liquids).[11−15] In this sense, it is expected that the length of the alkyl chain will also play a role on the aggregation.

This work provides the first step in characterizing and evaluating FILs, ILs with fluorinated alkyl chains equal or greater than four carbon atoms, for the development of new and improved fluorinated media to be used in areas where solvation in fluorinated media is the key. The new approaches and concepts can be clearly identified by the specific application of FILs in two main areas: PFCs environmental impact mitigation and biomedical applications.

PFCs environmental impact mitigation, through their use in extraction processes, is where FILs could be used as alternatives to currently used volatile organic solvents to efficiently separate perfluoroalkyl acid contaminants from industrial effluents. These compounds are particularly harmful for human health and the environment. They accumulate in living organisms, are transported by air, water, and migratory species and accumulate in terrestrial and aquatic ecosystems. FILs may also be used in gas separation processes, as supported or composite membranes reducing emissions of greenhouse gases of human origin that contribute to climate change. Reducing these emissions is the major goal of the Kyoto Protocol. Moreover, biomedical applications of FILs include newly improved oxygen therapeutic emulsions replacing, totally or in part, the inert PFCs presently used as oxygen carriers in these emulsions.

The study of novel, nonvolatile, recyclable FILs that will help to develop environmentally benign selective fluorinated systems will be addressed within the present work. However, some drawbacks need to be overcome in the future to develop and implement FIL-based processes. Among the most important, we highlight the need for lifetime, recyclability, safety, health, and environmental studies, and the high price of FILs, which are more expensive than conventional solvents. Although the price would drop for large scale production of these compounds, similar prices to those of conventional solvents will never be achieved because FILs are complex molecules that require advanced synthesis and purification steps.

Additionally, it is thought that the physicochemical properties of these FILs may be fine tuned through the careful selection of cations and anions leading to the desired physicochemical and toxicological properties for each application. However, this process requires a wide collection of accurate physicochemical property data for different families of FILs and the consequent understanding of the relationships between each macroscopic property and ionic liquid intermolecular forces. This paper provides a critical review and analysis of both the thermodynamic and thermophysical properties from the literature[11,13,16−27] and those measured in this work so that guidelines for selecting the most suitable FILs for each application can be established. The literature review on FILs is summarized in Table 1 together with an indication of the measured properties.[11,13,16−27] It is amazing to verify the great diversity of ILs that can be included in the FILs family. However, and more astonishing, is that most of these works only report the synthetic procedure and few properties such as melting and decomposition temperatures. In order to enlarge the understanding of the FILs thermodynamic behavior and thus to expand their possible applications, eight new FILs (Table 1 and Supporting Information) have been selected for the study of the effect of fluorination on the following properties: melting and decomposition temperature, density, refractive index, dynamic viscosity, and ionic conductivity in a temperature range from 283.15 to 353.15 K at atmospheric pressure. Finally, cytotoxicity was also evaluated because it is an important property regarding biomedical applications. As listed in Table 1, there are no refractive index and cytotoxicity data in the literature for this class of compounds. These data from the literature and the experimental measurements performed in this work are also discussed and evaluated to select the best fluorinated ionic liquid for each application.

■ CYTOTOXICITY ASSAYS

Information about the toxicity and biocompatibility of fluorinated ionic liquids is of vital importance for their application in numerous fields. In this work, cytotoxicity tests were performed using two different human cell cultures types, human colon adenocarcinoma cells, Caco-2, and liver carcinoma cells, HepG2, that are suitable and useful in vitro models for the intestinal barrier and hepatic metabolism studies, respectively.[28,29] The selected FILs were tested in a concentration range of 500−10000 μM, except for [(EtPFHex)MeIm][PF$_6$] that is poorly soluble in cell culture media and was tested in a concentration range of 50−1000 μM. It is important to emphasize that, to our knowledge, there are as yet no cytotoxicity data for fluorinated ionic liquids, defined as ionic liquids with fluorine tags equal or longer than four carbon atoms, in the open literature.

Dose-dependent toxicity curves were determined for all selected FILs. Some fluorinated ionic liquids, for concentrations higher than 2000uM, drastically decreased cellular viability, while others triggered decreases lower than 50% or insignificant changes.

It is known that in ILs based on the hexafluorophosphate anion ([PF$_6$]$^-$), toxicity is usually determined by the cation and, particularly for imidazolium-based cations, cytotoxicity increases with the length of the alkyl side chain.[30−33] These data suggest that the lipophilicity of the cation is an important factor in the ability of the ILs to induce cytotoxicity in a large number of cell models.[30−33] On the other hand, the results obtained in this work show that the substitution of an

hydrogenated alkyl chain 1-methyl-3-octylimidazolium hexafluorophosphate ([MeOcIm][PF$_6$]) by an homologue fluorinated alkyl chain ([(EtPFHex)MeIm][PF$_6$]) did not induce cytotoxicity after 4 h of exposure (this length of time was chosen according to digestion time), up to a concentration of 10000 uM. As shown in Figure 1, [MeOcIm][PF$_6$] induced
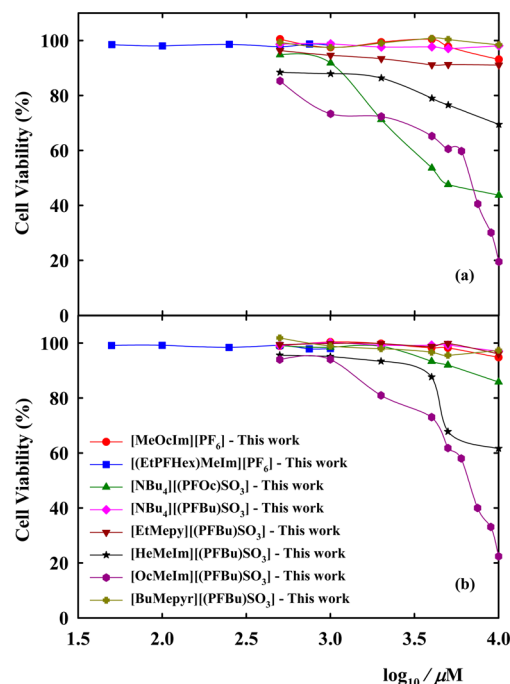
Figure 1. Experimental toxicity profile for fluorinated ionic liquids of this work using: (a) Caco-2 cells and (b) HepG2 cells.

negligible toxicity in intestinal epithelial cell models, while it had been previously observed that [MeOcIm][PF$_6$] induced cytotoxicity in Caco-2 cells for exposure periods of 24 h (effective concentration reducing cell viability to 50%, EC$_{50}$ = 5120 μM) and 48 h (EC$_{50}$ = 1460 μM).[32] These last results are in line with published data for the same IL.[34] However, using HepG2 as a cell-based model, it was observed that neither [MeOcIm][PF$_6$] nor [(EtPFHex)MeIm][PF$_6$] induced any cytotoxicity in the concentration range tested (Figure 1 and Table 2).

In this study, the influence of the size of the fluorinated chain of [R$_{fn}$SO$_3$]$^-$ anions in the cytotoxicity of ionic liquids was investigated for the first time. The increase in the fluorinated

Table 2. Cytotoxic Effective Concentration (EC$_{50}$) Values for Fluorinated Ionic Liquids Tested in Caco-2 and HepG2 Cells

ionic liquid	Log EC$_{50}$	
	Caco-2	HepG2
[MeOcIm][PF$_6$]	>4	>4
[(EtPFHex)MeIm][PF$_6$]	>4	>4
[NBu$_4$][(PFOc)SO$_3$]	3.65	>4
[NBu$_4$][(PFBu)SO$_3$]	>4	>4
[EtMepy][(PFBu)SO$_3$]	>4	>4
[HMIM][(PFBu)SO$_3$]	>4	>4
[OMIM][(PFBu)SO$_3$]	3.82	3.83
[BMPyr][(PFBu)SO$_3$]	>4	>4

Figure 2. continued

1	[(EtPFHex)MeIm][PF$_6$]	This work	**32**	[NBu$_3$(EtPFOc)][NTf$_2$]	26	**63**	[POc$_3$(EtPFDe)][I]	23
2	[(EtPFHex)BuIm][PF$_6$]	This work	**33**	[NOc$_3$(EtPFOc)][NTf$_2$]	26	**64**	[POc$_3$(EtPFDe)][BF$_4$]	23
3	[OcMeIm][(PFBu)SO$_3$]	This work	**34**	[NEt$_4$][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	**65**	[POc$_3$(EtPFDe)][PF$_6$]	23
4	[HeMeIm][(PFBu)SO$_3$]	This work	**35**	[NBu$_4$][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	**66**	[POc$_3$(EtPFDe)][OTs]	23
5	[(EtOEtRfn)MeIm][I]	17	**36**	[NOc$_3$Me][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	**67**	[POc$_3$(EtPFDe)][OTf]	23
6	[BuMeIm][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	**37**	[NEt$_2$Me(EtOMe)][N(PFBuSO$_2$)$_2$]	27	**68**	[P(EtPFOc)$_2$(EtPFHex)(triMePe)][I]	24
7	[EtMeIm][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	**38**	[PBu$_3$(EtPFBu)][I]	23	**69**	[P(EtPFOc)$_2$(EtPFHex)(triMePe)][BF$_4$]	24
8	[BuMe$_2$Im][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	25	**39**	[PBu$_3$(EtPFBu)][BF$_4$]	23	**70**	[P(EtPFOc)$_2$(EtPFHex)(triMePe)][PF$_6$]	24
9	[BuMeIm][(PFPh)NSO$_2$(PFBu)]	18	**40**	[PBu$_3$(EtPFBu)][PF$_6$]	23	**71**	[P(EtPFOc)$_2$(EtPFHex)(triMePe)][OTs]	24
10	[BuMe$_2$Im][(PFPh)NSO$_2$(PFBu)]	18	**41**	[PBu$_3$(EtPFBu)][OTs]	23	**72**	[P(EtPFOc)$_2$(EtPFHex)(triMePe)][OTf]	24
11	[BuMeIm][CF$_3$CHFO(CF$_2$)$_2$SO$_3$]	20	**42**	[PBu$_3$(EtPFBu)][OTf]	23	**73**	[P(EtPFOc)$_2$(EtPFHex)(triMePe)][NTf$_2$]	24
12	[BuMeIm][CF$_3$CF$_2$OCHFCF$_2$SO$_3$]	20	**43**	[PBu$_3$(EtPFHex)][I]	23	**74**	[P(EtPFHex)$_3$(DocHS)][Br]	24
13	[EtMepy][(PFBu)SO$_3$]	This work	**44**	[PBu$_3$(EtPFHex)][BF$_4$]	23	**75**	[P(EtPFHex)$_3$(DocHS)][NTf$_2$]	24

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dx.doi.org/10.1021/sc300163n | *ACS Sustainable Chem. Eng.* 2013, 1, 427−439

14 [(PFHep)1,2,4-oxadiazolMpy][I]	[19]	**45** [PBu$_3$(EtPFHex)][PF$_6$]	[23]	**76** [P(EtPFOc)$_2$(HexHS)(triMePe)][Br] [22]
15 [(PFHep)1,2,4-oxadiazolMpy][OTf]	[19]	**46** [PBu$_3$(EtPFHex)][OTs]	[23]	**77** [P(EtPFOc)$_2$(HexHS)(triMePe)][PF$_6$] [22]
16 [(EtPFHex)bipy][NTf$_2$]	[26]	**47** [PBu$_3$(EtPFHex)][OTf]	[23]	**78** [P(EtPFOc)$_2$(HexHS)(triMePe)][NTf$_2$] [22]
17 [(EtPFOc)bipy][NTf$_2$]	[26]	**48** [PBu$_3$(EtPFDe)][I]	[23]	**79** [PBu$_3$Me][(PFPh)NSO$_2$(PFBu)] [18]
18 [(EtSF$_5$PFBu)py][NTf$_2$]	[26]	**49** [PBu$_3$(EtPFDe)][BF$_4$]	[23]	**80** [(EtPFBu)BuTaz][NTf$_2$] [26]
19 [(EtPFHex)py][NTf$_2$]	[26]	**50** [PBu$_3$(EtPFDe)][PF$_6$]	[23]	**81** [(EtPFBu)HepTaz][NTf$_2$] [26]
20 [Etpy][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	[25]	**51** [PBu$_3$(EtPFDe)][OTs]	[23]	**82** [(EtPFBu)DeTaz][NTf$_2$] [26]
21 [Bupy][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$]	[25]	**52** [PBu$_3$(EtPFDe)][OTf]	[23]	**83** [(EtPFHex)MeTaz][NTf$_2$] [26]
22 [BuMepyr][(PFBu)SO$_3$]	This work	**53** [POc$_3$(EtPFBu)][I]	[23]	**84** [(EtPFHex)BuTaz][NTf$_2$] [26]
23 [NBu$_4$][(PFOc)SO$_3$]	This work	**54** [POc$_3$(EtPFBu)][BF$_4$]	[23]	**85** [(EtPFHex)HepTaz][NTf$_2$] [26]
24 [NBu$_4$][(PFBu)SO$_3$]	This work	**55** [POc$_3$(EtPFBu)][PF$_6$]	[23]	**86** [(PFOc)Me$_3$Taz][NTf$_2$] [26]
25 [NBu$_3$(EtPFBu)][I]	[26]	**56** [POc$_3$(EtPFBu)][OTs]	[23]	**87** [(PFOc)Me$_3$Taz][ClO$_4$] [26]
26 [NBu$_3$(EtPFOc)][I]	[26]	**57** [POc$_3$(EtPFBu)][OTf]	[23]	**88** [(PFOc)Me$_3$Taz][BF$_4$] [26]
27 [NOc$_3$(EtPFBu)][I]	[26]	**58** [POc$_3$(EtPFHex)][I]	[23]	**89** [(EtOCH$_2$(CF$_2$)$_3$CHF$_2$Ox)][NTf$_2$] [26]
28 [NOc$_3$(EtPFOc)][I]	[26]	**59** [POc$_3$(EtPFHex)][BF$_4$]	[23]	**90** [EtOCH$_2$(CF$_2$)$_3$CHF$_2$Ox][PF$_6$] [26]
29 [NOc$_3$(EtPFDe)][I]	[26]	**60** [POc$_3$(EtPFHex)][PF$_6$]	[23]	**91** [Et$_2$pipz][CHF$_2$(CF$_2$)$_3$CH$_2$SO$_4$] [25]
30 [NBu$_3$(EtPFOc)][C$_3$F$_7$CO$_2$H]	[26]	**61** [POc$_3$(EtPFHex)][OTs]	[23]	
31 [NBu$_3$(EtPFBu)][NTf$_2$]	[26]	**62** [POc$_3$(EtPFHex)][OTf]	[23]	

Figure 2. Decomposition temperature (onset temperature) versus melting temperature for fluorinated ionic liquids of this work and literature.[17−20,22−27] Line at $x = 185$ contains merely decomposition temperature data. Line at $y = 325$ refers only to melting temperature.

alkyl chain in the [R$_{fn}$SO$_3$]$^-$ anion, from R$_{fn}$ = PFBu (perfluorobutanesulfonate) to R$_{fn}$ = PFOc (perfluorooctanesulfonate), with [NBu$_4$]$^+$ as the cation, leads to an increase in FIL toxicity in Caco-2 cells (Figure 1). In fact, while [NBu$_4$]-[(PFBu)SO$_3$] was not toxic in the concentration range tested, [NBu$_4$][(PFOc)SO$_3$] dramatically reduced cell viability to 57%, presenting an EC$_{50}$ of 4467 μM (Figure 1 and Table 2). Stolte et al.[34] reported that the increase of the fluorinated chain, increasing the lipophobicity of the ionic liquids, is associated with a more pronounced cytotoxicity in all cell lines.[34,35] Greater cytotoxicity was observed for [NBu$_4$][(PFOc)SO$_3$] than [NBu$_4$][(PFBu)SO$_3$] in HepG2 cells. However, in this case, only a 15% reduction in cell viability was observed, whereas [NBu$_4$][(PFBu)SO$_3$] was still nontoxic (Figure 1). Moreover, maintaining the [(PFBu)SO$_3$]$^-$ anion, while [EtMepy][(PFBu)SO$_3$] remained unharmful, [HMIM]-[(PFBu)SO$_3$] and [OMIM][(PFBu)SO$_3$] induced similar toxicities in both cell lines with the latter attaining an EC$_{50}$ of 6607 μM for Caco-2 cells and 6760 μM for HepG2 cells (Figure 1). On the other hand, changing the cation to [BuMepyr]$^+$ did not induce any toxicity for the highest studied dose (10000 μM) in both Caco-2 and HepG2 cells. These results are in agreement with previous reports that show the absence of toxicity of this cation.[33]

Together, these results suggest that [R$_{fn}$SO$_3$]$^-$ toxicity depends on the size of the fluorinated chain, and consequently, that [(PFOc)SO$_3$]$^-$ is more toxic than [(PFBu)SO$_3$]$^-$. Nevertheless, data shows that FILs toxicity also depends considerably on the cation. Particularly, the presence of imidazolium-based cations induces toxicity depending on the cation alkyl chain length.

Except for [OMIM][(PFBu)SO$_3$], [HMIM][(PFBu)SO$_3$], for which the toxicity were similar in both cell lines, all ionic liquids proved to be less toxic in HepG2 than in Caco-2 cells. This is probably due to the higher metabolic capacity of HepG2 cells.

■ FLUORINATED IONIC LIQUID PROPERTIES

Thermal Properties. Melting and decomposition temperatures are some of the most important properties for ionic liquids, especially regarding their application as alternative solvents because they determine the liquid range of the fluids and their range of application. For example, the upper operating temperature of an ionic liquid is usually determined by its decomposition temperature. From this literature review (Table 1), it can be seen that the thermal properties of FILs are most commonly studied. The melting and decomposition temperatures for all the fluorinated ionic liquids found in the literature[17−20,22−27] as well as those measured in this work are illustrated in Figure 2. Two temperatures have been marked for the applications envisaged in this work: 25 °C, as a reference in separation processes for recycling/recovering the hazardous PFCs using fluorinated ionic liquids as solvents, and 37 °C, average body temperature and the reference for the development of new and improved oxygen therapeutic emulsions containing fluorinated ionic liquids. Eight different families of fluorinated ionic liquids are plotted in Figure 2, containing a total of 91 FILs, 46 of which have a melting temperature below 25 °C, and 51 of which are below 37 °C. Phosphonium-based ionic liquids are the most studied, and 20 out of the 42 selected are liquid in the full range of temperatures and present high decomposition temperatures. The second most studied FIL family is that ammonium-based ionic liquids, where 11 out of the 15 studied are also liquid below 37 °C. However, some these FILs either have the lowest decomposition temperatures, as in the example of [NBu$_4$]-[(PFOc)SO$_3$], or their decomposition temperature has not yet been determined. Imidazolium and pyridinium-based ionic liquids are less studied, but examples with low melting and high decomposition temperatures were reported in the literature.

The effect of the ionic liquid's anion nature on melting and decomposition temperatures can be studied using the phosphonium-based ionic liquids with fluorinated chains, where several different data sets (numbers 53−57, 58−62, and 63−67 from Figure 2) exist. For this cation family, the anions can be ranked by increasing thermal stability (the most
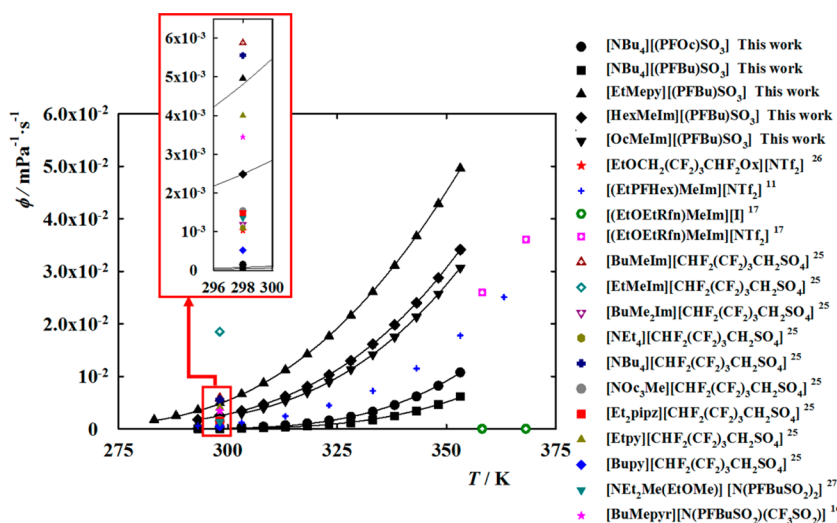
Figure 3. Fluidity (1/viscosity) and fitted curves as a function of temperature (T) for the fluorinated ionic liquids: black symbols indicate new data and color symbols show data from the literature.[11,16,17,25−27].

stable and with a wide liquid range) of the FILs: triflate ([OTf]⁻) > tosylate ([OTs]⁻) > iodide ([I]⁻) > tetrafluoroborate ([BF₄]⁻) > hexafluorophosphate ([PF₆]⁻). Regarding the cation effect on the thermal properties, Figure 2 shows that for the same anion perfluorobutanesulfonate $[(PFBu)SO_3]^-$ the decomposition temperatures of FILs with different cations are similar, while the melting points decrease in the following order, pyrrolidiums > ammoniums > imidazoliums > pyridiniums, indicating that the pyridinium cation (numbers 3, 4, 13, 22, and 24) is the best choice for the applications under consideration.

The increment in the fluorinated chain effect can be evaluated using ammonium-based ionic liquids ($[NBu_4]^+$ cation), where the change from $[(PFBu)SO_3]^-$ (number 24) to $[(PFOc)SO_3]^-$ (number 23) decreases both the decomposition and melting temperatures. This behavior is also observed in triazolium-based ionic liquids with the bis(trifluoromethylsulfonyl)imides anion ([(EtPFBu)BuTaz]-[NTf₂], number 80, and [(EtPFHex)BuTaz][NTf₂], number 84). In phosphonium-based ionic liquids with the triflate ([OTf]⁻) anion, the decomposition temperature also has the same behavior, but the melting point increases with the increment of the fluorinated chain ([PBu₃(EtPFBu)][OTf], number 42, [PBu₃(EtPFHex)][OTf], number 47, and [PBu₃(EtPFDe)][OTf], number 52). The effect of increasing the hydrogenated alkyl chain length of the cation in thermal properties can be studied in triazolium-based ionic liquids with the bis(trifluoromethylsulfonyl)imides anion, where the melting point decreases when the alkyl chain increases ([(EtPFHex)-MeTaz][NTf₂], number 83, [(EtPFHex)BuTaz][NTf₂], number 84, and [(EtPFHex)HepTaz][NTf₂], number 85; and [(EtPFBu)BuTaz][NTf₂] number 80, [(EtPFBu)HepTaz]-[NTf₂], number 81 and [(EtPFBu)DeTaz][NTf₂], number 82). The same behavior is observed in ammonium-based ionic liquids with the same anion ([NBu₃(EtPFOc)][NTf₂], number 32, and [NOc₃(EtPFOc)][NTf₂], number 33). Furthermore, in these last two FILs, thermal stability increases with the increment of the alkyl chain length of the cation. However, the opposite is found in phosphonium-based ionic liquids ([PBu₃(EtPFBu)][OTf], number 42, and [POc₃(EtPFBu)]-[OTf], number 57), where a fall in the decomposition

temperature can be observed when the alkyl chain of cation increases.

From these results, we can conclude that no specific overall rule can be extracted for melting and decomposition temperatures. However, if the fluorinated ionic liquids are analyzed as separate families, some consistent effects can be observed.

Viscosity and Ionic Conductivity. Transport properties, such as viscosity and ionic conductivity, are among the most relevant characteristics for chemical process design and development.[36] Viscosity is needed for the design of processing units to analyze the fluids' efficacy as a solvent in extraction processes, to study mass transfer processes, and to design equipment such as pumping systems. The high viscosity of some ionic liquids are a disadvantage in some industrial applications because it negatively affects processes such as pumping, mixing, stirring, and mass transfer operations.[37]

Accurate viscosity data for ionic liquids are still scarce[37] and even more so in the case of fluorinated ionic liquids. Values for merely 15 FILs were found in this review, and most of the data are reported at 298.15 K and atmospheric pressure. Fluidity (inverse of viscosity) data for these FILs,[11,16,17,25−27] together with the experimental data for the five FILs studied in this work are illustrated in Figure 3. The temperature effect on fluidity is very important because this property is very sensitive to temperature. Only one paper reported accurate values of dynamic viscosity for a large temperature range of between 293.15 and 363.15 K,[11] while for the other FILs, only discrete viscosity values at one temperature and atmospheric pressure were found. These data are completed with the experimental fluidity determined in this work for five new FILs in a temperature range from 283.15 to 353.15 K, depending on the melting temperature of each compound. A comparison carried out at 298.15 K shows that FILs composed of $[CHF_2(CF_2)_3CH_2SO_4]^-$ and $[(PFBu)SO_3]^-$ anions are the most fluid fluorinated ionic liquids and that this transport property is mainly governed by the cation.

The effect of the ionic liquid's cation nature on fluidity can be studied using FILs based on the $[CHF_2(CF_2)_3CH_2SO_4]^-$ anion, which presents the following trend in fluidity: $[EtMeIm]^+$ > $[BuMeIm]^+$ > $[NBu_4]^+$ > $[Etpy]^+$ > $[NOc_3Me]^+$ > $[Etpipz]^+$ > $[BuMe_2Im]^+$ > $[NEt_4]^+$ > $[Bupy]^+$. However, in the case of the $[(PFBu)SO_3]^-$ anion, pyridinium-
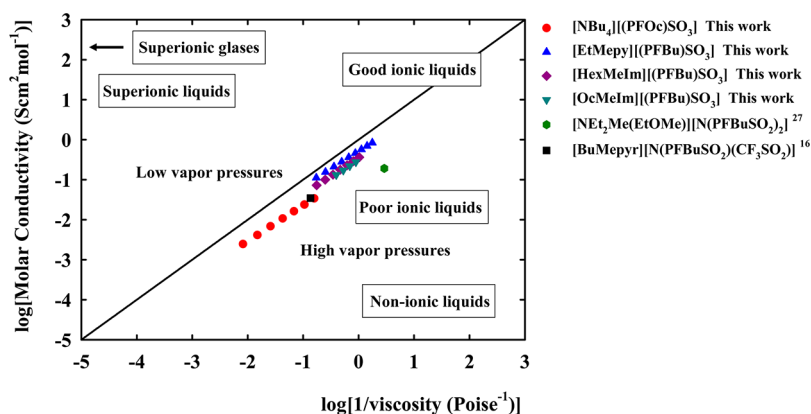
Figure 4. Classical Walden rule diagram for ionic liquids and a Walden plot for the fluorinated ionic liquids of this work and literature.[16,27]
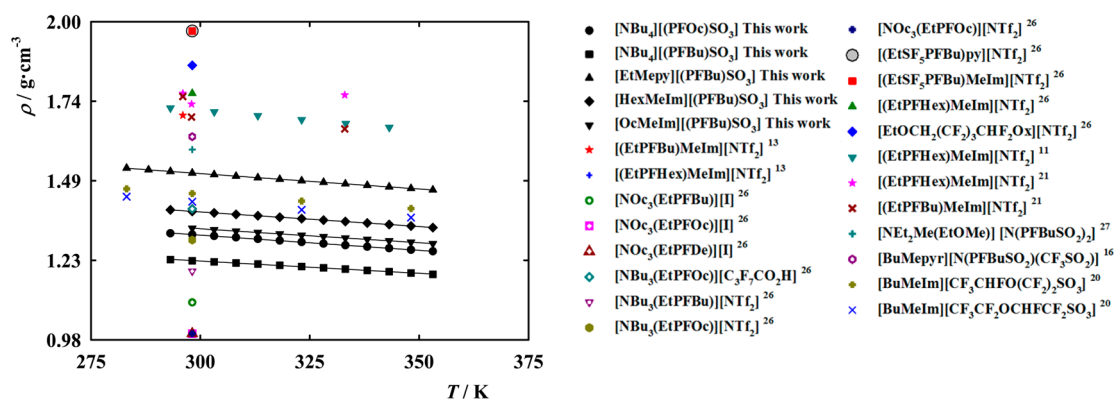

Figure 5. Density and fitted curves as a function of temperature (T) for the fluorinated ionic liquids of this work and literature.[11,13,16,20,21,26,27]

based ionic liquids show a higher fluidity: the less viscous FIL is $[EtMepy][(PFBu)SO_3]$, followed by imidazolium-based ionic liquids and ammonium-based ionic liquids.

The effect of increasing the hydrogenated alkyl chain length of the cation can be studied using imidazolium-based ionic liquids combined with $[(PFBu)SO_3]^-$ and $[CHF_2(CF_2)_3CH_2SO_4]^-$ anions, where the fluidity decreases when the alkyl chain length increases (for the $[(PFBu)SO_3]^-$ anion, $[HexMeIm]^+ > [OcMeIm]^+$; and for the $[CHF_2(CF_2)_3CH_2SO_4]^-$ anion, $[EtMeIm]^+ > [BuMeIm]^+$). Opposite behavior is observed for ammonium-based ionic liquids where, for the $[CHF_2(CF_2)_3CH_2SO_4]^-$ anion, the following rank of cations was found: $[NBu_4]^+ > [NEt_4]^+$. However, if the increment of hydrogenated alkyl chain is asymmetric, the behavior is the same as that observed for the imidazolium-based ionic liquids: $[NBu_4]^+ > [NOc_3Me]^+$.

The effect of the extension of the fluorinated chain in FIL viscosity can be studied using the ammonium-based ionic liquids ($[NBu_4]^+$ cation), where the increment of the fluorinated chain increases the fluidity of the fluorinated ionic liquid: $[(PFOc)SO_3]^-) > [(PFBu)SO_3]^-$.

Additional transport properties such as ionic conductivity/ionicity are also important for industrial purposes. One of the most important properties of inorganic salts is their high ionicity, which is intimately connected with their effectiveness as additives for separation processes. The same relationship between ionicity and performance as a solvent in the separation of azeotropic mixtures has recently been shown for ionic liquids.[38]

The Walden plot is a convenient and versatile tool for measuring the ionicity of ionic liquids[39,40] because it establishes a relationship between the molar conductivity and viscosity of a solution. Figure 4 is a plot based on the classical concept of the Walden plot for organizing the different possible relationships between molar conductivity and fluidity. The straight line fixes the position of the "ideal" Walden line that corresponds to aqueous potassium chloride solutions (ideal electrolyte) in which the system is known to be fully dissociated and to have ions of equal mobility. For the unit chosen, the ideal line runs from corner to corner of a square diagram.[41] This literature review revealed that experimental information on FIL ionicity is extremely scarce, as data are available for only two fluorinated ionic liquids. The data measured for the four fluorinated ionic liquids (the other selected FILs are solid in the temperature range studied) and the two FILs of the literature[16,27] are represented in Figure 4 together with the classification proposed by Angell and co-workers[39,42] for "good" and "poor" ionic liquids, depending on whether their behavior is close to or far from the ideal electrolyte behavior. For each fluorinated ionic liquid, the Walden plot has linear behavior with temperature. The behavior of $[EtMepy][(PFBu)SO_3]$ is the closest to ideal electrolyte (straight black line), and ionicity decreases in the following order: $[EtMepy][(PFBu)SO_3] > [HexMeIm][(PFBu)SO_3] > [OcMeIm][(PFBu)SO_3] > [BuMepyr][N(PFBuSO_2)(CF_3SO_2)] \approx [NBu_4][(PFOc)SO_3] > [NEt_2Me(EtOMe)][N(PFBuSO_2)_2]$.

Density. Density is one of the most relevant properties for any fluid. This thermophysical property is required for the application as a solvent in liquid−liquid extraction processes or
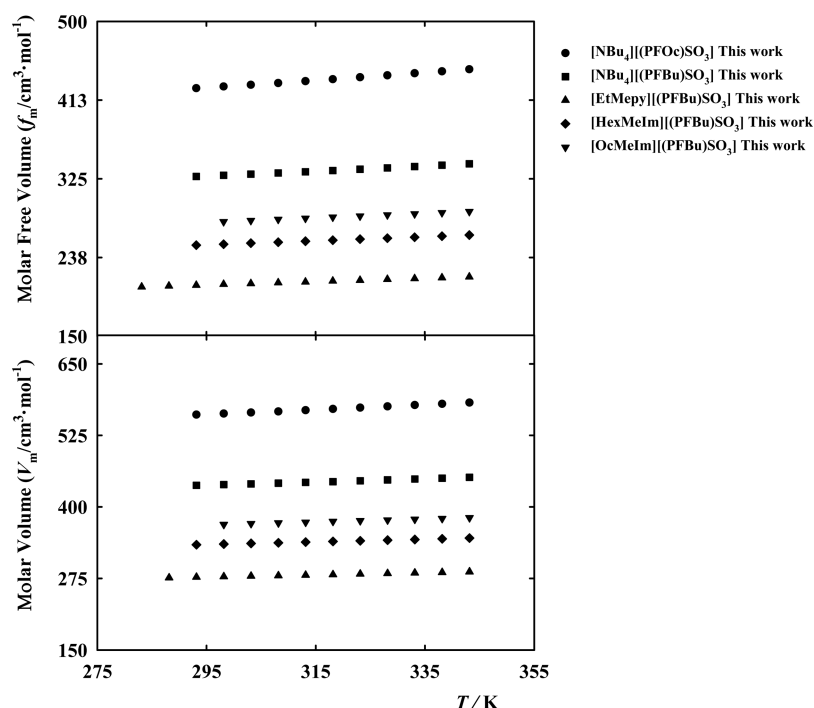
435

dx.doi.org/10.1021/sc300163n | ACS Sustainable Chem. Eng. 2013, 1, 427–439

Figure 6. Molar free volume (f_m) and molar volume (V_m) as a function of temperature (T) for the fluorinated ionic liquids studied in this work.

for the design of different types of equipment such as separation trains. For atmospheric pressure, the density of fluorinated ionic liquids is in the 1−2 g cm^{-3} range. The present literature review for FILs shows two main problems. First, data are centered at temperatures close to 298.15 K and atmospheric pressure conditions; second, less accurate methods, such as pycnometry, were used. The accuracy of the measuring technique is very important because it directly affects the accuracy of the results. For example, wide deviations are observed when literature data for [(EtPFHex)MeIm]-[NTf$_2$][11,13,21,26] are compared (Figure 5). The values of density are linear with temperature when an accurate U-shaped vibrating-tube densimeter is used, as is in the case of this work and some literature data.[13,20] However, if a pycnometer is used, a nonlinear temperature dependence is observed for the fluorinated ionic liquid [(EtPFHex)MeIm][NTf$_2$].[11,21,26] This fact demonstrates that the pycnometer is not the most accurate method for the measurement of density, and special care is needed when data benching. Nevertheless, this literature review reveals that the pycnometer is the most commonly used method for measuring the density of FILs.

The densities of the fluorinated ionic liquids measured herein and those found in the literature[11,13,16,20,21,26,27] appear in Figure 5 as a function of temperature. The effect of the ionic liquid's cation nature with fluorinated chains on the density can be studied using FILs based on the [NTf$_2$]$^-$ anion, where density decreases in the following order: [(EtSF$_5$PFBu)py]$^+$ ≈ [(EtSF$_5$PFBu)MeIm]$^+$ > [EtOCH$_2$(CF$_2$)$_3$CHF$_2$Ox]$^+$ > [(EtPFHex)MeIm]$^+$ > [(EtPFBu)MeIm]$^+$ > [NBu$_3$(EtPFOc)]$^+$ > [NBu$_3$(EtPFBu)]$^+$ > [NOc$_3$(EtPFOc)]$^+$. The same effect of the cation's nature can be addressed using FILs based on the [(PFBu)SO$_3$]$^-$ anion, but for now, it is addressed for cations with hydrogenated chains, where the following order of density was observed: [EtMepy]$^+$ > [HexMeIm]$^+$ > [OcMeIm]$^+$ > [NBu$_4$]$^+$. Furthermore, an increment in the fluorinated chain increases, as expected, the density of the fluorinated ionic

liquid: [NBu$_4$][(PFOc)SO$_3$] > [NBu$_4$][(PFBu)SO$_3$]; [(EtPFHex)MeIm][NTf$_2$] > [(EtPFBu)MeIm][NTf$_2$] and [NBu$_3$(EtPFOc)][NTf$_2$] > [NBu$_3$(EtPFBu)][NTf$_2$].

Refractive Index and Molar Free Volumes. The gasphylic behavior of fluorinated compounds in general and ionic liquids, in particular, is well known. In gas separation processes, fluorinated ionic liquids might be used as supported or composite membranes reducing emissions of greenhouse gases.[13] Taking into account the nature of FILs, molar free volume (calculated from density and refractive index, Supporting Information) is one of the most important properties for the use of these ILs in gas separation processes.

The analysis of the molar free volumes may be related to the solubility of different species in ILs and ILs mixtures, especially low molecular weight solutes that are gaseous at normal conditions.[43] However, for the purpose of solvent−solute interactions, the molar free volume is not entirely accessible, but an increment on this parameter will increment the available free space for gases to dissolve.[44] For the determination of the molar free volume, density and refractive index data are needed. This work reports the first data on the refractive index for fluorinated ionic liquids. The calculated molar free volumes and molar volumes are illustrated in Figure 6. The very strong C−F bonds existent in FILs cause an increase in rigidity of the molecular structure and a decrease in polarity. This fact justifies the increment of molar free volumes and molar volumes of FILs with long fluorinated chains when compared with those of conventional ionic liquids.[44]

A study of the cation's nature carried out for fluorinated ionic liquids based on the [(PFBu)SO$_3$]$^-$ anion shows that the molar free volume decreases in the following order: ammoniums > imidazoliums > pyridiniums. Moreover, as expected, the increment of the alkyl or the fluorinated chain increases the molar free volume, increasing the capacity for dissolving gases: [NBu$_4$][(PFOc)SO$_3$] > [NBu$_4$][(PFBu)SO$_3$] and [OcMeIm]-[(PFBu)SO$_3$] > [HexMeIm][(PFBu)SO$_3$].

■ FLUORINATED IONIC LIQUID APPLICATIONS

Recovery/Recycling of PFC Contaminants. One of the main objectives of this paper was to take the first steps toward the selection of fluorinated ionic liquids for application in more efficient separation processes for recycling/recovering the PFCs used in a wide number of industrial applications. A study of the properties of the fluorinated ionic liquids is carried out to select the best solvents to apply in more efficient and environmentally friendly processes for the separation of perfluoroalkyl acid contaminants by liquid–liquid extraction processes, significantly reducing the hazard of aquatic industrial effluents. The characterization is centered on the fluidity (inverse of dynamic viscosity), ionicity, and density of fluorinated ionic liquids.

From fluidity, ionicity, and density data, it can be concluded that the fluidity of fluorinated ionic liquids mainly depends on the anion and that $[(PFBu)SO_3]^-$ and $[CHF_2(CF_2)_3CH_2SO_4]^-$ anions comprise the FILs with the greatest fluidity. However, for the $[CHF_2(CF_2)_3CH_2SO_4]^-$ anion, no data currently exists for ionicity and density, and thus, no conclusions can be taken about the application of FILs based on this anion. In terms of the $[(PFBu)SO_3]^-$ anion, $[EtMepy][(PFBu)SO_3]$ has both the highest fluidity and also the greatest ionicity and density (similar to that of perfluoroalkyl acids). Therefore, 1-ethyl-3-ethylpyridinium perfluorobutanesulfonate may be a good candidate as a solvent in liquid–liquid extraction processes of perfluoroalkyl acids from aquatic industrial effluents.

Greenhouse Gases. It is well known that the mechanisms of solvation of some gases, for example, CO_2,[41,45] depend on interactions and also on free volume effects[46] according to the solvent. In the case of fluorinated ILs, although some debate has been heard regarding which factor controls solubility, the role of the large free volume cannot be neglected.[47] Therefore, refractive data can be useful for evaluating the importance of the dispersive molecular interactions and the size of the apolar domains (dominated by dispersive molecular interactions) in the pure ionic liquids or mixtures with ionic liquids.[43] If solubility is controlled by interactions, high density increases the specific interactions of the fluorinated domains. In this case, the density of fluorinated ionic liquids with the $[(PFBu)SO_3]^-$ anion decreases in the following order: $[EtMepy][(PFBu)SO_3]$ > $[HexMeIm][(PFBu)SO_3]$ > $[OcMeIm][(PFBu)SO_3]$ > $[NBu_4][(PFOc)SO_3]$ > $[NBu_4][(PFBu)SO_3]$.

Both parameters, molar free volume and density, present opposite behavior in the case of pyridinium and ammonium cations, but these parameters are independent. When solubility is controlled by physical absorption, the free volume present in the FILs is the most important parameter, but when solubility is controlled by chemical absorption, density is more so. Fluorinated ionic liquids based on an imidazolium cation can be a good option for this application because the behavior of both parameters is intermediate.

Biomedical Applications. The past decade of the 20th century has yielded remarkable progress in the field of first generation artificial blood substitutes. These products, suitable only as oxygen carriers and often referred to as oxygen therapeutics, are now in clinical trials. Their potential is enormous, especially in surgery with its risk of extensive blood loss, and a variety of substitutes have already been developed. Perfluorocarbons are totally fluorinated inert organic compounds that can dissolve large volumes of respiratory gases.[2,48] As they are immiscible in aqueous systems, they must be emulsified for intravascular administration. In fact, the transport and delivery of oxygen in vivo by means other than red blood cells has become one of the most challenging research topics of the last 25 years, and PFC-based emulsions have become one of the main candidates for a safe and reliable artificial blood substitute.[2,48]

This work also explores the possibility of replacement (either partially or totally) of PFCs with selected fluorinated ionic liquids in oxygen therapeutic emulsions. It is thought that FILs are more able to solubilize respiratory gases than PFC emulsions. The potential use of FILs as gas carriers have just been proposed in the literature,[49] and FILs have also shown a good behavior as a surfactant, remarkably facilitating the stabilization of dispersions of perfluorocarbons in a conventional IL.[50] Nonetheless, physiological safety and health studies among others will have to be carried out to evaluate this possible application. In this work, cytotoxicity studies of FILs have been carried out for the first time, which are of vital importance for this application.

This work is the first step to evaluate the potential of a new and improved generation of oxygen therapeutics containing fluorinated ionic liquids. With this aim, a study of the thermophysical and thermodynamic properties of fluorinated ionic liquids, specifically dynamic viscosity, density, and refractive index, was carried out. All fluorinated ionic liquids have a viscosity higher than water and PFCs. Therefore, the addition of FILs to a PFC emulsion will always increase viscosity. Care should be taken in choosing a specific FIL because it runs the risk of promoting the dispersion of fluorinated compounds in the water. On the other hand, the density of PFCs in oxygen therapeutic emulsions, approximately 1.5, is similar to that of FILs, making the latter good candidates for this application. Figures 3 and 5 suggest that $[EtMepy][(PFBu)SO_3]$ may be a good candidate due to its capacity to increase the viscosity of PFC-based emulsions and its similarity of density to that of PFCs. However, this fluorinated ionic liquid presents the lowest value of molar free volume (calculated from density and refractive index). Nevertheless, the fluorinated domains of these emulsions are expected to increase with the addition of $[EtMepy][(PFBu)SO_3]$, increasing the capacity for solubilizing respiratory gases.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information for this article contains the experimental section (materials, methods and procedures) and the experimental data (thermal properties, density, dynamic viscosity, refractive index and ionic conductivity) for the eight fluorinated ionic liquids studied in this work. The fit of the density, refractive index, fluidity and ionic conductivity for the FILs selected and the molar volume, molar refraction and free volume calculated from experimental results also appear. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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