Understanding the phase and solvation behavior of fluorinated ionic liquids

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ABSTRACT

Fluorinated ionic liquids (FILs) are defined as molecules having fluorinated tags equal to or longer than 4 carbon atoms in the anion and/or cation structures. They present nanosegregated domains making them *3-in-1* solvents with exceptional properties, including an attractive solubility power. This work is an important contribution towards understanding the current research on the phase behavior of FILs, which may be used as task-specific materials for industrial applications. An overview of the main works published in the last two decades is presented, concerning gas solubility in FILs, the application of membranes to improve the gas absorption in FILs, and the use of modeling approaches to ease the application of FILs in gas capture and separation processes, with emphasis on the relationship between the structural properties and their performance. Contributions concerning the liquid-liquid and solid-liquid equilibria behavior of FILs, including the liquid-liquid equilibria (LLE) of FILs in water and perfluoroalkanes, and the solid-liquid equilibria (SLE) of solid FILs in water and mixtures of FILs are also presented. Regarding the absorption of gases in FILs, a careful analysis of the published works reveals that: (1) an optimal density of fluorine atoms in FILs structure is required to positively impact the absorption of different gases, (2) the functionalization of membranes can be also a useful method to improve the performance in separation processes, and (3) modeling tools can ease the screening of the features that promote the absorption of gases by FILs. The study of FILs LLE showed a rich phase behavior with water and perfluoroalkanes and the enhanced surfactant power of FILs, which is highly dependent on the length of the hydrogenated and fluorinated side chains. Finally, studying the SLE of FILs mixtures allowed the formation of deep eutectic systems that enlarges the applicability of FILs.

Contents

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1. Introduction

Ionic liquids (ILs) are well-known compounds used in the most diverse fields of research as improved and "greener" solvents [1–9]. They have gained high popularity because they can be designed by choosing different combinations of cations and anions, allowing the control of their thermophysical and thermodynamic properties, toxicity, and biocompatibility [10–13]. Therefore, their environmental and health impact can be positively manipulated, as well as their molecular interactions, maintaining the desired characteristics for a specific ending. In general, ILs have highly attractive properties such as low flammability, wide liquid range, high thermal stability, easiness in recycling, insignificant vapor pressure at room temperature, and tunable toxicity, compared to conventional organic solvents [10–13]. Hence, the study of phase equilibria of ILs mixed with other substances such as other ILs, conventional solvents (water, organic solvents, fuels, hydrocarbons, etc.), and solutes (gases, salts, biomolecules, among others) is of great importance from a technological point of view [5–8,14–21]. Of particular interest are studies concerning phase equilibria of ILs with other substances leading to separation and extraction processes, which can be applied in the most diverse areas, from the chemical to the pharmaceutical and biomedical industry [8,15,22]. There are several excellent reviews regarding applications of ILs and how to model them, and the reader is referred to them for further details [23–28].

Fluorinated ILs (FILs) are a specific family of ILs structurally composed of anions and/or cations with fluorinated tags equal to or longer than 4 carbons [19,29,30]. This feature ensures that FILs have enhanced properties due to the nanosegregation into three different domains: one polar (negative and positive charges) and two non-polar (hydrogenated and fluorinated) [31–35]. Therefore, FILs can solubilize solutes with three different natures, guaranteeing an enhanced solubilization power relative to conventional ILs. This review is focused on the research that has been done since the 2000s, regarding the phase equilibria and other key properties of FILs [19,29,30], as well as a critical evaluation of the lessons learned from these studies and the remaining gaps. To our knowledge, this is the first review focused on this family from the phase equilibria and thermodynamic perspective.

FILs have common characteristics with conventional fluorinated compounds and can be used as a potential substitute in the fields where these compounds play an important role: from industrial processes to biomedical devices [36–39]. The physical and chemical properties of traditional fluorinated compounds include low surface tension, high surfactant power, the high solubility of gases, self-assembling into colloidal structures, and chemical and biological inertness [40–43]. These characteristics are related to the presence of carbon–fluorine bonds, which are the strongest, making these compounds indestructible substances [40–43]. While a class of innocuous fluorinated compounds are applied in different

biomedical proposes [22,36,37,44], other substances such as the perfluoroalkyl acids (PFAs) and the fluorinated greenhouse gases (F-gases), may pose health and environmental issues [39–43,45]. On the one hand, PFAs have a high environmental impact due to their bioaccumulation and persistency, contributing to the contamination of water, soils, biota, and food [39–43,45–49]. On the other hand, F-gases, mostly hydrofluorocarbons (HFCs), have a high global warming potential (GWP) and long atmospheric lifetime [39–43,45–49]. Therefore, these handicaps led to the exclusion of several fluorinated compounds from the market and to the need for promptly replacing them.

This review covers the most significant literature regarding the phase equilibria of FILs with other substances obtained by experimental and modeling approaches. The work is divided into four major sections. First, an overview of the FILs exceptional properties that differentiate them from the conventional ILs and traditional fluorinated compounds is presented. Then, the VLE of different gases with FILs is analyzed in three main groups: (i) the direct measurement of the solubility of gases, such as carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), hydrogen (H_2), and F-gases, in FILs; (ii) the use of membranes as a platform to improve the absorption of gases in FILs; and (iii) the use of molecular modeling approaches to predict the VLE behavior of gas + FILs systems. The review also includes the few works found in the literature related to the LLE and SLE behavior of FILs, that have high significance for their potential applications. The last section focuses on the analysis and discussion of the main findings related to the phase behavior of FILs, and the remaining challenges associated with the experimental and theoretical studies of these systems. The nomenclatures and structures of the compounds included in this work can be found in Table 1.

2. Effect of the fluorinated domains on selected properties of fluorinated ionic liquids

FILs have exceptional properties that can be enhanced through the fine-tuning of their three nanosegregated domains (polar, hydrogenated, and fluorinated) [29–31]. This has a clear effect on their rich phase behavior as well as their environmental impact [31,32].

The use of FILs for several applications is limited by their liquid range, which is defined by their phase behavior and thermal stability. Since this is a direct result of the constitution of the FILs, a careful selection of the cations and anions is needed, according to the desired application. While the extension of the fluorinated domain of the anion increases the melting temperature without affecting the thermal stability, the extension of the hydrogenated domain in the family $[C_nC_1Im][C_4F_9SO_3]$ leads to an increased melting temperature and a decreased thermal stability [33–35,50,51]. Moreover, higher thermal stability is achieved when carboxylate anions are substituted by sulfonate anions [19,31–33,50,52]. The
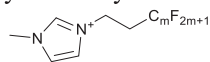
Table 1

Structure and nomenclatures of the cations and anions composing the ionic liquids, the fluorinated gases, and the perfluorocarbons mentioned in this study.
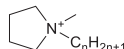
Cations
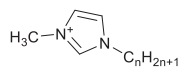
$[C_nC_1Im]^+$, n = 2, 4, 5, 6, 8, 10, 12

1-alkyl-3-methylimidazolium

$[C_2(C_mF_{2m+1})C_1Im]^+$, m = 4, 6

1-methyl-3-ethyl(perfluoroalkyl)imidazolium

$[C_nC_1pyr]^+$, n = 2,4

N-alkyl-N-methylpyrrolidinium
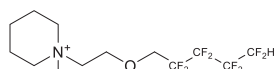
$[C_{2(O)1(4F)}C_1pip]^+$

N-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-
N-methylpiperidinium
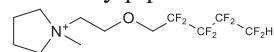
$[C_{2(O)1(4F)}C_1pyr]^+$

N-((2,2,3,3,4,4,5,5-octafluoropentoxy)ethyl)-
N-methylpyrrolidinium
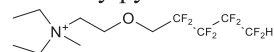
$[N_{2212(O)1(4F)}]^+$

N,N-diethyl-N-methyl-N-((2,2,3,3,4,4,5,5-
octafluoropentoxy)ethyl)-N-ammonium

$[C_2C_1py]^+$

1-ethyl-3-methylpyridinium
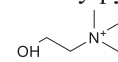
$[N_{1112(OH)}]^+$

Cholinium
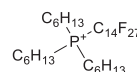
$[P_{66614}]^+$

Trihexyltetradecylphosphonium
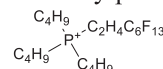
$[P_{4442(6F)}]^+$

Tributyl-(3,3,4,4,5,5,6,6,7,7,8,8,8-
tridecafluorooctyl)-phosphonium
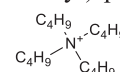
$[N_{4444}]^+$

Tetrabutylammonium
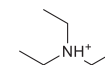
$[N_{0222}]^+$

Triethylammonium

Anions

$[C_mF_{2m+1}SO_3]^-$, m = 1, 4, 6, 8

Perfluoroalkylsulfonate

$[C_mF_{2m+1}CO_2]^-$, m = 4, 7, 8

Perfluoroalkylcarboxilate

$[BF_4]^-$

Tetrafluoroborate

$[SCN]^-$

Thiocyanate
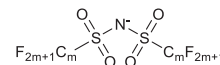
$[N(C_mF_{2m+1}SO_2)_2]^-$, m = 1, 2, 4

Bis(perfluoroalkylsulfonyl)imide
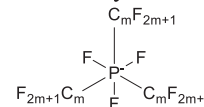
$[C_mFAP]^-$, m = 2, 4

Tris(perfluoroalkyl)trifluorophosphate

$[PF_6]^-$

Hexafluorophosphate

$[C_1CO_2]^-$

Acetate

Fluorinated Gases

R-32 (CH$_2$F$_2$)

Difluoromethane

R-14 (CF$_4$)

Tetrafluoromethane

R-125 (C$_2$HF$_5$)

Pentafluoroethane
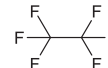
R-116 (C$_2$F$_6$)

Hexafluoroethane

R-134a (C$_2$H$_2$F$_4$)

1,1,1,2-Tetrafluoroethane

R-218 (C$_3$F$_8$)

Octafluoropropane

R-23 (CHF$_3$)

Trifluoromethane

R-143a (C$_2$H$_3$F$_3$)

1,1,1-Trifluoroethane

R-152a (C$_2$H$_4$F$_2$)

1,1-difluoroethane

R-1234yf (C$_3$H$_2$F$_4$)

2,3,3,3-Tetrafluoropropene

Perfluorocarbons

C$_8$F$_{18}$

Perfluorooctane
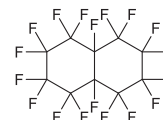
C$_{10}$F$_{18}$

Perfluorodecalin

thermodynamic properties are also influenced by the size of both non-polar domains; the increment of the hydrogenated chain decreases the FILs density, while the increment of the fluorinated chain increases it [19,33,50,51]. Furthermore, the functionalization of the imidazolium cations with hydroxyl groups increases the FILs density [52], which is also increased when sulfonated-based anions are used [19,50,52]. Viscosity increases with the increment of both hydrogenated and fluorinated side chain length in FILs containing imidazolium cations with hydroxyl groups, and with bulkier cations and sulfonate-based anions instead of carboxylate-based ones [19,33,50–52]. The increment of hydrogenated and fluorinated side chain length decreases the ionicity and increases the molar free volume of FILs [19,33,50–52].

FILs are surface-active compounds and their surface tension allied to their surfactant behavior makes them unique compounds to improve the solubility of different compounds and form different structures in aqueous solutions [32,34,50,52–55]. In the [C$_n$C$_1$-Im][C$_4$F$_9$SO$_3$] family, the increment of the hydrogenated chain up to 8 carbons ([C$_8$C$_1$Im][C$_4$F$_9$SO$_3$]) leads to a decrease in the surface tension values, and for longer hydrogenated chains, that seize more space at the surface, higher surface tension values are found in the literature [34].

FILs based on imidazolium, pyridinium, and cholinium cations have complete miscibility in water [53]. The study of the FILs aggregation behavior using their critical aggregation concentrations revealed the presence, in some cases, of up to four self-assembled structures which can be the main reason for the total water miscibility of FILs [53]. The surfactant feature of these compounds is supported by their low critical micellar concentration (CMC) values. Although the CMC value decreases with the increment of both hydrogenated and fluorinated side chains, the presence of four carbon atoms in the anion is sufficient for an improved surfactant behavior in comparison to traditional surfactants with eight carbon atoms [52–55]. Additionally, the cation nature has a slight influence on the aggregation dimension, since both pyridinium and tetrabutylammonium have lower CMC values than pyrrolidinium, cholinium, and imidazolium [52–55].

A detailed investigation on the hydrogen ability and polarizability of FIL in water has shown that the increment of the fluorinated

chain limits the influence of water and maintains their hydrogen bond acceptability [56]. Then the FILs self-aggregation will induce the water aggregation in a polar network that increases and becomes closer to the FIL polar domain [56].

3. Toxicity and environmental impact of fluorinated ionic liquids

Regarding the environmental impact of FILs, cytotoxicity is a critical parameter to evaluate their use for a variety of applications. According to the works published in the literature, this parameter is highly dependent on a variety of factors, such as the organism where tests are performed and the exposure time [19,57–60]. The cytotoxicity of several FILs has been evaluated in different human cell lines (human colon carcinoma cells (Caco-2), human hepatocellular carcinoma cells (HepG2), human umbilical vein cell line (EA.hy926), and spontaneously immortalized human keratinocyte cell line (HaCaT)) [19,57,58]. It was obtained that FILs with short hydrogenated and fluorinated side chains, and with cholinium and pyrrolidinium cations, have clearly reduced their toxicities compared to traditional fluorinated compounds [19,57,58], which is even more pronounced in the ones containing a perfluoropentanoate anion [19,57,58]. However, the elongation of the hydrogenated or fluorinated side chains leads to a higher charge delocalization and lipophilicity, resulting in a higher permeation of cellular membranes, and consequently higher cytotoxicity [19,57]. Furthermore, hemolytic tests reveal that red blood cell lysis only occurs at high FIL concentrations [59]. Herein, the lowest hemolytic rates were achieved with both imidazolium and pyridinium cations conjugated with the perfluoropentanoate anion [59]. Although the limited FILs solubility in the tested medium hampers a proper analysis about the effect of the hydrogenated and fluorinated side chain elongation, it was clear by the profiles achieved that the hemolysis accomplished higher levels in long chain-based FILs at similar or reduced concentrations than short chain-based ones [59].

FILs have an eco-friendly nature and have low acute aquatic hazards [60]. The ecotoxicological screening in *Lemna minor* plant, *Daphnia magna* crustacean, and *Vibrio fischeri* bacterium reveals that FILs based on cholinium and functionalized imidazolium cations have the lowest toxicities. Besides, FILs conjugated with the perfluoropentanoate anion generally induce less toxicity than the sulfonate equivalent [60]. For the Gram-negative *Pseudomonas*

stutzeri, the inhibition of the bacterial growth was only achieved at very high FIL concentrations, the cholinium cation was shown to be the least toxic, especially when conjugated with the perfluoropentanoate anion, and the increment of either hydrogenated or fluorinated alkyl generated more ecotoxic FILs [60].

The biodegradation is other key parameter to access the environmental danger of the FILs. The microbial degradation of some FILs was studied, and a lack of microbial degradability was found for compounds composed of imidazolium cations with short-alkyl chains [60]. Increased biodegradation is found for pyridinium cation, and the highest microbial degradability was obtained to the cholinium cation [60]. Both $[C_4F_9SO_3]^-$ and $[C_4F_9CO_2]^-$ have shown resistance to biodegradation and new alternatives must be find to solve this environmental issue [60]. Even though the strong C-F bonds present in the anions make FILs highly inert compounds, in one hand the resistant to biotic and abiotic degradation raises concerns about their persistence in the environment and in other hand their degradation can generate even more toxic intermediate compounds. Therefore, strategies to overcome the lack of biodegradability of FILs must be found to enable the usage of FILs in their potential applications. This will be further discussed in this work concerning the phase equilibria behavior of FILs (Section 6).

4. Gas solubility in fluorinated ionic liquids

4.1. Solubility of carbon dioxide in fluorinated ionic liquids

One of the main features of FILs is their ability to solubilize gases, and a great amount of work has focused on the solubility of CO_2 in FILs as a way to capture it, given its relevance in the context of reducing CO_2 emissions. Baltus *et al.* [61] were the first to report the solubility of CO_2 in the $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$. A Henry constant ($H_C$) of 0.45 ± 0.1 MPa was obtained at 298.15 K, [61] and later corrected to 0.6 ± 0.1 MPa [62]. Muldoon *et al.* [63] later measured the solubility of CO_2 in $[C_2(C_4F_9)C_1Im][N(CF_3SO_2)_2]$ and obtained a H_C almost five times greater than that obtained by Baltus and co-workers [62] for $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$, showing that an increment in 2 carbons of the fluorinated side chain of an imidazolium cation highly favored the solubility of CO_2 (lower value of H_C). Muldoon *et al.* [63] measured solubility in $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$ obtaining a H_C value of 2.73 ± 0.02 MPa at 298.15 K, which is close to the value for $[C_2(C_4F_9)C_1Im][N(CF_3SO_2)_2]$, 2.84 ± 0.01 MPa (see Fig. 1). Hou *et al.* [64] also determined the absorption and diffusivity of CO_2 in $[C_2(C_4F_9)C_1Im][N(CF_3SO_2)_2]$ obtaining a H_C of 3.1 ± 0.2 MPa at 298.15 K [64]. As can be seen in Fig. 1, this value is identical to the results obtained by Muldoon *et al.* [63] agreeing within 4%. Later on, Almantariotis *et al.* [65] measured the CO_2 uptake by $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$ resulting in a H_C value near to the one obtained by Muldoon and co-workers, [63] agreeing in 3% (Fig. 1). The large difference in the H_C obtained from different authors derives from the use of different experimental methods; hence, care must be taken when selecting the method.

Therefore, the introduction of a fluorinated alkyl chain in the imidazolium cation increases the ability to absorb CO_2. However, it reaches a point that an increment of the fluorinated tag does not significantly increase the uptake of CO_2 by FILs [65]. It is important to point out that the comparison with analogous non-fluorinated FILs demonstrated that the presence of a fluorinated side chain significantly increases the solubility of CO_2 [61–65]. Almantariotis *et al.* [65] used molecular simulations to explain the molecular mechanism of solvation of FILs, concluding that CO_2 is solvated near the charged domains, but also close to the cationic fluorinated chain, increasing the areas of absorption.
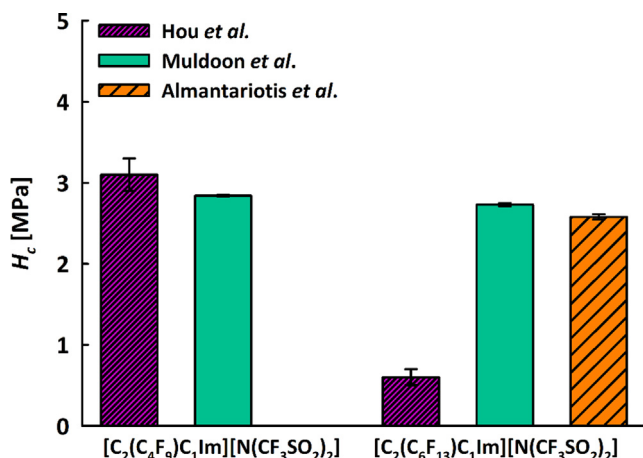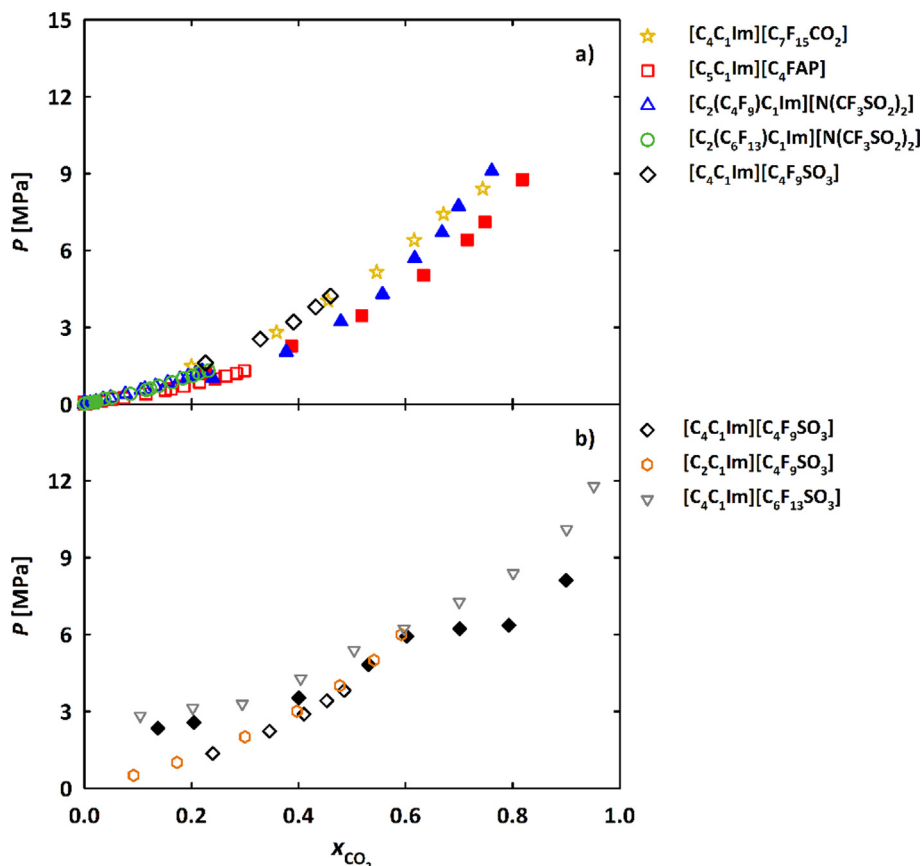

Fig. 1. Comparison of H_C for CO_2 in FILs with cationic fluorinated tags at 298 K. The values of Hou *et al.* are from [64] for $[C_2(C_4F_9)C_1Im][N(CF_3SO_2)_2]$, and [62] for $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$, Muldoon *et al.* from [63]; and Almantariotis *et al.* from [65]. Adapted from references [62–65].

Fig. 2. Solubility data (from literature) of CO_2 in FILs at a) 333.15 K and b) 313.15 K. The stars, squares, and upward-pointing triangles up refer to the work of Muldoon *et al.*, [63] where two techniques were used for high (filled symbols) and low (empty symbols) pressures. The empty circles refer to data of Muldoon *et al.* [63] and the filled circles of Almantariotis *et al.* [65]. The empty diamonds represent the data of Zhou *et al.* [67] and the filled diamonds of Hong *et al.* [66]. The hexagons and downward-pointing triangles are from references [68] and [69], respectively. Adapted from references [63,65–69].

As depicted in Fig. 2, the solubility of CO_2 in $[C_2(C_4F_9)C_1Im][N$ $(CF_3SO_2)_2]$, $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$, $[C_4C_1Im][C_7F_{15}CO_2]$, $[C_5C_1Im][C_4FAP]$, and $[C_4C_1Im][C_4F_9SO_3]$ at 333.15 K [63,66,67], is similar for all the FILs, with $[C_5C_1Im][C_4FAP]$ presenting the highest solubilization capacity, followed by the FILs with fluorinated cations. The FILs with less ability to solubilize CO_2 are the ones with linear fluorinated anions. The FIL with a bulky anion showed higher CO_2 solubilization capacity than the ones with linear anions, indicating that the number and disposition in the space of the fluorine atoms are two factors influencing the gas solubility. It is important to underline the similarity of the values for $[C_4C_1Im]$ $[C_7F_{15}CO_2]$ and $[C_4C_1Im][C_4F_9SO_3]$, which can indicate that the sulfonate functional group might have a positive effect on the solubility of CO_2 or the fluorinated chain with seven carbons diminish the solubility of CO_2.

In order to show the effect of increasing the linear fluorinated chain of the anion on the CO_2 solubility, Fig. 2b, showcases a comparison between the solubility of CO_2 in $[C_2C_1Im][C_4F_9SO_3]$, $[C_4C_1Im][C_4F_9SO_3]$, and $[C_4C_1Im][C_6F_{13}SO_3]$ [66–69]. While the increment of the hydrogenated chain from 2 carbon atoms ($[C_2C_1Im][C_4F_9SO_3]$) to 4 carbon atoms ($[C_4C_1Im][C_4F_9SO_3]$) does not change CO_2 solubility, the increment of the fluorinated alkyl chain of the anion from 4 carbon atoms ($[C_4C_1Im][C_4F_9SO_3]$) to 6 carbon atoms ($[C_4C_1Im][C_6F_{13}SO_3]$) slightly reduces the gas solubility. Therefore, similarly to the cations, there is a point at which the increase of fluorination content of the anion does not favor the solubility of CO_2. This behavior was also observed by Raveendran and Wallen [70] when studying the solubility of CO_2 in fluorocarbons using computational methods, and discussed by Muldoon *et al.*,

[63], inferring that an optimum density of fluorine atoms is required to have an ideal CO_2-philicity.

4.2. Solubility of oxygen, nitrogen, and hydrogen in fluorinated ionic liquids

To the best of our knowledge, only three works reported the direct solubility of O_2, N_2, and H_2 in FILs [68,71,72]. Watanabe *et al.* [68] measured the solubility of these three gases in $[C_4C_1Im][C_4F_9SO_3]$ at 323.15 K, as presented in Fig. 3a. $[C_4C_1Im]$ $[C_4F_9SO_3]$ has a higher affinity to O_2, followed by N_2 and H_2, with selectivity values (determined from the H_C for each gas) for the separation of CO_2/O_2, CO_2/N_2, and CO_2/H_2 of 8, 6, and 22, respectively [68]. These results highlight this FIL as a great candidate for gas capture and separation processes. Vanhoutte *et al.* [71] studied the solubility of O_2 at 298.15 K in FILs based on $[C_{2(O)1(4F)}-C_1pip]^+$, $[C_{2(O)1(4F)}C_1pyr]^+$, and $[N_{2212(O)1(4F)}]^+$) cations and on the $[N(CF_3SO_2)_2]^-$ anion, as well as in $[C_4C_1pyr][C_8F_{17}CO_2]$ (Fig. 3b). The fluorination was shown to significantly increase the solubility of O_2, being five times higher than that of the corresponding non-fluorinated IL [71]. Moreover, the solubility of O_2 is higher in the FIL based on $[C_{2(O)1(4F)}C_1pyr]^+$, followed by $[N_{2212(O)1(4F)}]^+$ and $[C_2$ $_{(O)1(4F)}C_1pip]^+$. The FIL $[C_4C_1pyr][C_8F_{17}CO_2]$ has the lowest O_2 absorption. Kang *et al.* [72] measured the N_2 solubility in phosphonium-based FILs at 303.15 K (Fig. 3b) and observed that increases by incrementing the anionic fluorinated chain: $[C_4F_9SO_3]^- < [C_6F_{13}SO_3]^- < [C_8F_{17}SO_3]^-$ and $[C_4F_9CO_2]^- < [C_8F_{17}CO_2]^-$. This increment is more significant from $[C_4F_9SO_3]^-$ to $[C_6F_{13}SO_3]^-$ than from $[C_6F_{13}SO_3]^-$ to $[C_8F_{17}SO_3]^-$. The same
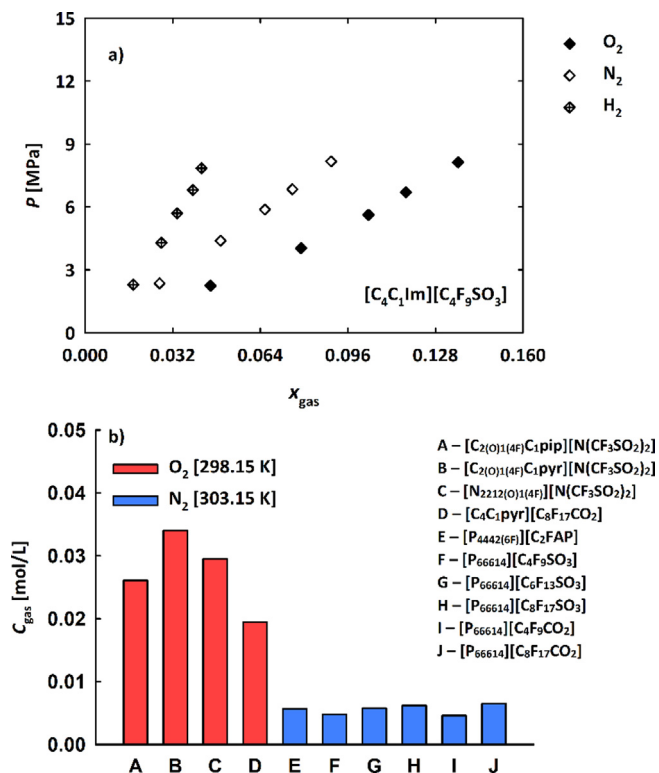
Fig. 3. Solubility of O_2, N_2, and H_2 in FILs at a) 323.15 K [68] and b) atmospheric pressure [71,72], from literature data adapted from references [68,71,72].

can be concluded by the similar uptake of N_2 by $[P_{4442(6F)}][C_2FAP]$ (with a cationic fluorinated chain of 6 carbons atoms and a bulky fluorinated anion) and $[P_{66614}][C_6F_{13}SO_3]$.

4.3. Solubility of fluorinated greenhouse gases in fluorinated ionic liquids

As mentioned, most of the studies on gas solubilization in FILs have focused on CO_2. However, the investigation of less common greenhouse gases (GHGs), such as the fluorinated gases (F-gases), is still scarce, although clearly relevant. These F-gases have high GWP and their emission into the atmosphere must be avoided. Most of the research on the absorption of HFCs, such as R-32, R-125, R-134a, R-23, R-143a, and R-152a, in ILs is focused on imidazolium- and pyridinium- based ILs containing the anions $[BF_4]^-$, [73–78] $[PF_6]^-$, [73–75,78,79] $[N(CF_3SO_2)_2]^-$, [75,76,80–84] and $[CF_3SO_3]^-$ [75,77,85]. Additionally, some authors have focused on phosphonium-based ILs [86,87]. These studies showed that the hydrogen–fluorine interactions established between the ILs and the HFCs lead to different solubilization degrees in each IL-HFC pair. A positive correlation was found between the presence of fluorine atoms in the cations and anions of the ILs and the solubilization of F-gases, at least up to a certain fluorination degree [74,76,88,89]. Additionally, the chain length/volume and dipole moment of F-gases, which are related to their structures and fluorination degree, were also shown to strongly affect solubilization [90]. By changing the constitution of each IL and the operational conditions (e.g., temperature and pressure) it is possible to develop separation processes where the solubilization of one gas is favored in relation to other gases in a mixture, hence, increasing the selectivity. Therefore, ILs have been investigated for the separation of azeotropic HFC refrigerant mixtures, such as R-410A (50 wt% R-125 + 50 wt% R-32) [84] and of blends of HFCs with other gases [91].

Regarding FILs investigation for the solubilization of F-gases, Sosa and co-workers [84] compared the solubilization of the HFCs R-32, R-125, and R-134a in imidazolium-based ILs containing $[C_1CO_2]^-$, $[CF_3SO_3]^-$, and $[N(CF_3SO_2)_2]^-$ anions with that obtained in imidazolium- and pyridinium-based FILs containing $[C_4F_9CO_2]^-$ and $[C_4F_9SO_3]^-$ anions. Their work demonstrated the relevance of the fluorination of the anions of FILs and the nanosegregated domains for the establishment of FIL-gas interactions and increasing gas solubility.

To circumvent the unfavorable properties of some FILs, such as the toxicity, poor biodegradability, high viscosity, high melting temperature of those with long fluorinated alkyl side chains, and high production costs, deep eutectic solvents (DESs) are emerging as an alternative. Despite having different chemical properties from the ones of ILs, they share some physical properties such as high tuneability, low vapor pressure, and non-flammability [92]. Some authors have studied the solubility of HFCs in DES prepared from ILs, but no higher solubilities were determined when compared with the corresponding ILs [89,93]. Nevertheless, Castro and co-workers [93] prepared new DES by mixing FILs with high melting points, based on cholinium, imidazolium, or tetrabutylammonium cations, with 4-carbon perfluoroalkyl acids, showing the advantages of the properties of FILs in the liquid state at a wider range of temperatures for the solubility of a variety of HFCs compared to traditional ionic liquids [93].

4.4. Molecular modeling of gas solubility in fluorinated ionic liquids

The great diversity of ILs that can be synthesized by different cation/anion combinations and by different functionalization makes their fully experimental characterization almost an impossible task. This has urged the use of theoretical tools to predict and model ILs to fasten the determination of their properties and the characterization of their mixtures. A rising number of publications have been released concerning the implementation of theoretical methods to carry out the characterization of the behavior of different gases in ILs and DESs [5–7,17,94–97]. In this review, we focused our attention on the works that have been published related to FILs.

Almantariotis *et al.* [65] carried out molecular simulations of $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$, searching for a solvation mechanism to explain the solubilization of CO_2. Sistla *et al.* [95] computed the solubility parameters of several FILs through molecular simulations. The prediction of 210 ILs solubility parameters was obtained and compared with the ones of CO_2, concluding that the fluorinated anions and phosphonium cations favor the capture and separation of CO_2 [95].

Atomistic force field methods are of great relevance to clarify the molecular features and local structure of ILs, elucidating mechanisms of ILs behavior that sometimes cannot be explained by experimental methods. However, it is a time-consuming approach and other tools based on correlative methods, hybrid quantum chemical/statistical thermodynamics, and molecular-based equations approaches have gained importance. Recently, Liu *et al.* [98] proposed an ionic polarity index parameter based on quantum chemical methods to correlate the CO_2 solubility in ILs. The authors presented a useful strategy to pre-screen possible cations and anions to design ILs with high CO_2-philicity [98]. Several works have focused, with the support of modeling approaches, on the development of technologies to mitigate the environmental impact of F-gases [84,90,93,99]. A COSMO-based/Aspen Plus methodology was successfully employed to evaluate the performance of $[C_2C_1Im][C_4F_9SO_3]$, $[C_2C_1Im][C_8F_{17}SO_3]$, $[C_2C_1Im][C_4F_9CO_2]$, $[C_2C_1Im][N(C_4F_9SO_2)_2]$, $[C_2C_1py][C_4F_9SO_3]$, $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$ and $[C_2(C_6F_{13})C_1Im][N(C_2F_5SO_2)_2]$ as HFCs (R-32 and R-134a) absorbents in a commercial packing column at process scale.

ILs with shorter fluorinated chains were demonstrated to have the best thermodynamic performance for HFC capture. The longer FILs have a higher viscosity, which results in lower efficiencies because the process is controlled by mass transfer kinetics [99]. Moreover, the absorption of F-gases in FILs [84] and on DESs based on mixtures of FILs and perfluorinated acids [93] have been successfully correlated with the non-random two-liquid (NRTL) model, allowing the implementation of simulation studies to the development of new separation processes.

Equations of state (EoS) have been established as one of the most used ways to predict the phase behavior of gases in FILs. Hong and co-workers [66,69] have used two classical cubic EoS, the Peng-Robinson EoS and the Soave-Redlich-Kwong EoS, to correlate the VLE data of CO_2 in $[C_4C_1Im][C_4F_9SO_3]$ and $[C_4C_1Im]$ $[C_6F_{13}SO_3]$. Zhou *et al.* [67] employed the Krichevsky-Kasarnovsky equation to correlate the experimental data of CO_2, O_2, N_2, and H_2 solubility in the FIL $[C_4C_1Im][C_4F_9SO_3]$. Watanabe *et al.* [68] used the Sanchez-Lacombe EoS to correct the buoyancy effects at high pressures of experimental data of $[C_2C_1Im][C_4F_9SO_3]$ with CO_2 gas system. Among the most used EoS are the molecular-based SAFT approaches, based on Statistical Mechanics, which explicitly consider structural details of the ILs, including the molecular size, shape, and hydrogen bonding formation in the formulation of the equation. The soft-SAFT EoS, proposed by Blas and Vega, [100,101] has been applied in the description of gas behavior in FILs and DESs. Ferreira *et al.* [102] showed a comprehensive analysis of several FILs studied in literature by using soft-SAFT, predicting their CO_2 solubility. Soft-SAFT EoS has also been used to predict the solubilities of atmospheric gases (CO_2, N_2, and O_2) in pyridinium and imidazolium-based FILs conjugated with the $[C_4F_9CO_2]^-$ and $[C_4F_9SO_3]^-$ anions [103]. These works allowed the finding of FILs structural features that favor the solubilization of those gases, using a limited amount of experimental data. Alkhatib *et al.* [97] have successfully applied the soft-SAFT EoS to the screening of potential ILs, including some FILs such as $[C_nC_1Im]$ $[C_4F_9SO_3]$, n = 2,4, and DESs for CO_2 capture by assessing their performance in terms of key process indicators, such as cyclic working capacity, enthalpy of desorption, and CO_2 diffusion coefficient. It was concluded that the majority of ILs have superior performance to capture CO_2 compared with DES. Jovell *et al.* [90] employed the soft-SAFT framework to model the solubility of F-gases, such as R134a, in FILs and DESs based on PFAs. Finally, Ferreira et al. [104] also successfully used the soft-SAFT EoS to infer the solubility of F-gases such as HFCs (R-32, R-125, R-134a) and PFCs (R-14, R-116, R-218) in FILs with different anionic and cationic fluorinated chains.

4.5. Gas separation processes using fluorinated ionic liquids-based membranes

Ionic liquid-based membranes present improved properties for their application in gas separation processes, as has been recently reviewed by Friess *et al.* [105]. Despite the great advantages of using FILs-based membranes for separation processes, they are still poorly explored. Given their relevance, and in order to avoid repetition, in this review, we focus on FILs-based membrane platforms studied for the separation of CO_2, F-gases, and other gases, not considered in reference [105]. Most works are related to gas permeability and selectivity in supported ionic liquid membranes (SILMs), prepared by impregnating a small amount of FIL into a porous membrane. Bara *et al.* [106] were the first ones to apply FILs ($[C_2(C_4F_9)C_1Im][N$ $(CF_3SO_2)_2]$ and $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2])$ into a SILMs configuration, determining the permeation of CO_2, O_2, N_2, and CH_4. at 296 K. Soon after, Pereiro *et al.* [107] studied the single gas permeability,
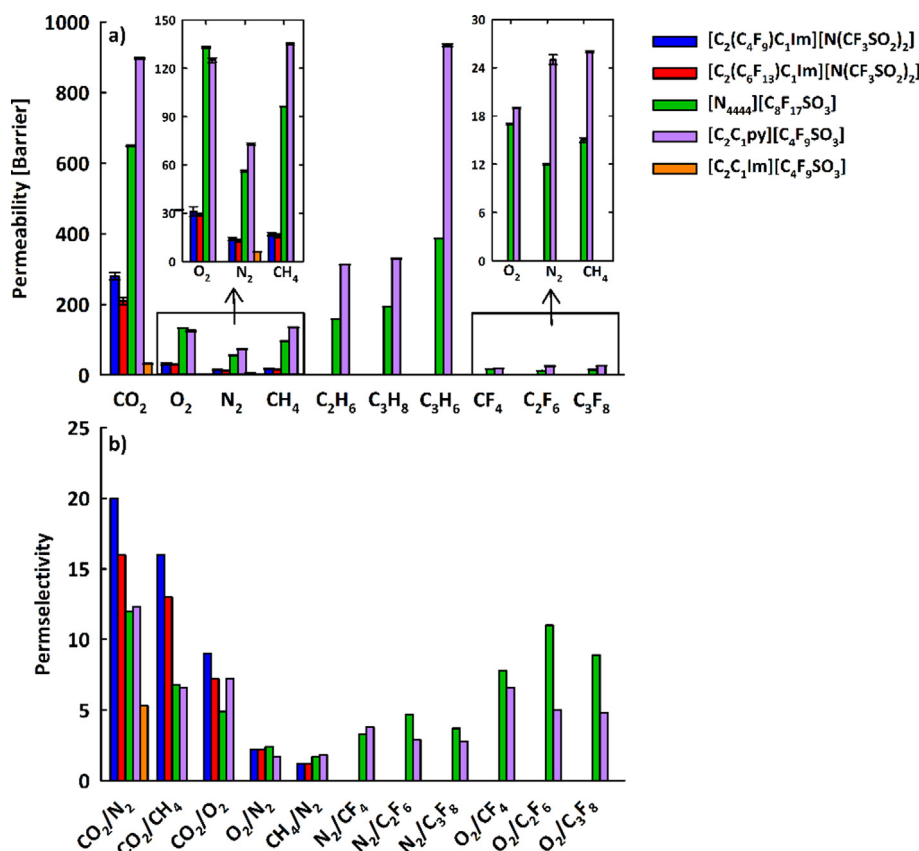

Fig. 4. Comparison of literature data of a) permeability and b) ideal permselectivity of SILMs based on FILs. Adapted from references [106–108].

diffusivity, and solubility of CO_2, O_2, N_2, CH_4, C_2H_6, C_3H_8, C_3H_6, CF_4, C_2F_6, and C_3F_8 in $[N_{4444}][C_8F_{17}SO_3]$- and $[C_2C_1py][C_4F_9SO_3]$-based SILMs at 294 K. Gouveia *et al.* [108] assessed the permeation, diffusion, and solubility of CO_2 and N_2 in $[C_2C_1Im][C_4F_9SO_3]$-based SILM at 293 K. All these permeabilities results are represented in Fig. 4a. $[C_2C_1py][C_4F_9SO_3]$ shows the highest permeation for all gases except O_2). Interestingly, when comparing the permeation of CO_2 in SILMs based on $[C_2C_1py][C_4F_9SO_3]$ and $[C_2C_1Im][C_4F_9SO_3]$, the latter has a permeation 28 times lower than the former, showing that the cation has a huge influence on the permeation of CO_2. Moreover, the fluorination of SILMs is only beneficial for gas permeation until a certain point, similar to what is observed for pure FILs. $[C_2C_1py][C_4F_9SO_3]$ shows higher permeation for almost all gases compared with the $[N_{4444}][C_8F_{17}SO_3]$ and the permeation of CO_2, O_2, N_2 and CH_4 is higher for $[C_2(C_4F_9)C_1Im][N(CF_3SO_2)_2]$ than $[C_2(C_6F_{13})C_1Im][N(CF_3SO_2)_2]$ (Fig. 4a).

The ideal permselectivities of some systems are represented in Fig. 4b [106–108]. The FILs containing a fluorinated cation have a higher selectivity for the separation of CO_2/N_2 and CO_2/CH_4, and therefore are of interest to be used in the separation of CO_2 from industrial flue gases and natural gas. Regarding the F-gases separation performance, $[N_{4444}][C_8F_{17}SO_3]$ has the highest efficiency and thus is useful for the development of technologies to mitigate climate change.

Sood *et al.* [109] studied proton conducting ionic liquids (PCILs), such as $[N_{0222}][C_4F_9SO_3]$ and $[N_{0222}][C_8F_{17}SO_3]$, as dopants of Nafion® membranes. The permeabilities of H_2 and O_2, studied at 293.15 K, using the doped membranes were identical. The authors found out that the FILs form crystalline domains, which sharply increased the gas permeability. This is a result of the diffusion paths formed in the interface between the crystalline PCIL domains and the membrane [109].

Recently, experimental data were collected for the first time regarding the gas permeation properties of HFCs commonly blended with other HFCs or with hydrofluoroolefins (HFOs) [110]. Polymeric membranes functionalized with ILs, the so-called composite ionic liquid–polymer membranes (CILPMs), started to be investigated as an advantageous technology for the separation of HFC blends and of HFC/HFO blends used for refrigeration applications. Pebax membranes functionalized with the ILs $[C_2C_1Im][SCN]$ and $[C_2C_1Im][BF_4]$ were tested for the separation

of the refrigerant R-410A (a near-azeotropic system of the HFCs R-32 and R-125), showing improvement in the permeability towards R-32 and of the R-32/R-125 selectivity, relatively to the neat polymer membranes [111]. Additionally, CILPMs were prepared by functionalizing Pebax membranes with $[C_2C_1Im][SCN]$, $[C_2C_1Im][BF_4]$, $[C_2C_1Im][CF_3SO_3]$, and $[C_2C_1Im][N(CF_3SO_2)_2]$ and were tested for the solubility and permeation of R-32, R-134a, and the HFO R-1234yf [112]. In this study, the CILPM based on $[C_2C_1Im][BF_4]$ showed higher permeability towards the HFCs R-32 and R-134a compared to the HFO R-1234yf, demonstrating to be useful for the separation of HFC/HFO blends [112]. Furthermore, Pebax membranes were functionalized with the so-called ioNanofluids, a suspension of exfoliated graphene nanoplatelets in the FIL $[C_2C_1py][C_4F_9SO_3]$, and used for the separation of the R-410A refrigerant, showing enhanced gas permeation relative to the neat membranes [113].

5. Liquid-liquid and solid-liquid fluorinated ionic liquids phase equilibria

Recently, efforts are being made to evaluate the liquid-liquid equilibria and solid-liquid equilibria, of several families of FILs with water, perfluorocarbons, as well as with other FILs [53–55,114,115]. A summary of the main contributions is presented here.

5.1. Liquid + liquid equilibria of fluorinated ionic liquids with water

The impact of the hydrogenated alkyl chain length increment from 1-butyl-3-methylimidazolium to 1-dodecyl-3-methylimidazolium ($[C_nC_1Im]^+$; n = 4, 6, 8, 10, 12) in FILs containing the $[C_4F_9SO_3]^-$ anion on the phase equilibria is illustrated in the phase diagrams depicted in Fig. 5 [54,55]. The systems show a classic LLE behavior in which temperature has a small impact on the solubility increment. In the presence of the $[C_4F_9SO_3]^-$ anion, the solubility of water in the FIL-rich-phase increases with lengthier hydrogenated alkyl chains [54,55]. The increment of the hydrogenated alkyl chain length induces a better phase separation since it increases the nanosegregation of the nonpolar regions that impels the water aggregates to the polar region of the IL [31,56].
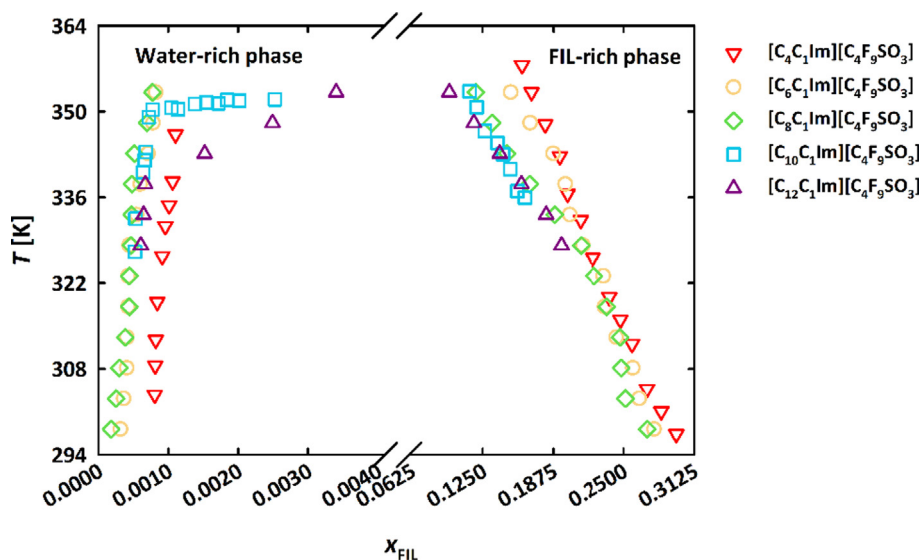
Fig. 5. Liquid-liquid phase diagrams for binary mixtures of $[C_nC_1Im][C_4F_9SO_3]$ + water as a function of FIL molar fraction $[C_4C_1Im][C_4F_9SO_3]$, [55] $[C_6C_1Im][C_4F_9SO_3]$, [54] $[C_8C_1Im][C_4F_9SO_3]$, [54] $[C_{10}C_1Im][C_4F_9SO_3]$, [55] and $[C_{12}C_1Im][C_4F_9SO_3]$ [54]. Adapted from references [54] and [55].
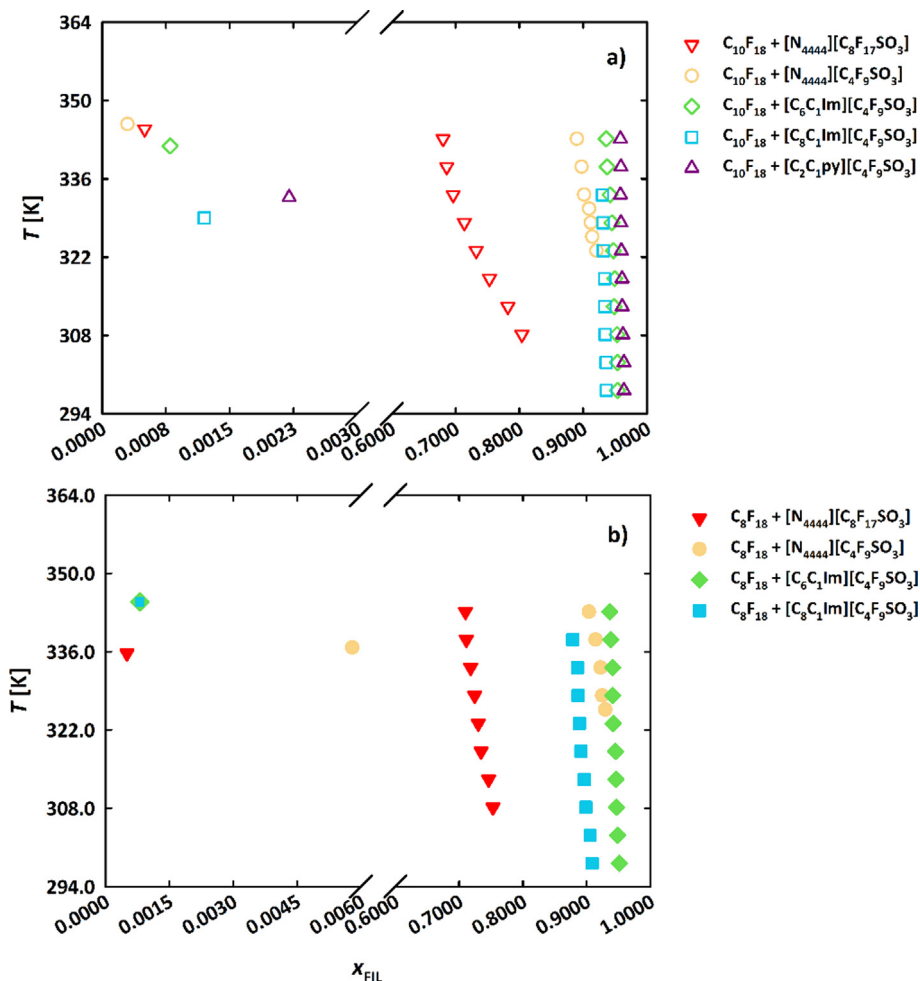
Fig. 6. Liquid-liquid phase diagrams for binary mixtures of a) perfluorodecalin + FILs and b) perfluorooctane + FILs as function of FIL molar fraction. Adapted from reference [114].

As illustrated in Fig. 5, the solubility of FILs in the water-rich-phase is very small and it decreases with the increment of the hydrogenated content up to an alkyl chain of C_6/C_8 in the imidazolium-based FILs, due to the increment of their hydrophobic behavior [54,55]. The opposite behavior was noticed for $[C_{10}C_1Im]$ $[C_4F_9SO_3]$ and $[C_{12}C_1Im][C_4F_9SO_3]$ and can be explained by their higher surfactant behavior and different structural arrangement that lead to an increased solubility in water, caused by a competition between the nonpolar domains of FILs (hydrogenated and fluorinated domains) [34,54,55].

Based on the solubility data obtained from the LLE experiments, several thermodynamic properties were determined to better understand the solvation mechanism of the FIL-water systems, including standard molar Gibbs energy ($\Delta_{sol}G_m^0$), standard molar enthalpy ($\Delta_{sol}H_m^0$) and standard molar entropy ($\Delta_{sol}S_m^0$) of solution [54,55,116–118]. These parameters explain the transfer of one molecule of solute to a theoretical dilute ideal solution and were calculated for all studied systems. In FIL + water systems, the solubility of water was linearly correlated with temperature [54,55]. The calculated molar enthalpies of water in this class of imidazolium-based FILs show that the solubilization process of water in FILs is endothermic [54,55]. Furthermore, the increment of the hydrogenated alkyl chain length also increases the values of these parameters, and major entropic contributions to the solution process were observed for the dodecyl-based cation [54,55]. This behavior can be associated with the higher free volume and

surfactant behavior of the longer chain-based FILs that might boost the solubility of the water in this FIL [19,54,55]. Additionally, the thermodynamic standard properties of solution and solvation, proposed by the standard state model of Ben-Naim, decrease with the increase of the alkyl side chain length of the imidazolium-based FILs [54,55,119,120]. Under the conditions established by Ben-Naim, the Gibbs free energy of solvation is negative, indicating a spontaneous and favorable solvation process, mainly induced by enthalpic contributions [54,55]. Additionally, the results suggest that spontaneous solvation is caused by the existence of interactions between water and FILs [54,55].

5.2. Liquid + liquid equilibria of perfluorocarbons with fluorinated ionic liquids

Martinho *et al.* studied the phase behavior of several families of FILs with traditional PFCs, perfluorooctane (C_8F_{18}), and perfluorodecalin ($C_{10}F_{18}$) [114]. The phase diagrams depicted in Fig. 6 show the classic LLE behavior, with higher solubilities associated with the increment of temperature. The low solubility of the FILs in both $C_{10}F_{18}$ and C_8F_{18}-rich phases is observed; however, the solubility in the PFC-rich phase was only determined at one point, corresponding to lower FIL compositions [114]. The lack of data for higher compositions is due to the high vapor pressure and boiling temperature of the PFCs, which limits a temperature rise until the point in which only one phase is observed. The solubility of

$C_{10}F_{18}$ in the studied FILs increased accordingly to the following trend: $[C_2C_1py][C_4F_9SO_3]$ < $[C_6C_1Im][C_4F_9SO_3]$ < $[C_8C_1Im][C_4F_9SO_3]$ < $[N_{4444}][C_4F_9SO_3]$ < $[N_{4444}][C_8F_{17}SO_3]$, whereas for C_8F_{18} the solubility in $[C_8C_1Im][C_4F_9SO_3]$ is higher than in $[N_{4444}][C_4F_9SO_3]$.

The increment of solubility associated with higher hydrogenated alkyl chains observed in the water-FIL binary systems was also observed for both PFCs in imidazolium-based FILs, but more pronounced in the case of C_8F_{18} [54,55,114]. Yet, the highest solubility of C_8F_{18} and $C_{10}F_{18}$ occurred for $[N_{4444}]^+$ when conjugated with $[C_8F_{17}SO_3]^-$ [114]. In this case, the temperature plays a significant role since up to 323.15 K the solubility is superior for C_8F_{18}, whereas for higher temperatures the behavior shift, and the solubility is higher for $C_{10}F_{18}$ [114]. The most pronounced difference between the solubility of PFCs was achieved with $[C_8C_1Im][C_4F_9SO_3]$ in which the solubility of C_8F_{18} was always superior to that of $C_{10}F_{18}$ [114].

Several thermodynamic parameters can be determined from the LLE diagram depicted in Fig. 6, as detailed in the previous section. In all binary systems, the solubility of PFCs in the FILs-rich phase was linearly correlated with temperature and the molar enthalpies of solution for both PFCs in all tested FILs indicate that their solubilization is an endothermic process [114]. As noticed for FIL-water binary systems, the increment of the hydrogenated alkyl chain length increases the values of these thermodynamic parameters, with the major entropic contribution to the solution process found for the ammonium-based FILs [114]. This can be associated with the higher free volume of the ammonium cation in comparison to the imidazolium and pyridinium cations, which also leads to a higher solubility of the PFCs.

According to the conditions proposed by Ben-Naim [119,120], the Gibbs free energy of solvation is always negative, resulting in a spontaneous and favored solvation process, for which the main contributions are enthalpic [114,119,120]. The local standard enthalpies of solvation indicate that pyridinium and imidazolium-based FILs interact strongly with the PFCs in comparison with the ammonium-based FILs [114]. Since the entropic contribution cannot be neglected, these results imply that the spontaneous solvation is mainly caused by the strong chemical F-F interactions, by the rigid organic fluorine (C-F···F-C) bond between FILs anions and PFCs, and by the hydrogen bonding interactions (C-H···F-C) between the FILs cations and the PFCs [114,121,122].

5.3. Solid + liquid equilibria of fluorinated ionic liquids with water

The solubility of solid FILs in water is essential to define the operational concentration ranges for any industrial application. To our knowledge, the only study available in the literature is the study performed by Teixeira *et al.* [54] for $[C_4C_1pyr]^+$ and $[N_{4444}]^+$ cations both conjugated with the $[C_4F_9SO_3]^-$ anion was studied. Remarkably, the solubility equilibrium took 24 h and 22 days to be achieved for $[C_4C_1pyr][C_4F_9SO_3]$ and $[N_{4444}][C_4F_9SO_3]$, respectively [54]. The solubility at 298.15 K increases in the following order: $[N_{4444}]^+$ (0.0035 in mass fraction) < $[C_4C_1pyr]^+$ (0.0206 in mass fraction). The pyrrolidinium-based FIL has the highest solubility due to its larger alkyl chain length and localized positive charge, whereas the high degree of symmetry of the ammonium cation difficult its solubility in water [54].

5.4. Solid + liquid equilibria of binary mixtures of fluorinated ionic liquids

Besides their unique properties, some FILs have limitations regarding industrial applications, related to their high melting temperatures, fomented by their fluorinated region [33,50,123]. To overcome this situation, eutectic mixtures based on different FILs and fluorine-containing ILs have been investigated. [33,50,115,123]. Although the advantages of these mixtures are notable, the number of studied combinations is very scarce, and the complexity of the observed phase behavior is notorious [115].

The solid–liquid equilibria of these binary mixtures studied by Teles *et al.* [115] revealed the existence of three distinct SLE behavior. The distinct phase diagrams elucidate the complex behavior of FILs mixtures. A quasi-ideal behavior, with a eutectic profile was determined, with eutectic points over the room temperature, and with a partial miscibility close to neat FILs. A negative deviation from the ideal behavior was also observed, in accordance with the formation of solid solution [115].

A very distinct phase behavior was observed by the same authors for $[C_4C_1pyr][N(C_4F_9SO_2)_2]$ + $[C_2C_1pyr][N(C_4F_9SO_2)_2]$ with a total miscibility in the solid phase. Herein, the melting temperature of $[C_2C_1pyr][N(C_4F_9SO_2)_2]$ is reduced by the addition of $[C_4C_1pyr][N(C_4F_9SO_2)_2]$ [115]. This continuous solid solution profile occurs due to the size similarity between the two cations. The solid phase structure was supported by the X-ray diffraction, suggesting the incorporation of $[C_2C_1pyr][N(C_4F_9SO_2)_2]$ in the crystalline structure of $[C_4C_1pyr][N(C_4F_9SO_2)_2]$ [115].

Another very complex behavior was observed with the presence of several polymorphs in the cholinium-based FIL systems [115]. As depicted in Fig. 7, this complex system presents: i) an intermediate compound, identified as A_2B; ii) a region, identified as α *s.s*, indicating a limited solubility of the polymorph, α, and the intermediate A_2B; iii) solid–solid phase transitions between the polymorphs β and γ at 400 K; and iv) an eutectoid reaction after the cooling step of polymorph β, revealing the existence of a solid–solid transition, from the solid polymorph β to the two solid phases correspondent to α *s.s* + A_2B [115].

6. Findings and remaining challenges of FILs phase equilibria determination

As inferred from the previous sections, most of the FILs phase equilibria studies have focused on gas solubility measurements or modeling, with few works dealing with liquid–liquid and solid–liquid equilibria.

Key main conclusions extracted from these studies are that the FILs present a high capacity to: i) solubilize gases due to their surfactant nature; ii) obtain three domains involved in the interaction
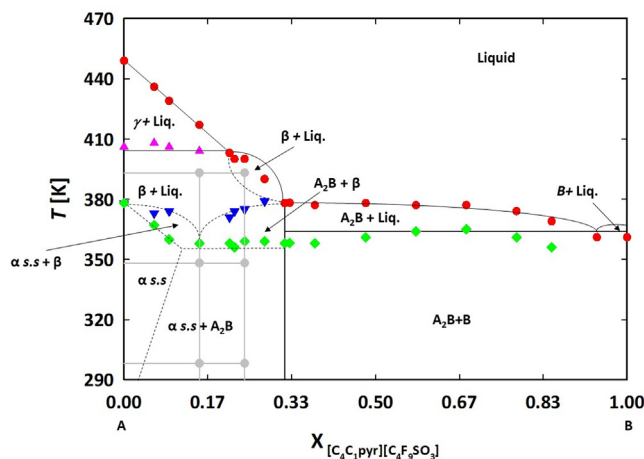
Fig. 7. Solid-liquid phase diagram from the $x[C_4C_1pyr][N(C_4F_9SO_2)_2]$ + (1 - x)[N_{1112}(OH)][$C_4F_9SO_3$], temperature versus mole fraction of [C_4C_1pyr][$N(C_4F_9SO_2)_2$]. Solid–liquid transition (●), eutectoic and eutectic thermal transitions (◆), and solid–solid transitions (▼) and (▲), obtained by DSC. Solid and dashed lines correspond to the interpretation of the diagram. Figure adapted from reference [115].

with solutes; and iii) have a rigid molecular backbone that forms large cavities to accommodate solutes. The presence of perfluoroalkyl chains either in the cation and/or in the anion promotes the solubility of gases, such as CO_2 and HFCs, with the solubility capacity being proportional to the size of the chain until a certain number of carbons (between 6 and 8 carbons atoms in the cases reported). Solubility power is also promoted by the presence of bulky anions, probably as a result of the generation of a structural asymmetry that provides more space to accommodate gas molecules. In the case of F-gases, the volume of the chains and their dipole moment also contribute to the solubilization process.

Despite promoting gas solubility, fluorine atoms may have negative effects on toxicity and biodegradability, as stated in Section 3, and therefore a fine tune of the fluorine content of FILs is needed to increase the benefits/risks ratio. Some new strategies can be followed to increase their biodegradability, such as: i) inserting specific chemical groups (such as esters, amides, hydroxyl, and carboxyl groups) in between the fluorinated chains; and ii) the use of more biodegradable cations, such as cholinium, conjugated with appropriate anions (with up to four carbon perfluorinated chains, for example). The combination of the cholinium cation with the perfluoropentanoate anion has enabled the design of a FIL with negligible toxicity, completely miscible in water, and improved biodegradability [55,58,60].

As highlighted in this work, the use of theoretical tools to predict gas solubility in FILs has been of great relevance to advance in the use of these compounds for several applications. Molecular simulations have provided insights on the mechanisms of solvation and the determination of solubility parameters, easing the study of the gas-philicity of a great number of FILs structural features. Other methods based on correlative and hybrid quantum chemical/statistical thermodynamics approaches, such as the COSMO-based/ Aspen Plus and NRTL models, have been successfully implemented. These models capture the behavior of the absorption of GHGs in different FILs, facilitating the development of separation processes. In this topic, equations of state can be highlighted as the most used method to predict the phase behavior of gases in FILs. Different equations have been applied and have allowed the computation of these complex systems with good agreement with experimental data. The molecular-based soft-SAFT equation of state stands out as the most used equation and is a promising tool to accelerate the actual implementation of FILs for gas solubility applications. The robust and simple way in which the interaction of these complex systems with gases can be modeled enables the accurate prediction of the vapor–liquid behaviors. Additionally, this tool can capture the influence of the structural features of FILs and enables the search for properties that favor the solubilization of gases, such as CO_2 and HFCs. The theoretical models show great benefit to the study of phase behavior, and more time should be invested in this topic to envisage new ILs for gas solubility and other applications.

Considering the high impact of some GHGs on the environment and living organisms, the use of FILs with low toxicity, improved biodegradability, high adsorption capacity, and high selectivity may have a positive environmental impact, with clear benefits when compared to other sustainable options with lower efficiency. In this context, the development of smart and sustainable technologies based on FILs must be considered. For example, as stated in this review, the combination of FILs with membrane technologies would allow reducing the amounts of FILs needed and to increase efficiency, with clear environmental and economic benefits. Other approaches can also be taken to bypass some properties of FILs that hamper their efficient application, such as their viscosity. Therefore, the use of FILs-based eutectic mixtures may be considered.

Three main factors have been shown to influence the LLE behavior of FILs in water, such as their water miscibility, high surfactant behavior, and the presence of three nanosegregated domains. The increment of the hydrogenated chain in the $[C_nC_1Im][C_4F_9SO_3]$ family increases the solubility of water in the FIL-rich phase. The reverse is found for the water-rich phase; solubility decreases with the increasing of the hydrogenated chain up to a certain number of carbon atoms. The further increment of the hydrogenated chain leads to a rearrangement between the nanosegregated domains and consequently to an increase in the solubility of the FIL in water. The study of FILs phase behavior with traditional PFCs highlights that FILs have very low solubility in the PFCs-rich phase. The larger hydrogenated and fluorinated chains increase the solubility of PFCs in the FILs-rich phase. However, the determination of FILs solubility in the PFC-rich phase is hindered by the high vapor pressure and boiling point of the PFCs that severely limits the possible temperature working range. The solid–liquid equilibria behavior of solid FILs in water shows the influence of the cation in the solubility. FILs having bulkier content of fluorine tend to have shorter liquid ranges and the increment of this interval has huge relevance in their industrial applications. The study of the solid–liquid equilibria of FILs mixtures revealed that they can assume a liquid form in a wider interval of temperatures.

The phase diagrams of FILs mixtures are very challenging to determine and evaluate due to the large number of different behaviors found in the few works studied in the literature, which hinders the studies on them. Therefore, it is extremely important to further study liquid–liquid and solid–liquid equilibria of FILs, not only to learn how the fluorination affects their behavior but also to progress in the study of FILs mixtures, creating new opportunities for applications. Moreover, the use of theoretical tools should greatly benefit the still unexplored area of study of LLE and SLE of the highly surfactant FILs with different solvents. The promising applications would vastly benefit from exploring more theoretical methods that can ease the screening of FILs complex properties. Therefore, studies concerning the phase behavior of FILs with compounds that have significant value in the environmental, biomedical, and chemical industries, such as GHGs gases, industrial solvents, pharmaceuticals, refrigerants, etc. are still needed.

7. Conclusions and perspectives

In the last two decades, a vast amount of work has been produced on the phase equilibria of FILs, mostly focused on gas solubility. These studies show that the fluorine content of FILs, up to a certain length, impacts positively the absorption of different gases. However, fluorinated chains with more than 6 carbons do not compensate for the increased toxicity of these FILs. In this sense, outstanding contributions have been published on modeling FILs + gases VLE, showing that this is a powerful method to decrease the time of screening a vast amount of FILs, being highly accurate and useful when only scarce experimental data is available.

The LLE of FILs showed that they have a rich phase behavior in the presence of water. They can be designed to be totally miscible and to have a high aggregation behavior in water, making them enhanced surfactant compounds through an appropriate balance between the hydrogenated and fluorinated side chain length. The LLE of PFCs with FILs show that the mechanism of solvation depends on the length of the fluorinated and hydrogenated chain, and the temperature. Finally, the SLE of FILs mixtures show that different FILs combinations can be tested and introduced as viable options for industrial processes, namely for the substitution of environmentally dangerous compounds, such as methanol or toluene. The formation of eutectic mixtures, which allows FILs to be in a liquid state at a wider temperature range has been already

reported, which is also a great advantage for several industrial applications. However, more work should be done to apply the benefits of this approach to different commercial processes.

The three-nanosegregated domains of FILs are responsible for most of their final performance. In this work, a detailed analysis has been provided on the impact of both cation and anion nature, as well as hydrogenated and fluorinated side chain length in many properties, which directly influences the formation and size of the nanosegregated domains Then, this work demonstrated a structure–activity relationship between FILs structure and properties, easing a future FIL design accordingly to the final application and enabling the manipulation of their properties, such as: thermal and thermophysical properties, surface tension, surfactant behavior, cytotoxicity, and ecotoxicity.

The design of FILs with high surfactant power and aggregation behavior, enabling the formation of self-assembled structures, total miscibility in water, negligible cytotoxicity and ecotoxicity, and ease to regenerate favors their application in fields where greener and biocompatible substances are required. FILs are a sustainable solution for gas capture and separation processes, and for biomedical purposes where the immiscibility of PFCs in water is a major drawback, such as artificial gas carriers and as drug delivery systems.

Considering the great potential of using FILs for gas capture and separation processes, greater efforts must be taken regarding the development of FIL-based membranes to ease the capture and separation of GHGs gases as well as the design and optimization of processes involving them as well as the development of scale-up strategies of promising FILs to facilitate the transfer of these systems from laboratory to industrial scale. On the fundamental side, studies regarding ions dissociation to infer in the phase equilibria of FILs with water and other solvents are still missing in the literature should be carried out to assess its possible role on the performance of FILs for this application.

The selection of biocompatible FILs for biomedical applications is a subject of growing interest. Several FILs with different structures and properties can be designed resulting in specific interactions of FILs with different biomolecules. Therefore, it is of high importance to study FILs interactions with biomolecules. It is also imperative to advance in the studies concerning the development of stable formulations based on FILs and biomolecules. These delivery platforms can be undertaken by inferring the phase equilibria of FILs with excipients of great relevance in the pharma industry. Moreover, it must be initiate *in vivo* studies of FILs formulations, opening the possibility to use FILs as biomaterials.

In conclusion, the detailed study of FILs phase equilibria is a key first step to optimize their use for applications where the changes in phase behavior are critical. The exceptional tuneability of FILs makes them optimal candidates for the design of alternative and sustainable solutions for almost unlimited applications and therefore the study of FILs is an area with great potential and key advances are expected in the next years.

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CRediT authorship contribution statement

Margarida L. Ferreira: Formal analysis, Visualization, Investigation, Writing – original draft. **Nicole S.M. Vieira:** Visualization, Investigation, Writing – original draft. **Paulo J. Castro:** Visualization, Investigation, Writing – original draft. **Lourdes F. Vega:** Methodology, Software, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing. **João M. M. Araújo:** Conceptualization, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Ana B. Pereiro:** Conceptualization, Resources, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The Authors declares that they have no Known Competing Financial Interests or Personnel Relationships that could has appeared to influence the work reported in this paper. I, Ana B. Pereiro: corresponding author of this paper, declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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