

# Phase Equilibria, Diffusivities, and Equation of State Modeling of HFC-32 and HFC-125 in Imidazolium-based Ionic Liquids for the Separation of R-410A

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## Abstract

Growing concerns about the global warming potential (GWP) of hydrofluorocarbons (HFCs) has led to increasing interest in developing technologies to effectively recover and recycle these refrigerants. Ionic liquids (ILs) have shown great potential to selectively separate azeotropic HFC gas mixtures such as R-410A composed of HFC-32 ( $\text{CH}_2\text{F}_2$ ) and HFC-125 ( $\text{CHF}_2\text{CF}_3$ ), based on solubility differences between the refrigerant gases in the respective IL. Isothermal vapor–liquid equilibrium (VLE) data for HFC-32 and HFC-125 were measured in ILs containing fluorinated and non-fluorinated anions using a gravimetric microbalance at pressures ranging from 0.05 to 1.0 MPa and a temperature of 298.15 K. The van der Waals Equation of State (EoS) model was applied to correlate the experimental solubility data of each HFC refrigerant / IL mixture. The solubility differences between HFC-32 and HFC-125 vary significantly depending on the choice of IL. The diffusion coefficients for both HFC refrigerants in each IL were calculated by fitting Fick's law to time-dependent absorption data. HFC-32 has a higher diffusivity in most ILs tested due to its smaller molecular radius relative to HFC-125. Based on the calculated Henry's law constants and the mass uptake for each system, the  $[\text{C}_6\text{C}_{1\text{im}}][\text{Cl}]$  was found to have the highest selectivity difference for separating R-410A at 298.15 K.

## 1. Introduction

Hydrofluorocarbons (HFCs) are a family of refrigerants extensively used in air-conditioning and refrigeration systems. HFCs were developed to replace chlorofluorocarbons that were linked to the depletion of the Earth's ozone layer. HFCs have zero ozone depletion potential (ODP)<sup>1</sup>, but some have high global warming potential (GWP).<sup>2, 3</sup> The Kyoto Protocol of the United Nations Framework Convention on Climate Change (UNFCCC)<sup>4</sup> has recommended the phase-out of HFCs under the Kigali Amendment to the Montreal Protocol.<sup>5</sup> In addition, the EU Regulation No. 517/2014 that mandates the reduction of up to two thirds of the 2010 fluorinated greenhouse gas (GHG) emissions by 2030 has been implemented.<sup>6</sup>

R-410A is a near-azeotropic HFC mixture composed of 50.0 mass % HFC-32 ( $\text{CH}_2\text{F}_2$ , NBPT = 221.3 K) (Normal Boiling Point Temperature) and 50.0 mass % HFC-125 ( $\text{CHF}_2\text{CF}_3$ , NBPT = 224.9 K) that was developed as a replacement for HCFC-22 ( $\text{CHClF}_2$ ) in residential and commercial air-conditioning and heat pump systems.<sup>7</sup> Currently there is no commercial technology available for separation of HFC-32 and HFC-125; therefore, if R-410A cannot be recycled in the future it will have to be incinerated.<sup>8,9</sup> The need for a sustainable process to separate R-410A such that HFC-32 can be used in low-GWP blends with hydrofluoroolefins (HFOs) and HFC-125 can be utilized as a feedstock for future products is critically important considering the pending and new regulations that will limit the use of HFCs.

Ionic liquids (ILs) are of particular interest for absorption-based gas separation processes.<sup>10</sup> These low-melting salts, which are composed of an organic cation, such as imidazolium, pyridinium, and ammonium, combined with either an organic (e.g.,  $\text{HCOO}^-$  and  $\text{CH}_3\text{COO}^-$ ) or an inorganic anion (e.g.,  $\text{Cl}^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ ), can be molecularly designed to selectively increase the solubility of either HFC-32 or HFC-125 for optimal separation of R-410A. Many ILs have a negligible vapor

pressure, which makes them ideal entrainers for gas separation processes because of the minimal loss to the gas phase. ILs provide opportunities to develop new gas separation technologies due to their high chemical and thermal stability with HFCs. While a large number of publications available in the literature focus on the use of ILs for separation and purification of natural gases, such as  $\text{CO}_2/\text{CH}_4$ <sup>11</sup> and  $\text{CO}_2/\text{N}_2$ ,<sup>12</sup> not many reports have been published on the use of ILs for the separation of azeotropic HFC refrigerant mixtures. Shiflett and Yokozeki proposed using ILs to separate R-507 (50 wt % HFC-125 and 50 wt % HFC-143a (1,1,1-trifluoroethane,  $\text{CH}_3\text{CF}_3$ )) and R-404a (44 wt % HFC-125, 52 wt % HFC-143a and 4 wt % HFC-134a (1,1,1,2-tetrafluoroethane,  $\text{CH}_2\text{FCF}_3$ )) when they discovered large differences in the solubility of HFCs in 1-butyl-3-methylimidazolium tetrafluoroborate  $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$  and 1-butyl-3-methylimidazolium hexafluorophosphate  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ .<sup>13</sup> Also, the same authors have investigated the use of  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  as an entraining agent for extractive distillation to separate R-410A into HFC-32 and HFC-125.<sup>14</sup> The separation was simulated using ASPEN Plus™, and resulted in an efficient separation of R-410A into 99 mol% HFC-32 and 99 mol% HFC-125. Additional measurements on HFC-32 and HFC-125 in ILs have been recently measured by Sosa et al., Liu et al., Sousa et al. and Asensio-Delgado et al.<sup>15-20</sup>

The present study aims to contribute to the development and implementation of IL-based separation processes for recovering and recycling of HFC refrigerants. To assess the impact varying the anions has on solubility and diffusivity, imidazolium-based cations with a range of different anions were examined. This was done to test the hypothesis that anions have a larger effect on physical gas solubility than cations. In this context, the vapor-liquid equilibria (single-component absorption) of the R-410A components, *i.e.*, HFC-32 and HFC-125, in 1-butyl-3-methylimidazolium acetate ( $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{CO}_2]$ ),  $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ ,  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ , 1-butyl-3-

methylimidazolium thiocyanate ( $[\text{C}_4\text{C}_{1\text{im}}][\text{SCN}]$ ), 1-hexyl-3-methylimidazolium chloride ( $[\text{C}_6\text{C}_{1\text{im}}][\text{Cl}]$ ), and 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ( $[\text{C}_6\text{C}_{1\text{im}}][\text{FAP}]$ ) were measured using a gravimetric microbalance at 298.15 K and pressures up to 1.0 MPa. The temperature of 298.15 K was chosen for this study to screen ILs for capacity and selectivity differences. The most promising candidates will be studied in more depth over a range of temperatures in the future.

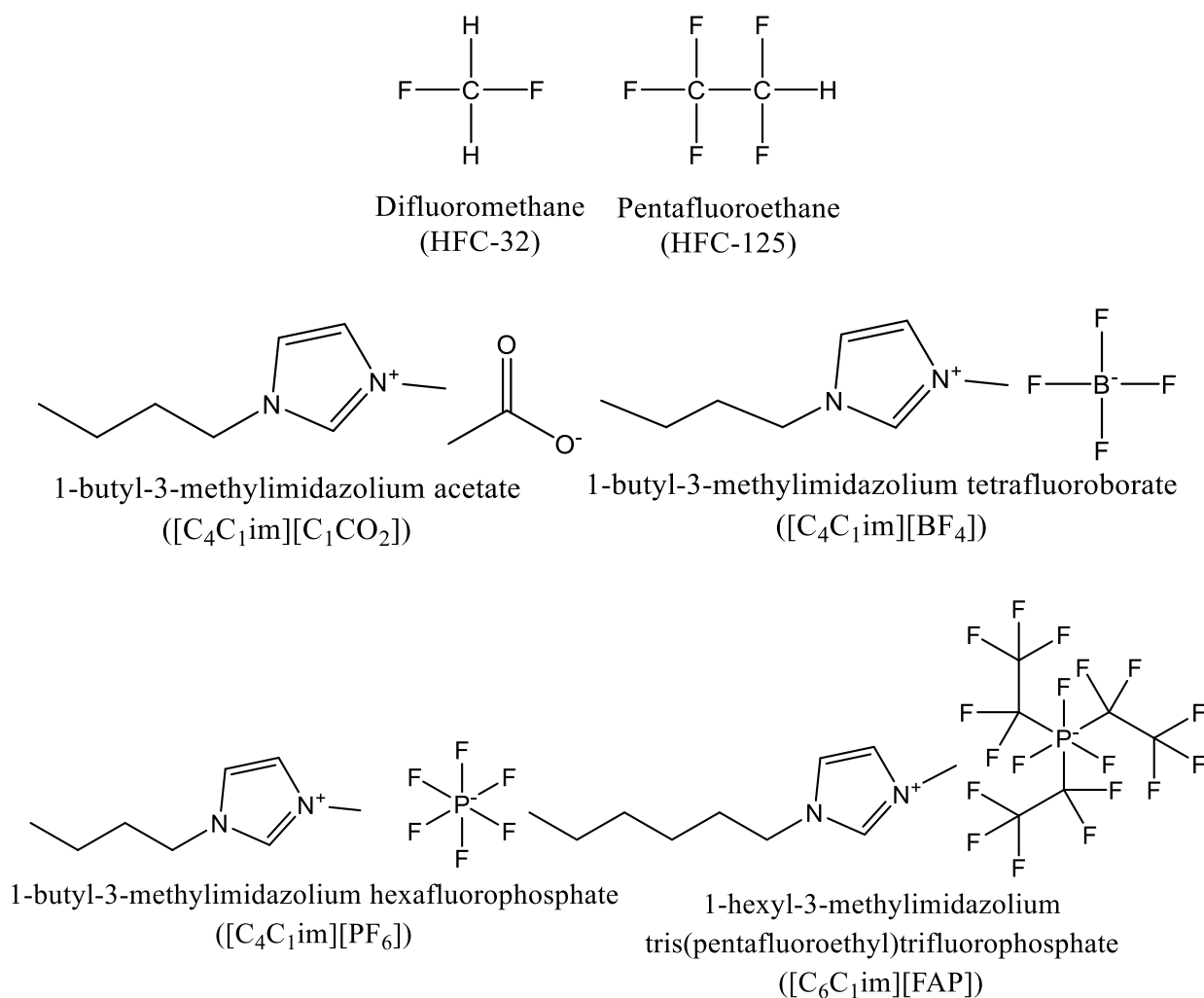
One of the motivations for this work is to develop a framework where accurate engineering models can be developed and used for process optimization to select the best IL from a total cost and performance standpoint. No single IL property such as solubility or viscosity can be used to make such an assessment. The van der Waals EoS model was applied to correlate and predict the phase equilibria for each HFC-32 / IL and HFC-125 / IL mixture using the experimental solubility data. In addition, the time-dependent behavior of the HFC / IL systems was analyzed using the one-dimensional Fick's law. Finally, the ideal selectivity of the separation of R-410A for each IL was calculated by taking the ratio of the Henry's law constants at 298.15 K and the ratio of the mass absorption at 1.0 MPa and 298.15 K.

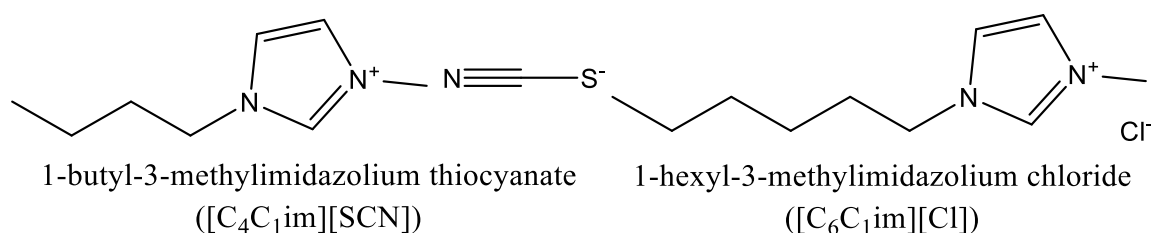
## **2. Materials and Methods**

### **2.1. Materials**

HFC-32 (CAS# 75-10-5) and HFC-125 (CAS# 354-33-6) were obtained from The Chemours Company (Newark, DE) with a minimum purity of 99.9 wt %, and used as received. Ionic liquids were purchased from commercial suppliers as follows:  $[\text{C}_4\text{C}_{1\text{im}}][\text{C}_1\text{CO}_2]$  (assay,  $\geq 95$  wt%, CAS No. 284049-75-8, Lot and Filling Code S25803 444041302),  $[\text{C}_4\text{C}_{1\text{im}}][\text{BF}_4]$  (assay,  $\geq 97$  wt%, CAS No. 174501-65-6, Lot and Filling Code No. 1116280 23404335),  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$  (assay,  $\geq 96$  wt%, CAS No. 174501-64-5, Lot and Filling Code No. 1242554 304070904),  $[\text{C}_4\text{C}_{1\text{im}}][\text{SCN}]$

(assay,  $\geq 95$  wt %, CAS No. 344790-87-0, Lot and Filling code, S25812 14804B3), and  $[\text{C}_6\text{C}_1\text{im}][\text{Cl}]$  (assay,  $\geq 97$  wt %, CAS No. 171058-17-6, Lot and Filling code, 1086333 41705081) were obtained from the Fluka Chemika (Switzerland). The  $[\text{C}_6\text{C}_1\text{im}][\text{FAP}]$  (assay,  $\geq 99$  wt%, CAS No. 713512-19-7, Lot and Filling code, S4872378 733) was purchased from EMD Millipore, Inc. (United States). The densities of HFC-32 and HFC-125 were obtained from the National Institute of Standards and Technology (NIST) REFPROP V.10.0 database.<sup>21</sup> The densities and molecular weight of the ILs were obtained from the literature.<sup>13, 22</sup> Figure 1 provides the chemical structures and acronyms for the HFC refrigerants and ILs studied in this work.





**Figure 1.** Chemical structures and acronyms of the HFC refrigerants and ILs.

## 2.2. Experimental Methodology

The gas absorption measurements were performed using a gravimetric microbalance (Hidden Isochema Ltd., IGA 003, Warrington, United Kingdom). The experimental equipment and protocols for the gas solubility measurements have been described in detail in a prior reference; therefore, only a brief description is provided here.<sup>13</sup> Approximately 50 mg of IL was loaded in a flat bottom Pyrex sample container and degassed under vacuum ( $10^{-10}$  MPa) at 348.15 K for 12 hours to remove any trace amounts of water and / or other volatile impurities prior to the measurements. The water content in the halogen containing ILs was estimated to be less than 100 ppm and in the acetate containing IL to be less than 1000 ppm after in situ pretreatment. This estimation was validated by pulling a comparable vacuum on select IL samples using a Schlenk line and then analyzing them using a coulometric Karl Fisher titration method. Note that it has been demonstrated that  $[\text{PF}_6]$  and  $[\text{BF}_4]$  anions are hydrolytically unstable at elevated temperatures.<sup>23</sup> However, because the application under investigation involves moderate temperatures and the HFCs can be scrupulously dried, the  $[\text{PF}_6]$  and  $[\text{BF}_4]$  anions have demonstrated good stability. To ensure enough time to reach vapor-liquid equilibrium at 298.15 K, each pressure setpoint was held for a minimum of 8 hours. The kinetic sorption profile and balance stability were monitored by the HISorp software program to ensure that the HFC / IL mixtures had reached thermodynamic equilibrium. The gas sorption measurements were

performed in “static mode”, where set point pressures were maintained constant within the system through simultaneous adjustments in admit and exhaust valves. The sample and counterweight temperatures were measured using an *in-situ* K-type thermocouple with an uncertainty of  $\pm 0.1$  K. Both temperature and pressure transducers in the microbalance were calibrated using NIST certified reference instruments. The *in-situ* thermocouple was calibrated using a standard platinum resistance thermometer (Hart Scientific SPRT model 5699 and readout Hart Scientific Blackstack model 1560 with a SPRT module 2560) with an accuracy of  $\pm 0.005$  K. Pressures under vacuum ( $10^{-10}$  to  $10^{-5}$  MPa) were measured using a Pfeiffer vacuum gauge (model PKR251) and pressures from vacuum ( $10^{-5}$  MPa) to higher pressure (2.0 MPa) were measured using a Druck pressure transducer (model PDCR4010) with an accuracy of  $\pm 0.0008$  MPa. The IGA microbalance had a mass resolution of 0.0001 mg for absorption and desorption measurements at any given temperature and pressure. The gas sorption data were corrected for buoyancy and volume expansion as described previously by Minnick et al.<sup>24</sup> Previous measurements for HFC-32 in [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] and [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and HFC-125 in [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] were repeated to ensure that the new experimental setup being used for this study was able to reproduce previous work (see SI).

### 2.3. Equation of State Modeling

Solubilities of gases including hydrofluorocarbons in ionic liquids have been accurately modeled using cubic EoS models as well as activity coefficient models, including NRTL, Wilson, and Margules.<sup>19, 22, 25-34</sup> To utilize experimental or computed solubility data in a process optimization framework, it is necessary to have analytic equations to represent the data. A particularly effective way of representing HFC/IL solubility data is with a cubic EoS. In 2010, Yokozeki and Shiflett showed a generic van der Waals EoS could accurately predict solubilities of gases including CO<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>, and hydrofluorocarbons such as HFC-134a, in room temperature ionic liquids (RTILs).<sup>35</sup> In this

work, parameters have been fit to the same generic van der Waals model for mixtures of HFC-32 and HFC-125 in the ILs studied. The van der Waals Equation of State (EoS) is modeled by the equation:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V^2} \quad (1)$$

$$a_i(T) = \frac{0.421875R^2T_{Ci}^2\alpha_i(T)}{P_{Ci}} \quad (2)$$

$$b_i = \frac{0.125RT_{Ci}}{P_{Ci}} \quad (3)$$

$$\alpha_i(T) = \sum_{k=0}^{\leq 3} \beta_{ki} \left( \frac{1}{T_{ri}} - T_{ri} \right)^k, \quad \left( T_{ri} \equiv \frac{T}{T_{Ci}} \right) \quad (4)$$

where  $\alpha$  represents the temperature dependence of the  $a$  parameter. The critical constant,  $\beta$ , the critical temperature,  $T_c$ , and the critical pressure,  $P_c$ , for HFC-32 and HFC-125 were obtained from prior calculations by Yokozeki<sup>36</sup> and are shown in Table 1.

**Table 1.** HFC Critical Parameters

| Compound | $T_c$ (K) | $P_c$ (kPa) | $\beta_{\text{HFC, A}}$ | $\beta_{\text{HFC, B}}$ | $\beta_{\text{HFC, C}}$ | $\beta_{\text{HFC, D}}$ |
|----------|-----------|-------------|-------------------------|-------------------------|-------------------------|-------------------------|
| HFC-32   | 351.26    | 5782        | 1.0019                  | 0.48333                 | -0.07538                | 0.00673                 |
| HFC-125  | 339.19    | 3637        | 1.0001                  | 0.47736                 | -0.01977                | -0.0177                 |

Yokozeki proposed the following temperature dependence for the  $a$  parameter for ILs:<sup>36</sup>

$$\alpha(T) = 1 + \beta_{IL,i} \left( \frac{1}{T_{r,IL}} - T_{r,IL} \right) \quad (5)$$

where  $\beta_{IL}$  is an adjustable fitting parameter and calculated for each IL. In this work, the  $T_c$  and  $P_c$  used for all ILs were set to 1000 K and 2.5 MPa. The model fit is extremely insensitive to the choice of IL  $T_c$  and  $P_c$  as shown in Section 3.

The following mixing rules were originally developed for refrigerant-lubricant mixtures involving large molecular-size differences and/or asymmetric interactions with respect to compositions and were extended to refrigerant/ionic liquid mixtures.<sup>35, 36</sup>

$$a = \sum_{i,j=1}^N \sqrt{a_i a_j} f_{ij}(T) (1 - k_{ij}) x_i x_j \quad (6)$$

$$f_{ij}(T) = 1 + \frac{\tau_{ij}}{T} \quad (7)$$

$$k_{ij} = \frac{l_{ij} l_{ji} (x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}, \quad \text{where } k_{ii} = 0 \quad (8)$$

$$b = 0.5 \sum_{i,j=1}^N (b_i + b_j) (1 - k_{ij}) (1 - m_{ij}) x_i x_j \quad (9)$$

Here  $l$ ,  $m$ , and  $\tau$  are binary interaction parameters,  $x_i$  is the mole fraction of species  $i$ , and  $R$  is the universal gas constant. We assume  $l_{ii} = l_{jj} = 1$ ,  $m_{ij} = m_{ji}$  and  $m_{ii} = 0$ , and  $\tau_{ij} = \tau_{ji}$  and  $\tau_{ii} = 0$ , which leaves only four of these parameters ( $l_{ij}$ ,  $l_{ji}$ ,  $m_{ij}$ , and  $\tau_{ij}$ ) to be estimated via nonlinear regression. These simplifying assumptions are consistent with previous generic van der Waals EoS model calculations by Yokozeki and Shiflett.<sup>35, 36</sup>

With  $\beta_{IL}$  and the four binary interaction parameters, five total parameters were fit in this model. Many combinations for the parameters  $l_{ij}$ ,  $l_{ji}$ ,  $m$ ,  $\tau$ , and  $\beta_{IL}$  are possible for which the model predictions closely match the experimental data; therefore, the choice of binary interaction parameters has negligible impact on the quality of the fit.

The fugacity coefficient is defined as:

$$\ln \phi_i = \ln \left( \frac{RT}{P(V-b)} \right) + \frac{b'_i}{V-b} - \frac{a'_i + a}{VRT} \quad (10)$$

where,

$$a'_i = 2 \sum_{j=1}^N \sqrt{a_i a_j} f_{ij} x_j \left\{ 1 - k_{ij} - \frac{l_{ij} l_{ji} (l_{ij} - l_{ji}) x_i x_j}{(l_{ji} x_i + l_{ij} x_j)^2} \right\} - a \quad (11)$$

$$b'_i = \sum_{j=1}^N (b_i + b_j) (1 - m_{ij}) x_j \left\{ 1 - k_{ij} - \frac{l_{ij} l_{ji} (l_{ij} - l_{ji}) x_i x_j}{(l_{ji} x_i + l_{ij} x_j)^2} \right\} - b \quad (12)$$

and equilibria between the liquid and vapor phases is determined by:

$$(x_i \phi_i)^L = (y_i \phi_i)^V \quad (13)$$

The amount of IL in the vapor phase is assumed to be zero, due to the negligible vapor pressure of ILs; therefore, the vapor mole fraction of HFC is unity ( $y_{HFC} = 1$ ) and its phase equilibria is modeled by:

$$x_{HFC} \phi_{HFC}^L = \phi_{HFC}^V \quad (14)$$

To fit the ionic liquid critical parameter and binary interaction parameters for each mixture, nonlinear regression was used to solve the following:

$$\min_{l_{ij}, l_{ji}, m, \tau, \beta_{IL}} (P_{vdW} - P_{exp})^2 \quad (15)$$

constrained by Equations (1) – (14) to calculate  $P_{vdW}$ .  $P_{exp}$  are the experimentally measured pressures at equilibrium.

## 2.4. Henry's law constant at infinite dilution

Henry's law constants ( $k_H$ ) were used to evaluate the refrigerant absorption in ILs at infinite dilution concentrations, where lower  $k_H$  values indicate higher refrigerant solubility in the solvent.<sup>37</sup> In this work, both HFC-32 and HFC-125 solubilities increase linearly with increasing pressure up to about 0.2 MPa, indicating the Henry's law regime; therefore, the refrigerant partial pressure was directly proportional to its liquid composition in the liquid phase, under dilute conditions. The Henry's law constant can be calculated from experimental refrigerant solubility ( $PTx$ ) data assuming the hydrostatic pressure correction (Krichevsky-Kasarnovsky equation) is not required:

$$k_H = \lim_{x_1 \rightarrow 0} \frac{f_1^V(T, P, y_1)}{x_1} \approx \left( \frac{df_1^V}{dx_1} \right)_{x_1=0} \quad (16)$$

where  $f_1^V$  is the vapor phase fugacity of HFC-32 and HFC-125 ( $y_1 = 1$ ) absorbed in the IL, which was calculated using an EoS model at given temperature and pressure.<sup>21</sup> The Henry's law constants were calculated by determining the slope of a linear regression, fitting the experimental solubility data up to about 0.2 MPa, including the theoretical point with no refrigerant in the IL at zero pressure.

## 2.5. Fickian Diffusion Analysis

In addition to the equilibrium solubility, the time-dependent absorption data for HFC-32 and HFC-125 in the ILs were also measured using the gravimetric microbalance at 298.15 K and pressures ranging from 0.05 to 1.0 MPa. Details on how to apply Fick's law to the current physical situation have been previously reported; therefore, only a few important assumptions and conditions will be provided here.<sup>28</sup> In this simplified Fickian diffusion model, the following assumptions for the dissolving refrigerant in IL were applied:<sup>13</sup> (i) the interactions between the HFC and IL are physical; (ii) HFC dissolves through a one-dimensional (vertical) diffusion process, and there is

no convective flow in the IL; (iii) a thin boundary layer exists between HFC and IL at given  $T$  and  $P$ , where the thermodynamic equilibrium is established with the saturation concentration ( $C_s$ ); (iv) HFC / IL mixture is a dilute solution, and thermophysical properties do not change at given  $T$  and  $P$ . These assumptions allow describing the dissolution of the HFC in ILs based on the one-dimensional mass diffusion, due to local concentration difference:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (17)$$

Initial Condition:

$$t = 0, 0 < z < L, \text{ and } C = C_0 \quad (18)$$

Boundary Conditions (*i* and *ii*):

$$(i) \ t > 0, z = 0, \text{ and } C = C_s \quad (19)$$

$$(ii) \ t > 0, z = L, \text{ and } \frac{\partial C}{\partial z} = 0 \quad (20)$$

where  $C$  is the concentration of the HFC in the IL as a function of time ( $t$ ),  $z$  is the vertical location,  $z = 0$  corresponds to the vapor–liquid boundary,  $L$  is the depth of the IL in the sample container, and  $D$  is the diffusion coefficient that was assumed to be constant. The depth ( $L$ ) was estimated by knowing the cylindrical geometry of the sample container, mass, and average weight fraction density of the HFC / IL mixture at initial ( $C_0$ ) and saturation concentration ( $C_s$ ) at a given  $T$  and  $P$ . Equation 17 was solved analytically by applying the proper initial and boundary conditions (Equations 18-20), and the separation of variables or Laplace transform methods to yield the following:<sup>38</sup>

$$\langle C \rangle = C_s \left[ 1 - 2 \left( 1 - \frac{C_o}{C_s} \right) \sum_{n=0}^{\infty} \frac{\exp(-\lambda_n^2 Dt)}{L^2 \lambda_n^2} \right] \quad (21)$$

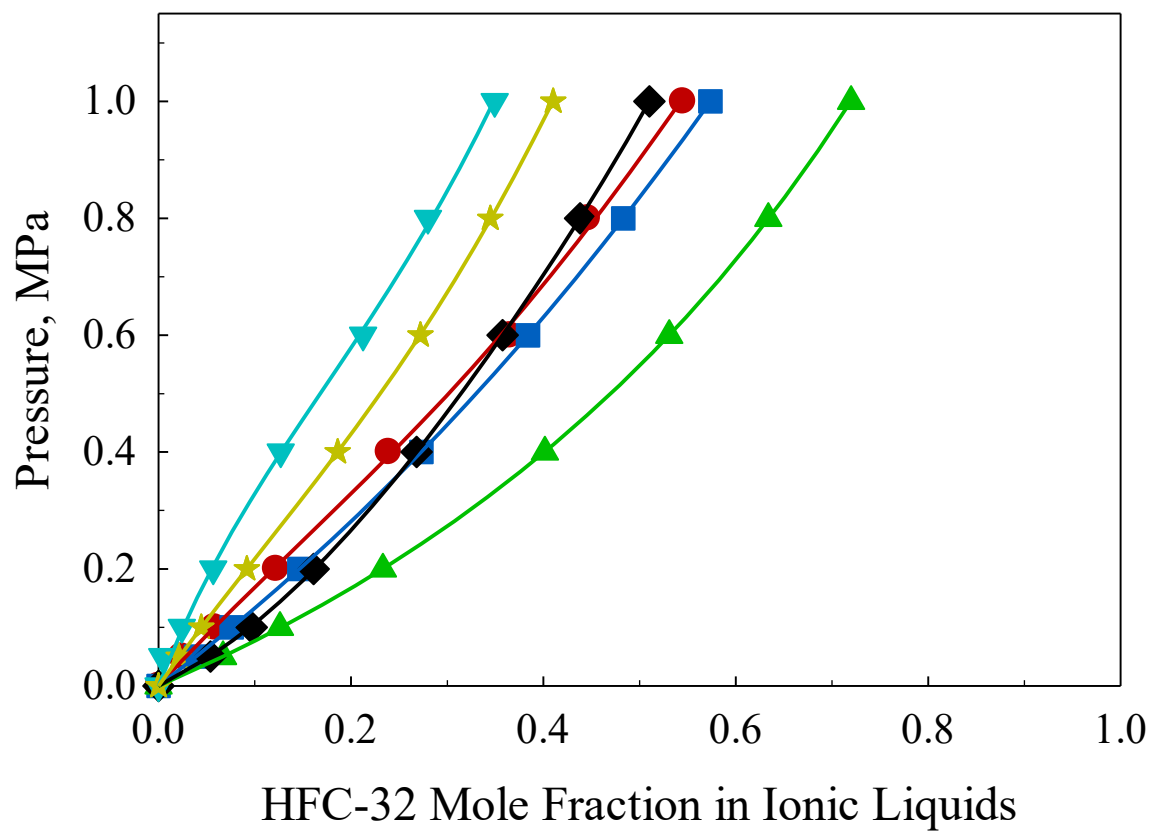
where  $\lambda_n = [n + (1/2)](\pi/L)$

Although Equation 21 has an infinite summation term, only the first ten terms were applied in this analysis. The diffusion coefficient ( $D$ ) and solubility limit at equilibrium ( $C_s$ ) for each HFC in IL data set were calculated through nonlinear regression of Equation 21 using MATLAB software, and the best model fit was obtained by selecting the proper  $C_o$  value (see Supplemental Information for additional details).

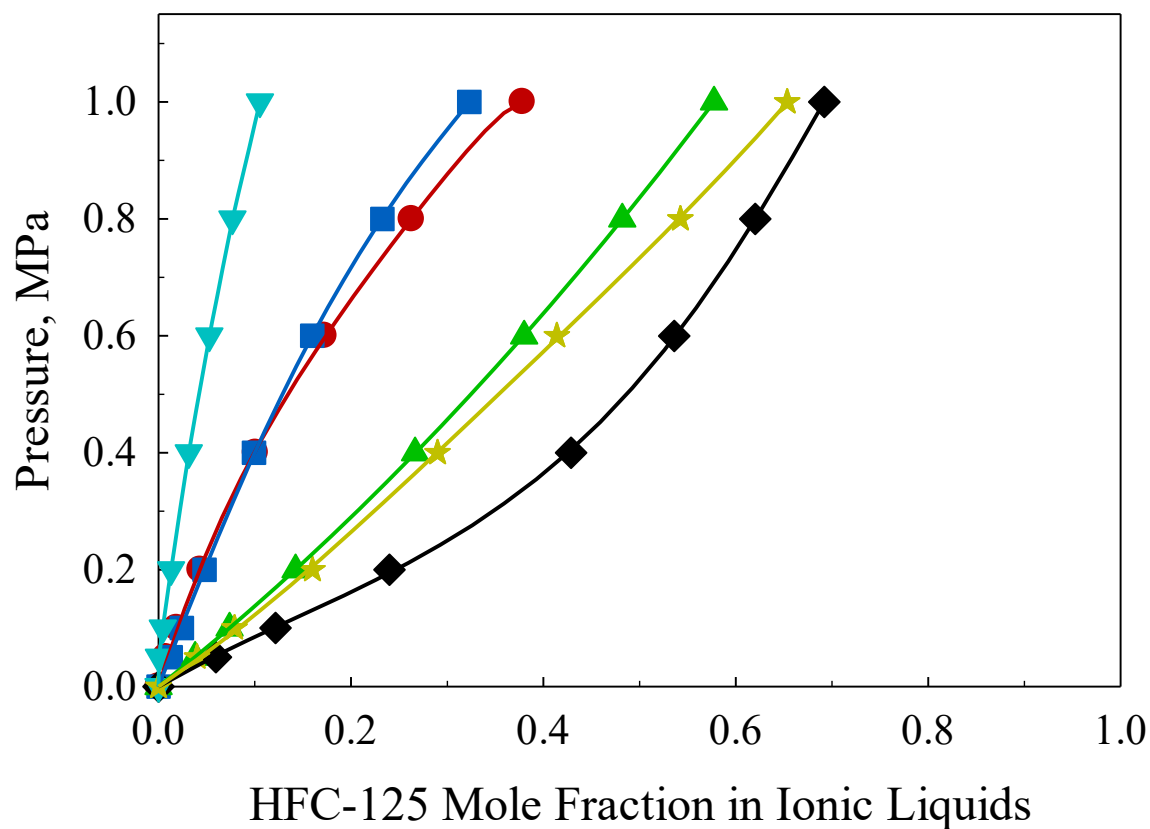
### 3. Results and Discussion

#### 3.1. Vapor Liquid Equilibrium Results

Previous studies indicate that the HFC solubility in ILs depends primarily on the interaction strength between the refrigerant and the IL anion.<sup>39</sup> For instance, Shiflett et al. reported that HFC-32 is more soluble in ILs containing fluorinated anions than in those with non-fluorinated anions due to hydrogen bonding between the hydrogen on the refrigerant and the fluorine on the anion.<sup>28</sup> In addition, the same authors found large solubility differences for HFC-32 relative to HFC-125 in  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ . For example, HFC-32 /  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  had a Henry's law constant of  $8.8 \pm 0.7$  bar, while HFC-125 /  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$  had a Henry's law constant of  $23.1 \pm 2.3$  bar at 298.15 K.<sup>13</sup> To validate this theory, experimental solubility data of HFC-32 and HFC-125 in three ILs with fluorinated anions ( $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ ,  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ , and  $[\text{C}_6\text{C}_1\text{im}][\text{FAP}]$ ) and in three ILs with non-fluorinated anions ( $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{CO}_2]$ ,  $[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$ , and  $[\text{C}_6\text{C}_1\text{im}][\text{Cl}]$ ) at pressures ranging from 0.05 to 1.0 MPa and at 298.15 K were measured (Tables 2 to 7) and correlated using the van der Waals EoS model as shown in Figures 2 and 3.



**Figure 2.** VLE for HFC-32 in  $[C_4C_{1im}][SCN]$  ( $\blacktriangledown$ ),  $[C_6C_{1im}][Cl]$  ( $\star$ ),  $[C_4C_{1im}][C_1CO_2]$  ( $\blacklozenge$ ),  $[C_4C_{1im}][BF_4]$  ( $\bullet$ ),  $[C_4C_{1im}][PF_6]$  ( $\blacksquare$ ), and  $[C_6C_{1im}][FAP]$  ( $\blacktriangle$ ) at 298.15 K. Symbols are measured experimental data ( $PTx$ ) and lines are van der Waals EoS model predictions.



**Figure 3.** VLE for HFC-125 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{SCN}]$  ( $\blacktriangledown$ ),  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$  ( $\blacksquare$ ),  $[\text{C}_4\text{C}_{1\text{im}}][\text{BF}_4]$  ( $\bullet$ ),  $[\text{C}_6\text{C}_{1\text{im}}][\text{FAP}]$  ( $\blacktriangle$ ),  $[\text{C}_6\text{C}_{1\text{im}}][\text{Cl}]$  ( $\star$ ), and  $[\text{C}_4\text{C}_{1\text{im}}][\text{C}_1\text{CO}_2]$  ( $\blacklozenge$ ) at 298.15 K. Symbols are measured experimental data ( $PTx$ ) and solid lines are van der Waals EoS model predictions.

**Table 2.** Experimental VLE for HFC-32 / [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and HFC-125 / [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] mixtures at 298.15 K.

| HFC-32 (1) + [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ] (2) |                     |                 | HFC-125 (1) + [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ] (2) |                     |                 |
|-----------------------------------------------------------------------|---------------------|-----------------|------------------------------------------------------------------------|---------------------|-----------------|
| $P$<br>(MPa)                                                          | $100x_I$<br>(mol %) | $w_I$<br>(wt %) | $P$<br>(MPa)                                                           | $100x_I$<br>(mol %) | $w_I$<br>(wt %) |
| 0.05                                                                  | 2.4                 | 0.6             | 0.05                                                                   | 0.8                 | 0.4             |
| 0.1                                                                   | 5.8                 | 1.4             | 0.1                                                                    | 1.9                 | 1.0             |
| 0.2                                                                   | 12.2                | 3.1             | 0.2                                                                    | 4.3                 | 2.3             |
| 0.4                                                                   | 23.9                | 6.8             | 0.4                                                                    | 10.1                | 5.6             |
| 0.6                                                                   | 36.5                | 11.8            | 0.6                                                                    | 17.2                | 10.0            |
| 0.8                                                                   | 44.6                | 15.8            | 0.8                                                                    | 26.3                | 15.9            |
| 1.0                                                                   | 54.5                | 21.9            | 1.0                                                                    | 37.8                | 24.4            |

$P$  – Pressure;  $100x_I$  and  $w_I$  - HFC composition (mol % and wt %) in IL.

Standard uncertainties:  $u(T) = 0.1$  °C;  $u(P) = 0.0008$  MPa and  $u(100x_I) = 0.5$  mol%.

**Table 3.** Experimental VLE for HFC-32 / [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] and HFC-125 / [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] mixtures at 298.15 K.

| HFC-32 (1) + [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ] (2) |                     |                 | HFC-125 (1) + [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ] (2) |                     |                 |
|-----------------------------------------------------------------------|---------------------|-----------------|------------------------------------------------------------------------|---------------------|-----------------|
| $P$<br>(MPa)                                                          | $100x_I$<br>(mol %) | $w_I$<br>(wt %) | $P$<br>(MPa)                                                           | $100x_I$<br>(mol %) | $w_I$<br>(wt %) |
| 0.05                                                                  | 3.9                 | 0.7             | 0.05                                                                   | 1.2                 | 0.5             |
| 0.1                                                                   | 7.6                 | 1.5             | 0.1                                                                    | 2.4                 | 1.0             |
| 0.2                                                                   | 14.6                | 3.0             | 0.2                                                                    | 4.8                 | 2.1             |
| 0.4                                                                   | 27.3                | 6.4             | 0.4                                                                    | 9.9                 | 4.4             |
| 0.6                                                                   | 38.4                | 10.2            | 0.6                                                                    | 16.0                | 7.2             |
| 0.8                                                                   | 48.3                | 14.6            | 0.8                                                                    | 23.2                | 11.0            |
| 1.0                                                                   | 57.4                | 19.8            | 1.0                                                                    | 32.3                | 16.1            |

$P$  – Pressure;  $100x_I$  and  $w_I$  - HFC composition (mol % and wt %) in IL.

Standard uncertainties:  $u(T) = 0.1$  °C;  $u(P) = 0.0008$  MPa and  $u(100x_I) = 0.5$  mol%.

**Table 4.** Experimental VLE for HFC-32 / [C<sub>6</sub>C<sub>1</sub>im][FAP] and HFC-125 / [C<sub>6</sub>C<sub>1</sub>im][FAP] mixtures at 298.15 K.

| HFC-32 (1) + [C <sub>6</sub> C <sub>1</sub> im][FAP] (2) |                     |                 | HFC-125 (1) + [C <sub>6</sub> C <sub>1</sub> im][FAP] (2) |                     |                 |
|----------------------------------------------------------|---------------------|-----------------|-----------------------------------------------------------|---------------------|-----------------|
| $P$<br>(MPa)                                             | $100x_I$<br>(mol %) | $w_I$<br>(wt %) | $P$<br>(MPa)                                              | $100x_I$<br>(mol %) | $w_I$<br>(wt %) |
| 0.05                                                     | 6.7                 | 0.6             | 0.05                                                      | 3.8                 | 0.8             |
| 0.1                                                      | 12.6                | 1.2             | 0.1                                                       | 7.4                 | 1.5             |
| 0.2                                                      | 23.3                | 2.5             | 0.2                                                       | 14.2                | 3.1             |
| 0.4                                                      | 40.2                | 5.4             | 0.4                                                       | 26.7                | 6.6             |
| 0.6                                                      | 53.1                | 8.8             | 0.6                                                       | 38.0                | 10.7            |
| 0.8                                                      | 63.4                | 12.9            | 0.8                                                       | 48.2                | 15.3            |
| 1.0                                                      | 72.0                | 18.1            | 1.0                                                       | 57.8                | 20.9            |

$P$  – Pressure;  $100x_I$  and  $w_I$  - HFC composition (mol % and wt %) in IL.

Standard uncertainties:  $u(T) = 0.1$  °C;  $u(P) = 0.0008$  MPa and  $u(100x_I) = 0.5$  mol%.

**Table 5.** Experimental VLE for HFC-32 / [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] and HFC-125 / [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] mixtures at 298.15 K.

| HFC-32 (1) + [C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> CO <sub>2</sub> ] (2) |                     |                 | HFC-125 (1) + [C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> CO <sub>2</sub> ] (2) |                     |                 |
|--------------------------------------------------------------------------------------|---------------------|-----------------|---------------------------------------------------------------------------------------|---------------------|-----------------|
| $p$<br>(MPa)                                                                         | $100x_I$<br>(mol %) | $w_I$<br>(wt %) | $p$<br>(MPa)                                                                          | $100x_I$<br>(mol %) | $w_I$<br>(wt %) |
| 0.05                                                                                 | 5.4                 | 1.5             | 0.05                                                                                  | 6.0                 | 3.7             |
| 0.1                                                                                  | 9.7                 | 2.7             | 0.1                                                                                   | 12.2                | 7.7             |
| 0.2                                                                                  | 16.1                | 4.8             | 0.2                                                                                   | 24.0                | 16.0            |
| 0.4                                                                                  | 26.8                | 8.7             | 0.4                                                                                   | 42.9                | 31.0            |
| 0.6                                                                                  | 35.7                | 12.6            | 0.6                                                                                   | 53.6                | 40.8            |
| 0.8                                                                                  | 43.8                | 16.8            | 0.8                                                                                   | 62.0                | 49.1            |
| 1.0                                                                                  | 51.0                | 21.2            | 1.0                                                                                   | 69.2                | 56.9            |

$P$  – Pressure;  $100x_I$  and  $w_I$  - HFC composition (mol % and wt %) in IL.

Standard uncertainties:  $u(T) = 0.1$  °C;  $u(P) = 0.0008$  MPa and  $u(100x_I) = 0.5$  mol%.

**Table 6.** Experimental VLE for HFC-32 / [C<sub>4</sub>C<sub>1</sub>im][SCN] and HFC-125 / [C<sub>4</sub>C<sub>1</sub>im][SCN] mixtures at 298.15 K.

| HFC-32 (1) + [C <sub>4</sub> C <sub>1</sub> im][SCN] (2) |                     |                 | HFC-125 (1) + [C <sub>4</sub> C <sub>1</sub> im][SCN] (2) |                     |                 |
|----------------------------------------------------------|---------------------|-----------------|-----------------------------------------------------------|---------------------|-----------------|
| $p$<br>(MPa)                                             | $100x_I$<br>(mol %) | $w_I$<br>(wt %) | $p$<br>(MPa)                                              | $100x_I$<br>(mol %) | $w_I$<br>(wt %) |
| 0.05                                                     | 0.4                 | 0.1             | 0.05                                                      | < 0.1               | < 0.1           |
| 0.1                                                      | 2.4                 | 0.6             | 0.1                                                       | 0.4                 | 0.3             |
| 0.2                                                      | 5.7                 | 1.6             | 0.2                                                       | 1.3                 | 0.8             |
| 0.4                                                      | 12.7                | 3.7             | 0.4                                                       | 3.1                 | 1.9             |
| 0.6                                                      | 21.2                | 6.6             | 0.6                                                       | 5.3                 | 3.2             |
| 0.8                                                      | 28.0                | 9.3             | 0.8                                                       | 7.7                 | 4.7             |
| 1.0                                                      | 34.9                | 12.4            | 1.0                                                       | 10.5                | 6.5             |

$P$  – Pressure;  $100x_I$  and  $w_I$  - HFC composition (mol % and wt %) in IL.

Standard uncertainties:  $u(T) = 0.1$  °C;  $u(P) = 0.0008$  MPa and  $u(100x_I) = 0.5$  mol%.

**Table 7.** Experimental VLE for HFC-32 / [C<sub>4</sub>C<sub>1</sub>im][Cl] and HFC-125 / [C<sub>4</sub>C<sub>1</sub>im][Cl] mixtures at 298.15 K.

| HFC-32 (1) + [C <sub>6</sub> C <sub>1</sub> im][Cl] (2) |                     |                 | HFC-125 (1) + [C <sub>6</sub> C <sub>1</sub> im][Cl] (2) |                     |                 |
|---------------------------------------------------------|---------------------|-----------------|----------------------------------------------------------|---------------------|-----------------|
| $p$<br>(MPa)                                            | $100x_I$<br>(mol %) | $w_I$<br>(wt %) | $p$<br>(MPa)                                             | $100x_I$<br>(mol %) | $w_I$<br>(wt %) |
| 0.05                                                    | 2.1                 | 0.5             | 0.05                                                     | 4.0                 | 2.4             |
| 0.1                                                     | 4.4                 | 1.2             | 0.1                                                      | 7.9                 | 4.8             |
| 0.2                                                     | 9.2                 | 2.5             | 0.2                                                      | 16.0                | 10.2            |
| 0.4                                                     | 18.6                | 5.6             | 0.4                                                      | 29.0                | 19.5            |
| 0.6                                                     | 27.2                | 8.8             | 0.6                                                      | 41.4                | 29.6            |
| 0.8                                                     | 34.5                | 11.9            | 0.8                                                      | 54.3                | 41.3            |
| 1.0                                                     | 41.0                | 15.2            | 1.0                                                      | 65.4                | 52.8            |

$P$  – Pressure;  $100x_I$  and  $w_I$  - HFC composition (mol % and wt %) in IL.

Standard uncertainties:  $u(T) = 0.1$  °C;  $u(P) = 0.0008$  MPa and  $u(100x_I) = 0.5$  mol%.

It is worth mentioning that the absorption equilibrium isotherms shown in Figures 2 and 3 were measured up to 1.0 MPa in order to not exceed the saturation vapor pressure at 298.15 K of the HFCs studied in this work, *i.e.*, 1.69 and 1.38 MPa for HFC-32 and HFC-125, respectively.<sup>21</sup>

To validate the experimental method and general solubility trends reported in this work, the solubility data for HFC-32 and HFC-125 in fluorinated and non-fluorinated anion-based ILs were compared with those reported in the literature. In general, the experimental VLE data obtained are in good agreement with previous reports (Figures S1-S3).<sup>13</sup> For example, the solubility data for HFC-32 and HFC-125 in [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] and [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] are on average within 0.6 to 2.8 mol% of those data reported by Shiflett and Yokozeki in 2006.<sup>13</sup>

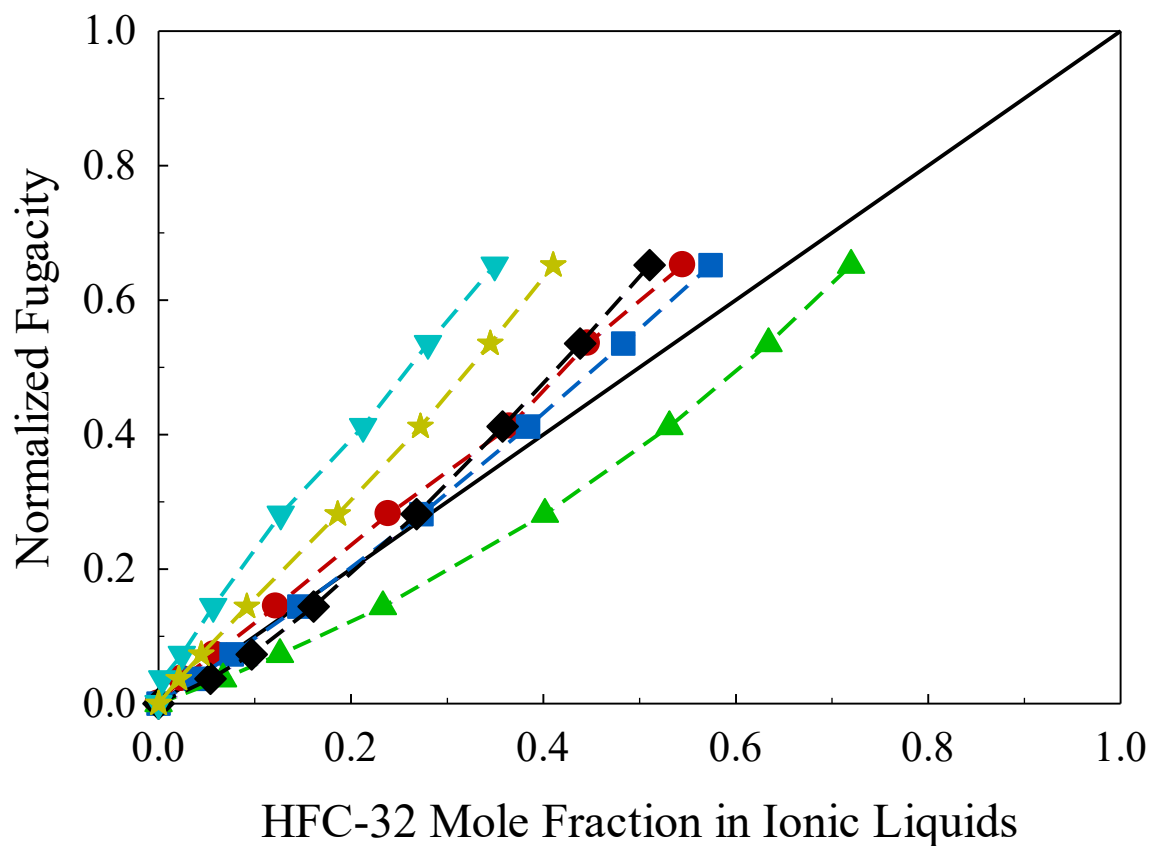
As expected, the solubility of HFC-32 and HFC-125 increase with increasing pressure for any given IL. However, it is the relative differences in solubility for either HFC-32 or HFC-125 that is most important, particularly for selective separation of R-410A. For example, HFC-32 is 44.2 % (mole fraction basis) more soluble than HFC-125 in [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] at 298.15 K and 1.0 MPa. Similar trend was obtained by Liu et al., who found that HFC-32 is more soluble than HFC-125 in [C<sub>6</sub>C<sub>1</sub>im][NTf<sub>2</sub>] at a given temperature and pressure.<sup>18</sup> However, the more important comparison for designing separation systems is the difference in solubility based on a mass fraction basis. In this case due to molecular weight differences (HFC-32 MW = 52.024 g·mol<sup>-1</sup> and HFC-125 MW = 120.02 g·mol<sup>-1</sup>) the HFC-125 is only 11.4 % more soluble than HFC-32 at 298.15 K and 1.0 MPa. Similar differences in solubility were found for the other ILs with fluorinated anions, [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] and [C<sub>6</sub>C<sub>1</sub>im][FAP], as shown in Tables 3 and 4, respectively.

In addition to the anion fluorination of the imidazolium-based ILs, a longer alkyl chain length for the cation may play a role in increasing the HFC-32 and HFC-125 absorption in the [C<sub>6</sub>C<sub>1</sub>im][FAP] ionic liquid. For example, comparing HFC-134a solubility in various ILs at 298.15 K, it is clear

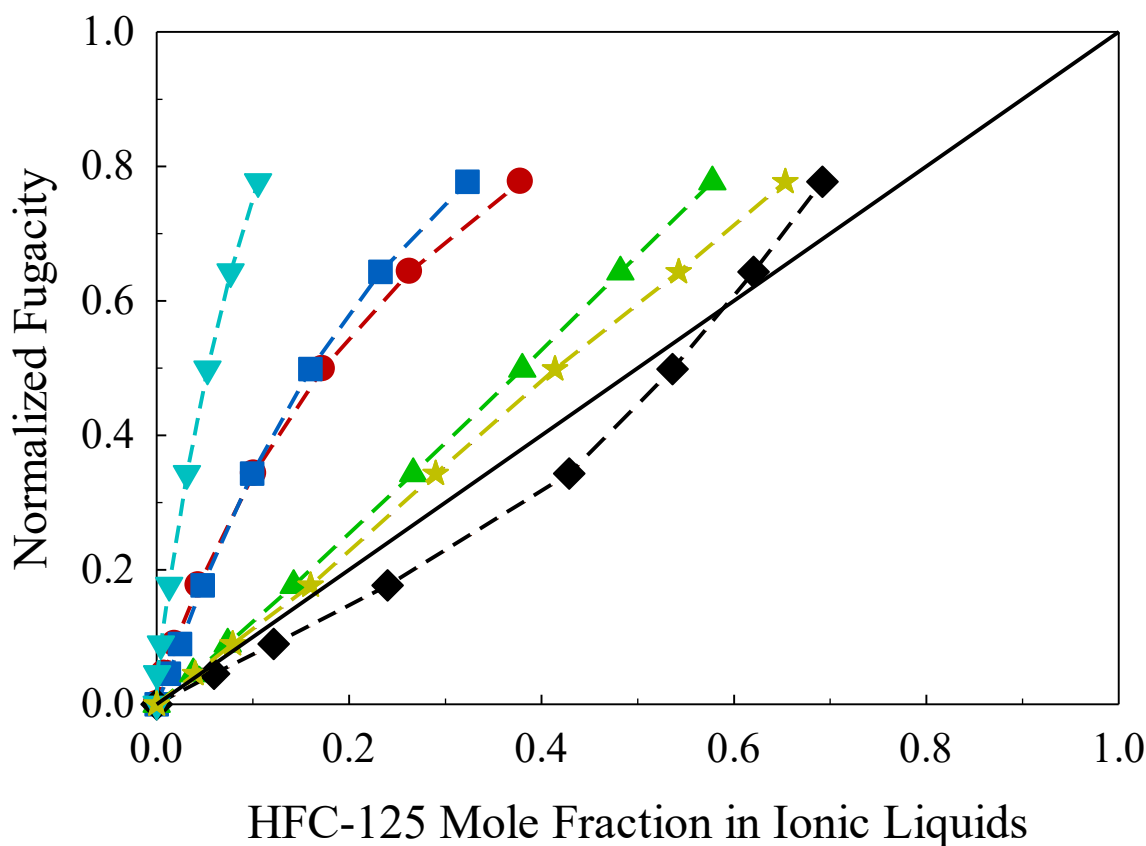
that longer alkyl chain on the cation increases the absorption of HFC-134a, as lower HFC-134a solubility was observed in [C<sub>2</sub>C<sub>1</sub>im][NTf<sub>2</sub>] relative to [C<sub>6</sub>C<sub>1</sub>im][NTf<sub>2</sub>].<sup>39</sup> Also, Shiflett et al. found higher HFC-32 solubilities in [C<sub>6</sub>C<sub>1</sub>im][TFES] relative to [C<sub>4</sub>C<sub>1</sub>im][TFES].<sup>40</sup> It is worth mentioning that IL cations with longer hydrogenated chains and/ or anions with a larger number of fluorine atoms have been associated with increasing levels of IL toxicity.<sup>41</sup>

### 3.2. Deviation from Ideality (Raoult's law)

To evaluate the non-ideality of HFC-32 and HFC-125 in IL, the normalized fugacity as a function of HFC molar compositions in the liquid phase was evaluated. The normalized fugacity was expressed as  $f^v/f^{sat}$ , where  $f^v$  refers to the vapor phase fugacity of the HFC resulting from the negligible vapor pressure of the IL,<sup>42</sup> such that  $y_{ref} = 1$ , and  $f^{sat}$  corresponds to the fugacity of the HFC at saturated vapor pressure with a temperature of 298.15 K. Figures 4 and 5 show the normalized fugacity for HFC-32 and HFC-125 in the ILs studied in this work as a function of molar compositions at 298.15 K.



**Figure 4.** Normalized fugacity for HFC-32 in  $[C_4C_{1im}][SCN]$  ( $\blacktriangledown$ ),  $[C_6C_{1im}][Cl]$  ( $\star$ ),  $[C_4C_{1im}][C_1CO_2]$  ( $\blacklozenge$ ),  $[C_4C_{1im}][BF_4]$  ( $\bullet$ ),  $[C_4C_{1im}][PF_6]$  ( $\blacksquare$ ), and  $[C_6C_{1im}][FAP]$  ( $\blacktriangle$ ) as a function of refrigerant molar composition at 298.15 K. Solid line represents Raoult's law. Dashed lines were added as a guide for the reader.



**Figure 5.** Normalized fugacity for HFC-125 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{SCN}]$  ( $\blacktriangledown$ ),  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$  ( $\blacksquare$ ),  $[\text{C}_4\text{C}_{1\text{im}}][\text{BF}_4]$  ( $\bullet$ ),  $[\text{C}_6\text{C}_{1\text{im}}][\text{FAP}]$  ( $\blacktriangle$ ),  $[\text{C}_6\text{C}_{1\text{im}}][\text{Cl}]$  ( $\star$ ), and  $[\text{C}_4\text{C}_{1\text{im}}][\text{C}_1\text{CO}_2]$  ( $\blacklozenge$ ) as a function of refrigerant molar composition at 298.15 K. Solid line represents Raoult's law. Dashed lines were added as a guide for the reader.

It is most interesting that these refrigerants within the same family of HFCs show quite distinct solubility behaviors depending on the choice of IL. For instance, HFC-32 had a strong negative deviation from Raoult's law in  $[\text{C}_6\text{C}_{1\text{im}}][\text{FAP}]$  across the entire refrigerant composition range, suggesting that the phase behavior was dominated by stronger van der Waals interactions between HFC-32 and this IL. In addition, HFC-32 exhibited a nearly ideal solubility behavior in  $[\text{C}_4\text{C}_{1\text{im}}][\text{C}_1\text{CO}_2]$  and  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$  for lower refrigerant compositions (up to 0.3 mole fraction),

whereas at higher refrigerant mole fractions, it showed a slightly positive deviation from Raoult's law. HFC-32 showed positive deviations over all compositions in [C<sub>4</sub>C<sub>1</sub>im][SCN], [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and [C<sub>6</sub>C<sub>1</sub>im][Cl]. Similar findings were obtained by Shiflett et al., who found that HFC-32 exhibited negative and positive deviations from Raoult's law in ILs with fluorinated and non-fluorinated anions, respectively, depending on refrigerant composition.<sup>13</sup> The strong absorption mechanism for HFC-32 in ILs with fluorinated anions has been proposed to be due to hydrogen bonding between the electronegative fluorinated IL anion (BF<sub>4</sub>, PF<sub>6</sub>, and FAP) and the acidic hydrogen atoms on the fluorocarbon (CH<sub>2</sub>F<sub>2</sub>).<sup>13</sup> Unlike HFC-32, HFC-125 exhibited a strong positive deviation from Raoult's law in ILs with fluorinated anions (BF<sub>4</sub>, PF<sub>6</sub>, and FAP), which may indicate that the cohesive forces between HFC-125 and the IL are weaker than cohesive forces between HFC / HFC and / or IL / IL. Interestingly, HFC-125 in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] showed mixed negative and positive deviations from Raoult's law depending on the molar concentration of the refrigerant. For instance, HFC-125 exhibited negative deviation for lower refrigerant mole fractions (up to approximately 0.6), whereas, at higher refrigerant compositions, it showed positive deviation from Raoult's law. These results suggest that the carboxylate group in the IL anion plays an important role in increasing the solubility of HFC-125. Similar findings were reported by Sosa et al., who reported that HFC-125 is significantly more soluble than HFC-32 in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] at 303.15 K and any given pressure.<sup>15</sup> The excess Gibbs energy for HFC-32 and HFC-125 were calculated in each of the IL and can be found in the Supplemental Information (Figures S4 and S5). The differences in excess Gibbs energy for HFC-32 and HFC-125 for each IL correlate with the differences in solubility based on mole fraction. It is worth mentioning that molecular dynamic simulations and calorimetric studies are underway to fully understand the observed HFC solubility trends.

### 3.3. van der Waals EoS modeling

Figures 2 and 3 show the van der Waals EoS model predictions for the solubilities of HFC-32 and HFC-125 in ILs using the best fit parameters reported in Tables 8 and 9, respectively.

**Table 8.** van der Waals EoS model parameters for HFC-32

| Ionic liquid                                                        | HFC-32/IL van der Waals Parameters |          |          |        |              |
|---------------------------------------------------------------------|------------------------------------|----------|----------|--------|--------------|
|                                                                     | $l_{ij}$                           | $l_{ji}$ | $m$      | $\tau$ | $\beta_{IL}$ |
| [C <sub>6</sub> C <sub>1</sub> im][FAP]                             | 0.76263                            | 0.76227  | -3.1790  | 1070.6 | 0.80407      |
| [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]                | 0.84646                            | 0.84015  | -5.2491  | 1492.4 | 0.25646      |
| [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]                | 0.77015                            | 0.76988  | -3.3283  | 1079.2 | 0.96279      |
| [C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> CO <sub>2</sub> ] | 0.68425                            | 0.68604  | -2.1789  | 1152.3 | 4.9624       |
| [C <sub>6</sub> C <sub>1</sub> im][Cl]                              | 0.86666                            | 0.85663  | -5.8300  | 1500.0 | 0.24679      |
| [C <sub>4</sub> C <sub>1</sub> im][SCN]                             | 0.90109                            | 0.87156  | -6.72538 | 1499.8 | 0.033817     |

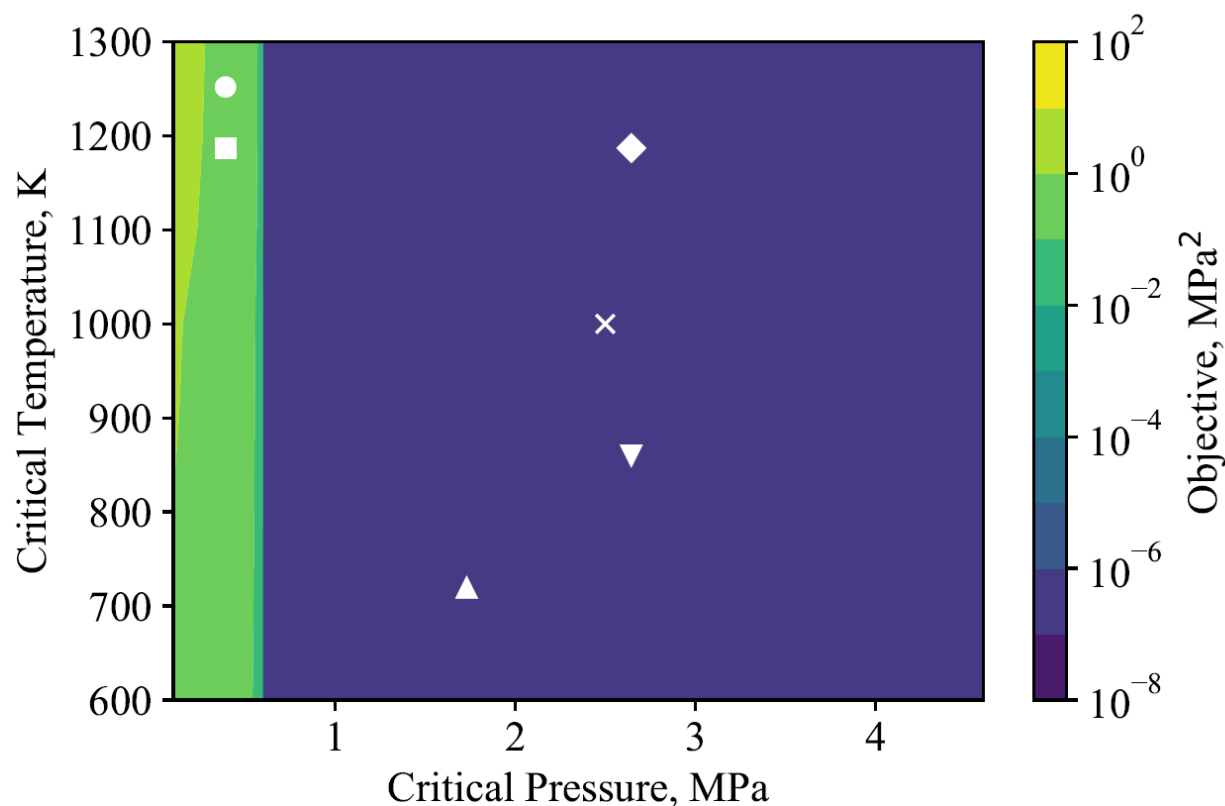
**Table 9.** van der Waals EoS model parameters for HFC-125

| Ionic liquid                                                        | HFC-125/IL van der Waals Parameters |          |          |        |              |
|---------------------------------------------------------------------|-------------------------------------|----------|----------|--------|--------------|
|                                                                     | $l_{ij}$                            | $l_{ji}$ | $m$      | $\tau$ | $\beta_{IL}$ |
| [C <sub>6</sub> C <sub>1</sub> im][FAP]                             | 0.75724                             | 0.75777  | -3.1236  | 1096.9 | 0.84396      |
| [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]                | 0.94755                             | 0.88067  | -9.7377  | 1495.6 | -0.19398     |
| [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]                | 0.63148                             | 0.63317  | -1.7454  | 1187.0 | 4.9560       |
| [C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> CO <sub>2</sub> ] | 0.40726                             | 0.24824  | -0.34565 | 115.93 | 0.053203     |
| [C <sub>6</sub> C <sub>1</sub> im][Cl]                              | 0.79991                             | 0.80272  | -4.0687  | 1440.3 | 0.83820      |
| [C <sub>4</sub> C <sub>1</sub> im][SCN]                             | 0.96174                             | 0.92967  | -9.9840  | 1.6323 | 0.75431      |

These results are consistent with Yokozeki and Shiflett,<sup>35</sup> who show the van der Waals EoS model can accurately predict phase equilibria for HFC-134a and the ionic liquid [C<sub>2</sub>C<sub>1</sub>im][Tf<sub>2</sub>N] mixtures. However, there is no guarantee that the parameters presented in Tables 8 and 9 are at the

global optimum because Equation (15) is a non-convex optimization problem and there may exist other parameter values that give similar high-quality fits.

Because ILs decompose before reaching their critical temperatures<sup>43, 44</sup> and actual critical points cannot be determined experimentally, hypothetical values (pseudocritical points) were used for ILs in this analysis. Multiple studies have sought to predict the pseudocritical points for ILs. For the IL [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>], pseudocritical property estimation methods include density and surface tension-based empirical equations,<sup>43</sup> group contribution methods,<sup>45</sup> Gibbs ensemble Monte Carlo,<sup>44</sup> and the critical-volume based Vetere's method.<sup>35</sup> However, these various methods result in estimates for [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] pseudocritical temperatures and pressures ranging from 600-1300 K and 0.39-3.0 MPa, respectively. Previous analysis by Yokozeki and Shiflett suggested the generic van der Waals model was not sensitive to IL critical properties.<sup>35, 36</sup> To verify this, a systematic analysis of the model fit was performed, quantified by the sum of residuals squared, with respect to  $T_c$  from 600 K to 1400 K and  $P_c$  from 0.1 MPa to 5.0 MPa for the mixture of HFC-32 in [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>]. The objective function is shown in Figure 6 as colored contours with respect to  $T_c$  and  $P_c$  and the critical points estimated by the methods listed above are marked by symbols. For  $P_c$  values below 0.5 MPa the objective function is on the order of  $10^{-1}$  to  $10^{+1}$ , which indicates a poor fit of the experimental data. For  $P_c$  values greater than 0.5 MPa and all  $T_c$ , the model returns feasible solutions with objective function values on the order of  $10^{-6}$ . This indicates the van der Waals EoS model is insensitive to  $T_c$  and  $P_c$ 's for ILs; therefore, it is unnecessary to determine highly accurate IL pseudocritical properties when fitting the van der Waals EoS model parameters to binary mixture solubility data; any critical point estimate can be used if its critical pressure is greater than 0.5 MPa. As mentioned in section 2.3, the  $T_c$  and  $P_c$  for each IL were set at 1000 K and 2.5 MPa, respectively. This is also likely true for other EoS models but should be tested.



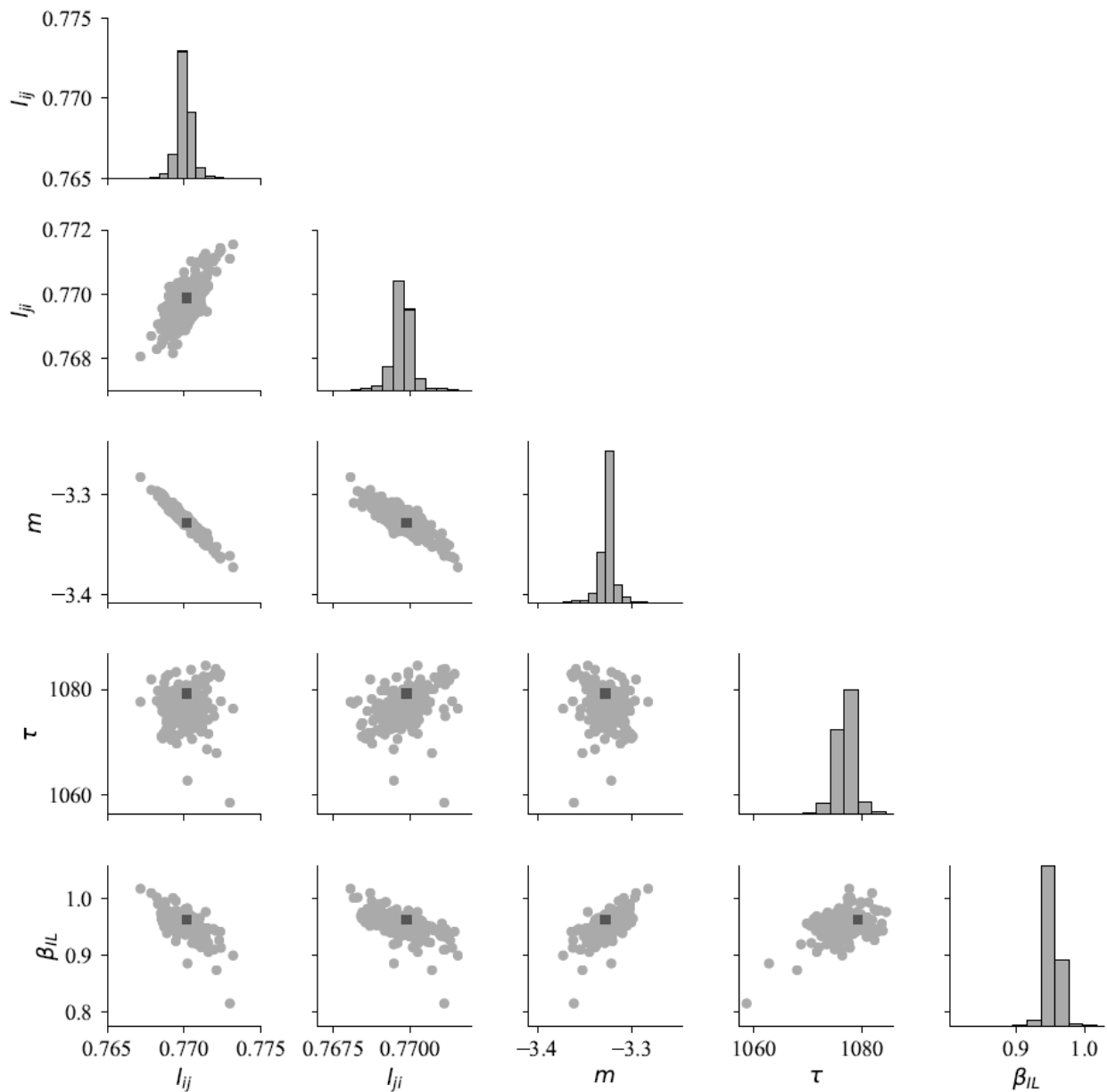
**Figure 6.** Critical temperature and pressure sensitivity analysis for the solubility of HFC-32 in the IL  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$ . The markers indicate critical temperatures and pressures calculated by: Vetere’s Method<sup>35</sup> (▼), Gibbs ensemble Monte Carlo<sup>44</sup> (●), surface tension based empirical equations to calculate critical temperature and Vetere’s method critical pressure<sup>35, 43</sup> (◆), surface tension based empirical equations to calculate critical temperature and Gibbs ensemble Monte Carlo critical pressure<sup>43, 44</sup> (■), and group contribution methods<sup>45</sup> (▲). The x marker indicates the critical temperature and pressure values used in this work.

Monte Carlo uncertainty analysis<sup>46, 47</sup> was also performed for the fitted parameters of the mixture of HFC-32 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$ . To summarize, normally distributed random error was added to the experimental  $x$ ,  $T$ , and  $P$  in Table 3 to create a new “simulated” experimental dataset. The values of error were chosen to correspond with experimental precision for  $x$ ,  $T$ , and  $P$  and the normal distribution over which the errors were randomly chosen was located within each measurement’s standard uncertainty:  $\pm 0.005$  (unitless) for mole fraction,  $\pm 0.1$  K for temperature, and  $\pm 0.0008$

MPa for pressure. Using the simulated data, the van der Waals parameters  $l_{ij}$ ,  $l_{ji}$ ,  $m$ ,  $\tau$ , and  $\beta_{IL}$  were refit and the results recorded. This procedure was repeated one thousand times. Thus, one thousand simulated experimental datasets, with  $x$ ,  $T$ , and  $P$  values varying within the experimental precisions, were generated and van der Waals parameters were fit to each simulated dataset. This provided a multivariate distribution of the fitted parameters, which is shown in Figure 7. The Monte Carlo procedure provides the expected deviation in the fitted results if the experiments were repeated hundreds of times.

Three important insights about our experimental data and fitted model can be gained from Figure 7. The plots along the diagonal of Figure 7 are histograms for the five fitted parameters. The first insight is that parameter  $l_{ij}$  has a variability of 0.785%,  $l_{ji}$  has a variability of 0.454%,  $m$  has a variability of 2.66%,  $\tau$  has a variability of 2.44%, and  $\beta_{IL}$  has a variability of 25.0%. This variability is induced by random errors of similar magnitude to the experimental precision. In other words, a variability of at least this large is expected if the experiments were repeated with the same equipment. The variability of fitted parameter  $\beta_{IL}$  is one to two orders of magnitude larger than the other parameters. This gives the second insight:  $\beta_{IL}$  is a sloppy parameter,<sup>48</sup> which means it cannot be determined uniquely from these data. This is because the quality of fit (sum of residuals squared) is insensitive with respect to  $\beta_{IL}$ . Scatter plots below the diagonal of Figure 7 show pairwise variability in the fitted parameters. The highest histogram bars (on the diagonal) correspond with the tightest clusters of parameters in the scatter plots (off the diagonal). The dark gray squares mark the parameter values for HFC-32 in [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] reported in Table 8, which were calculated with the original experimental data from Table 3. In each scatter plot, this dark gray square is located in the densest regions of parameters. From these scatter plots, we get our third key insight: parameters  $l_{ij}$ ,  $l_{ji}$ ,  $m$ , and  $\beta_{IL}$  are correlated. This suggests there exists an alternate

thermodynamic model with one or fewer fitted parameters that gives a similar quality of fit (sum of residuals squared).



**Figure 7.** Uncertainty analysis of van der Waals EoS model parameters for the solubility of HFC-32 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$ . Histograms for each parameter are shown on the diagonal, depicting the variability of each parameter. Scatter plots below the diagonal show the pairwise variability of the fitted parameters, with the dark gray squares indicating the parameters calculated with the original dataset shown in Table 8.

### 3.4. Ideal Selectivity based on Henry's law constants

The most suitable IL for a specific gas separation process hinges on the gas absorption capacity, the ability to preferentially absorb one gas over another from a mixture, and the ability to facilitate gas diffusion (as discussed in Section 3.5). In this context, the ideal selectivity has been reported as a parameter to assess the ability of a given pure IL to separate HFC-32 and HFC-125 in R-410A.<sup>15, 49</sup> The ideal selectivity can be defined as the ratio of the Henry's law constants of the HFC refrigerants at a given temperature, as follows:<sup>15</sup>

$$S_{Hij} = \left( \frac{k_{Hi}}{k_{Hj}} \right)_T \quad (22)$$

where  $k_{Hi}$  and  $k_{Hj}$  are the Henry's law constants calculated for the HFC refrigerants,  $i$  = HFC-32 and  $j$  = HFC-125, respectively.

Henry's law constants for HFC-32 and HFC-125 in the ILs were calculated using the method described in Section 2.5, and the results are summarized in Table 10.

**Table 10.** Henry's law constants (MPa) for HFC-32 and HFC-125 in ILs at 298.15 K.<sup>a</sup>

| Ionic liquid                                                        | Henry's law constants ( $k_H$ ) ( $kH, MPa$ ) |            | Selectivity<br>$S_{Hij}$ |
|---------------------------------------------------------------------|-----------------------------------------------|------------|--------------------------|
|                                                                     | HFC-32                                        | HFC-125    |                          |
| [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]                | 1.54±0.06                                     | 4.19±0.17  | 0.37                     |
| [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]                | 1.34±0.01                                     | 4.05±0.06  | 0.33                     |
| [C <sub>6</sub> C <sub>1</sub> im][FAP]                             | 0.84±0.03                                     | 1.37±0.01  | 0.61                     |
| [C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> CO <sub>2</sub> ] | 1.20±0.11                                     | 0.81±0.00  | 1.48                     |
| [C <sub>4</sub> C <sub>1</sub> im][SCN]                             | 3.11±0.37                                     | 13.32±2.44 | 0.23                     |
| [C <sub>6</sub> C <sub>1</sub> im][Cl]                              | 2.00±0.00                                     | 1.16±0.03  | 1.72                     |

<sup>a</sup> The uncertainties are the standard error of the coefficient obtained in the linear regression.

Comparing the Henry's law constants calculated for HFC-32 in ILs at 298.15 K shows that  $k_H$  (MPa) follows the order: [C<sub>6</sub>C<sub>1</sub>im][FAP] < [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] < [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] < [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] < [C<sub>6</sub>C<sub>1</sub>im][Cl] < [C<sub>4</sub>C<sub>1</sub>im][SCN], which is in good agreement with the general solubility trends

reported in Tables 2-7. On the other hand, HFC-125  $k_H$  (MPa) follows the order:  $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{CO}_2] < [\text{C}_6\text{C}_1\text{im}][\text{Cl}] < [\text{C}_6\text{C}_1\text{im}][\text{FAP}] < [\text{C}_4\text{C}_1\text{im}][\text{PF}_6] < [\text{C}_4\text{C}_1\text{im}][\text{BF}_4] < [\text{C}_4\text{C}_1\text{im}][\text{SCN}]$ . Based on this analysis, the ILs with the highest solubility (i.e. lowest Henry's law constants) for HFC-32 and HFC-125 are  $[\text{C}_6\text{C}_1\text{im}][\text{FAP}]$  and  $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{CO}_2]$ , respectively.

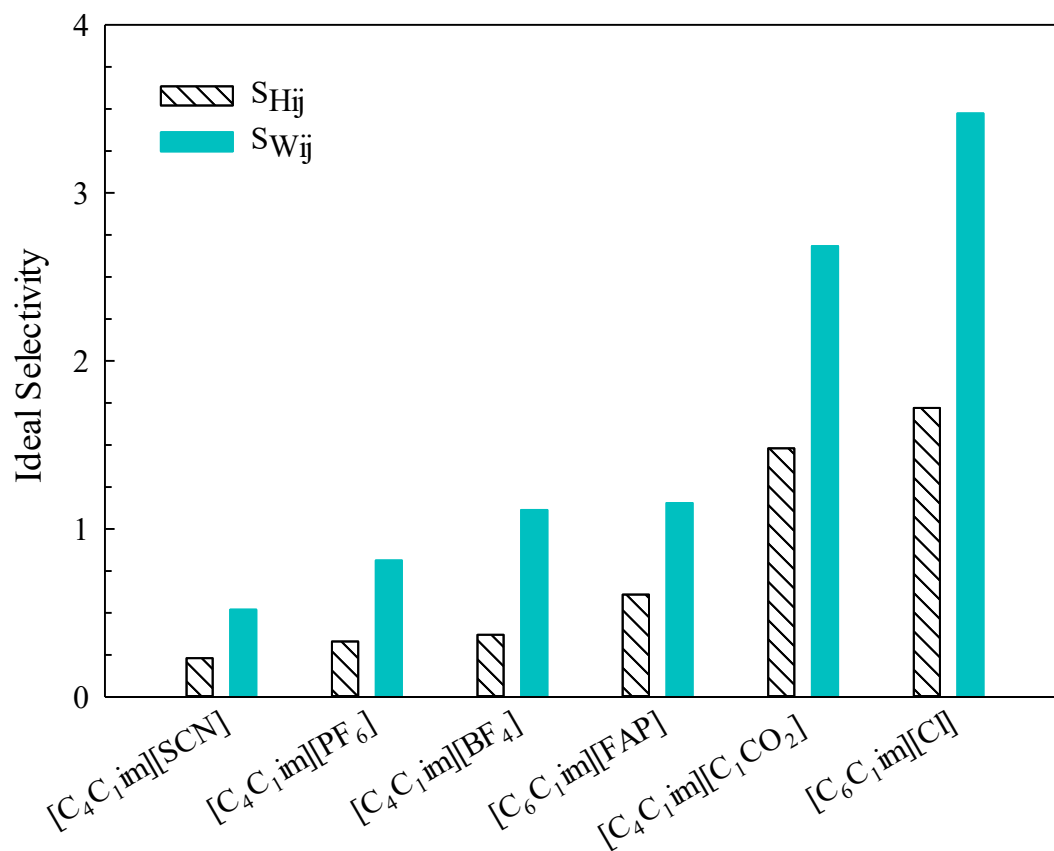
The ideal selectivity can also be defined as the ratio of the pure refrigerant solubilities on a molar or mass basis in the IL. The mass basis is more relevant to the design of separation systems; therefore, the selectivity can be defined as follows:

$$S_{Wij} = \left( \frac{w_{vi}/w_{li}}{w_{vj}/w_{lj}} \right)_{T,P} \quad (23)$$

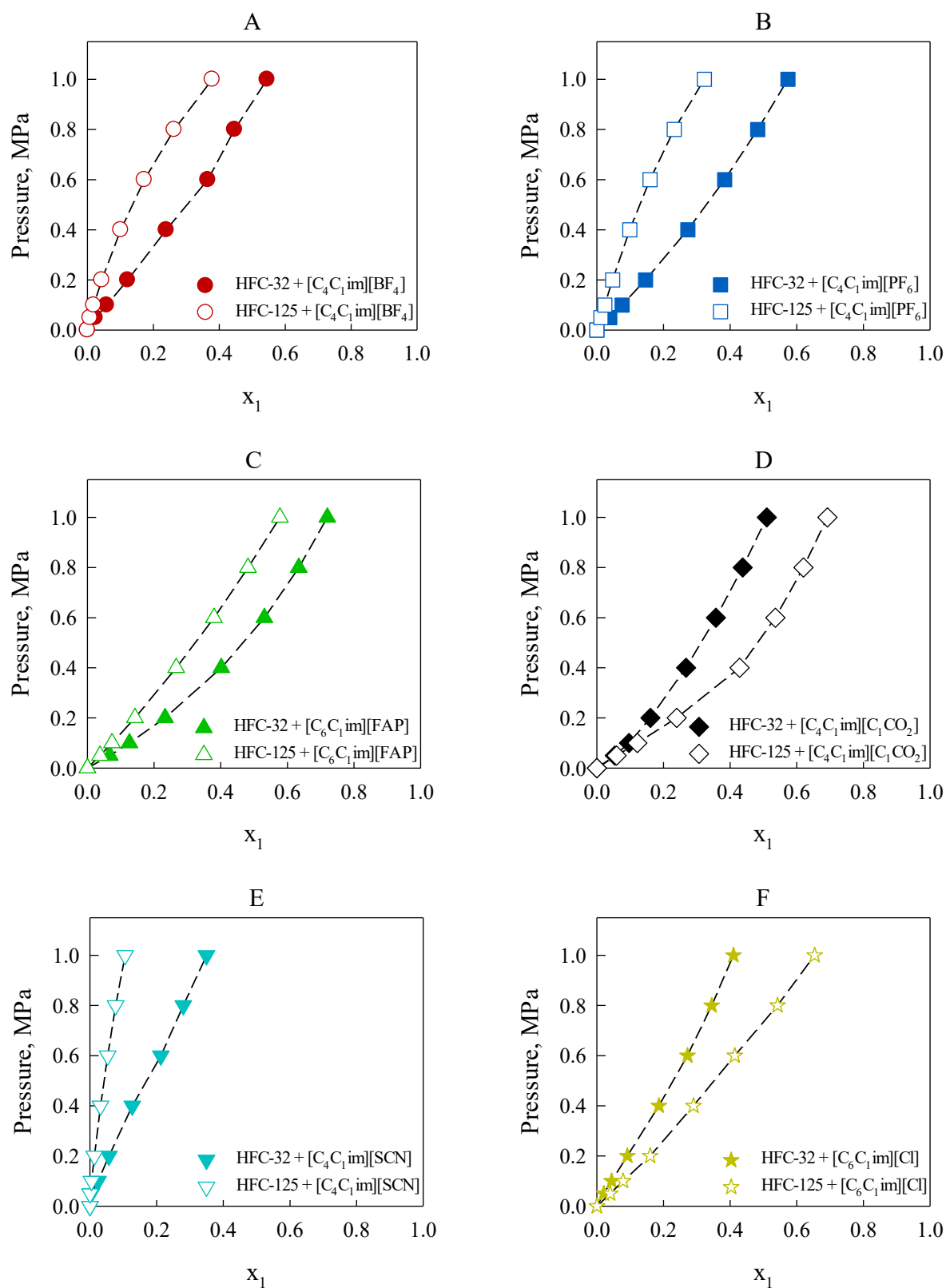
where  $w_{vi}$  and  $w_{li}$  are the vapor and liquid mass fractions of the dissolved refrigerants ( $i = \text{HFC-32}$  and  $j = \text{HFC-125}$ ) in the IL at  $T = 298.15 \text{ K}$  and  $P = 1.0 \text{ MPa}$ , respectively (where  $w_{vi}$  and  $w_{vj} = 1.0$ ).

In both cases ( $S_{Hij}$  and  $S_{Wij}$ ), the IL with the highest overall selectivity for the separation of R-410A, based on the ratio of the Henry's law constants ( $S_{Hij}$ ) or the ratio of the mass fractions ( $S_{Wij}$ ) for the separation of R-410A mixture was obtained using  $[\text{C}_6\text{C}_1\text{im}][\text{Cl}]$ . The ideal selectivity trends obtained with Equations 22 and 23 are shown in Figure 8.

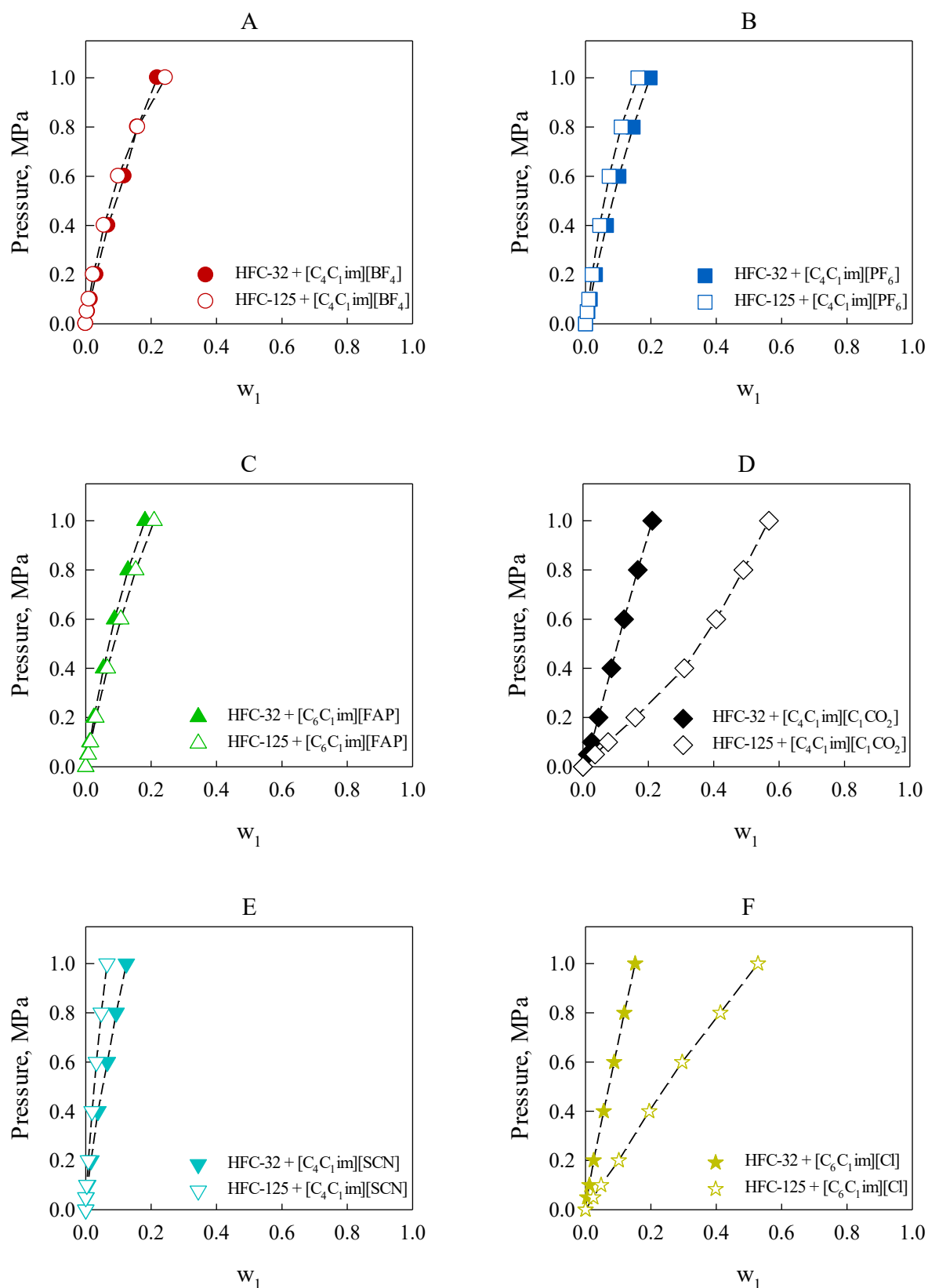
Too often in the literature, comparisons are made of the mole fraction solubility as a function of  $T$  and  $P$  as shown in Figure 9. The most relevant comparison for designing a separation process is to evaluate the difference in the mass fraction solubility as a function of  $T$  and  $P$  as shown in Figure 10.



**Figure 8.** Ideal selectivity for the absorption of HFC-32 and HFC-125 in ILs. The ideal selectivity was calculated based on the ratio of the Henry's law constants ( $S_{Hij}$ ) in the ILs at 298.15 K and the ratio of the weight fractions ( $S_{Wij}$ ) in the ILs at 1.0 MPa and 298.15 K.



**Figure 9.** Comparison of HFC-32 and HFC-125 VLE (mol fraction,  $x_1$ ) in ionic liquids: (A)  $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ , (B)  $[\text{C}_4\text{C}_1\text{im}][\text{PF}_6]$ , (C)  $[\text{C}_6\text{C}_1\text{im}][\text{FAP}]$ , (D)  $[\text{C}_4\text{C}_1\text{im}][\text{C}_1\text{CO}_2]$ , (E)  $[\text{C}_4\text{C}_1\text{im}][\text{SCN}]$ , and (F)  $[\text{C}_6\text{C}_1\text{im}][\text{Cl}]$  at 298.15 K.



**Figure 10.** Comparison of HFC-32 and HFC-125 VLE (mass fraction,  $w_1$ ) in ionic liquids: (A)  $[C_4C_1im][BF_4]$ , (B)  $[C_4C_1im][PF_6]$ , (C)  $[C_6C_1im][FAP]$ , (D)  $[C_4C_1im][C_1CO_2]$ , (E)  $[C_4C_1im][SCN]$ , and (F)  $[C_6C_1im][Cl]$  at 298.15 K.

In some cases such as for [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>], [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>], and [C<sub>6</sub>C<sub>1</sub>im][FAP] what appears to be a large difference in the mole fraction solubility for HFC-32 and HFC-125 turns out to be only a small or negligible difference in the mass fraction solubility that is needed for designing a separation process. Alternatively, small differences in the mole fraction solubility for HFC-32 and HFC-125 in [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>] and [C<sub>6</sub>C<sub>1</sub>im][Cl] result in larger differences in mass fraction solubility, and therefore these two ILs are possible candidates for separation of R-410A.

The most suitable IL for a specific gas separation must also consider practical aspects, such as the viscosity and cost of the ILs. For example, Gomez et al., reported a dynamic viscosity of 18.1 Pa·s for [C<sub>6</sub>C<sub>1</sub>im][Cl] at 298.15 K and ambient pressure that is higher than the other ILs in this study and this must be taken into consideration in separation processes.<sup>50</sup> Ideally, the ILs must also be recycled and used continuously in a separation process, such as extractive distillation. However, IL losses must be expected, whereby inexpensive ILs are more desirable for lowering the *operational expenses* (OPEX) of the separation process. Additional considerations include the toxicity and corrosivity of the IL.

### 3.5. Fickian Diffusion Coefficients

The diffusivity of HFCs in ILs is also required to design and develop new IL-based separation processes.<sup>51</sup> The time-dependent absorption behavior of HFC-32 and HFC-125 in the ILs was analyzed using a simplified Fickian diffusion model (see Section 2.5). The calculated diffusion coefficients for HFC-32 and HFC-125 in each IL at 0.05 MPa and 298.15 K are shown in Table 11 along with the viscosity of the ILs at 298.15 K.

**Table 11.** Estimated Fickian diffusion coefficients for HFC-32 / IL and HFC-125 / IL systems at 298.15 K and 0.05 MPa and reported viscosities for ILs at 298.15 K and 0.1 MPa.<sup>a</sup>

| Ionic liquid                                                        | Viscosity<br>(Pa·s)       | HFC-32 (1) / IL (2)                              |              | HFC-125 (1) / IL (2)                             |              |
|---------------------------------------------------------------------|---------------------------|--------------------------------------------------|--------------|--------------------------------------------------|--------------|
|                                                                     |                           | $D$ ( $10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ ) | $C_s$ (wt %) | $D$ ( $10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ ) | $C_s$ (wt %) |
| [C <sub>6</sub> C <sub>1</sub> im][Cl]                              | $18.1 \pm 1.8^{50}$       | 1.5                                              | 0.5          | 0.4                                              | 3.2          |
| [C <sub>4</sub> C <sub>1</sub> im][C <sub>1</sub> CO <sub>2</sub> ] | $0.448 \pm 0.019^{52}$    | 0.5                                              | 1.5          | 1.3                                              | 3.7          |
| [C <sub>4</sub> C <sub>1</sub> im][PF <sub>6</sub> ]                | $0.271 \pm 0.021^{53}$    | 8.5                                              | 0.7          | 1.7                                              | 0.5          |
| [C <sub>4</sub> C <sub>1</sub> im][BF <sub>4</sub> ]                | $0.1014 \pm 0.0027^{54}$  | 7.8                                              | 0.6          | 2.4                                              | 0.4          |
| [C <sub>6</sub> C <sub>1</sub> im][FAP]                             | $0.0882 \pm 0.0021^{55}$  | 19.6                                             | 0.6          | 5.5                                              | 0.8          |
| [C <sub>4</sub> C <sub>1</sub> im][SCN]                             | $0.0517 \pm 0.00055^{56}$ | -                                                | -            | -                                                | -            |

<sup>a</sup> The estimated diffusivity uncertainty was estimated to be within a factor of two in the calculated diffusivity.<sup>13</sup>

The diffusion coefficient ( $D$ ) of HFCs in the ILs is dependent on the refrigerant solubility ( $C_s$ ), the viscosity of the IL,<sup>38</sup> and the molecular radius of the solute molecule, according to the Stokes-Einstein equation.<sup>57</sup> The largest  $D$  values for HFC-32 and HFC-125 were found in [C<sub>6</sub>C<sub>1</sub>im][FAP] (HFC-32  $D = 19.6 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$  and HFC-125  $D = 5.5 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ ), which has one of the lowest viscosities of the ILs tested (see Supplemental Information for details). The 3.5 times higher HFC-32 diffusion coefficient in [C<sub>6</sub>C<sub>1</sub>im][FAP] can be attributed to the approximately 22 % smaller molecular radius for HFC-32 (0.18 nm) relative to HFC-125 (0.23 nm).<sup>58, 59</sup> In general, the calculated diffusion coefficients are in good agreement with previous reports.<sup>60</sup> For example, the diffusion coefficients for HFC-32 and HFC-125 in ILs are of the same order of magnitude, *i.e.* between  $10^{-11}$  and  $10^{-10} \text{ m}^2\cdot\text{s}^{-1}$ , for those previously reported in other fluorinated ILs.<sup>13</sup> In addition, the diffusion coefficient for R-22 (chlorodifluoromethane, CHClF<sub>2</sub>) in [C<sub>4</sub>C<sub>1</sub>im][BF<sub>4</sub>] and [C<sub>4</sub>C<sub>1</sub>im][PF<sub>6</sub>] reported by Minnick et al., are also within the same order of magnitude ( $10^{-10}$  to  $10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ ) as the data reported here.<sup>29</sup> The trend in diffusion coefficient with the inverse in viscosity ( $D \sim 1/\mu$ ) generally holds true for HFC-32 and HFC-125, except for HFC-32 + [C<sub>4</sub>C<sub>1</sub>im][C<sub>1</sub>CO<sub>2</sub>], which might indicate some chemical interaction

between HFC-32 and the acetate anion  $[C_1CO_2]$ . Molecular modeling studies are underway to elucidate this effect.

#### 4. Conclusions

A separation process for recycling R-410A is necessary so that HFC-32 can be reused in new HFO containing low-GWP refrigerant blends, and HFC-125 can be used as a fluorine-containing feedstock in more sustainable products. The absorption of HFC-32 and HFC-125 in six imidazolium-based ILs containing fluorinated and non-fluorinated anions was accurately measured using a microbalance at 298.15 K and pressures ranging from 0.05 to 1.0 MPa. HFC-32 was found to be more soluble in ILs with fluorinated anions than HFC-125, which is most likely due to hydrogen bonding between the refrigerant ( $CH_2F_2$ ) and the fluorinated anion ( $[BF_4]$ ,  $[PF_6]$ , and  $[FAP]$ ). HFC-125 was found to be more soluble in ILs with non-fluorinated anions ( $[C_1CO_2]$  and  $[Cl]$ ). The  $[C_4C_1im][SCN]$  had low solubility for both HFC-32 and HFC-125 relative to the other ILs tested. These results clearly demonstrate that the anion plays a major role in governing the solubility of HFCs in ILs. In future work, molecular modeling will be used to try and elucidate the physical reason for these trends. The experimental VLE data sets were successfully correlated using the van der Waals EoS and the model was insensitive to the choice of critical parameters ( $600 < T_c < 1400$  K and  $0.5 < P_c < 5.0$  MPa). The  $[C_6C_1im][Cl]$  and  $[C_4C_1im][C_1CO_2]$  ILs provided the highest ideal selectivity (2.7 to 3.5 on a mass basis) for separating R-410A at 298.15 K among the ILs studied in this work. The one-dimensional diffusion model was applied to time-dependent absorption data for each HFC / IL binary system. HFC-32 and HFC-125 had a higher diffusion coefficient in  $[C_6C_1im][FAP]$  relative to the other ILs due to its lower viscosity. HFC-32 had a higher diffusion coefficient (up to 3.5 for  $[C_6C_1im][FAP]$ ) relative to HFC-125 due to its smaller molecular radius (0.18 nm versus 0.25 nm). Molecular simulations (Monte Carlo and molecular dynamics) are underway to better understand the unique interactions and forces between HFCs and ILs. The present work

provides important insights into the solubility, diffusivity, EoS modeling, and ideal selectivity of HFC-32 and HFC-125 in ILs for the design of a separation process for recycling R-410A.

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Supporting Information – Comparison of VLE data for HFC-32 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$  and  $[\text{C}_4\text{C}_{1\text{im}}][\text{BF}_4]$ , and HFC-125 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$  obtained in this work with those available in the literature; comparison of excess Gibbs energy for HFC-32 and HFC-125 in  $[\text{C}_4\text{C}_{1\text{im}}][\text{PF}_6]$ ,  $[\text{C}_4\text{C}_{1\text{im}}][\text{BF}_4]$ ,  $[\text{C}_6\text{C}_{1\text{im}}][\text{FAP}]$ ,  $[\text{C}_6\text{C}_{1\text{im}}][\text{Cl}]$ ,  $[\text{C}_4\text{C}_{1\text{im}}][\text{C}_1\text{CO}_2]$ , and  $[\text{C}_4\text{C}_{1\text{im}}][\text{SCN}]$ ; and diffusion coefficient analysis for HFC-125 in  $[\text{C}_6\text{C}_{1\text{im}}][\text{FAP}]$ .

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