**Molecular Insights of Refrigerants (R32, R125, R134a) In Amino acid based Ionic Liquids**

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**ABSTRACT**

The increase in greenhouse gases contributes to the global warming potential, leading to the enhanced utilization of refrigeration and air conditioning fluids. Ionic liquids (ILs) have shown promise in the separation of refrigerants. In this paper, we employ molecular dynamics simulation to understand the molecular-level insights of refrigerants in ILs derived from amino acids (AA). Utilization of AA-derived ILs and their underlying structure with unexplored refrigerants. We considered three refrigerants, R32, R125, and R134a, tetra-butyl-phosphonium [TBP] as a common cation, and AA-derived molecules leucine [LEU], and isoleucine [ILE] as anions. We performed detailed structural, dynamic, and thermodynamic analyses to understand the underlying molecular behavior of R32, R125, and R134a in ILs. Among the three refrigerants, R32 self-diffusivity is one-fold higher than R125 and R134a in two ILs. Based on the detailed structural insights, [ILE] enhances the strong interaction with the refrigerants compared to other anions. These refrigerants' detailed free energy analysis shows that R134a presents ~ 75 % more negative free energy than R32 in [TBP][ILE]. Overall, the results presented in this manuscript guide the selection of various IL combinations for separating refrigerants, which stimulates further work on AA-based ILs.

**Keywords:** Refrigerants, Ionic liquid, tetra-butyl-phosphonium, leucine, and isoleucine

1. **Introduction**

Refrigerant and air conditioning systems are crucial in daily life, encompassing various industries, commercial, and domestic uses. There is a significant need to reduce the adverse effects of climate change, rising sea levels, global warming, and ecosystem disruptions.1, 2 One of the main reasons is the harmful greenhouse gas emissions, which contain fluorine, hydro-chloro-fluoro-carbons (HCFCs), and chloro-fluoro-carbons (CFCs).3, 4 In this context, third-generation refrigerants, hydrofluorocarbons (HFCs), are the most economical and environmentally friendly alternatives for the large-scale production and consumption of refrigerants and the air conditioning sector (RAC).5 Consequently, the release of HFCs into the atmosphere has consistently risen since 1990.6 Some countries have come up with a few regulations for the gradual reduction of HFC production and usage across several phases.7

However, there are no current replacements for HFCs that can fulfill the needs of refrigerants,8 domestic air conditioning systems,9 fire extinguishers,10 cooling systems for automobiles,11 aerosol-based propellants,12 etc. However, the development of Low Global Warming Potential (GWP) refrigerant blends that merge HFCs and hydrofluoroolefins (HFOs) is progressing rapidly in the marketplace, for example, R455A, R513A, R454A, R454C, R448A, etc.13-15 Moreover, apart from formulating the new blends, recycling and reuse of refrigerants is a promising approach to increase the lifetime of refrigerants.16,17 However, the separation of pure component refrigerants is difficult with traditional distillation techniques because of the formation of azeotropic mixtures.18, 19 For the separation of azeotropic refrigerant mixtures, extractive distillation20 is an effective method because of its wide variety of applications, low energy consumption, and large separation volumes.21

Ionic liquids (ILs)22 has been utilized as an extractant for the effective separation of HFC because of its incredible properties, such as high thermal stability, low melting point, and ease of solubility with different compounds.23 A series of studies has been reported on the separation of refrigerants with different ILs. Morais et al.,24 studied IL-based separation techniques for HFC (R-410A) refrigerant recovery and recycling by using different combinations of ILs 1-butyl-3-methylimidazolium acetate ([C4C1im][C1CO2]), 1-butyl-3-methylimidazolium tetrafluoroborate [C4C1im][BF4], 1-butyl-3-methylimidazolium hexafluorophosphate [C4C1im][PF6], 1-butyl-3-methylimidazolium thiocyanate ([C4C1im][SCN]), 1-hexyl-3-methylimidazolium chloride ([C6C1im][Cl]), and 1-hexyl-3-methylimidazolium tris(penta-fluoro-ethyl)tri fluoro-phosphate ([C6C1im][FAP]) at 298.15 K and up to 1.0 MPa. Sun et al.,25  studied the separation capacity of R-134a, R-227ea, R-32, R-152a, and R-125 blends in tri-hexyl(tetra-decyl)-phosphonium chloride [P6,6,6,14] [Cl] ILs using a temperature range of 293.15 to 343.15 K.

Asensio et al.,26, 27 focused on the separation of fluorinated refrigerant gases, R32, R125, R134a, R1234yf, and R1234ze, with three different combinations of ionic liquids, 1-Ethyl-3-methylimidazolium dicyanamide [C2mim][DCA], 1-butyl-3-methylimidazolium dicyanamide [C4mim][DCA], 1-Ethyl-3-methylimidazolium thiocyanates [C2mim][SCN] at 283.15 to 323.15 K and pressures up to 1 MPa. Finberg et al.,28 designed a process for the separation of refrigerants, such as R-404A, R-407C, and R-410A, with HCFC-22. At high pressure, pure R404A achieved 99.5 wt.% in the presence of [BMIM][PF6] and [EMIM][TF2N], R407C was achieved 99.7 wt.%, in the presence of [BMIM][PF6] and R410A was achieved 95.5 wt.% in the presence of [BMIM][PF6]. Viar et al.,29 provided insights into the design of extraction distillation to separate the R410A by using seven different combinations of ILs, such as [C4C1im] [PF6], [C4C1im] [BF4], [C4C1im] [DCA], [C4C1im] [SCN], and [C4C1im] [TF2N]. In many of the literature works on the refrigerants, Imidazolium-based ILs have been used significantly. Arishi et al.30 have utilized imidazolium and phosphonium-based ILs tri-hexyl-tetra-decyl-phosphonium chloride [P6,6,6,14][Cl] for separating the azeotropic mixture of R-450A, R-456A, R-515B, and R-516A. Liu et al.31 have used tri-hexyl-tetra-decyl-phosphonium bis(2,4,4-trimethylpentyl)phosphonate IL to understand the solubility of R32, R227EA, R236FA, and R245FA**.**

Despite the widely available ILs for capturing the various refrigerants, there is a known limitation of being expensive and viscous. However, Recker et al.32 utilized an anion derived from the branched-chain amino acids (AA), i.e., valine, leucine, and isoleucine, using ammonium and phosphonium-based cations for direct air capture of CO2. These types of AA are generally found in human hair, feathers, and fur, which are not expensive, thereby reducing the overall cost of ionic liquids. To the best of our knowledge, no literature has been found on utilizing the amino acid-based ILs to understand the structure and properties of refrigerants. Therefore, it is intriguing to understand the role of the phosphonium-based ILs on the refrigerants. In our previous work, we considered the tetra-butyl-phosphonium [TBP] as a cation and the amino acid-derived anion valine [VAL] as an anion to understand the separation properties of benzene, toluene, and p-xylene.33 In that work, we understand that the [TBP][VAL] was found to be favorable for the separation of benzene at room temperature and pressure. However, there is a lack of significant understanding of the role of AA and phosphonium-based ILs and their role in refrigerants. On the other hand, the role of amino acid-derived anions is shown to be promising.

In this paper, we investigate intermolecular structure, dynamics, and thermodynamic behavior of two different IL combinations, using tetra-butyl phosphonium ([TBP]) as a common cation and two independent amino acid-derived anions, such as (a) leucine ([LEU]), and (b) isoleucine ([ILE]) were considered. We considered three refrigerants—R32, R125, and R134a to understand the underlying molecular insights. The following sections describe the methodology and the molecular structure, dynamics, and thermodynamic properties in detail.

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**Figure 1.** Chemical structures of (a)TBP, (b) Isoleucine, (c) Leucine, (d) R32, (e) R125, (f) R134a using ChemSketch. Molecular models of (i)TBP, (ii) Isoleucine, (iii) Leucine, (iv) R32, (v) R125, (vi) R134a. Color codes: red: oxygen, white: hydrogen, gray: carbon, dark blue: nitrogen, orange: phosphorus, light blue: fluorine.

1. **Modeling and Simulation Methodology**

Avogadro software34 was used to model the various refrigerants (R32, R125, R134a), cation (TBP), and anions (LEU, and ILE) molecules, and ChemSketch software35 was used for the representation of schematic structures, as shown in Figure 1. The molecular geometry optimization was performed using the density functional theory (DFT) with a basis set of B3LYP/def2-SVP. The partial charges of atoms were calculated using the ChelPG method as implemented in the ORCA software.36 The force field parameters of refrigerants and anions were adapted from the LigParGen Server37-39, and the force field of TBP is taken from the literature.40 Figure S1 represents the detailed labeling of each molecule, and Table S1 provides the forcefield parameters of all the molecules. All bonds are constrained by the LINCS algorithm.41

OPLS-AA force fields42 were used to model the bonded and non-bonded interactions for the entire simulation systems. The particle-mesh-Ewald (PME) method43 was used to calculate the Coulomb interactions with a cutoff radius of 1.4 nm. The Lennard-Jones 12-6 method44 was used to observe the van der Waals interactions with a cutoff radius of 1.4 nm. The Parrinello-Rahman barostat and Nose-Hoover thermostat were used to maintain the pressure at 1 bar and temperature at 298 K, respectively, with a time constant of 5ps for both.

Energy minimization of the system was performed using the steepest descent (SD) algorithm with a step size of 0.01. The SD45, 1st order derivative is simple and easy to implement, very stable, especially with highly distorted structures, and effective at removing large forces quickly. The equation of motion is solved by using the leap-frog algorithm46 This method is being used for its stability, especially when long simulation timescales are required. The periodic boundary conditions (PBC) were applied in all three directions. We considered a cubic box of 6 nm, and all the simulations are performed using GROMACS 2022.4.47

Initially, we prepared the independent simulations involving refrigerants and ILs of all molecules to benchmark against the experimental density data using NPT-MD simulations of 50 ns. Then, we prepared six different mixed systems with a combination of refrigerants, cation, and anions. Each mixed simulated system was subjected to a 100 ns NPT-MD simulation. We used the block sum averaging method to analyze the data and statistical uncertainties. In total, we have performed two sets of simulations with varying concentrations of refrigerants (Cref), 0.142 M and 0.625 M. The details of the simulation system are summarized in Table 1.

**Table 1.** Simulation System details.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Number of molecules | | | | | | |
| **System name** | **TBP** | **LEU** | **ILE** | **R32** | **R125** | **R134a** |
| **Cref = 0.124 M** | | | | | | |
| **TBP+LEU+R32** | 300 | 300 | - | 100 | - | - |
| **TBP+LEU+R125** | 300 | 300 | - | - | 100 | - |
| **TBP+LEU+R134a** | 300 | 300 | - | - | - | 100 |
| **TBP+ILE+R32** | 300 | - | 300 | 100 | - | - |
| **TBP+ILE+R125** | 300 | - | 300 | - | 100 | - |
| **TBP+ILE+R134a** | 300 | - | 300 | - | - | 100 |
| **Cref = 0.625 M** | | | | | | |
| **TBP+LEU+R32** | 300 | 300 | - | 1000 | - | - |
| **TBP+LEU+R125** | 300 | 300 | - | - | 1000 | - |
| **TBP+LEU+R134a** | 300 | 300 | - | - | - | 1000 |
| **TBP+ILE+R32** | 300 | - | 300 | 1000 | - | - |
| **TBP+ILE+R125** | 300 | - | 300 | - | 1000 | - |
| **TBP+ILE+R134a** | 300 | - | 300 | - | - | 1000 |

We performed the free-energy-solvation of refrigerant using the thermodynamic integration technique and the detailed method described in the literature reports.48-50 The following equation was used for the calculation of the solvation of free energy (ΔGSol),

ΔGSol = ΔGelectrostatic + ΔGvan der Waals  ------------------------ (i)

Where, ΔGelectrostatic is free energy due to the electrostatic decoupling and ΔGvan der Waals is free energy due to the van der Waals decoupling. We performed the electrostatic and van der Waals interactions separately in the solvation-free energy. Separating the two different non-bonded energy terms would help in understanding the responsible and favorable non-covalent interactions. We performed 21 simulations for electrostatics and 21 simulations for van der Waals and electrostatic decouplings. The numerical integration problems are possible for short-chain and long-chain molecules due to the simultaneous (de)coupling of both van der Waals and electrostatic interactions. Thus, we decouple both electrostatic and van der Waals interactions separately with the window size of 0.05. Each window simulation was performed by a 5 ns NPT-MD simulation. One among the 101 refrigerants is used to probe the free energy calculation for all three refrigerants in different IL combinations.

1. **Results and discussion**
   1. **Density**

We first observe the system density (ρ) behavior. The pure refrigerants (R32, R125, and R134a) and neat ILs ([TBP][LEU] and [TBP][ILE]) ρ values are presented in Table 2. It is observed that IL ρ values vary at 0.9313 g/cc for [TBP][LEU] and 0.9349 g/cc for [TBP][ILE]. These ρ show a good agreement with the available experimental and theoretical ρ data, with the deviation as ~ 0.5 %.40,51 However, there is no direct experimental data available for pure refrigerants at the simulated conditions of 298 K and 1 bar. Instead, the available data52-54 for refrigerants is reported as shown in Table 2. It is observed that the ρ values do not vary significantly from those of experimental data.

**Table 2.** Density (ρ) of pure refrigerant and IL in the system. The standard deviation values are given in parentheses.

|  |  |  |  |
| --- | --- | --- | --- |
| **Molecules** | **Simulation data (g/cm3)** | | **Experimental density (g/cm3)** |
| **TBP+LEU** | 0.931 | (0.002) | 0.926951 |
| **TBP+ILE** | 0.935 | (0.002) | 0.929651 |
| **R32** | 0.824 | (0.008) | 0.96052a |
| **R125** | 1.164 | (0.001) | 1.18353b |
| **R134a** | 1.180 | (0.001) | 1.20754c |

a binary mixture of R32 and R123yf with R32 mole fraction 0.904 and at 30 bar and 303 K.

b at 18 bar and 300 K.

c at 8.2 bar and 298 K.

**Table 3.** Density (ρ) of refrigerant and IL mixtures in the system. The standard deviation values are given in parentheses.

|  |  |  |
| --- | --- | --- |
| **Mixed system** | **Mixed system density (ρ) (g/cc)** | |
| **Cref = 0.142M** | **Cref = 0.625M** |
| **R32+TBP+LEU** | 0.833 (0.008) | 0.880 (0.007) |
| **R125+TBP+LEU** | 0.871 (0.008) | 1.105 (0.006) |
| **R134a+TBP+LEU** | 0.860 (8.147) | 1.041 (0.006) |
| **R32+TBP+ILE** | 0.832 (8.087) | 0.882 (0.007) |
| **R125+TBP+ILE** | 0.868 (0.008) | 1.104 (0.006) |
| **R134a+TBP+ILE** | 0.858 (0.008) | 1.041 (0.006) |

Table 3 presents the IL + refrigerant ρ data at Cref = 0.142 M and 0.625 M. It is observed that with an increase in concentration of refrigerant, we observe ρ increase. While the IL density remains at 0.93 g/cc, there is a variation in the ρ values of refrigerants due to variation in the Cref. For instance, ρ of R125+IL mixture shows higher than R134a+IL and R32+IL. This implies that the pentafluorine atoms on R125 lead to significant interactions with the ILs compared to R32 and R134a. Compared to the ρ of neat refrigerant systems, we see a decrease in the ρ in IL-mixed systems. Overall, at 0.142 M and 0.625 M, we observe that ρ of the mixed system follows a sequence given as R125 + IL > R134a + IL and > R32+IL. It is derived that the higher the fluorine atoms, the enhanced the densities.

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**Figure 2(i).** Snapshots of equilibrated refrigerants with different ionic liquid systems at Cref = 0.142M as (a)TBP+LEU+R32, (b)TBP+LEU+R125, (c)TBP+LEU+R134a, (d)TBP+ILE+R32, (e)TBP+ILE+R125, (f)TBP+ILE+R134a. Color codes: orange: TBP, ice-blue: LEU, blue: ILE, yellow: R32, light green: R125, green: R134a.

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**Figure 2(ii).** Snapshots of equilibrated refrigerants with different ionic liquid systems at Cref = 0.625M as (g)TBP+LEU+R32, (h)TBP+LEU+R125, (i)TBP+LEU+R134a, (j)TBP+ILE+R32, (k)TBP+ILE+R125, (l)TBP+ILE+R134a. Color codes: orange: TBP, ice-blue: LEU, blue: ILE, yellow: R32, light green: R125, green: R134a.

To underline the observed density behavior, we analyze the equilibrated simulated snapshots of refrigerants and IL mixed systems. Figure 2 (i and ii) represents the equilibrated snapshots of the systems at 0.142M and 0.625M. We observe that TBP molecules show significant aggregation themselves in the dilute systems, 0.142 M. Interestingly, we see an interaction with anions also. On the other hand, we observe the refrigerants distributed throughout the simulations. Similarly, in the concentrated systems 0.625 M, we observe that the refrigerators show dominant aggregates than the ILs.

Overall, despite the aggregations observed, we see that increased molecular packing is going from 0.142 M to 0.625 M., which influences the overall system density increase. There were some important contributions from the mixture of refrigerants and IL, which may influence the overall polarity of the system, intermolecular interactions, hydrogen bonding interactions, etc. It is observed that ILs tend to interact with refrigerants. Anions belonging to the amino acid groups with an alkyl group show an interaction with refrigerants in both dilute and concentrated solutions. During the mixing process, TBP forms a strong hydrogen bond with the amino acid group anions; on the other hand, IL with refrigerants may form the van der Waals interactions and dipole-dipole interactions. These detailed analyses are further quantified by calculating pair-wise distribution functions.

* 1. **Radial distribution function**

The radial distribution function (RDF) analysis is used to understand the intermolecular interaction properties between the molecular and atomic pairs. Based on observations, all the peaks in the graphs initially fluctuated and then eventually stabilized into a straight line at g(r) = 1. The first peak defines the interaction between atoms or molecules, the second peak onwards defines the solubility of atoms within the system, and the straight end line represents the ideal behavior of the system.

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**Figure 3.** Radial distribution function plots at 0.142 M (a) PTBP with C1Refrig, and (b) PTBP with F1Refrig.

Figure 3 (a) represents the RDFs for atom-atom interactions between the phosphorus of TBP (PTBP) and carbon atoms of the refrigerants (C1Refrig). Similarly, Figure 3 (b) presents PTBP and Fluorine atoms of refrigerants (F1Refrig). The atomic pair corresponding coordination number (Ncr) is provided in Table S3. From Figure 3 (a), RDF between the PTBP - C1Refrig shows peaks located in the range of ~0.54 – 0.58 nm for all the mixed systems R32+LEU+TBP, and R32+ILE+TBP. Interestingly, for the mixture of R32 + IL, we observe that the PTBP - C1Refrig RDF shows variation in intensity of the peak given as [TBP][LEU] > [TBP][ILE]. This is also reflected in the coordination number calculation, when compared to the other refrigerants, and in all the ILs, the C1 of refrigerant R32 highly interacts with the P of TBP, as observed from Table S4. Similarly, RDF between the PTBP - F1Refrig was presented. In Figure 3 (b). We only observe a significant structure between the Fluorine atoms of R32 and PTBP. In the case of R32 + IL mixture, we see the first peak located at ~0.45 nm in [TBP][ILE] and in [TBP][LEU], with an Ncr value of 0.092 and 0.099, respectively. Interestingly, we do not see any structure between R125 and R134a with [TBP] in two ILs. R32 presents strong interaction with the cations when compared to R125 and R134a. Despite more Fluorine atoms on the R125 and R134a, we do not see a significant structure with the PTBP, -PTBP.

To understand the responsible molecular factors, we plot the atomistic RDF between the cation and anion. Figure S2 represents the pair distribution function analysis between the atom PTBP with the O1, O2, N1, and C1 atoms of anions (LEU and ILE) in the mixed system containing R32+TBP+ILE, R125+TBP+ILE, and R13a+TBP+ILE at CRef = 0.625 M. The O1 atom of the ILE anion exhibited the strongest interaction, with PTBP at a distance of 0.42 nm. Similar behavior was observed with the atom O2 of ILE and PTBP at 0.42 nm. However, interactions between the N1 of anions with PTBP show higher peaks (at 0.41 nm) with LEU anions than with ILE. In contrast, carbon C1 of ILE interacts more strongly with PTBP  than the system containing LEU and VAL. It is intriguing that the influence of refrigerant on the IL-IL interactions remains unaffected. Meanwhile, interactions between PTBP- C1Refrig and PTBP-F1Refrig remain similar at CRef =0.625 M (see Figure S2 (c,d) and Figure 3). Several interesting observations can be made, such as that TBP-ILE interactions are stronger than TBP-LEU. R32 possesses strong interaction with the TBP in the presence of LEU anions. Because of these observations, we observe the weak local structure between TBP-LEU.

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**Figure 4.** RDF plots of LEU with refrigerants (a) O1LEU-C1Refrigerants, (b) O1LEU-F1Refrigerants, (c) O2LEU-C1Refrigerants, (d) O2LEU-F1Refrigerants, (e) N1LEU-C1Refrigerants, (f) N1LEU-F1Refrigerants. Similarly, RDF function plots of ILE with refrigerants. (g) O1ILE-C1Refrigerants, (h) O1ILE-F1Refrigerants, (i) O2ILE-C1Refrigerants, (j) O2ILE-F1Refrigerants, (k) N1ILE-C1Refrigerants, (l) N1ILE-F1Refrigerants.

Figure 4 represents the RDFs for atom-atom interactions between the atoms O1, O2, and N1 of anions with C1 and F1 atoms of refrigerants R32, R125, and R134a at 0.124 M. Their corresponding coordination number (Ncr) is provided in Table S3. From Figure 4 (a), the highest interaction occurs with the refrigerant R32 at 0.36 nm. However, in Figure 4 (b), the highest interaction occurs with R125, with a slight fluctuation in the interaction at 0.31 nm Similarly, in Figure 4 (c), the R32 refrigerant exhibits a strong interaction with O2 of VAL at 0.34 nm and in Figure 4 (d), the R125 refrigerant shows a strong interaction with O2 of VAL at 0.30 nm with an Ncr value of 0.017. Furthermore, C1 of R32 refrigerants shows high interaction with N1 of VAL at 0.38 nm, and the interaction of F1 of R125 refrigerant with N1 of VAL is highest among all the refrigerants at 0.28 nm with an Ncr of 0.010. From Figure 4, it is observed that R32 shows a strong intermolecular interaction with VAL.

When compared to the RDF between O1, O2, and N1 of ILE as well as LEU with C1 and F1 atoms of the refrigerants R32, R125, and R134a, we observe that R32 presents a strong coordinating structure with ILE and LEU, with the peak located at ~0.36 nm C1 and F1 of the refrigerants. The peak intensity is higher for R32, followed by R125 and R134a. These peak locations remain similar at 0.625 M as shown in Figures S3, S4, and S5. Similarly, the RDFs for atom-atom interactions between the atoms C1VAL, C1LEU, and C1ILE with the C1 and F1 atoms of refrigerants, R32, R125, and R134a. C1 of VAL has the same interaction with C1 and F1 of R32 at 0.43 nm, 0.39 nm, and 0.39 nm for VAL, LEU, and ILE, respectively. Overall, we observe that the C1 of anions interacts more with C1refreig. This is due to the relatively negative charge on the carbon atoms of the anion and the positive charge on the carbon atoms of the refrigerants. Similar behavior is seen in the refrigerant concentration of 0.625 M. The strong electrostatic interaction between the refrigerant and cation leads to molecular packing between R32-TBP, R125-TBP, and R134a-TBP. We further evaluate the RDF between the center of mass of molecular RDFs.

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**Figure 5.** Centre of mass of Pair distribution function plots at 0.142M of (a) TBP-R32, (b) TBP-R125, (c) TBP-R134a, (d) R32-R32, (e) R125-R125, (f) R134a-R134a, (g) LEU-REFRIG, (h) ILE-REFRIG.

In the label of graph, R32LT: system [R32][LEU][TBP], R32IT: system [R32][ILE][TBP], R125LT: system [R125][LEU][TBP], R125IT: system [R125][ILE][TBP], R134aLT: system [R134a][LEU][TBP], R134aIT: system [R134a][ILE][TBP].

Figure 5(a, b, and c) RDF between the TBP with refrigerants in the presence of two anions. We see a significant coordination structure between cation and refrigerant with peaks located at 0.51 nm, 0.59 nm, and 0.56 nm, respectively, for TBP-R32, TBP-R125, and TBP-134a. The peak heights do not change significantly with the presence of two different anions, LEU and ILE. On the other hand, we do not see any significant structure between the Anions-refrigerant, whereas we see a minimal first peak located at 0.52 nm – 0.59 nm for the anion-R32, anion-R125, and anion-R134a. Therefore, cations interact strongly with the refrigerants. In addition, despite the presence of different anions, we see that refrigerants show a strong coordination structure among themselves. For instance, the location of the first peak is 0.45 nm for R32-R32, 0.52 nm for R125-R125, and 0.52 nm for R134a-R134a. The corresponding coordination values are appended in Table S4.

In Figure S6, at 0.142 M, plots (a) and (b) represent the C1Leu with C1Refrigerant and F1Refrigerant. C1R32 showed a sharp peak at 0.41 nm with an Ncr value of 0.133, while C1R125 and C1R134a had the same peak of interaction at the same distance, 0.46 nm, with an Ncr value of 0.163 and 0.165. Additionally, F1R125 had an instant peak with C1Leu at 0.36 nm with an Ncr value of 0.045, while F1R32 and F1R134a had peaks at 0.37 nm with Ncr values of 0.059 and 0.058, respectively. Furthermore, plots (c) and (d) represent the interaction of C1Ile with C1Refrigerant and F1Refrigerant. The C1R32 and F1R32 showed a strong peak of interaction at 0.44 nm and 0.36 nm, with an Ncr value of 0.392 and 0.142 compared to R125 and R134a. However, in Figure S7 at 0.625 M, the same interaction combination was observed between refrigerants with C1Leu and C1Ile. In contrast with anions, LEU and ILE have larger, more branched side chains. These bulkier groups block, making it harder for R32 to get close. As a result, the RDF peaks for LEU and ILE are lower or shifted, showing weaker interactions.

Figure S8 represents the RDF of a pair of TBP with anions, anions with themselves, and a cation with itself. It is interesting to see that the presence of IL does not alter the IL structure at Cref =0.124 M and 0.625 M. The Anions LEU-LEU and ILE-ILE, as well as TBP-TBP, present strong structure formation in all three refrigerant systems. For instance, the interaction of cation with itself is more in the presence of ILE anion with the refrigerants. These observed structural transitions remain intact in the concentrated systems CRef =0.625 M, as shown in Figures S9 and S10. The fluorine atoms in R32 had a weak interaction with the COO group in anions, while R125 and R134a had multiple fluorine atoms as compared to R32, which presents a weak interaction because of the dominant van der Waals interactions with anions.

* 1. **Diffusivity**

Self-diffusivity (D) defines the random movement of the molecule within the system as being driven by its kinetic energy, and the average distance traveled by each molecule from the initial position is calculated by mean square displacement (MSD) at various time intervals. The D value of the molecule is calculated by Einstein's relation55, and the corresponding MSD plots are provided in Figures S11 and S12. The D values of individual molecules, with their standard deviation, are provided in Table S5. Figure 6 presents the D values of the refrigerants in the different combinations of ILs with different refrigerant concentrations. In a low concentration regime, 0.124 M, we observe that D values of R32, R125, and R134a are higher in [TBP][ILE]. Relatively higher D values are observed in high-concentration systems. However, when compared with the D values of refrigerant systems, we see two-fold higher values in concentrated systems. Deng et al.56 studied the evaporation behaviors of R32/R1234ze(E) mixtures on a copper surface using molecular dynamics simulations. The D value of R32 is greater than that of R1234ze(E), which indicates the R32 molecule experiences a lower binding force to the copper surface than the R1234ze(E) molecule. However, there is no reported experimental self-diffusivity data available for R32 or R125.

A comparison of a graph

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**Figure 6.** Self-diffusivity coefficient of Refrigerants in different combinations of IL systems (a) at 0.142M, and (b) at 0.625M.

Figure 6 illustrates the self-diffusivity of refrigerants at different concentrations in the presence of different IL combinations. While comparing Figure 6 (a) and (b), we understand that by varying concentration, such as 0.142M and 0.625 M, D values show more than two-fold higher. at 0.625 M with the different combinations of ILs. At 0.142M, the diffusivity of refrigerants varies with different combinations of ILs. For instance D value of R32, in IL (TBP+ILE), with the D obtained 1.144 (± 0.121) × 10-5 cm2/sec, is 0.883 (± 0.043) × 10-5 cm2/sec in IL (TBP+LEU), which indicates that R32 presents weak intermolecular interactions with TBP and ILE that led to higher D values. Similar observations were shown with refrigerant R125. The hydrogen bonding capability may also affect the D values as observed in RDF calculations, as the atoms of refrigerants had weak interaction with anions due to lower van der Waals interactions and had weak hydrogen bonding capability, especially in R32. Furthermore, while observing refrigerant R134a, the lower D values are observed in IL combination (TBP+LEU) with the D value of 0.332 (± 0.022) × 10-5 cm2/sec. In addition, the overall D values follow a sequence given as: DR32 > DR125 > DR134a.

Furthermore, in Figure 6 (b) at 0.625M, we observed the opposite behavior due to the higher concentration of refrigerants. In (TBP+LEU) and (TBP+ILE), the diffusivity occurs in the same way in R32, with the D value of 2.793 (± 0.046) × 10-5 cm2/sec and 2.783 (± 0.023) × 10-5 cm2/sec, respectively, and approx. 0.35% of changes occur. R125 and R134a D values are lower in (TBP+LEU) with the D value of 0.819 (± 0.029) × 10-5 cm2/sec and 0.922 (± 0.014) × 10-5 cm2/sec, respectively. Similar observations were observed in RDF plots (atom-wise and pair-wise distribution), R32 freely moves in the presence of ILs, while R125 and R134a had a strong bond with IL, indicating that the higher the fluorine atoms, the higher the densities. Among all the refrigerants, the highest diffusion occurs in R32. However, this is due to the higher concentration of refrigerants.

On the other hand, the D values of cation and anion are relatively lower for the IL [TBP][ILE] in the low and higher refrigeration concentration systems. However, when compared to D values of refrigerants and ILs, the D values are an order of magnitude higher for R32, R125, and R134a than ILs. This indicates that the presence of fluorine atoms leads the refrigerants to show a significant enhancement in the D values in the ILs.

In self-diffusivity analysis, at 0.142 M concentration, we observed that R32 exhibits higher diffusivity in systems containing the anion ILE, compared to LEU. This trend aligns with the RDF data, where R32 shows weaker interactions with all anions, particularly with ILE. Furthermore, RDF indicates that in the LEU system, R32 shows a stronger coordination with the TBP cation, which may slightly hinder its mobility due to more frequent interactions. In contrast, ILE-containing systems, R32, are less associated with both ionic molecules, thereby facilitating higher diffusivity.

For R125 and R134a, which both contain multiple electronegative fluorine atoms, lower self-diffusivity was observed, particularly in the presence of LEU. With RDF peaks, this outcome pronounced interaction between these refrigerants and IL, especially hydrogen bonding and dipole interactions with TBP. These structured interactions, as seen in sharper and higher RDF peaks, correlate with reduced mobility, particularly in dilute conditions. For instance, in the RDF plots, R125 shows a notable peak at distances corresponding to hydrogen bonding with the TBP cation.

In 0.625 M, the overall diffusivity values are significantly higher compared to 0.142 M. This may happen due to an increase in the number of molecules. In the RDF and pair distribution function data, we also observed that R125 and R134a have more persistent first-shell interactions, especially with the LEU and ILE systems. In contrast, R32 had less intense RDF peaks, confirming weaker interactions, particularly with the anions. This observation explains the relatively higher diffusivity of R32, which supports the weaker van der Waals and hydrogen bonding capabilities, allowing for greater molecular mobility.

To summarize our discussion, our combined analysis suggests that diffusivity is inversely related to the strength and structure of solute-solvent interactions, as revealed by RDF data. Stronger interactions, indicated by sharper RDF peaks and closer coordination shells, result in lower diffusivity, especially for refrigerants like R125 and R134a in the presence of more interactive anions like LEU. Conversely, weaker and more diffuse interactions, as seen in R32 with ILE, allow for enhanced mobility.



**Figure 7.** Solvation-free energy (ΔGsolv) of refrigerants with different combinations of ILs.

* 1. **Solvation of free energy**

To understand the detailed thermodynamic behavior, solvation free-energy (ΔGsolv) analysis was used through the thermodynamics integration technique, as given in equation (i). We calculated the ΔGsolv of refrigerants in a different system, i.e., perturbing one refrigerant molecule into the system, as provided in Table 1 for Cref = 0.142 M. The multistage thermodynamics integration involves the ΔGsolv due to the electrostatic coupling (λele) and van der Waals coupling (λvdW), i.e., ΔGele and ΔGvdW, respectively, as shown in Figure S13. We have provided intermolecular interactions of the combination of the TBP cation and different anions (LEU and ILE) with different refrigerants (R32, R125, and R134a), which specifically calculate the electrostatic and van der Waals contributions to the total solvation free energy. Meanwhile, the solvation-free energy is majorly dominated by the electrostatic contribution to the total solvation-free energy when compared to the van der Waals interactions. Their interactions are indeed highly dominant due to the presence of P and O atoms of the TBP cation, which contribute to electrostatic interactions, while the butyl group on the TBP promotes the dispersive interaction57, 58. Based on the thermodynamic profiles, we observe that electrostatic coupling is stronger than van der Waals coupling. Figure 7 presents the solvation-free energy (ΔGsolv) of refrigerants with different combinations of ILs, and their corresponding values are provided in Table S6. The total ΔGsolv specifically shows the electrostatic and van der Waals contributions. Whereas, compared to van der Waals, the electrostatic contribution is more dominant in the system. We observed that in the presence of LEU anions, R134a is more negative compared to others, but in the presence of anion ILE, R125 is more negative than others. In the case of R32, the ΔGsolv is less negative with all the combinations of ILs. R134a, a larger molecule with four fluorine atoms, exhibits a higher degree of polarizability.59, 60 This higher polarizability enhances both the electrostatic and dispersive interactions between R134a and the IL, [TBP][ILE], resulting in a more thermodynamically favorable solvation process. In contrast, the geometry of R32 contains only two fluorine atoms and has a slightly smaller, less polarizable molecule.61, 62 Consequently, it forms weaker dispersion and electrostatic interactions with ILs, resulting in a less negative ΔGsolv. The observed D values are aligned well with the structural transition observed in the RDF. The solvation is more prominent due to the significant interactions with the TBP. The ΔGsolv varies in a sequence given as R134a > R125 > R32. However, there is no significant variation in the ΔGsolv in different ILs. Their proper selection of cation might influence the solvation structure and its underlying thermodynamic behavior.

1. **Conclusion**

In this study, the MD simulation was carried out to investigate the interactions between various refrigerants (R32, R125, R134a) and various combinations of ILs, such as cation [TBP] and anions [LEU and ILE]. The structural, dynamic, and thermodynamic behavior of these systems was analyzed to estimate their potential for the separation of refrigerants.

The [TBP][LEU] combination shows the most favorable interaction with refrigerants. In RDF analysis, we observed the sharp peak of FC1R32 with CA1LEU, OA2LEU, and NA1LEU at 0.37 nm, 0.33 nm, and 0.30 nm, respectively, indicating a weak hydrogen bonding with the fluorine atoms of refrigerants and functional group (COO- and NH2), compared to R125 and R134a. The self-diffusivity analysis showed R32 had the highest value. In comparison, R125 was about 60.6% lower, and R134a was around 59.4% lower than R32. This trend is observed with all the systems, indicating R32 had low interaction with ILs, which makes it easier to separate.

Furthermore, in solvation free energy analysis, R134a showed the strongest interaction. On the otherhand, R125 was about 11.2% weaker, and R32 was around 43% weaker when compared the solvation free energy of R134a. Based on these outcomes, the combination of [TBP][ILE], IL is most suitable for the effective separation of R134a. In summary, the results presented in this manuscript provide detailed molecular-level insights that can guide the selection of IL combinations for the effective separation of refrigerants.

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**Supporting Data**

Forcefield of molecular systems, additional simulation snapshots, additional radial distribution functions, density and free energy data.

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**Graphical Abstract**

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