

Coarse-grained molecular dynamics study for optimizing the solvent-to-feed mass ratio in diesel purification by LLE using an imidazolium-based ionic liquid

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Abstract– This work aims to determine the optimal solvent-to-feed mass ratio in a liquid–liquid extraction (LLE) process, simulating four systems through the compression of an ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF₄ and an impure diesel model represented by dodecane, considering pyridine, thiophene, and toluene as representative impurities. The systems were simulated using a coarse-grained molecular dynamics (CGMD) approach with the MARTINI 3 force field. The amount of IL was kept constant, while the impure diesel content was varied to obtain solvent-to-feed mass ratios of 1:0.5, 1:1, 1:2, and 1:3. In all four systems, the impure diesel composition remained fixed, consisting of 70% dodecane and 10% of each impurity. The optimal ratio was evaluated in terms of extraction efficiency, distribution ratio, and selectivity. The 1:2 system exhibited the highest extraction efficiency for all three impurities, reaching 49% for toluene, 77% for thiophene, and 84% for pyridine. The distribution ratio mirrored the extraction efficiency trend, with the highest values likewise observed for the 1:2 system across all three impurities; pyridine exhibited the highest distribution ratio, reaching 9.0, followed by thiophene (5.4) and toluene (1.9). Selectivity increased with increasing impure diesel mass, indicating a stronger preference of the IL for the impurities. The highest selectivity was observed for pyridine, indicating its preferential extraction over the other system components. Consistently, the RDF analysis for the optimized system followed the same trend with the pyridine closer to the [BMIM], confirming a strong affinity.

Keywords–computer simulation, ionic solvent, fossil fuel, pollution, refining.

I. INTRODUCTION

Air pollution is a global concern, as numerous studies have demonstrated its adverse effects on human health even at low concentrations. According to the World Health Organization (WHO), approximately 99% of the world's population breathes air that exceeds the limits established in the global air quality guidelines [1], which primarily address pollutants such as particulate matter, ozone, nitrogen dioxide, sulfur dioxide, and carbon monoxide [2].

A significant fraction of these pollutants is associated with the combustion of fossil fuels [1]. Crude oil, a complex mixture of organic compounds predominantly composed of hydrocarbons, is the primary feedstock for the production of a range of fuels, including diesel, through distillation and refining processes. Diesel fuel is widely used in the transportation sector and in stationary power generation systems [3]. From a chemical standpoint, diesel consists of fractions of paraffins, isoparaffins, cycloalkanes, and aromatic compounds, whose presence influences its physicochemical properties, operational characteristics, and overall performance as a fuel [3], [4].

Despite ongoing efforts to promote biofuels and renewable energy sources for power generation, fossil fuels remain the dominant global energy source, supplying more than 80% of worldwide energy demand [5], [6], [7]. Within this context, diesel continues to play a significant role in transportation, electricity generation, and industrial applications, where it remains one of the most extensively used fossil fuels [8].

However, diesel contains various impurities, including aromatic compounds such as toluene, nitrogen-containing species such as pyridine, and sulfur-containing compounds such as thiophene. The combustion of these species contributes to the emission of environmentally and medically relevant pollutants, including volatile organic compounds (VOCs), particulate matter, nitrogen oxides (NO_x), and sulfur oxides (SO_x). Beyond their adverse environmental and health impacts, the presence of these impurities may also affect fuel performance and efficiency [9], [10].

One of the most employed approaches for the removal of sulfur- and nitrogen-containing compounds involves catalytic processes such as hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), which operate under high hydrogen pressures and elevated temperatures conditions. Nevertheless, these techniques exhibit limitations in the removal of heterocyclic aromatic compounds such as thiophene and pyridine, due to their high chemical stability and resistance to hydrogenation. Consequently, more severe operating

conditions and higher energy consumption are often required [11].

In addition to catalytic processes, alternative strategies for impurity reduction in fuels have been investigated [12]. Among them, liquid-liquid extraction (LLE) has emerged as an industrially viable alternative due to its economic feasibility, operational flexibility, and scalability. However, process efficiency strongly depends on the properties of the solvent employed, as many conventional organic solvents exhibit drawbacks such as limited selectivity, high volatility, recovery challenges, and toxicity-related concerns [13], [14].

In this context, the development of more efficient, selective, and sustainable methods for removing impurities such as thiophene, pyridine, and toluene remains an active area of research. As an alternative to conventional solvents in LLE processes, ionic liquids (ILs) have been proposed. These systems, typically composed of low-melting organic salts, exhibit negligible volatility due to their high enthalpies of vaporization. Furthermore, their potential for recovery and reuse contributes to reducing the environmental impact of the process, making them attractive candidates for the development of more sustainable separation technologies [15], [16].

In recent years, ILs have been extensively investigated as solvents in LLE and purification processes involving organic compounds from various matrices, often achieving satisfactory extraction performance [16], [17]. Several studies have demonstrated their selective affinity toward nitrogen, sulfur, and aromatic-containing compounds in gas oil streams intended for diesel production [18], [14].

Computational approaches, particularly molecular dynamics simulations, provide significant insights into molecular level mass transfer mechanisms and support the rational design of ionic liquids prior to experimental synthesis. Among these approaches, coarse-grained molecular dynamics (CGMD) simulations using MARTINI force field constitute a widely employed computational approach for biomolecular systems [19], [20], [21]. This methodology has been extended to soft matter applications and has been useful to investigate the structure and dynamics of pure ILs, aqueous biphasic mixtures, and interfacial systems without requiring full atomistic reparameterization. Additionally, CGMD offers the added advantage of improved time and length scales [19], [22], [23]. To adequately describe interactions involving polar and ionic compounds, the MARTINI 3 force field was employed in this study. This version introduces a chemically organized framework that distinguishes ions, organic species, and water, allowing improved optimization of interactions within each category and enabling better balance between polarity, charge distribution, and solvation effects. Overall, MARTINI 3 provides a robust and broadly adaptable platform for simulating complex molecular processes [24].

Although ILs have been extensively studied for diesel purification using molecular dynamics, most studies rely on atomistic simulations and fixed operating conditions. The application of CGMD, particularly with the MARTINI 3 force

field, remains limited in this context. Furthermore, systematic evaluation of the solvent-to-feed mass ratio as an optimization variable is scarce. Therefore, this work aims to bridge this gap by integrating CGMD simulations with a parametric analysis of the solvent-to-feed mass ratio to optimize extraction performance, providing both molecular-level insight and process-relevant design criteria.

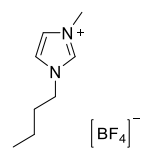
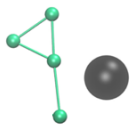
In this study, a LLE was simulated by four systems through the compression of an ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄) and an impure diesel model represented by dodecane, considering pyridine, thiophene, and toluene as representative impurities. The systems were simulated using a coarse-grained molecular dynamics (CGMD) approach with the MARTINI 3 force field. The objective of this work is to determine the optimal solvent-to-feed mass ratio (1:0.5, 1:1, 1:2, and 1:3) through calculations of efficiency extraction, distribution ratio and selectivity. Structural information such as phase separation, IL structural stability, and impurity orientation with respect to the IL is also being investigated.

II. METHODOLOGY

A. Simulation details

The simulation process was performed using the computational package GROMACS 2022.1 [25] and MARTINI 3 coarse-grained (CG) force field [24]. The compound list, chemical structure, CG model, and the natures beads within the force field are presented in Table I. Newton's equation of motion was integrated using the leap-frog algorithm [26] with a time step of 20 fs. Energy minimization to relax molecules was developed through the steepest descent algorithm [27] with a target convergence energy criterion of 100 kJ mol⁻¹ nm⁻¹. The cutoff distance was defined as 1.1 nm for coulomb and Lennard-Jones interactions [28]. The neighbor list was updated every 20 steps. Long-range interactions were measured using the Particle Mesh Ewald (PME) [29] method and bonds constraints were applied using the LINCS algorithm [30]. The temperature was controlled using the velocity-rescale (v-rescale) thermostat [31] with a coupling time constant of 1 ps, while pressure was regulated using the Parrinello-Rahman barostat [32] with a coupling time constant of 12 ps. The systems were equilibrated for 100 ns in a NVT ensemble at 298 K, followed by one microsecond molecular dynamics simulation performed with a semi-isotropic NPT ensemble, using a reference pressure of 1 bar and a compressibility constant of 3.0x10⁻⁴ bar⁻¹. All snapshots were generated with the VMD program [33].

TABLE I
COMPOUND LIST, CHEMICAL STRUCTURE, AND CG MODELS

Compound	Chemical structure	CG model	Beads
1-butyl-3-methylimidazolium cation (green) and tetrafluoroborate anion (black)			Q2
			TN2q
			TN2q
			TC6
Dodecane			SC3
			C1
			C1
Toluene			C1
			SC4
			TC5
Thiophene			TC5
			TC6
			TC5
Pyridine			TN6a
			TC5
			TC5

B. System setup

Four systems were constructed with solvent-to-feed mass ratios of: 1:0.5, 1:1, 1:2, and 1:3 using GROMACS tools. The first step consisted of constructing and equilibrating a cubic box of 6.7 x 6.7 x 6.7 nm, containing 844 IL molecules of [BMIM]BF₄. The gmxc editconf program was used to define the system to the segment of interest during the setup. The IL cubic box was centered, and two boxes at each side were constructed. Toluene, thiophene, pyridine, and dodecane molecules were inserted with the gmxc insert-molecules program, as indicated in Table II for each system. In all four systems, the composition of the impure diesel was kept constant at 70% dodecane and 10% of each impurity. The final simulation maintained the same XY dimensions as the IL box, while the Z dimension range was set from 16.7 to 26.7 nm, as shown in Figure 1 (A). Two structural analyses were computed using the last 200 ns of the CGMD results: normalized density profile, and radial distribution function (RDF). The final configuration state is shown in Figure 1 (B).

TABLE II
NUMBER OF TOLUENE, THIOPHENE, PYRIDINE, AND DODECANE MOLECULES FOR THE SYSTEMS: 1:0.5, 1:1, 1:2 AND 1:3

System	Toluene	Thiophene	Pyridine	Dodecane
1:0.5	104	114	120	392
1:1	208	226	240	784
1:2	416	452	480	1568
1:3	624	678	720	2352

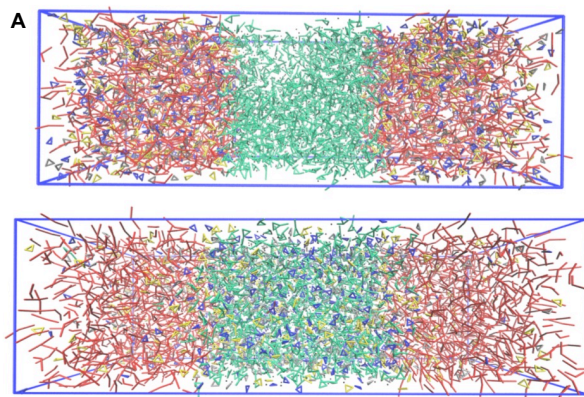


Figure 1. Initial (A) and final (B) system setup snapshot. Dodecane (red), 1-butyl-3-methylimidazolium cation (green), tetrafluoroborate anion (black), toluene (yellow), thiophene (gray), and pyridine (blue) for the 1:2 system.

C. Calculated properties

Extraction efficiency was estimated using the methodology proposed by Gabric et al., following equations 1 and 2 [17], [34]. In these equations, subscript 2 represents any impurity, such as toluene, thiophene or pyridine. Initially, two phases were defined: an IL (II) rich phase and a dodecane-rich phase (I).

$$E(\%) = \frac{n_{2,initial} - n_{2,I}}{n_{2,initial}} \quad (1)$$

In equation 1, $n_{2,initial}$ corresponds to the total initial number of impurity molecules dissolved in the diesel phase, while $n_{2,I}$ represents the number of molecules remaining in the dodecane-rich phase after extraction. The $n_{2,I}$ value is determined from the density profile of each impurity $\rho_2(Z)$, as follows:

$$n_{2,I} = \left(\int_{Z'}^{Z''} \rho_2(Z) dZ \right) \frac{L_x L_y N_a}{M_2} \quad (2)$$

In equation 2, Z' and Z'' define the integration limits along the Z direction, which corresponds to the IL-rich phase (II) and dodecane-rich phase (I), L_x and L_y correspond to the transverse dimensions of the simulation box, M_2 is the molar mass of the impurity, and N_a is Avogadro's number. In this work the IL-

rich phase (II) was defined as the region where the density profiles of IL and dodecane intersect.

Distribution ratio and selectivity were calculated for each contaminant according to equations 3 and 4, respectively. Mass fractions were obtained from the mass density profile of each component [9], [35].

$$\beta_2 = \frac{w_2^{II}}{w_2^I} \quad (3)$$

$$S = \frac{\beta_2}{\beta_1} \quad (4)$$

In equation 3, w_2 is the mass fraction for each impurity in phases I or II. In equation 4, the subscript 1 corresponds to dodecane.

III. RESULTS AND DISCUSSION

The solvent-to-feed mass ratio is an operational variable in extraction processes. Aiming its optimization can reduce the required amount of IL while maintaining the same extraction efficiency. The normalized density profiles are shown in Figure 2 for four solvent-feed mass ratios: 1:0.5 (A), 1:1 (B), 1:2 (C), and 1:3 (D). In all of them, effective impurity separation is observed, as well as a clear phase separation between the IL and dodecane-rich phases. The normalized density profiles were obtained by dividing the density profile of each component by its maximum value respectively. The IL phase extends in the Z direction from 3.5 to 5 nm, increasing as the number of impurities observed rise. In all systems, except 1:0.5, pyridine exhibits the highest density through the IL phase. In contrast, thiophene and toluene maximum density values varies from the interphase towards the center of the phases depending on the system. Toluene exhibits this behavior more markedly in all systems, reflecting its comparatively weak partitioning into the ionic phase. This can be attributed to its low polarity and limited capacity to establish directional intermolecular interactions, which restrict favorable solvation within the ionic medium.

This trend is consistent with previous experimental and atomistic molecular dynamics studies, where toluene has been reported to interact mainly through weak π -cation and dispersive forces, while the strong cation-anion interactions in imidazolium-based ionic liquids hinder the deep penetration of toluene into the ionic regions. As a result, toluene preferentially accumulates near the interfacial region or within less polar domains, rather than being strongly stabilized in the bulk ionic phase, which explains its lower selectivity compared with aromatic compounds containing sulfur or nitrogen and exhibiting higher polarity [36].

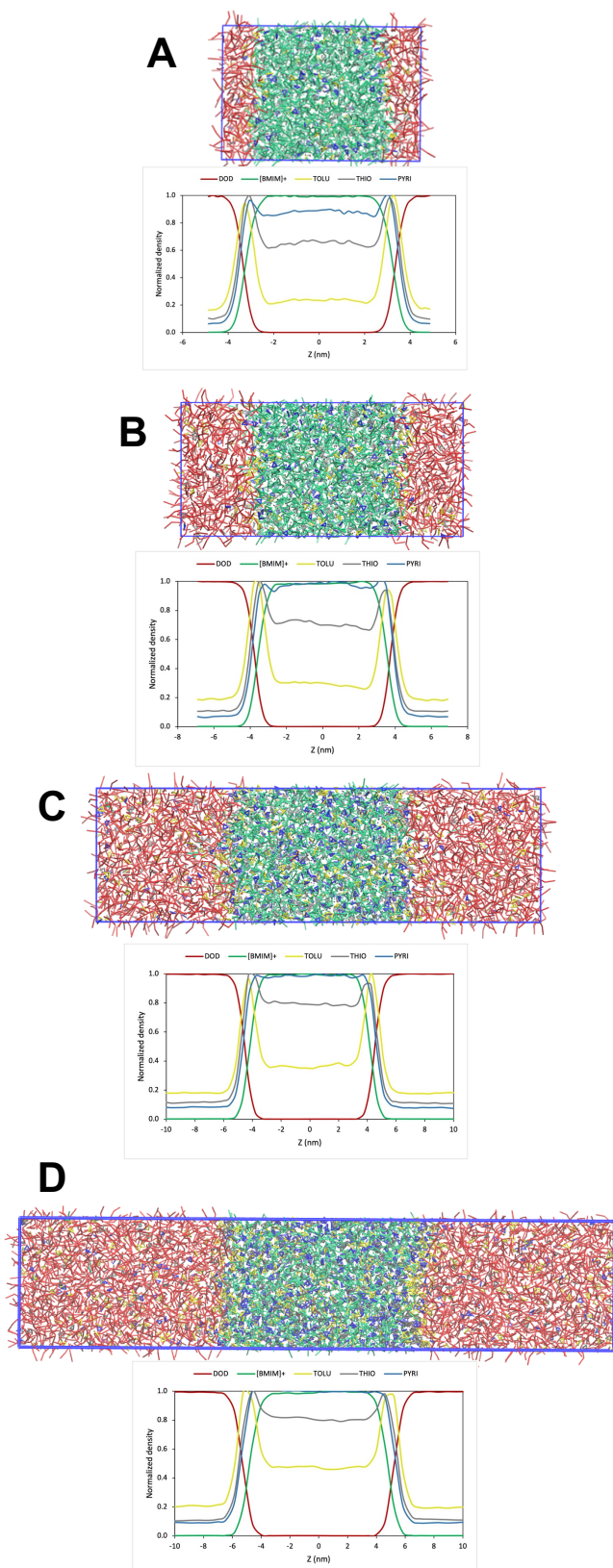


Figure 2. Normalized density profile of 1-butyl-3-methylimidazolium cation (green), dodecane (red), toluene (yellow), thiophene (gray), and pyridine (blue) for the 1:0.5 (A), 1:1 (B), 1:2 (C), and 1:3 system.

Figure 3 (A) shows the RDF for the system 1:2 of the IL beads head TN2q-TN2q-TC6 and the bead tail SC3 report in Table I taking the BF_4 anion center of mass as reference. The RDF describes the spatial distribution of one particle relative to a reference particle in condensed-phase systems. This analysis reveals the position of the IL structure with respect to BF_4 anion, showing BF_4 anion is located closer to the IL head than to the tail. This behavior is consistent with the expected electrostatic attractions of the IL, where the anion preferentially interacts closer to the positively charge head of the cation. The extraction efficiency varies among the impurities across all systems, with pyridine being the most effectively separated, followed by thiophene and, lastly, toluene, as shown in Figure 2. This separation profile is also reflected in the RDF analysis in Figure 3 (B), where, using [BMIM] as a reference, pyridine exhibits the highest interaction peak, followed by thiophene, and finally toluene.

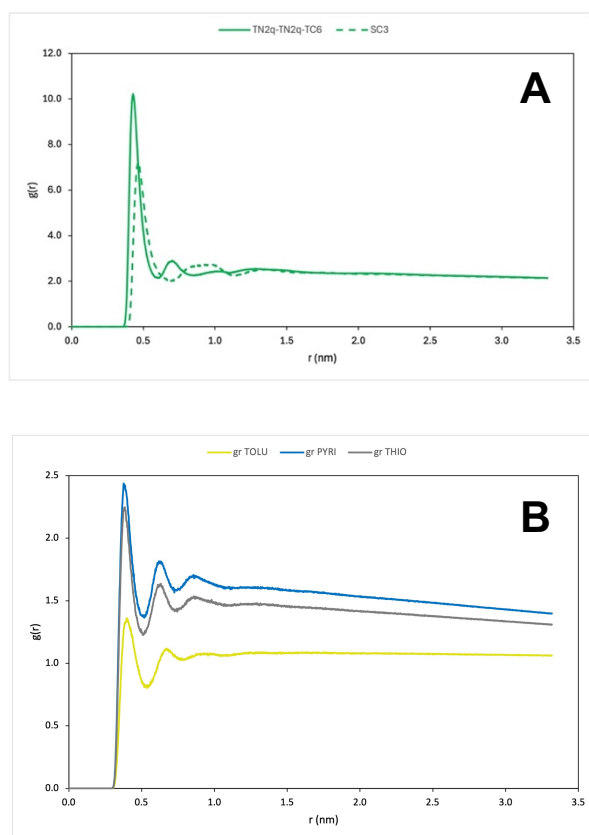


Figure 3. RDF of IL beads head center of mass TN2q-TN21-TC6 and bead tail SC3 for the system 1:2 with BF_4 ion mass center as reference. (B) RDF of toluene (yellow), thiophene (gray), and pyridine (blue) for the system 1:2 taking the [BMIM] mass center as a reference.

The density profile was used to calculate the extraction efficiency shown in Figure 4. The interphase boundary performed with Equation 2, was determined at the points where dodecane and IL phases intersect in each system, as illustrated in Figure 2. The 1:2 solvent-to-feed mass ratio exhibits the

highest extraction efficiency for all three impurities: toluene (49%), thiophene (77%), and pyridine (84%). In all four systems, pyridine consistently shows the highest extraction efficiency, followed by thiophene and, lastly, toluene. In the first three systems (1:0.5, 1:1, and 1:2), the extraction efficiency for pyridine remains essentially constant (83–84%). In contrast, in the (1:3) system, the extraction efficiency decreases to 75%, representing a 9% reduction compared to the most efficient system. Previous theoretical studies have reported stronger interaction energies between pyridine and imidazolium-based ionic liquids than between neutral aromatic compounds and these solvents, which supports its preferential extraction[37]. Thiophene shows moderate variation in the first three systems, ranging from 73 to 77%; however, the extraction efficiency decreases significantly in the 1:3 system to 64%, which is 13% lower than that of the 1:2 system. This behavior can be attributed to its sulfur-containing aromatic ring, which provides higher polarizability and favorable π -type interactions with the imidazolium cation, although weaker than those observed for pyridine. Computational studies have shown that thiophene interacts favorably with ionic liquids, although with lower binding strength than pyridine, which explains its lower yet still significant extraction efficiency[37]. From these results, it can be inferred that, even when the mass of impure diesel decreases, the extraction efficiency does not increase appreciably, indicating that the IL has reached its maximum loading capacity. This behavior suggests a saturation point can be identified at the maximum efficiency extraction. This saturation has been reported in previous studies, where the solvent-to-feed volume ratio varied from 1:1 to 2.5:1 [38]. On the other hand, toluene exhibits greater variation in the first three systems, with extraction efficiencies ranging from 39% to 49%. This impurity shows the largest variation, approximately 10%, suggesting that toluene saturation has not yet been reached at the 1:1 ratio. In the 1:3 system, toluene presents the most pronounced change in extraction efficiency, with a decrease of 18%. A previous atomistic computational study of LLE, using a different imidazolium-based IL and a diesel model containing thiophene and pyridine as impurities, reported extraction efficiencies ranging from 43.99% to 54.30% for thiophene and from 80.36% to 85.91% for pyridine [17]. These results indicate that the pyridine extraction efficiencies obtained in this study are in good agreement with both atomistic simulations and experimental data results. However, the values obtained using the CG approach for thiophene differ by approximately 20%. This could be explained by IL nature with a hydrophilic cation and a bulky anion, where small structure variations may produce significant differences in efficiency extraction [39].

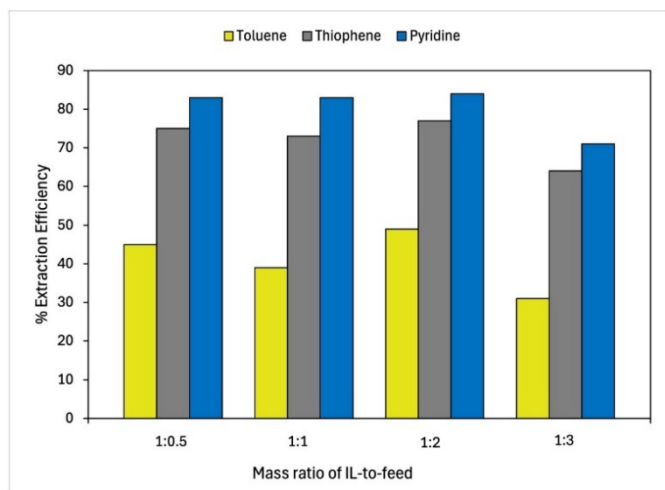


Figure 4. Extraction efficiency E (%) of toluene (yellow), thiophene (gray), and pyridine (blue) in dodecane at 298 K and 1 bar in an equilibrium liquid-liquid using [BMIM][BF₄] in four different mass ratios: 1:0.5, 1:1, 1:2, and 1:3.

The distribution ratio is interpreted as an indicator of the amount of solvent required; a higher distribution ratio value implies a smaller amount of IL needed to achieve high extraction efficiency. The distribution ratio maintains the efficiency extraction tendency, with the highest distribution ratio values obtained for the 1:2 system across all three impurities. Pyridine presents the highest value, followed by thiophene and toluene, Figure 5. In this system (1:2), toluene, thiophene, and pyridine reach a maximum value of 1.9, 5.4, and 9.0, respectively. All values above 1 indicate a higher mass fraction of each impurity in the IL phase.

A compilation of distribution ratio values from previous studies using a 1:1 solvent-to-feed ratio with imidazolium-based IL reports values of 2.0–2.5 for pyridine and 0.9–1.0 for thiophene [9]. In comparison: For toluene, values reported for different solvent extraction systems range between 0.1 and 0.9. In the case of benzene, in reference as an analogue to toluene, distribution ratio values vary between 0.75 and 1.35 have been reported for LLE using [BMpyr][DCA] [40].

For the mass ratio 1:3, the distribution ratio decreases for pyridine and toluene compared to the 1:2 system, although it is still higher than in the 1:0.5 and 1:1 system. However, and in contrast, thiophene and pyridine were the impurities that presented most significant increase in distribution ratio, while the less affected impurity is toluene exhibiting a variation range between 0.6 and 1.9. When contrasting our results with previous experimental and simulations studies, differences in distribution ratios are observed for all impurities, however, toluene shows the closest proximity with literature data.

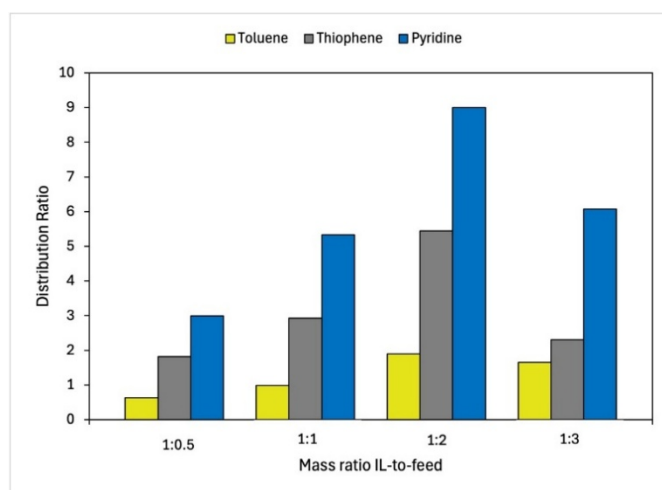


Figure 5. Distribution ratio (β) of toluene (yellow), thiophene (gray), and pyridine (blue) in the IL solvent and dodecane at 298 K and 1 bar in a liquid-liquid equilibrium using [BMIM][BF₄] in four different mass ratios: 1:0.5, 1:1, 1:2, and 1:3.

Selectivity measures the affinity of one component over another: in this case, impurities relative to dodecane. Moreover, high selectivity values indicate that fewer separation stages are required to achieve a target separation. In all four systems, selectivity increases for toluene, thiophene, and pyridine, with pyridine exhibiting the highest selectivity, as presented in Figure 6. Pyridine is the impurity that shows the greatest variation, followed by thiophene and toluene. In the 1:2 system, the selectivity values for toluene, thiophene, and pyridine were 74, 212, and 350, respectively. A compilation of selectivity values from previous studies using a 1:1 solvent-to-feed ratio with imidazolium-based ionic liquids reports values of <500 and 450–750 for pyridine and thiophene, respectively. For toluene, reported values range between 20 and 100, although these were obtained using different solvent extraction systems [9]. For benzene, used as a reference for toluene, selectivity values between 72 and 447 have been reported for LLE using [BMpyr][DCA] [40].

The computational results indicate that the IL exhibits promising performance in the LLE process across the evaluated solvent-to-feed mass ratios. Nevertheless, these findings would benefit from validation through complementary experimental studies on the same systems. Although the Martini 3 force field represents a substantial advancement in CG modelling, particularly in terms of improved transferability and parametrization of bead types for complex materials, it still presents inherent limitations associated with its reduced resolution. Specifically, the representation of multiple atoms as single isotropic interaction sites restricts the accurate description of fine structural and directional interactions. Moreover, the reduced chemical detail can affect the balance between enthalpic and entropic contributions in the estimation of thermodynamic properties, such as Gibbs free energy.

Despite these limitations, CGMD simulations provide valuable molecular-level insights that are not easily accessible through experimental methods alone, such as the characterization of interfacial behavior, nanoscale organization, and dynamic partitioning behavior. Therefore, combining CG simulations with experimental approaches constitutes a complementary strategy, where simulations enable mechanistic interpretation and hypothesis generation, while experimental data serve to validate and refine the computational models.

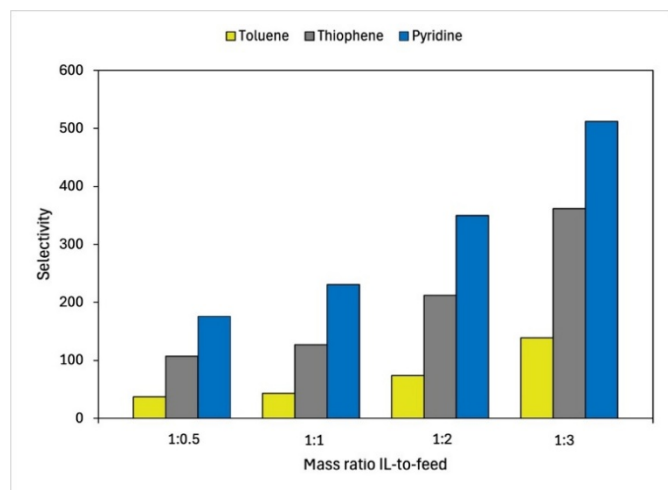


Figure 6. Selectivity (S) of toluene (yellow), thiophene (gray), and pyridine (blue) in an equilibrium liquid-liquid using [BMIM][BF₄] at 298 K and 1 bar in four different mass ratios: 1:0.5, 1:1, 1:2, and 1:3.

IV. CONCLUSION

The LLE of three impurities such as toluene, thiophene, and pyridine from a dodecane based diesel model using an imidazolium-based IL as solvent was successfully simulated using CGMD with the MARTINI 3 force field over a simulation time of one microsecond for each system. Four systems with different solvent-to-feed mass ratios (1:0.5, 1:1, 1:2, and 1:3) were evaluated.

Based on the extraction efficiency, the 1:2 system was identified as the optimal configuration, particularly for pyridine, which reached an extraction efficiency of 84%. Each solvent exhibits a saturation point or maximum loading capacity that differs for each impurity, depending on its chemical preferences, which explains why pyridine shows similar extraction efficiencies across most systems. Only when the impure diesel content is increased to a 1:3 ratio does the extraction efficiency decrease. The distribution ratio follows the same trend as the extraction efficiency, indicating that the 1:2 system requires the lowest amount of IL for an optimal LLE. Selectivity values increase solvent-to-feed mass ratio across all systems for all three impurities, obtaining the highest selectivity values for pyridine, indicating its preferential extraction over the other system components. Regarding structural information of the IL, the anion remains preferentially close to the cation

head group. On the other hand, among the impurities, pyridine remains the closest to the IL, followed by thiophene and, lastly toluene.

Overall, this study demonstrates the capability of CGMD simulations with the MARTINI 3 force field to capture key extraction trends and identify optimal operating conditions, highlighting its potential as a predictive tool for the design and optimization of ionic liquid-based separation processes.

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