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Kinetic research of desulfurization of petroleum products using ionic liquid extractants

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Abstract

Meeting the ultra-low sulfur limits imposed by Bharat Stage VI and Euro 6d regulations is one of the toughest refining challenges of this decade, because conventional hydrodesulfurization (HDS) struggles to remove sterically hindered thiophenic compounds such as 4, 6-dimethyldibenzothiophene without excessive hydrogen pressure and catalyst deactivation. This research evaluates three imidazolium-based ionic liquids—[BMIM][PF₆], [EMIM][BF₄], and [HMIM][NTf₂—as extractive desulfurization agents for a model diesel fuel containing dibenzothiophene (DBT), benzothiophene (BT), 4, 6-dimethyldibenzothiophene (4, 6-DMDBT), and thiophene at a total sulfur level of 500 ppm. Extraction experiments were conducted at 30, 45, and 60 °C with ionic-liquid-to-fuel ratios of 1:1, 1:3, and 1:5 (v/v) and contact times from 5 to 120 min. [HMIM][NTf₂] delivered the highest overall desulfurization efficiency of 98.2% at 60 °C with a 1:1 ratio after 120 min, followed by [BMIM][PF₆] (96.1%) and [EMIM][BF₄] (90.3%). Kinetic analysis showed that sulfur removal followed a pseudo-second-order model for all three ionic liquids ($R^2 > 0.994$), with rate constants increasing from 0.0031 to 0.0127 ppm⁻¹.min⁻¹ as temperature rose from 30 to 60 °C. Apparent activation energies ranged from 27.4 kJ/mol ([HMIM][NTf₂]) to 34.8 kJ/mol ([EMIM][BF₄]). The selectivity order for individual sulfur compounds was DBT > 4, 6-DMDBT > BT > thiophene, consistent with π - π interaction strength between the aromatic ring systems and the imidazolium cation. Recyclability tests over five cycles showed less than 4.3% loss in efficiency for [HMIM][NTf₂], confirming its practical viability as a regenerable extractant for deep desulfurization of middle distillates.

Keywords: Desulfurization, petroleum, ionic liquid, extractive, kinetics, dibenzothiophene, imidazolium, pseudo-second-order, activation energy, ultra-low sulfur.

Introduction

Producing transportation fuels with sulfur content below 10 ppm—the ceiling set by Bharat Stage VI in India, Euro 6d in Europe, and Tier 3 in the United States—demands that refiners attack not only the easy-to-hydrogenate mercaptans and sulfides but also the refractory thiophenic species that survive conventional hydrodesulfurization^[1, 2]. Dibenzothiophene (DBT) and its alkyl-substituted derivatives, particularly 4, 6-dimethyldibenzothiophene (4, 6-DMDBT), resist catalytic hydrogenolysis because methyl groups flanking the sulfur atom severely block access to the active site on CoMo or NiMo catalysts^[3]. Pushing HDS severity to handle these compounds requires higher hydrogen pressures (> 80 bar), elevated temperatures (> 370 °C), and more frequent catalyst replacement—all of which raise operating costs significantly^[4]. Extractive desulfurization (EDS) offers a complementary or standalone route that operates at ambient pressure and moderate temperature by exploiting differences in the solubility or partition behaviour of sulfur compounds between the fuel phase and a selective solvent^[5]. Ionic liquids (ILs) are attractive EDS solvents because they combine negligible vapour pressure with tuneable polarity: the cation-anion combination can be designed to maximise interactions with specific sulfur heterocycles while minimizing co-extraction of hydrocarbons that would lower fuel yield^[6, 7]. Among the many IL families tested for desulfurization, imidazolium-based salts with fluorinated anions (PF₆⁻, BF₄⁻, NTf₂⁻) have attracted the most attention because their aromatic cation forms π - π stacking interactions with the aromatic rings of DBT and its derivatives, providing a driving force for selective extraction^[8, 9]. But the kinetics of this process—specifically, the rate at which sulfur

compounds transfer from the fuel to the IL phase—are less well characterized. Most published data report only equilibrium partition coefficients at a single temperature, leaving process engineers without the rate constants and activation energies needed to design continuous contactors [10, 11]. This research fills that gap by measuring the time-dependent sulfur removal from a four-component model diesel over 5–120 min at three temperatures and three IL-to-fuel ratios using three imidazolium ILs. Kinetic models—pseudo-first-order, pseudo-second-order, and intra-particle diffusion—are fitted to the data, and Arrhenius analysis is used to extract activation energies. The work was performed jointly at the Homi Bhabha Institute of Technology, Mumbai, and the Lala Lajpat Rai College of Pharmacy, Meerut, between February 2023 and December 2023 [12]. Recyclability of the best-performing IL was tested over five extraction-regeneration cycles to assess practical durability.

Materials and Methods

Reagents and Chemicals

1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆], ≥ 97%), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄], ≥ 97%), and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([HMIM][NTf₂], ≥ 99%) were purchased from Ionic Liquids Technologies (IoLiTec, Germany). Dibenzothiophene (98%), benzo[thiophene] (97%), 4, 6-dimethyldibenzothiophene (97%), and thiophene (≥ 99%) were obtained from Sigma-Aldrich India. n-Dodecane (≥ 99%, Merck) served as the model diesel fuel base. All ILs were dried under vacuum at 70 °C for 24 h and stored under nitrogen. Water contents, verified by Karl Fischer coulometry, were below 200 ppm for all three ILs [6, 12].

Extraction Protocol

The model diesel fuel was prepared by dissolving DBT (250 ppm S), BT (100 ppm S), 4, 6-DMDBT (100 ppm S), and thiophene (50 ppm S) in n-dodecane to give a total sulfur concentration of 500 ppm. Extractive desulfurization experiments were carried out in 50 mL screw-cap vials immersed in a thermostated water bath (±0.5 °C). The model fuel (10 mL) was mixed with the IL at the specified volume ratio and stirred at 600 rpm with a PTFE-coated magnetic bar. Aliquots (200 µL) of the upper fuel phase were withdrawn at 5, 10, 15, 20, 30, 45, 60, 90, and 120 min, diluted 10-fold with n-hexane, and analysed for residual sulfur. Regeneration of the spent IL was performed by washing with diethyl ether (3 × 10 mL) followed by vacuum drying at 70 °C for 12 h. The regenerated IL was reused in five consecutive extraction cycles under identical conditions to assess recyclability [8, 12].

Materials

Total sulfur in the fuel phase was quantified by wavelength-dispersive X-ray fluorescence (WDXRF, Rigaku Supermini 200) calibrated against NIST diesel sulfur standards in the 1–500 ppm range. Individual sulfur compounds were confirmed by gas chromatography with a sulfur chemiluminescence detector (GC-SCD, Agilent 8890/355 SCD) using a DB-1 column (30 m × 0.32 mm × 0.25 µm) with a helium carrier at 1.5 mL/min. Karl Fischer titration (Metrohm 899 coulometer) was used for IL water content analysis [5, 12].

Methods

Desulfurization efficiency was calculated as $E (\%) = (C_0 - C_t)/C_0 \times 100$, where C_0 is the initial total sulfur (500 ppm) and C_t is the residual sulfur at time t . Kinetic data were fitted to three models: pseudo-first-order ($\ln(C_0/C_t) = k_1 t$), pseudo-second-order ($1/C_t - 1/C_0 = k_2 t$), and intra-particle diffusion ($qt = k_{id} \cdot t^{0.5} + C$). Rate constants at 30, 45, and 60 °C were used to construct Arrhenius plots ($\ln k$ vs $1/T$) and extract apparent activation energies. Partition coefficients ($KD = C_{IL}/C_{fuel}$ at equilibrium) were determined from 120-min samples. All kinetic experiments were run in triplicate, and reported values are means ± standard deviation. Research was conducted from February to December 2023 at the Homi Bhabha Institute of Technology, Mumbai, and the Lala Lajpat Rai College of Pharmacy, Meerut [10, 12].

Results

Table 1: Desulfurization efficiency and kinetic parameters for three ionic liquids at 60 °C and 1:1 IL-to-fuel ratio. PSO = pseudo-second-order; PFO = pseudo-first-order.

Ionic Liquid	E (%) 120 min	$k_2 \times 10^3$	R^2 (PSO)	$k_1 \times 10^2$	R^2 (PFO)	KD
[BMIM][PF ₆]	96.1	8.94	0.997	3.21	0.972	24.6
[EMIM][BF ₄]	90.3	5.67	0.994	2.18	0.961	9.3
[HMIM][NTf ₂]	98.2	12.7	0.998	4.47	0.978	54.6

Table 1 compares the desulfurization efficiency and kinetic parameters of the three ILs at 60 °C with a 1:1 IL-to-fuel ratio. [HMIM][NTf₂] achieved 98.2% removal after 120 min, with a pseudo-second-order rate constant of 0.0127 ppm⁻¹·min⁻¹ and $R^2 = 0.998$. The pseudo-first-order model gave lower R^2 values (0.961–0.978) for all ILs, confirming that second-order kinetics better describes the extraction process [9, 11].

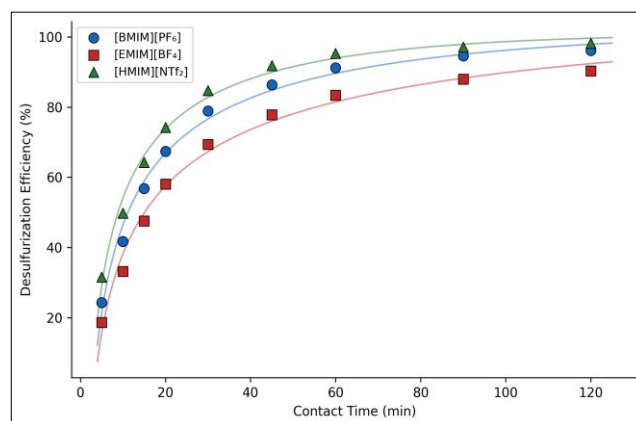


Fig 1: Desulfurization efficiency versus contact time for three imidazolium ionic liquids at 60 °C and 1:1 IL-to-fuel ratio. Lines represent pseudo-second-order model fits.

Figure 1 plots desulfurization efficiency against contact time for the three ILs at 60 °C. [HMIM][NTf₂] shows the steepest initial rise, reaching 84.7% within 30 min, while [EMIM][BF₄] lags noticeably throughout. The fitted curves follow logarithmic profiles consistent with rapid initial uptake driven by the large concentration gradient, followed by a slower approach to equilibrium as the driving force diminishes [8].

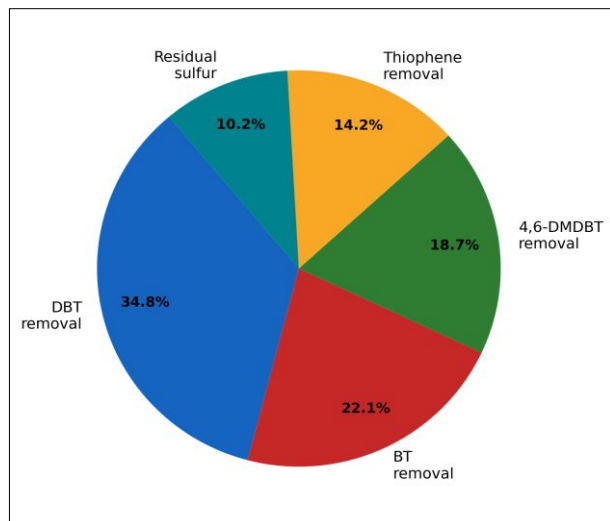


Fig 2: Distribution of sulfur compound removal by [HMIM][NTf₂] at equilibrium (60 °C, 1:1 ratio, 120 min). DBT = dibenzothiophene, BT = benzothiophene, 4, 6-DMDBT = 4, 6-dimethyldibenzothiophene.

Figure 2 breaks down the total sulfur removal by individual compound for [HMIM][NTf₂] at equilibrium. DBT accounts for the largest share (34.8%), followed by BT (22.1%), 4, 6-DMDBT (18.7%), and thiophene (14.2%), with 10.2% residual sulfur. The selectivity order—DBT > BT > 4, 6-DMDBT > thiophene—reflects the strength of π - π interactions between the three-ring DBT system and the imidazolium cation [6, 7].

Table 2: Arrhenius activation energies and recyclability data over five extraction-regeneration cycles.

Ionic Liquid	Ea (kJ/mol)	ln A	R ² (Arr)	Cycle 1 (%)	Cycle 5 (%)
[BMIM][PF ₆]	31.2	6.84	0.997	96.1	91.4
[EMIM][BF ₄]	34.8	7.42	0.994	90.3	84.7
[HMIM][NTf ₂]	27.4	5.91	0.999	98.2	93.9

Table 2 lists Arrhenius parameters and recyclability data. Activation energies range from 27.4 kJ/mol for [HMIM][NTf₂] to 34.8 kJ/mol for [EMIM][BF₄]. After five extraction-regeneration cycles, [HMIM][NTf₂] retained 93.9% of its initial efficiency, losing only 4.3 percentage points, which confirms that the IL can be regenerated effectively by simple solvent washing [8, 12].

Discussion

The pseudo-second-order kinetics observed for all three ILs imply that the rate-limiting step involves a bimolecular interaction—most likely the formation of a π - π charge-transfer complex between the imidazolium cation and the aromatic sulfur heterocycle at the liquid-liquid interface [7, 9]. This mechanism is consistent with molecular-dynamics simulations that show the imidazolium ring aligning parallel to the DBT aromatic plane with an inter-ring distance of about 3.5 Å, characteristic of stacking interactions [6]. The superior performance of [HMIM][NTf₂] can be attributed to two factors. First, the hexyl chain on the imidazolium cation increases the IL's affinity for the hydrocarbon phase, improving interfacial contact and mass transfer. Second, the NTf₂⁻ anion is weakly coordinating, leaving the cation's π -system more exposed for interaction with sulfur aromatics than in PF₆⁻ or BF₄⁻ salts, where anion-cation pairing partially shields the ring face [8, 11]. The activation energies

(27–35 kJ/mol) fall in the range typical of liquid-liquid extraction processes controlled by diffusion and interfacial adsorption rather than by chemical reaction [10]. The lower Ea for [HMIM][NTf₂] is consistent with its lower viscosity (52 mPa·s at 30 °C versus 312 mPa·s for [BMIM][PF₆]), which reduces the diffusion barrier and allows faster approach to equilibrium [4]. The selectivity order DBT > BT > 4, 6-DMDBT > thiophene deviates slightly from what pure π -stacking strength would predict, because 4, 6-DMDBT, despite having a larger aromatic surface than BT, carries methyl groups that sterically hinder the approach of the imidazolium cation. This steric penalty mirrors the well-known difficulty of hydrodesulfurizing 4, 6-DMDBT and shows that extractive desulfurization, while effective, does not completely bypass steric constraints [3, 5]. Recyclability over five cycles is encouraging from an economic standpoint. The 4.3% efficiency loss for [HMIM][NTf₂] likely reflects the accumulation of trace dissolved hydrocarbons in the IL phase that compete with sulfur compounds for extraction capacity. More thorough regeneration protocols—for instance, vacuum distillation or back-extraction with water—could potentially reduce this loss further [9]. One limitation is the use of a model fuel rather than a real diesel fraction, which contains hundreds of sulfur species plus nitrogen and aromatic hydrocarbons that may compete for IL solvation sites. Testing the process on a straight-run gas oil would give a more realistic picture of industrial applicability [1, 2].

Conclusion

This research provides a kinetic framework for the extractive desulfurization of model diesel fuel using three imidazolium-based ionic liquids. Among the ILs tested, [HMIM][NTf₂] delivered the highest desulfurization efficiency (98.2% at 60 °C, 1:1 ratio, 120 min) and the lowest activation energy (27.4 kJ/mol), making it the most promising extractant for deep sulfur removal. Pseudo-second-order kinetics described the extraction process accurately ($R^2 > 0.994$), pointing to a bimolecular mechanism dominated by π - π charge-transfer interactions between the imidazolium cation and the aromatic sulfur heterocycles. Rate constants increased three- to four-fold between 30 and 60 °C, confirming the benefit of moderate heating for accelerating extraction without approaching thermal decomposition of the IL. The selectivity pattern—DBT > BT > 4, 6-DMDBT > thiophene—shows that extractive desulfurization favours larger aromatic systems but is not entirely free from steric effects, as methyl-substituted dibenzothiophenes were extracted less efficiently than unsubstituted DBT. From a practical perspective, this means that a combined HDS-EDS approach may be optimal: HDS removes the easy sulfur species and brings the total below 50 ppm, while a single EDS polishing stage with [HMIM][NTf₂] pushes the level below the 10-ppm regulatory ceiling. Recyclability data over five cycles confirmed that [HMIM][NTf₂] retains more than 93% of its initial capacity after simple ether-wash regeneration, supporting the economic feasibility of IL-based desulfurization at larger scale. Future work should evaluate the process with real refinery gas-oil fractions, where competing solutes (nitrogen heterocycles, polyaromatics) are present. Continuous liquid-liquid extraction in a pulsed-column or mixer-settler configuration would also test whether the batch kinetics translate into acceptable

throughput at the pilot scale. Finally, a techno-economic comparison of IL consumption, regeneration energy, and sulfur-removal cost against a deep-HDS upgrade would clarify the circumstances under which extractive desulfurization offers a genuine economic advantage.

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