



Extractive desulfurization of model oil using 1-methyl-4-ethyl pyridinium iodide ionic liquids with some Lewis acids

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Abstract

The ionic liquid (IL) (1-methyl-4-ethyl pyridine-1-ium iodide) [MEPy]I in this work was created through a direct reaction between 4-ethyl pyridine and methyl iodide. Subsequently, complex salts were prepared using Lewis acids (ferrous chloride and copper chloride) in molar ratios of 1:1 and 1:2, ionic liquid: metal chloride. Nuclear magnetic resonance spectroscopy (1H-NMR), elemental analysis (CHN), infrared spectra (FT-IR), and other methods were used to identify the prepared compounds. Moreover, the study of the thermal stability of the prepared compounds. These compounds were tested in the extractive desulfurization process (EDS). Using a model oil sample containing dibenzothiophene (DBT) as an aromatic organosulfur compound dissolved in solvent (n-decan) at a concentration of 1500 ppm. The sulfur percentage was estimated before and after treatment by gas chromatography technique GC-FID, and the conditions were determined (time and concentration of the extracted substance), as it was found that ionic liquids of pyridine base and its complex salts with ferrous and copper chlorides have good efficiency in the process of removing sulfur (EDS).

Keywords: Lewis acid ionic liquids, Desulfurization, Model oil, Thermal stability

Introduction

It is well known that the combustion process produces sulfur oxides, or SO_x, which are harmful pollutants. As a result, it is necessary to reduce these emissions by lowering the sulfur content of the fuel [1, 2]. That can affect the power and reduce the octane number and impact the devices used in oil refineries [3, 4]. Hydrogenation desulfurization processes are of limited use, particularly in aromatic organic sulfur compounds, due to their high cost and requirement for particular operating conditions from temperature and pressure. As a result, other methods, such as extraction and adsorption, were employed. The process is chosen based on the sulfur compound quality in the oil or treated oil derivative [5].

It is possible to use only solvents in the extractive desulfurization process (EDS), such as DMF and DMSO solvents. Still, they are non-selective in compound extraction because they can remove other compounds and require large amounts of solvent in the extraction process. As a result, adding additional materials to increase selectivity, such as ionic liquids (ILs), is preferable to improve selectivity and extraction efficiency [6, 7]. Controlling the quality of the positive ion and the negative ion helps manage ionic liquids' properties. One of the essential

properties of ionic liquids is their solubility, and their zero solubility in fuel is one of the main reasons for their use in the extraction process. As the dissolution of ionic liquids for nitrogen bases in fuel results in the emission of oxides of nitrogen and increased pollution, as well as the ease of recovery and reuse of ionic liquids [8].

Several ionic liquids for pyridine bases were tested in the extractive desulfurization process, and it was discovered that increasing the aromatic character of the organosulfur compounds in the fuel increases extraction efficiency under the same experimental conditions. The most likely explanation for the association in extraction processes is aromatic sulfur [9, 10]. In general, ionic liquids without metal are less efficient than those that do. Experiments have shown that ionic liquids containing Lewis acids (such as metal chlorides) provide good efficiency and promising results for the extraction process. The ionic liquid with Lewis acid mixtures is more efficient than without Lewis acid [11-13].

In this study, the pyridine base's ionic liquid [MEPy]I was prepared. Then systems of this ionic liquid were designed with ferrous chloride and copper chloride in different molar ratios, diagnosed using spectroscopic and physical methods, and the thermal stability of

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these systems was studied. It is then subjected to extractive desulfurization testing.

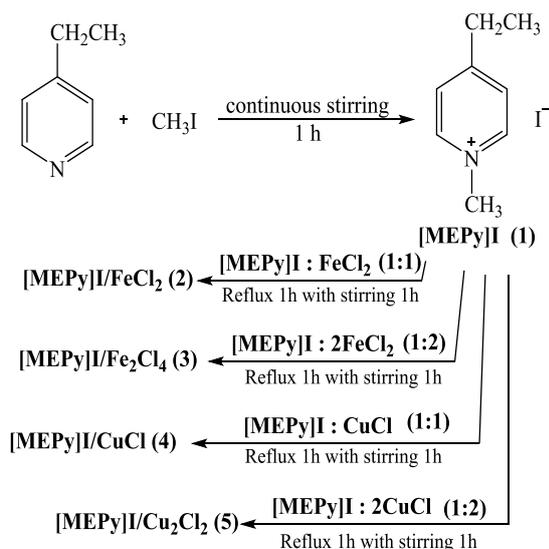
Materials and methods

Chemicals and Materials:

Chemicals and solvents from internationally approved sources (Sigma-Aldrich, Alfa Aesar, Fluka, and BDH) were used to prepare ionic liquid and ionic liquid systems and prepare the petroleum model (DBT).

Synthesis of IL-system:

The methods were adopted to prepare ionic liquids [14-16], the ionic liquid (1-methyl-4-ethyl pyridine-1-ium iodide) [MEPy]I was prepared for the base of the pyridine substitute by reacting (0.1 mol, 10.7g) of 4-ethyl pyridine with methyl iodide (15 g) by gradual addition of alkyl halide for an hour with continuous stirring. Then a mixture of ionic liquid with Lewis acids (complex salts) are prepared using ferrous chloride (FeCl_2) or copper chloride (CuCl) by reacting a different ratio of ionic liquid to metal chloride; then reflux the mixture for one hour with stirring. Upon completion of the reaction, the product was washed with n-hexane to remove the remaining methyl iodide. Scheme 1 shows the preparation of an ionic liquid and its salts for Lewis acids.



Scheme (1): Preparation of [MEPy]I ionic liquid and its Lewis acid salts (1-5)

Preparation of Model Oil and Extraction desulfurization (EDS):

The petroleum model was prepared [17, 18] by dissolving the organic sulfur compound (DBT) in the solvent n-decan at a concentration of 1500 ppm (by weight-to-weight ratio). A single-necked flask with a capacity of 100 ml was used for the extraction experiments. Introductory experiments were carried out using 10 ml of the petroleum model and using different temperatures from 20 to 50°C, using other

extraction times from 15 to 60 minutes as well as using different weights of the extracting agent (ionic liquid and Lewis acid for ionic liquid) dissolved in 10 ml of the solvent (DMSO). All these conditions were used to reach the optimum conditions for the extractive desulfurization process. After the specified time, the layers are separated in the extraction process (the upper layer of the oil model and the lower layer of the extracted and dissolved substance in the solvent). The residual sulfur concentration and removal percentage (the efficiency of the extraction process under the specified conditions) are measured based on the initial and final sulfur concentration in the oil model.

Instrumentation and Equipment:

To obtain the removal percentage, use many techniques and devices to characterize the ionic liquid and its salts and know the sulfur concentration before and after treatment. Bruker Avance DPX 400 MHz nuclear magnetic resonance spectrometry $^1\text{H-NMR}$ was used by DMSO-d_6 as a solvent; the device (JASCO Canvas FT/IR 4200) was also used to obtain the frequencies of the leading groups in the prepared compounds. To find out the proportions of the elements using the elemental analysis of the compounds, this device (Flash EA 1112 Series Thermo electron) was used. While (SensAA GCB) was used to determine the percentage of the metal elements using the (Avanta 2.02 software). Conductivity studied by BC3020 professional benchtop conductivity meter TRANS INSTRUMENTS using DMF as solvent. Thermal stability was studied by METTLER TOLEDO using the STARE evaluation software (16.00), the operating program from 25°C to 700°C with ten °C/min ramping temperature, using a ceramic pan under atmospheric pressure and air, and using water for cooling. GC-FID 4200 Carlo Erba using the SE-03 column measured before and after the extraction process using gas chromatography technology the sulfur content. Table 1 shows some physical properties of prepared compounds.

Table (1): Some physical properties of prepared compounds

No.	Compounds	Color	m.p °C	Conductivity*
1	[MEPy]I	Dark Brown	45	70
2	[MEPy]I/FeCl ₂	Brown Yellow	50	77
3	[MEPy]I/Fe ₂ Cl ₄	Brown Yellow	50	75
4	[MEPy]I/CuCl	Brown	56	78
5	[MEPy]I/Cu ₂ Cl ₂	Brown	58	80

* Λ ($\text{cm}^2/\text{ohm}^{-1}\cdot\text{mol}^{-1}$) at 25°C and 10^{-3}M , by using DMF as a solvent

Results and discussion

Characterization of IL and IL-system:

Figure 1. Shows the $^1\text{H-NMR}$ of [MEPy]I., $^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz) : δ 8.860 (2H, d, $J = 6.52$ Hz), δ 8.006 (2H, d, $J = 6.40$ Hz), δ 4.288 (3H, s), δ 2.904 (2H, q, $J = 7.56$ Hz), δ 1.255 (3H, t, $J = 7.56$ Hz). Mass spectroscopy data, MS m/z (relative intensity): 72 (0.39%), 73 (5.75%), 74 (100.00%), 75 (3.62%), 90 (2.12%), 91 (51.80%), 92 (2.03%), 117 (3.37%), 118 (14.50%), 119 (1.30%), 122 (0.02%). The elemental analysis of prepared IL-systems are: [MEPy]I (1) Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{IN}$: C, 38.57; H, 4.86; N, 5.62. Found C, 38.23; H, 4.62; N, 5.44. [MEPy]I/FeCl₂ (2) Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{FeIN}$: C, 25.57; H, 3.22; N, 3.73; Fe, 14.86. Found C, 24.80; H, 3.02; N, 3.56; Fe, 15.62. [MEPy]I/Fe₂Cl₄ (3) Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{Cl}_4\text{Fe}_2\text{IN}$: C, 19.12; H, 2.41; N, 2.79; Fe, 22.22. Found C, 18.76; H, 2.22; N, 2.56; Fe, 22.88. [MEPy]I/CuCl (4) Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{ClCuIN}$: C, 27.60; H, 3.47; N, 4.02; Cu, 18.26. Found C, 25.56; H, 3.55; N, 3.82; Cu, 20.16. [MEPy]I/Cu₂Cl₂ (5) Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{Cu}_2\text{IN}$: C, 21.49; H, 2.71; N, 3.13; Cu, 28.43. Found C, 20.82; H, 2.45; N, 29.50; Cu, 29.50.

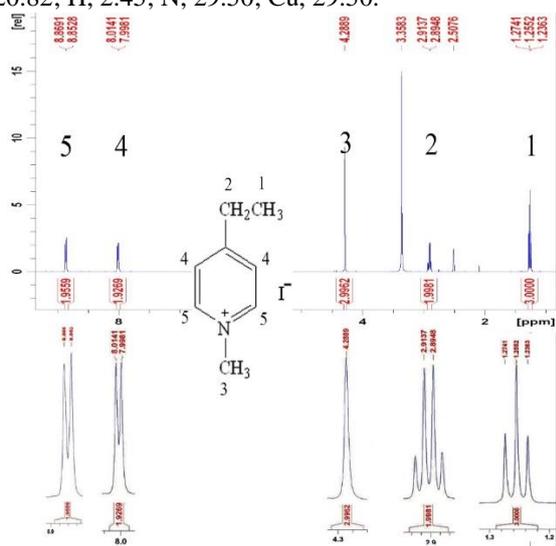


Fig (1): $^1\text{H-NMR}$ of [MEPy]I in DMSO- d_6

While studying the stretch frequencies of the [MEPy]I (1) pyridine aromatic ring and its Lewis acid mixture (Table 2), a (C=C) group appeared in the region of (1610-1650 cm^{-1}). The region's KBr disk (600-4000 cm^{-1}) was used for infrared measurements, while the region's CsI disk (200-500 cm^{-1}) was used. The leading group stretching frequencies of the (C=N) and (C-N) bands appeared in the (1435-1475 cm^{-1}) and (1100-1240 cm^{-1}) regions, respectively, while the (C-H) bands appeared in the (3020-3375 cm^{-1}) region. The metal-halide bond (M-X) (X= Cl, I) was realized at (230-340 cm^{-1}); furthermore, the new active group (N^+-CH_3) was realized at (2350-2860 cm^{-1}), all these values are compatible with the literature [4, 19-21].

Thermal Analysis:

The thermal stability of the prepared ionic liquids mixtures was verified. Figure 2 shows the thermal curve and the thermal differential curve for the ionic liquid. Figure 3 compares the thermal analysis curves of the ionic liquid and its complex salts of Lewis acids. It was noted that the ionic liquid [MEPy]I (1) is thermally stable to more than 200°C and degraded in one main phase, indicating the presence of one substance [22, 23]. In contrast, in the thermal analysis scheme for ionic liquids mixed with Lewis acids, the dissociation occurs in two primary stages, indicating the presence of two components in the mixture (ionic liquid and metal chloride) [24, 25]. The percentages of mass loss and corresponding heat ranges are shown in Table 3.

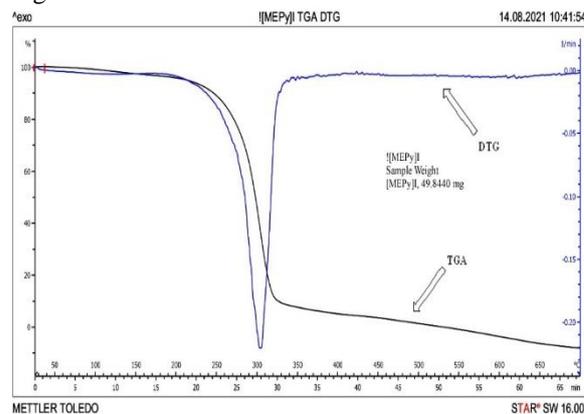


Fig (2): Thermal analysis of [MEPy]I, (1) (TGA and DTG)

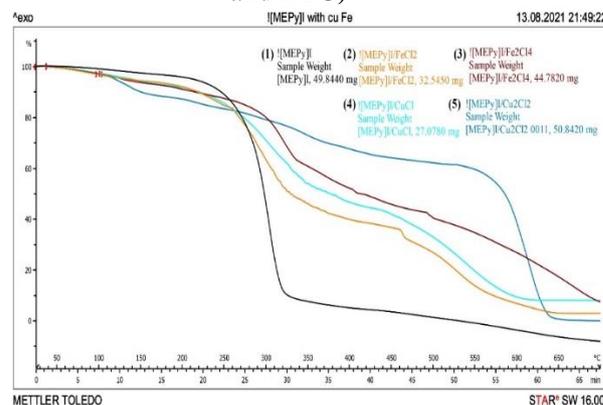


Fig (3): TGA analysis of prepared compounds (1-5)

By observing the data for the thermal analyses of the prepared compounds, it is clear that all of these compounds (ionic liquids and its mixture with Lewis acid) are stable under the experimental conditions of the extractive desulfurization process (EDS) used in this work, and this is consistent with the literature [22-26].

Table (2): Infrared Str. frequencies (cm⁻¹) values of the leading group of prepared compounds

No.	Compounds	$\nu(\text{N}^+-\text{CH}_3)$	$\nu(\text{M}-\text{X})$	$\nu(\text{C}-\text{H})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$
1	[MEPy]I	---	---	3020s	1190m	1475m	1650s
2	[MEPy]I/FeCl ₂	255m,315s	2850w	3320s	1120m	1445w	1645s
3	[MEPy]I/Fe ₂ Cl ₄	245s,330s	2370w	3335s	1110m	1455w	1646s
4	[MEPy]I/CuCl	240s,330s	2355w	3370s	1215s	1455m	1610m
5	[MEPy]I/Cu ₂ Cl ₂	245s,330s	2845w	3360s	1245w	1430m	1610m

s = strong, m = medium, w = weak

Table (3): Thermal analysis, degradation stages, and mass loss % data of prepared compounds

No.	Compounds	1 st degradation		Mass loss%	2 nd degradation		Mass loss%
		Onset °C	Endset °C		Onset °C	Endset °C	
1	[MEPy]I	195	350	94	---	---	---
2	[MEPy]I/FeCl ₂	54	374	58	374	687	40
3	[MEPy]I/Fe ₂ Cl ₄	58	377	46	377	692	38
4	[MEPy]I/CuCl	79	381	52	381	687	44
5	[MEPy]I/Cu ₂ Cl ₂	64	419	35	419	691	64

EDS optimization conditions:

Experiments on extractive desulfurization were carried out at room temperature 25 °C because temperature changes had no discernible effect on the extraction process's efficiency [1, 4]. The following parameters were used in the GC-FID quantitative determination of the DBT compound: injector temperature 275 °C, oven temperature 280 °C, detector temperature 280 °C, helium gas as a carrier, and a hydrogen gas flame in the detector using a GC column of type PB SE-03. 0.25 mm ID. 0.25 m. 25 m. All ionic liquid systems (1-5) were tested for half an hour with 0.05 g of an ionic liquid dissolved in 10 ml of DMSO solvent. The efficiency results of the extractive desulfurization process are shown in table 4.

Effect of EDS experiment time:

Consistent with earlier extractive desulfurization process experiments (Table 4), it was determined that the best extracting is compound (5), which will be used to determine the optimal conditions. The effect of time was investigated using 0.05 g of the extracted agent at 25°C with a range of times (15, 30, 45, 60 minutes). Increasing the extraction time improves sulfur removal efficiency, but only until a certain

point is reached; after 30 minutes, the sulfur removal capacity appears to have been established. The equilibrium state between the layers is consistent with what is mentioned in the literature [1, 4]. On the contrary, increasing the extraction time may increase efficiency in some cases, depending on the quality of the extracted material and the sulfur compounds [2]. The best efficacy at 60 min (58%), figure 4 depicts the percentage of sulfur removed at various times.

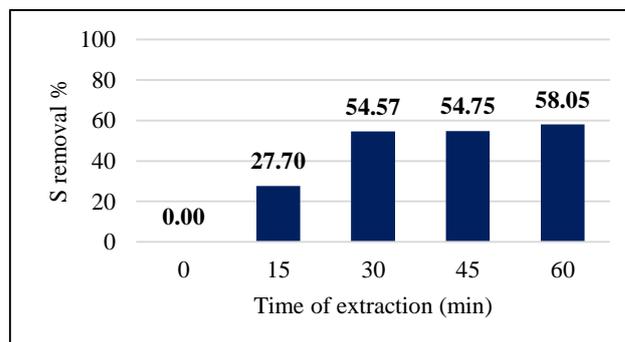


Fig (4): The effect of time, EDS conditions (extractant = [MEPy]I/Cu₂Cl₂, weight = 0.05 g, at 25°C)

Table (4): Sulfur removal percentage, (EDS) conditions (time = 30 min, extractant weight = 0.05 g, at 25°C)

No.	Extractant	DBT area (counts)	DBT conc. (ppm)	S _{removal} %
1	[MEPy]I	79602	1206.02	22.41
2	[MEPy]I/FeCl ₂	84009	1063.22	31.60
3	[MEPy]I/Fe ₂ Cl ₄	75051	908.95	41.52
4	[MEPy]I/CuCl	96483	964.39	37.96
5	[MEPy]I/Cu ₂ Cl ₂	64631	706.10	54.57

Effect of extractant weight:

One of the essential factors influencing the extraction process's efficiency and feasibility is the weight factor for the extracted material. Because the effect of time is imperceptible, 30 minutes was chosen, at the same temperature as the previous experiments, and by changing the weight of the extracted factor (0.025, 0.05, 0.075, 0.1 g). It is noted that the extraction process's efficiency increases with the percentage of extracted substance, which is consistent with the literature [1, 2], where the highest value is 58% with the use of 0.1 g of extractant. It is possible to claim that the removal efficiency of sulfur compounds is 100%, but only if a large amount of the extracting agent is used compared to the oil model [8, 13, 27]. As shown in Figure 5, the percentage of sulfur removal increased as the weight increased.

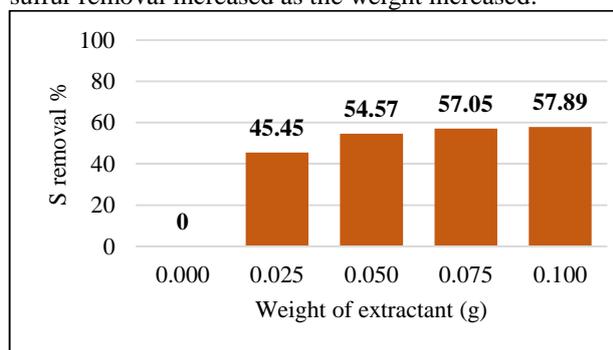


Fig (4): The effect of time, EDS conditions (extractant = [MEPy]I/Cu₂Cl₂, weight = 0.05 g, at 25°C)

Conclusion:

This study shows that pyridinium-based ionic liquids are highly efficient in the extractive desulfurization process. In addition to the ionic liquids of pyridinium bases containing Lewis acids, it has been observed that the presence of Lewis acids (ferrous chloride and copper chloride) increases the efficiency of the process and that the efficiency of ionic systems containing Lewis acids is higher than that of systems without them. That is due to an increase in the (π - π) interactions between the aromatic electrons in organic sulfur compounds and the metal ion. It was also discovered that increasing the ratio of Lewis acid to an ionic liquid increases extraction efficiency and improves sulfur removal percentage.

Increasing the extraction time and weight of the extracted material positively affects the sulfur removal process, but only to a certain extent, as the increase is not noticeable. It is also clear that the efficiency of the sulfur removal process is not 100%, which is due to the use of small quantities of the extracted substance, as large quantities give good results and the efficiency of removal can reach 100%, but it is economically expensive.

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References:

1. Butt, H.S., K.C. Lethesh, and A. Fiksdahl, *Fuel oil desulfurization with dual functionalized imidazolium based ionic liquids*. Separation and Purification Technology, 2020. **248**: p. 116959.
2. Balinge, K.R., et al., *Deep-desulfurization of the petroleumdiesel using the heterogeneous carboxyl functionalized poly-ionic liquid*. Resource-Efficient Technologies, 2016. **2**: p. S105-S113.
3. Syntyhaki, E. and D. Karonis, *Oxidative and extractive desulfurization of petroleum middle distillates, using imidazole ionic liquids*. Fuel Communications, 2021. **7**: p. 100011.
4. Dharaskar, S.A., et al., *Synthesis, characterization and application of 1-butyl-3-methylimidazolium tetrafluoroborate for extractive desulfurization of liquid fuel*. Arabian Journal of Chemistry, 2016. **9**: p. 578-587.
5. Wu, Q., et al., *Synthesis of Surface-Active Heteropolyacid-Based Ionic Liquids and Their Catalytic Performance for Desulfurization of Fuel Oils*. ACS omega, 2020. **5**(48): p. 31171-31179.
6. Kulkarni, P.S. and C.A. Afonso, *Deep desulfurization of diesel fuel using ionic liquids: current status and future challenges*. Green Chemistry, 2010. **12**(7): p. 1139-1149.
7. Chica, A., A. Corma, and M.E. Dómine, *Catalytic oxidative desulfurization (ODS) of diesel fuel on a continuous fixed-bed reactor*. Journal of Catalysis, 2006. **242**(2): p. 299-308.
8. Zhang, L., et al., *Deep oxidative desulfurization of fuels by superbase-derived Lewis acidic ionic liquids*. Chemical Engineering Journal, 2017. **328**: p. 445-453.
9. Holbrey, J.D., et al., *Liquid clathrate formation in ionic liquid-aromatic mixtures*. Chemical Communications, 2003(4): p. 476-477.
10. Su, B.-M., S. Zhang, and Z.C. Zhang, *Structural elucidation of thiophene interaction with ionic liquids by multinuclear NMR spectroscopy*. The Journal of Physical Chemistry B, 2004. **108**(50): p. 19510-19517.
11. Gao, H., et al., *Desulfurization of fuel by extraction with pyridinium-based ionic liquids*. Industrial & Engineering Chemistry Research, 2008. **47**(21): p. 8384-8388.
12. Zhao, D., Y. Wang, and E. Duan, *Oxidative desulfurization of fuel oil by pyridinium-based ionic liquids*. Molecules, 2009. **14**(11): p. 4351-4357.
13. Ko, N.H., et al., *Extractive desulfurization using Fe-containing ionic liquids*. Energy & Fuels, 2008. **22**(3): p. 1687-1690.

14. SABAH, A.A. „*Synthesis and Characterization of Some Transition Metals Complex Salts of Pyridinium Iodide Ionic Liquids: Application on Extractive Desulfurization*. Journal of the Turkish Chemical Society Section A: Chemistry, 2021. **8**(3): p. 763-774.
15. Singh, S.K. and A.W. Savoy, *Ionic liquids synthesis and applications: An overview*. Journal of Molecular Liquids, 2020. **297**: p. 112038.
16. Muhammad, N., et al., *An overview of the role of ionic liquids in biodiesel reactions*. Journal of Industrial and Engineering Chemistry, 2015. **21**: p. 1-10.
17. Li, F.-t., et al., *Deep extractive desulfurization of gasoline with x Et₃NHCl· FeCl₃ ionic liquids*. Energy & fuels, 2010. **24**(8): p. 4285-4289.
18. Wang, Q., et al., *Extractive desulfurization of fuels using trialkylamine-based protic ionic liquids*. Separation and Purification Technology, 2020. **231**: p. 115923.
19. Earle, M.J., P.B. McCormac, and K.R. Seddon, *Regioselective alkylation in ionic liquids*. Chemical communications, 1998(20): p. 2245-2246.
20. Ding, Y.-S., et al., *Synthesis, characterization and properties of geminal imidazolium ionic liquids*. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2007. **298**(3): p. 201-205.
21. Moshikur, R.M., et al., *Ionic liquids with N-methyl-2-pyrrolidonium cation as an enhancer for topical drug delivery: Synthesis, characterization, and skin-penetration evaluation*. Journal of Molecular Liquids, 2020. **299**: p. 112166.
22. Bittner, B., R.J. Wrobel, and E. Milchert, *Physical properties of pyridinium ionic liquids*. The Journal of Chemical Thermodynamics, 2012. **55**: p. 159-165.
23. Matandabuzo, M. and P.A. Ajibade, *Synthesis and surface functionalization of multi-walled carbon nanotubes with imidazolium and pyridinium-based ionic liquids: Thermal stability, dispersibility and hydrophobicity characteristics*. Journal of Molecular Liquids, 2018. **268**: p. 284-293.
24. Duan, Z., Y. Gu, and Y. Deng, *Green and moisture-stable Lewis acidic ionic liquids (choline chloride· x ZnCl₂) catalyzed protection of carbonyls at room temperature under solvent-free conditions*. Catalysis Communications, 2006. **7**(9): p. 651-656.
25. Xie, W. and H. Wang, *Synthesis of heterogenized polyoxometalate-based ionic liquids with Brønsted-Lewis acid sites: A magnetically recyclable catalyst for biodiesel production from low-quality oils*. Journal of Industrial and Engineering Chemistry, 2020. **87**: p. 162-172.
26. Tao, L., et al., *Application of choline chloride· x ZnCl₂ ionic liquids for preparation of biodiesel*. Chinese Journal of Chemical Engineering, 2010. **18** (2): p. 322-327.
27. Zhang, M., et al., *Deep oxidative desulfurization of dibenzothiophene with POM-based hybrid materials in ionic liquids*. Chemical engineering journal, 2013. **220**: p. 328-336.