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APPLICATION EXTRACTIVE DESULFURIZATION USING PIPERIDINIUM BASED IONIC SALT WITH $FeCl_3$ AS LEWIS ACID

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Abstract: *The study involves the synthesis of inorganic salts by reacting the organic salts with ferric chloride and organic salts* ***(1) [****mAMPi]Br****, (2) [****pAMPi]Br derived from the nitrogenous base of Piperidinium. Spectroscopic and physical techniques were used to characterize the prepared compounds, including mass spectrometry, infrared FT-IR, micro-elemental analysis, and* ^{1}*H-NMR nuclear magnetic resonance spectroscopy. The extractive desulfurization method was used in this study, and the produced compounds were examined using model oil that contained 1000 ppm of the sulfur compound. Dibenzothiophene (DBT) was dissolved in an n-hexane solvent, and ultraviolet (UV) was used as a quantitative analysis method to calculate the percentages of sulfur removal. Future research may be able to enhance the sulfur removal rate provided by the prepared compounds, which were showed an acceptable result.*

Keywords*: Ionic liquids, organic salts, Lewis acid, desulfurization*
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Introduction

Environmental concern has increased worldwide, and strict standards and regulations have been enacted to reduce the negative impacts of automobile exhaust on human health and the environment [1].

With increasing environmental awareness, limitations on restricting fuel sulfur content have been issued worldwide. The treatments must go ahead to reach the rigid regulation of the sulfur level in liquid fuels. To overcome the defects of monolayer ionic liquids (ILS) mentioned above, the devised SiO_2– immobilized bilayer ILS (SiO_2– Bill) [2]. With the development of industry, the global atmospheric environment gradually deteriorated. The sulfur component of fuel oil turns to sulfur oxides that will seriously pollute the atmosphere.

The essential desulphurization method is hydrodesulfurization (HDS) [3]. Social development demands large consumption of fossil fuels in industries as well as for other applications in different fields like transportation, power stations, power engines, aircraft, agricultural fields, etc. It is established that the presence of sulfur compounds in fossil fuels after the combustion process produces gaseous Sox in the environment, which is the cause of air pollution via acid rain and produces various other hazardous products that create several health issues [4].

Modern urbanization and industrial development have greatly stimulated global fossil energy consumption. Various methods have been tried for desulfurization, including hydro, bio-absorptive, extractive, and oxidative desulfurization (ODS). As OSCs' most popular removal method, hydro-desulfurization (HDS) is applied intensively in fossil fuel refining plants worldwide. The HDS technology has

been considered an efficient method for nearly a century in removing various sulfurous compounds from several fuel resources. In this process, sulfur is removed as H_2S gas; therefore, hydrodesulfurization comprises facilities for capturing and removing H_2S [5, 6].

Experimental part

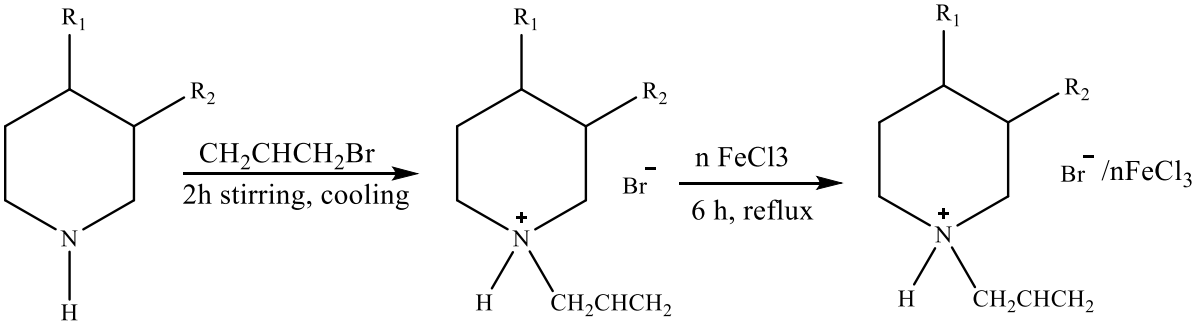
Methodology. Each and every chemical that is used comes from an authentic, ultra-pure source. The FT-IR spectra were obtained using the JASCO Canvas FT/IR 4200 infrared spectrophotometer. 1HNMR spectra were acquired on a Bruker 400MHz spectrometer with tetramethylsilane (TMS) as an internal reference and DMSO-d6 as a solvent. The microanalysis was performed at Thermo Electron Corporation's Flash EA 1112 Series using a Trio-1000 mass spectrometer.

Preparation of organic salts and complex salts of Fe(III).

1-allyl-3-methylpiperidinium bromide **[*m*AMPi]I (1)**

1-allyl-4-methylpiperidinium bromide **[*p*AMPi]I (2)**

The organic salts (ionic liquids) have been prepared according to the literature [7-11], considering that the reaction is exothermic and its yield increases with cooling. The Scheme below displays the reaction equation:



1: R_1 = H, R_2 = CH_3 , **[*m*AMPi]Br**
2: R_1 = CH_3, R_2 = H, **[*p*AMPi]Br**
3: R_1 = H, R_2 = CH_3 , n = 1,**[*m*AMPi]$FeCl_3$Br**
4: R_1 = CH_3, R_2 = H, n = 2 , **[*m*AMPi]Fe_2Cl_6Br**
5: R_1 = H, R_2 = CH_3 , n = 1, **[*p*AMPi]$FeCl_3$Br**
6: R_1 = CH_3, R_2 = H, n = 2 , **[*p*AMPi]Fe_2Cl_6Br**

By reacting different ratios of organic salt with ferric chloride in ratios of (1:1) and (1:2), respectively, ionic salts of iron were created. The prepared compounds' physical characteristics and the outcomes of their elemental microanalysis are displayed in the Table 1.

In order to prepare the model oil sample, the sulfur compound Dibenzothiophene (DBT) must first be dissolved in hexane solvent to achieve the initial concentration of 1000 ppm. Next, the optimal conditions for the sulfur removal process must be identified.

Table 1. Physical properties and results of elemental microanalysis of the prepared compounds

Compounds	Formula	Melting point (°C)	CHN (theory)/ Calculate			
			C%	H%	N%	Fe%
(1) [*m*AMPi]Br	$C_9H_{18}BrN$	157-159	(49.10) 48.24	(8.24) 8.23	(6.63) 6.33	---
(2) [*p*AMPi]Br	$C_9H_{18}BrN$	144-146	(49.10) 46.39	(8.24) 7.86	(6.63) 7.76	---
(3) [*m*AMPi]$FeCl_3$Br	$C_9H_{18}BrCl_3FeN$	150-152	(28.27)	(4.75)	(3.66)	(14.61)

			29.88	4.65	3.48	14.06
(4) [*m*AMPi]Fe_2Cl_6Br	$C_9H_{18}BrCl_6Fe_2N$	140-143	(19.85) 18.28	(3.33) 3.92	(2.57) 2.63	(20.51) 20.18
(5) [*p*AMPi]$FeCl_3Br$	$C_9H_{18}BrCl_3FeN$	148-150	(28.27) 27.88	(4.75) 4.35	(3.66) 3.68	(14.61) 15.00
(6) [*p*AMPi]Fe_2Cl_6Br	$C_9H_{18}BrCl_6Fe_2N$	141-143	(19.85) 18.76	(3.33) 3.48	(2.57) 2.66	(20.51) 21.24

Results and discussion

The ability of Piperidinium ionic liquids to extract sulfur from petroleum derivatives is one of their main characteristics. These liquids contain Lewis acids, iron in particular. Every produced chemical was thoroughly characterized and found to be in accordance with the data presented in the references [8, 12, 13].

The ^{1}H-NMR characterization data for organic salts (**1,2**) respectively are (DMSO-d_6, 400 MHz), δ0.88 (3H, C-CH_3, s), δ1.066 (1H, CH-C, bs), δ1.06, δ1.73, δ3.29, δ3.70 (cyclic, 2H, CH_2, bs), δ3.70 (2H, CH_2 for terminal group, bs), δ4.010 (2H, CH_2, d, for allylic group), δ5.74 (1H, = CH, bs), δ9.59 (1H, NH, s). The GC-mass data for organic salt (**1**), **[*m*AMPi]Br,** $C_9H_{18}BrN$, (*m/z*, intensity%): (140, 100%), (138.2, 1.04%), (126.1, 0.11%), (124.1, 0.39%), (112,1.08%), (98.1, 0.5%), (84, 0.32%), (82, 0.19%), (70, 0.06%), (68, 0.05%). (DMSO-d6, 400 MHz), δ0.90 (3H, C-CH_3, s), δ1.066 (1H, CH-C, bs), δ1.06, δ1.73, δ3.29, δ3.70 (cyclic, 2H, CH_2, bs), δ3.21 (2H, CH_2, d, for allylic group), δ5.38 (1H, =CH, bs), δ5.18 (2H, for terminal CH_2 group, bs) δ8.53 (1H, NH, s). The GC-mass data for organic salt (**2**), **[*p*AMPi]Br,** $C_9H_{18}BrN$, (*m/z*, intensity%): (140.2, 4.41%), (138.2, 0.15%), (100.1, 100%), (98.1, 2.26%), (96.1, 0.01%), (94.1, 0.03%), (82, 0.04%), (82, 0.02%), (70, 0.06%), (58, 0.04%).

In addition to the properties listed in the previous Table 1, the compounds have been well characterized [7, 14, 15] by spectroscopic and physical measurements, as shown in Table 2.

Table 2. Some characteristics data for the prepared compounds

Comp. No.	IR data (cm^{-1})				μ_{eff} (BM)	Conductivity** $ohm^{-1}.cm^2.mol^{-1}$
	C-N	N^+-R*	N-H	M-X		
1	1586	2368	3422	---	---	67
2	1592	2365	3412	---	---	72
3	1214	2356	3398	239,331	5.61	80
4	1110	2368	3434	242,327	5.86	88
5	1118	2368	3412	254,316	5.56	82
6	1245	2368	3422	246,331	5.82	86

* *R = CH_2CHCH_2*

** *(DMF) as solvent at 25°C, (10^{-3} M)*

The Extraction desulfurization. The optimal conditions for the extractive desulfurization process were determined in advance by determining the concentration of the salt prepared and used in the test, the time of the extraction process, and the temperature. The results showed optimal conditions (concentration in grams, extraction time 60 minutes, 30 degrees Celsius). Using ultraviolet technology with a Shimadzu UV 1800 device, and using an initial concentration of the petroleum model of sulfur using Dibenzothiophene (DBT) dissolved in hexane solvent at a concentration of 1000 ppm, a standard curve was plotted (Figures 1 and 2).

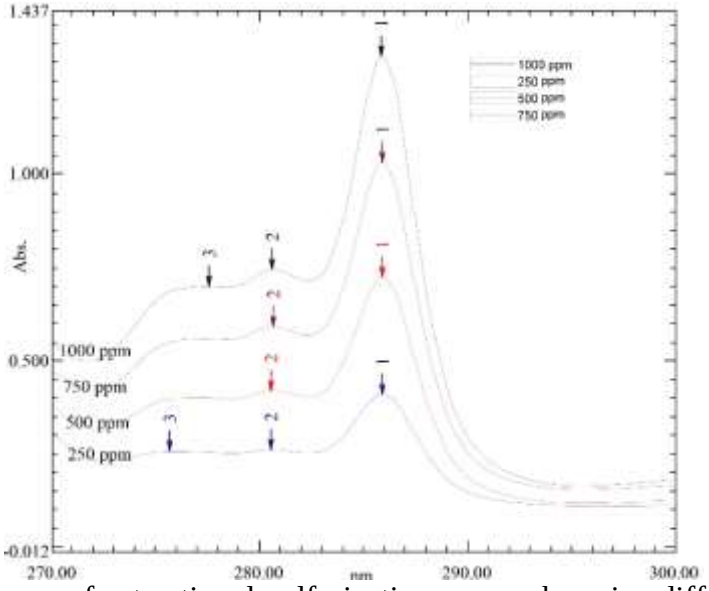


Fig. 1. Calibration curve of extraction desulfurization process by using different concentrations (standard solutions)

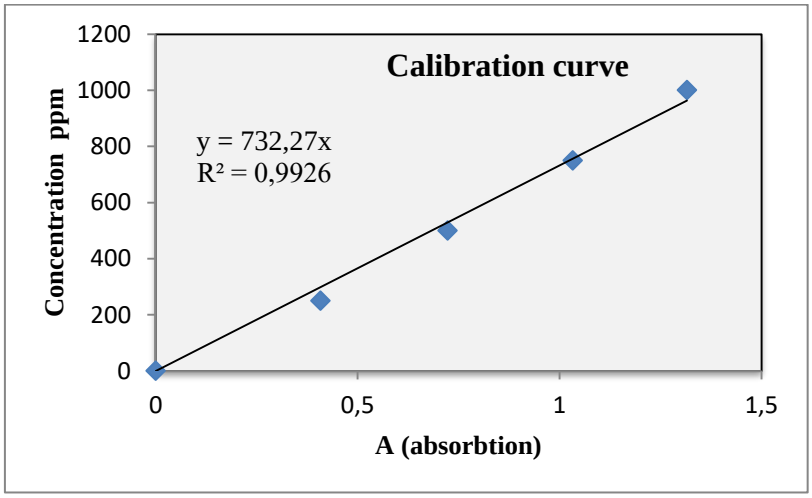


Fig. 2. The calibration curve of the extraction desulfurization process

The Table 3 illustrates how the extraction process' efficiency was determined by comparing the results of testing the prepared compounds with existing literature [8, 16-19].

Table 3. The extraction data of tested prepared salts by using optimal conditions (285 nm, 60 min, 0.1 gm of extractant at 30°C)

Comp. No.	A (absorption)	$S_{content}$ ppm	$S_{removal}$ %
1	1.129	826	17.4
2	1.145	838	16.2
3	1.060	776	22.4
4	1.058	774	22.6
5	0.901	659	34.1
6	0.898	657	34.3

Conclusion

Comparing the prepared salts to other studies [10, 16-18], it is evident from the earlier findings that they have an acceptable efficiency level in the sulfur removal process. It is also

evident that there is no variation in the extraction efficiency when comparing organic salts to one another. It is observed that there are no variations in efficiency due to the methyl group's replacement on the ring. It is found that the extraction efficiency rises with the addition of iron salt [10, 11, 20] and climbs as the quantity of iron salt increases. This is in agreement with the literature information.

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LYUİS TURŞUSU KİMİ $FeCl_3$ İLƏ PİPERİDİNİUM ƏSASLI İON DUZUNDAN İSTİFADƏ ETMƏKLƏ EKSTRAKSİYALI DESULFURİZASİYANIN TƏTBİQİ

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Xülasə: Tədqiqatda dəmir (III) xlorid və piperidiniumun azotlu əsaslarından alınmış üzvi duzları (1) [mAMPi]Br, (2) [pAMPi]Br ilə reaksiyası nəticəsində qeyri-üzvi duzların sintezi aparılmışdır. Alınmış birləşmələr mass-spektrometriya, infraqırmızı Furye spektroskopiya, mikroelement analizi və ^{1}H-NMR nüvə maqnit rezonans spektroskopiyası üsulları ilə xarakterizə edilmişdir. Bu tədqiqatda ekstraksiyalı kükürdsüzləşdirmə üsulundan istifadə edilərək, sintez edilmiş birləşmələr tərkibində 1000 ppm kükürd birləşmələri olan neftlə tədqiq edilmişdir. Dibenzotiofen (DBT) n-heksan həlledicidə həll edilmiş və kükürdün xaric olma faizini hesablamaq üçün kəmiyyət təhlili

üsulu kimi ultrabənövşəyi (UV) üsuldan istifadə edilmişdir. Gələcək tədqiqatlar yüksək nəticə göstərən birləşmələrdən istifadə etməklə kükürdün çıxarılması sürətini artıra bilər.
Açar sözləri: İon mayeləri, üzvi duzlar, Lyuis turşusu, desulfurizasiya

ПРИМЕНЕНИЕ ЭКСТРАКЦИОННОЙ ДЕСУЛЬФУРИЗАЦИИ С ИСПОЛЬЗОВАНИЕМ ИОННОЙ СОЛИ НА ОСНОВЕ ПИПЕРИДИНИЯ С $FeCl_3$ В КАЧЕСТВЕ КИСЛОТЫ ЛЬЮИСА

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Резюме: Исследование включает синтез неорганических солей путем взаимодействия хлорида железа с органическими солями (1) [mAMPi]Br, (2) [pAMPi]Br, полученными из азотистого основания пиперидиния. Для характеристики полученных соединений использовались спектроскопические и физические методы, включая масс-спектрометрию, инфракрасную Фурье-спектроскопию, микроэлементный анализ и спектроскопию ядерного магнитного резонанса ^{1}H-ЯМР. В этом исследовании использовался метод экстракционной десульфурации, а полученные соединения были исследованы с использованием модельной нефти, содержащей 1000 ppm сернистого соединения. Дибензотиофен (DBT) растворяли в растворителе н-гексане, а ультрафиолет (УФ) использовали в качестве количественного метода анализа для расчета процентов удаления серы. Будущие исследования могут повысить скорость удаления серы, обеспечиваемую приготовленными соединениями, которые показали приемлемый результат.
Ключевые слова: Ионные жидкости, органические соли, кислота Льюиса, десульфуризация.