

Catalytic Oxidative-Extractive Deep Desulfurization of Diesel Fuel by N-methyl-2-pyrrolidone-Based Protic Acidic Ionic Liquids (PAILs)

Akbari, Azam*⁺

Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186 Tehran, I.R. IRAN

Haji Andevary, Hojatollah

Mazandaran University of Science and Technology, Babol, I.R. IRAN

ABSTRACT: Inexpensive and low-viscosity Protic Acidic Ionic Liquids (PAILs) of N-methyl-2-pyrrolidone formate, acetate and propionate abbreviated as [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] respectively, were prepared and characterized by FT-IR and H-NMR. Deep oxidative and extractive desulfurization of a simulated oil and a real diesel containing 1000 ppmw sulfur were studied under the catalysis of the proposed PAILs without additional carboxylic acid and extraction solvent in the system. The desulfurization efficiency in this study was influenced by both amount of PAILs and concentration of the produced peroxyacids from H₂O₂. Comparing to [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] had a relatively higher extraction ability however the weaker acidic properties of them resulted in a lower activation of H₂O₂ to produce peroxyacids and finally led to a lower oxidative desulfurization (ODS) efficiency at a same condition. Additionally, the neutralization reaction may not be efficiently gone to right hand by weaker acids. The effects of main process variables were studied in detail. The highest desulfurization yield of 97% for BT and 99% for DBT and 4,6-DMDBT, were achieved using [Hnmp][HCOO] in the ODS system at temperature of 40 °C, H₂O₂/sulfur molar ratio of 10, V_{PAIL}/V_{oil} of 0.2 and reaction time of 90 min. The immiscibility of the proposed PAILs in this study with the oil phase caused easy separation of them after desulfurization. The possible ODS pathway was also proposed.

KEYWORDS: Oxidative desulfurization; Ionic liquid; Carboxylic acid; Catalyst; Thiophenic compounds.

INTRODUCTION

Efficient deep oxidative desulfurization (ODS) of aromatic sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and their alkylated derivatives

in fuels has been an important research subject in recent decades [1-3]. Deeply removal of these aromatic thiophenic compounds were highly difficult and costly

* To whom correspondence should be addressed.

+ E-mail: a.akbari@ccerci.ac.ir

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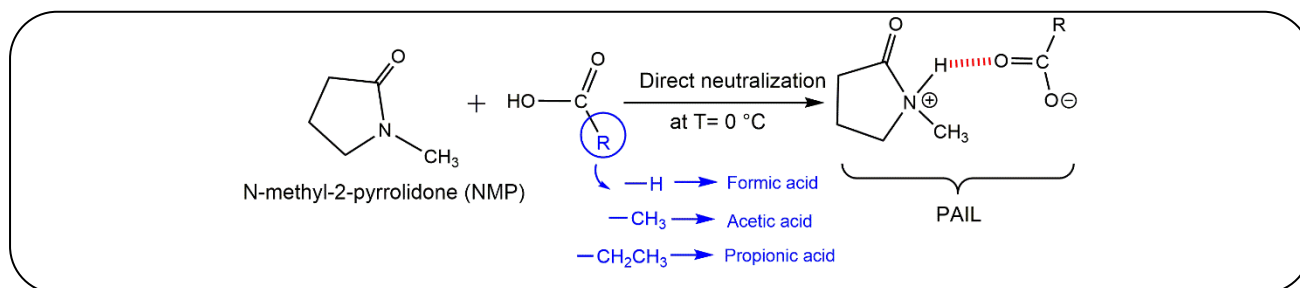
in the conventional industrial hydrodesulfurization (HDS) [4-6]. The ODS process, which operate at a mild reaction temperature (25-90 °C), atmospheric pressure, liquid phase and without using expensive hydrogen, can appropriately remove the residual refractory aromatic sulfur compounds after HDS to produce clean fuels [1,4,5]. In the ODS process, usually H₂O₂ was used as the oxidant, and a catalyst was also necessary for generation of active oxidant intermediates from H₂O₂ for oxidation of thiophenic compounds to polar sulfones. After oxidation, an extraction solvent was used for separation of the sulfone products from fuel [6-8]. For instance, high active peroxy-carboxylic acids could produce in situ by reaction of carboxylic acid catalysts with H₂O₂, that effectively oxidize thiophenic compounds to sulfones [6,9,10]. Then an organic solvent such as *N*-methyl-2-pyrrolidone (NMP), acetonitrile and methanol [6,11], or some Ionic Liquids (ILs) having higher ability than organic solvents [7,8,12-14], were utilized to extract sulfones from oil phase. For example, *Bui et al.* [14] synthesized and investigated non-halogen [Bmim]HSO₄ and [BPy]HSO₄ for removal of DBT using H₂O₂ and formic acid as catalyst. *Zhao et al.* [15] stated that DBT was efficiently removed in the ODS process using pyridinium-based ILs by H₂O₂ and formic acid catalyst. *Yu et al.* [12] studied the ODS of model fuel oils using acetic acid as catalyst, H₂O₂ as oxidant and low viscosity [C₂mim][N(CN)₂] IL as the extractant. In this system, 99% of DBT (with initial concentration of 758 ppmw in model oil) was removed at 70 °C, IL/oil mass ratio of 1 and during 6 h [12]. [C₄mim]PF₆ [13], Me₃NCH₂C₆H₅Cl₂ZnCl₂ [8] and (C₄H₉)NBr₂C₆H₁₁NO [7] were other typical examples of ILs applied in the ODS process by the carboxylic acid catalysts/H₂O₂ system. However, the application of additional catalysts elevated some problems such as difficult separation and regeneration of the carboxylic acids, and fuel pollution by residual dissolved catalysts [1,7]. To avoid these problems, recently many of the researchers suggested the use of some effective ILs which can simultaneous act as a catalyst and extractant in the ODS process [16-25]. The ILs dealing with this approach, usually included a *N*-methyl-2-pyrrolidone (NMP) [3,14,16], imidazolium [17-21], or Pyridinium [16,22,23] substituted cation, and [FeCl₄], [CH₃COO], [HSO₄], or [ZnCl₂] as the typical anions [11,14,22,23]. Furthermore, some supported and

unsupported polyoxometalate-based ILs have been recently reported to be efficient in ODS process [26-28]. The cation and anion structure, and acidic properties (Bronsted or Lewis) of these ILs were important for playing a dual catalyst-extractant role [17,22]. Based on the previous studies, it seems that combination of carboxylic acids and ILs properties in one material, would be attractive for catalyzing of ODS reaction simultaneous with the extraction of sulfone products in one step and at a short reaction time. The aim of this work was synthesis and application of non-halogen and low viscosity protic acidic ILs (PAILs) of [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO]. The motivation of this work was the use of one easy separable PAIL replaced with the use of both carboxylic acid and an extraction solvent for deep desulfurization of diesel fuel at a mild condition. The suggested PAILs in this work could be practically interesting Bronsted acidic ILs having catalytic activity and extraction ability in ODS process; the NMP ring can facile extract the aromatic sulfur compounds based on its similarity with the thiophenic ring [3]; At the same time, the carboxylic group of the anion can catalyze the oxidation reaction of sulfur compound by H₂O₂. Moreover, these PAILs present the advantage of being cost-effective while be easy prepared without formation of residual by-products [29]. In this work, the suggested PAILs of [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] were prepared by the neutralization of NMP with carboxylic acids (formic, acetic and propionic acids). The FTIR and H-NMR spectra were utilized to understand the coordinations. Oxidative desulfurization of simulated (BT, DBT and 4,6-DMDT in *n*-Octane) and real diesel were studied using the prepared PAILs. The effects of main process variables of temperature, H₂O₂/sulfur molar ratio (n_O/n_S) and V_{PAIL}/V_{oil} were investigated. The chemical behavior of the suggested PAILs in this ODS system were investigated and compared.

EXPERIMENTAL SECTION

Chemical Materials

The following chemical materials were purchased from different companies; *N*-methyl-2-pyrrolidone (NMP) from Fluka chemicals Ltd; Benzothiophene (BT), Dibenzothiophene (DBT), Formic acid, Acetic acid,



Scheme 1: Preparation of PAILs by direct neutralization.

Propionic acid, H_2O_2 (30 wt.% aqueous solution), ethyl acetate, hexadecane and n-Octane from Merck chemical company, Germany; 4,6-Dimethyldibenzothiophene (4,6-DMDBT) from Haohua Industry Company Ltd., China. The hydrotreated diesel was supplied from Tehran oil refinery, Iran. All chemicals were used without further purification.

Preparation of PAILs

The PAILs were prepared via the general neutralization reaction of NMP with carboxylic acids (formic, acetic and propionic acid) [30,31] as illustrated in Scheme 1. The neutralization method was utilized as follows: The carboxylic acid was added dropwise to a same molar amount of NMP under vigorous stirring in a round-bottom flask equipped with a reflux condenser. Because the reaction of carboxylic acid and NMP is exothermic, an ice bath was used during the dropwise addition of acids. After 30 min, the stirring was continued for 3 hr at ambient temperature. Finally, the residual NMP and acid impurities were evaporated using a rotary evaporator at 80-90 °C under reduced pressure to obtain the PAIL. The name, structure and abbreviation of the synthesized PAILs has been listed in Table 1.

Characterization methods

$^1\text{H-NMR}$ spectra were recorded on a Bruker DRX 400 MHz spectrometer at room temperature (400 MHz) and internally referenced to tetramethylsilane signal in CDCl_3 . Fourier transform infrared (FTIR) spectra were obtained by PerkinElmer FT-IR spectrometer using KBr pellets. GC-FID (Agilent 7890A, HP-5 capillary column, 30 m \times 0.32 mm id, temperature program: 200 °C for 3 min, temperature elevating of 10 °C/min up to 280 °C, 280 °C for 5 min, injector temperature: 280 °C, detector temperature: 300 °C, N_2 carrier gas with flow rate of

5 mL/min) was used to measure the desulfurization yield of model sulfur compounds. Hexadecane was employed as the internal standard to perform the sulfur concentration measurements. Total sulfur of the real diesel was determined by Multi EA 5000 (Analytik Jena, Germany), in accordance with international standard of ASTM D5453. Pulsed Flame Photometric detector (GC-PFPD) was employed to characterize desulfurization of real diesel. GC-MS (Varian, Saturn 2200, GC/MSD; VF-5 MS column, 30m \times 250 μm id \times 0.25 μm ; temperature program: 150 °C for 2 min, temperature rising of 10 °C/min up to 280 °C, 280 °C for 30 min; injector temperature: 280 °C) was used to characterize desulfurization products.

Oxidative and Extractive desulfurization procedures

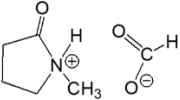
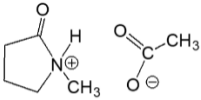
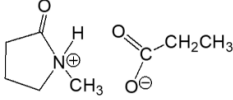
The desulfurization experiments were performed in a 25 mL glass batch reactor under magnetic stirring and reflux. A water bath was used to control the temperature. An equimolar mixture of BT, DBT and 4,6-DMDBT in n-octane (total sulfur content of 500 ppmw) was used as the simulated fuel feedstock in the reactor. In a typical oxidative desulfurization (ODS) run, the model fuel and H_2O_2 was added into the reactor, then the prepared PAIL catalyst was added under vigorous stirring at 1000 rpm. The extractive desulfurization (EDS) was performed in a same procedure without adding H_2O_2 . After a specified reaction time and phase separation, the oil sample was taken out and mixed with the solution of ethyl acetate in hexadecane as the internal standard for GC analysis.

RESULTS AND DISCUSSION

FTIR and $^1\text{H-NMR}$ of PAILs

Fig. 1 shows the FTIR spectra of NMP, carboxylic acids (formic, acetic and propionic acids) and the synthesized PAILs. As shown in Fig. 1, the band of C=O

Table 1: Name and structure of the synthesized PAILs.

| PAIL | Chemical structure | Abbreviation |
|-----------------------------------|---|-------------------|
| N-methyl-2-pyrrolidone formate |  | [Hnmp][HCOO] |
| N-methyl-2-pyrrolidone acetate |  | [Hnmp][CH3COO] |
| N-methyl-2-pyrrolidone propionate |  | [Hnmp][CH3CH2COO] |

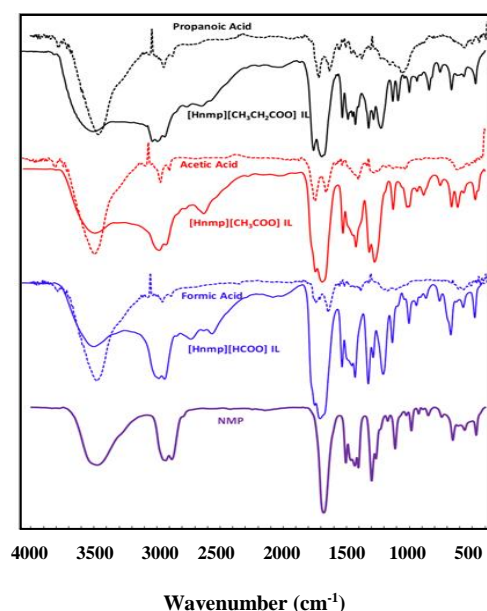


Fig. 1: FT-IR spectra of NMP, carboxylic acids and the synthesized PAILs.

at 1680 cm^{-1} in NMP spectra has been branched to two peaks and shifted to lower wavenumbers of 1665.3 , 1668 and 1667.6 cm^{-1} in [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO], respectively, proving the formation of the coordinated bond between NMP and carboxylic acids [3,16,32]. The observed peaks at 2882 and 2931.1 cm^{-1} in NMP spectra were ascribed to C-H vibrations of NMP ring. The bands at 1718.6 , 1722.7 and 1730.2 in [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO], respectively, were associated

to the carbonyl stretching of formyl, acetyl and propanoyl groups [32]. As a result, the effective interaction between NMP and carboxylic acids was well observed by the FTIR spectra of PAILs. To further realize these interactions, the H-NMR spectra of NMP and PAILs were also recorded (Fig. 2). A broad singlet ascribed to N-H proton can be observed at 9.2 ppm in [Hnmp][HCOO] spectra indicating proton transfer by interaction between NMP and formic acid. However, NMR spectra shows a weaker singlet of N-H proton at 7.51 and 10.2 ppm in the spectra of [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] respectively. This indicated more neutralization of NMP by strong formic acid comparing to weaker acetic acid and propionic acid. The resonance for the proton of formyl group in [Hnmp][HCOO] is observed as a sharp singlet at 8.05 ppm .

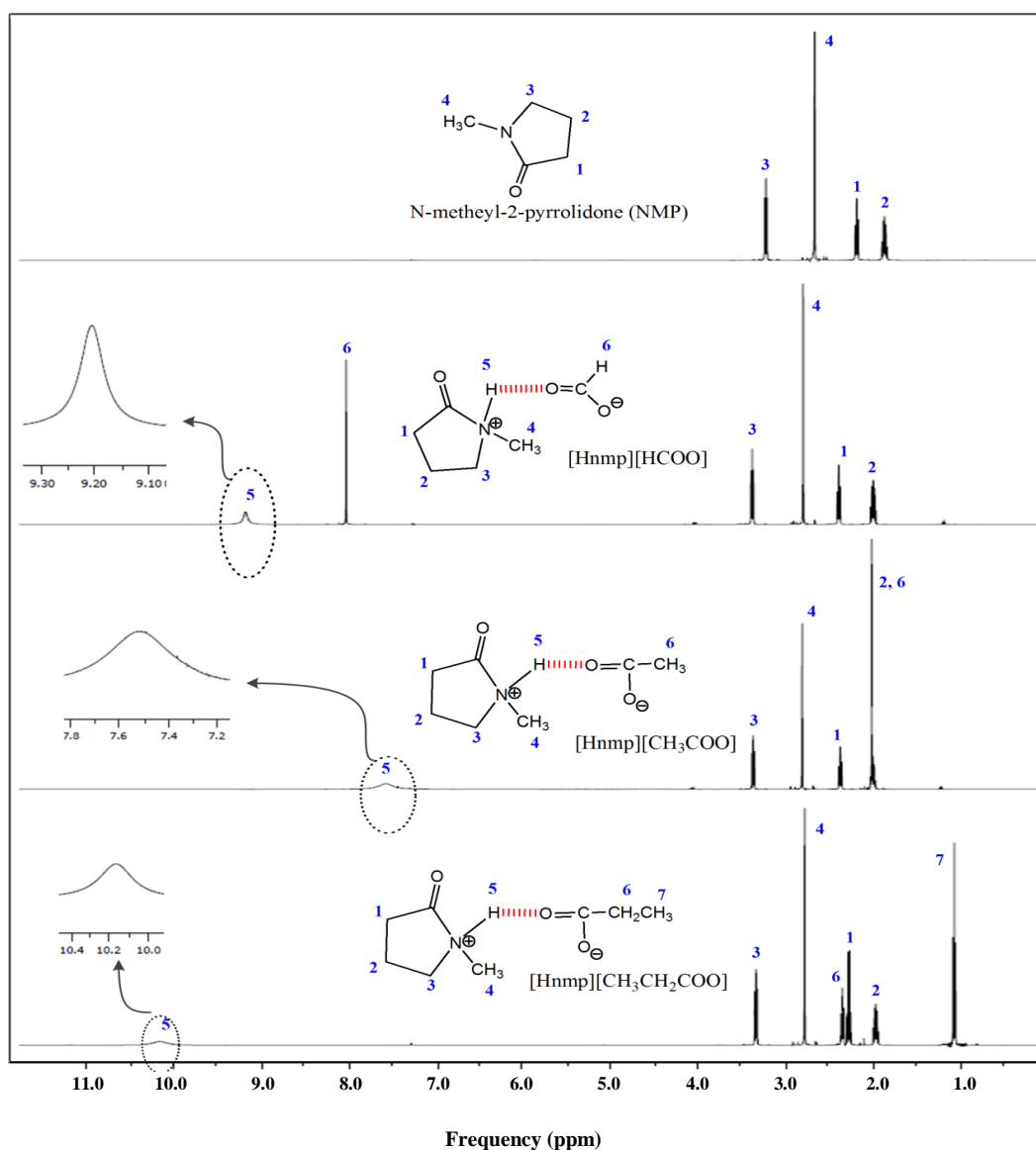
PAILs evaluation in oxidative-extractive desulfurization of simulated oil

As shown in Table 2, the experimentation was done in different desulfurization systems to investigate the capacity of different three PAILs in extraction and oxidation of aromatic sulfur compounds. In this study, BT, DBT and 4,6-DMDBT were used as the models of refractory sulfur compounds. These experiments were carried out at temperature of $40\text{ }^{\circ}\text{C}$, H₂O₂/sulfur molar ratio (n_o/n_s) of 10 (in ODS treatments), $V_{\text{PAIL}}/V_{\text{oil}}$ of 1.0 mL/mL , and reaction time of 90 min. The desulfurization results (average of 3 replicate experiments) were presented in Table 2.

At the used experimental conditions in Table 2, the removal of DBT was achieved in the range of 54-56.5%

Table 2: The results of BT, DBT and 4,6-DMDBT elimination (%) in different systems.

| Entry | Desulfurization system | Sulfur compound removal (%) | | |
|-------|---|-----------------------------|------|-----------|
| | | BT | DBT | 4,6-DMDBT |
| 1 | [Hnmp][HCOO] + H ₂ O ₂ | 84.7 | 94.8 | 92.7 |
| 2 | [Hnmp][CH ₃ COO] + H ₂ O ₂ | 79.6 | 91.6 | 75.7 |
| 3 | [Hnmp][CH ₃ CH ₂ COO] + H ₂ O ₂ | 78.3 | 85.7 | 64.5 |
| 4 | [Hnmp][HCOO] | 33.2 | 54.0 | 31.8 |
| 5 | [Hnmp][CH ₃ COO] | 38.7 | 55.1 | 34.2 |
| 6 | [Hnmp][CH ₃ CH ₂ COO] | 42.2 | 56.5 | 36.5 |

Fig. 2: ¹H-NMR spectra of NMP and the prepared PAILs.

by using PAILs in the extractive desulfurization (without adding H_2O_2 , Entry 3-4 in Table 2). These results revealed the extraction ability of the proposed PAILs for thiophenic compounds. A relatively higher extraction was provided by [Hnmp][CH_3CH_2COO] having a large carbon chain in the anion. Therefore, the carbon chain length of PAIL anion slightly affected the extractive performance before adding H_2O_2 . A similar effect was also reported by Nie et al. [22] related to the extraction performance of different ILs with diverse alkyl chain lengths. This could be attributed to a better lipotropism by large carbon chains consequently leading to more chances of entering the oil phase and then a better extraction of thiophenic compounds [17]. When H_2O_2 was added (Entry 1-3, Table 2), DBT removals were increased up to 94.8, 91.6 and 85.7% using [Hnmp][HCOO], [Hnmp][CH_3COO] and [Hnmp][CH_3CH_2COO] respectively. Similar trends were also observed for BT and 4,6-DMDBT substrates. The increase in removal of thiophenic compounds were caused from catalytic oxidation of them using peroxyacid generated from H_2O_2 and the acidic anion of PAILs. These results exhibited a more effective role of the proposed PAILs in catalytic oxidation of thiophenic sulfur compounds simultaneous to extraction of them. The highest desulfurization yield was achieved using [Hnmp][HCOO] in the ODS system when 84.7%, 94.8% and 92.7% of BT, DBT and 4,6-DMDBT were eliminated. This result come from a dual enhancing impact of [Hnmp][HCOO] in extraction of aromatic sulfur compounds by NMP ring as well as the efficiently catalytic generation of high active peroxyformic acid by H_2O_2 [6,7,32]. Comparing to [Hnmp][HCOO], the weaker acidic properties of [Hnmp][CH_3COO] and [Hnmp][CH_3CH_2COO] resulted in a lower activation of H_2O_2 to produce peroxyacids and finally led to a lower ODS efficiency. In addition, the neutralization reaction of weak acetic and propionic acids with NMP (Scheme 1) may not be efficiently gone to right hand; in these two cases, the synthesized reactions may reach a point of equilibrium [26]. Despite that the considerable catalytic efficiency of non-ionic liquid carboxylic acids in ODS systems have been demonstrated and reported in previous researches [6,9,10], the separation of carboxylic acids from oil and NMP extraction solvent could be difficult. The solubility of [Hnmp][HCOO] in the oil phase

has been measured using the standard gravimetric method [3] and replicated 3 times; The result demonstrated less than 0.9 wt.% dissolution of [Hnmp][HCOO] in the oil at temperature of 40 °C and V_{PAIL}/V_{oil} of 1.0. Therefore, one of the main advantages of the proposed PAILs in this study was immiscibility with the oil phase which caused easy separation of them after desulfurization. In addition, the use of high corrosive carboxylic acids in the reaction media has been avoided. Moreover, the recyclability of [Hnmp][HCOO] was examined in six ODS cycles. After each cycle, the used [Hnmp][HCOO] was mixed with tetrachloromethane (CCl_4) and stirred for 40 min, then separated via decantation and placed in a vacuum oven at 70 °C overnight to completely remove the ODS products and impurities residue. The recovered [Hnmp][HCOO] was used in the next ODS run. The results displayed that BT, DBT and 4,6-DMDBT elimination decreased to 80.7, 92.8 and 90.4 respectively after six recycles in the ODS reaction at a same condition used in Table 2. These results displayed well recyclability of [Hnmp][HCOO] suggesting the structural stability in the proposed ODS system.

Effects of V_{PAIL}/V_{oil} , H_2O_2 /sulfur molar ratio, and temperature as the main process variables

The effects of V_{PAIL}/V_{oil} and H_2O_2 /sulfur molar ratio (n_O/n_S) on the ODS of model sulfur compounds were illustrated respectively in Figs. 3 and 4. As shown in Fig. 3, the influence of V_{PAIL}/V_{oil} was different according to the type of PAIL which have different acidic properties. When V_{PAIL}/V_{oil} decreased from 1.0 up to 0.1, the ODS efficiency of [Hnmp][CH_3COO] and [Hnmp][CH_3CH_2COO] significantly decreased. This was related to the significant reduction in the amount of peroxyacid peroduction for oxidation of sulfur compounds at lower PAILs amounts. The peroxyacid intermediates, as the high active oxidants, have been generated from in situ reaction of H_2O_2 with acetic or propionic acid anion of the PAIL in the ODS system. From the results in Fig. 3, the amounts of peroxyacetic and peroxypropionic acid at low V_{PAIL}/V_{oil} of 0.1, were not sufficient for efficient desulfurization of thiophenic compounds. However, in the case of [Hnmp][HCOO] IL, the effect of V_{PAIL}/V_{oil} had a different trend; The ODS efficiency firstly increased by reduction of [Hnmp][HCOO] per oil volume ratio (V_{PAIL}/V_{oil}) from

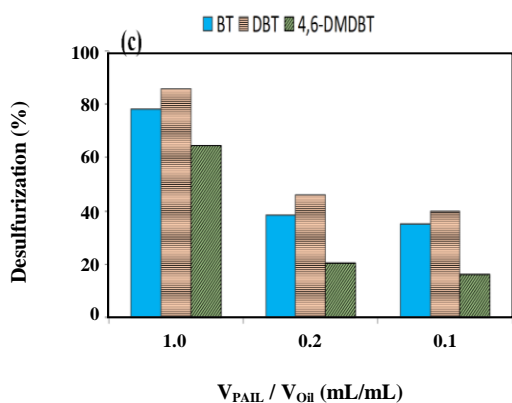
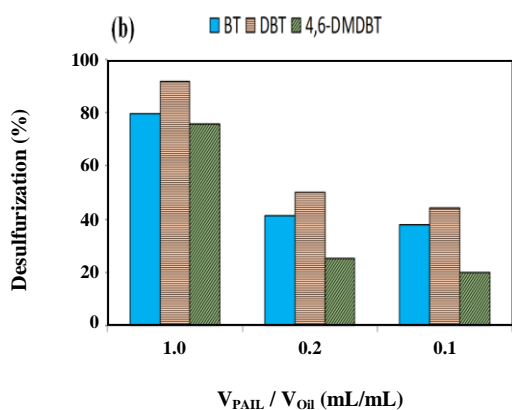
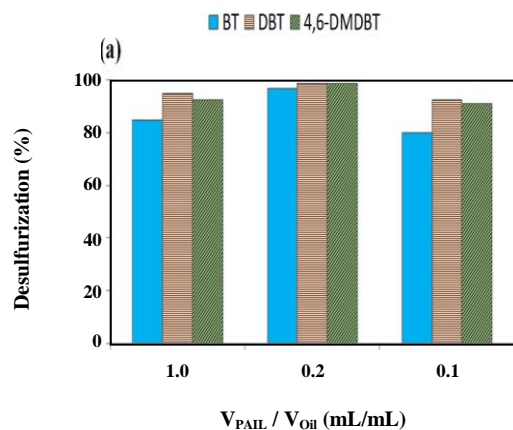


Fig. 3: The influence of V_{PAIL}/V_{oil} on the removal of different thiophenic compounds using $[Hnmp][HCOO]$ (a), $[Hnmp][CH_3COO]$ (b) and $[Hnmp][CH_3CH_2COO]$ (c) (Experimental condition: temperature=40 °C, $n_o/n_s=10$ mol/mol, reaction time= 90 min).

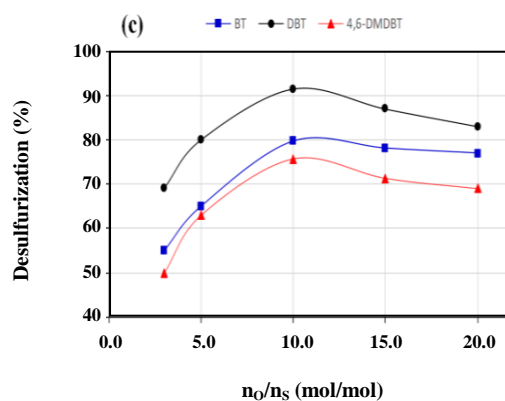
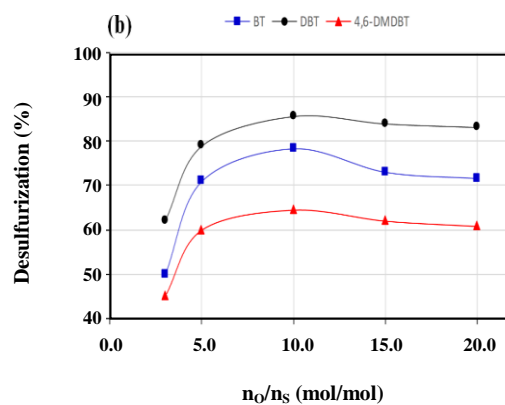
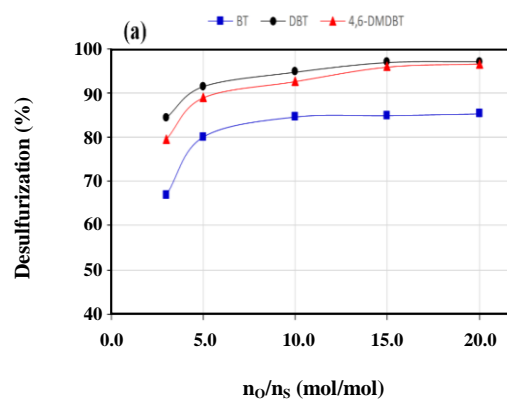


Fig. 4: The influence of n_o/n_s on the removal of different thiophenic compounds using $[Hnmp][HCOO]$ (a), $[Hnmp][CH_3COO]$ (b) and $[Hnmp][CH_3CH_2COO]$ (c) (Experimental condition: temperature=40 °C, $V_{PAIL}/V_{oil}=1.0$, reaction time= 90 min).

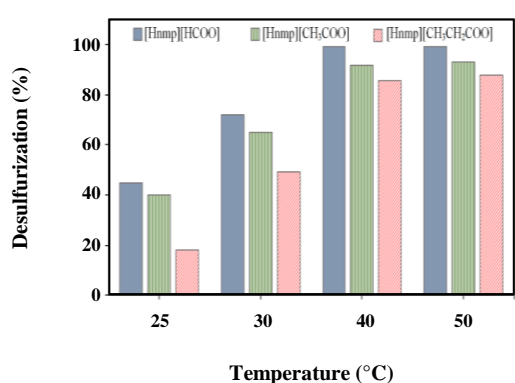


Fig. 5: The effect of reaction temperature on removal of DBT in ODS by PAILs.

1.0 to 0.2, and then declined by more reduction of $V_{\text{PAIL}}/V_{\text{oil}}$ up to 0.1. This verified that both the amount and concentration of generated peroxyformic acid at $V_{\text{PAIL}}/V_{\text{oil}}$ of 0.2, have been suitable for maximum oxidation of sulfur compounds (97% for BT and 99% for both DBT and 4,6-DMDBT removal) at $n_{\text{O}}/n_{\text{S}}$ of 10. At higher amount of $V_{\text{PAIL}}/V_{\text{oil}}$ of 1.0, the concentration of peroxyformic acid may decrease resulting in reduction of ODS efficiency. At $V_{\text{PAIL}}/V_{\text{oil}}$ of 0.1, the amount of generated peroxyformic acid was not enough to appropriately oxidize BT, DBT and 4,6-DMDBT. Therefore, the desulfurization efficiency of PAILs in this study should be adjusted by both IL amounts and the produced peroxyacids concentration. A maximum 93.3% removal of DBT was reported by Zhao *et al.* [15] using [BPy]HSO₄ IL and formic acid as the catalyst. Therefore, a considerable higher ODS efficiency was obtained in this work beside the prevention of formic acid addition.

As shown in Fig. 4, the removal of BT, DBT and 4,6-DMDBT has been increased by increasing $n_{\text{O}}/n_{\text{S}}$ from 3 up to 10, and has not changed significantly by further increasing of $n_{\text{O}}/n_{\text{S}}$. A higher generation of peroxyacid oxidants caused to increase ODS efficiency by increasing H₂O₂ amount from $n_{\text{O}}/n_{\text{S}}$ of 3 up to 10 mol/mol. When $n_{\text{O}}/n_{\text{S}}$ increased from 10 to 20, a little reduction in removal of some sulfur compounds was observed in the cases of [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] in Fig 4, for example DBT removal by [Hnmp][CH₃COO]; This may be related to reduction of peroxyacid concentration in the reaction media by increasing oxidant amount corresponded to $n_{\text{O}}/n_{\text{S}}$ of 20.

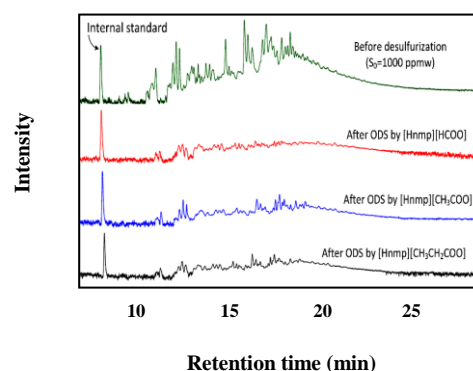


Fig. 6: GC-PFPD of real diesel before and after desulfurization by PAILs.

Another reason may be the inhibition effects of extra aqueous solution of H₂O₂ on the extraction ability of PAILs. This again confirmed the significant role of both amount and concentration of peroxyacids in this study.

The effect of reaction temperature on removal of DBT was examined at $n_{\text{O}}/n_{\text{S}}$ of 10 and $V_{\text{PAIL}}/V_{\text{oil}}$ of 0.2. The results are shown in Fig. 5. DBT removal has been efficiently increased by elevating the temperature from 25 up to 50 °C (similar trends have been also achieved for BT and 4,6-DMDBT). The possible undesirable decomposition of H₂O₂ at high temperature of 50 °C had not a significantly limiting influence on DBT removal in the investigated experimental conditions.

Desulfurization of hydrotreated diesel using PAILs

In practice, the real diesel involves many types of thiophenic sulfur compounds. To investigate the practical desulfurization capacity of the suggested PAILs, the hydrotreated diesel containing 1000 ppmw of sulfur was examined as the feedstock. The experimental conditions were as $n_{\text{O}}/n_{\text{S}}$ of 10, $V_{\text{PAIL}}/V_{\text{oil}}$ of 1, temperature of 40 °C, and duration of 90 min. GC-PFPD was employed to determine the desulfurization efficiency of PAILs. The results are shown in Fig. 6 indicating efficient removal of sulfur compounds of diesel by catalytic oxidative-extractive effects of the used PAILs. The obtained efficiency of diesel desulfurization by [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] were respectively 80, 71 and 68% measured by total sulfur analyzing. Based on the above discussion on ODS of simulated oil, the weaker acidic properties of

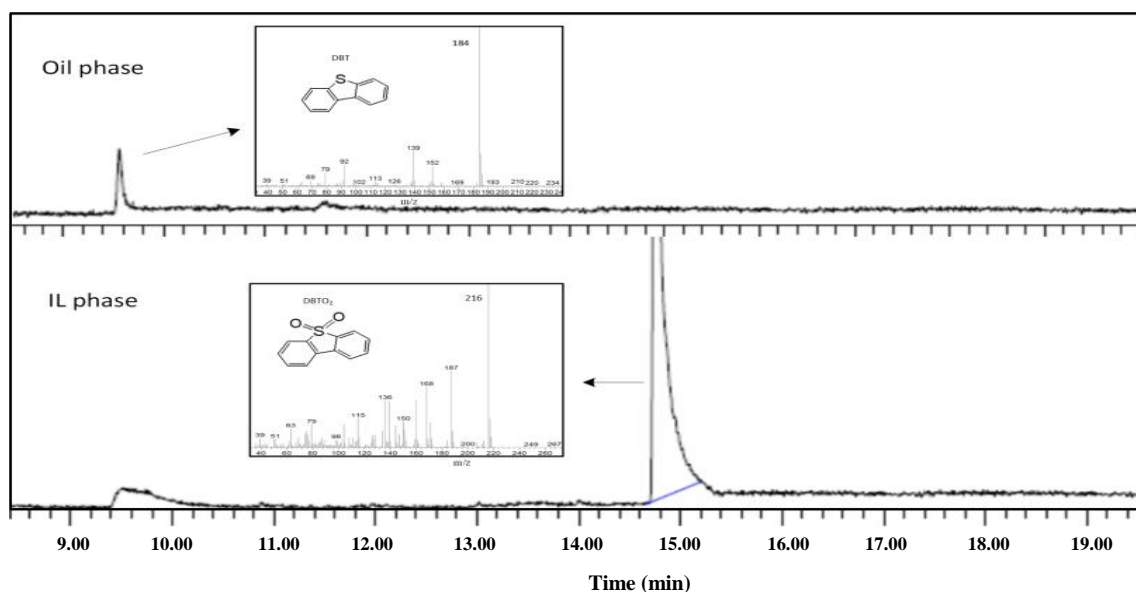


Fig. 7: GC-MS of model oil (DBT + *n*-octane) and IL phase after ODS by [Hnmp][HCOO].

[Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] led to a lower catalytic performance for peroxyacid generation from H₂O₂ and finally resulted in a lower ODS efficiency of diesel fuel. No new peaks corresponded to sulfones products were detected in Fig. 6. Therefore, the results clearly confirmed that PAILs can be able to be used in the ODS process without the need to use a further extractive solvent.

Extractive and Oxidative desulfurization pathway

Based on the literature [6-8], carboxylic acids played a catalytic role in the ODS process by generation of the strong oxidants of peroxyacids from H₂O₂. Furthermore, in the previous researches, it was stated that NMP ring can polarize thiophenic sulfur compounds and then facilitate the extraction of them from oil phase [3,16,33]. Since the prepared and used PAILs in this research had both acidic anions and NMP groups, a dual above-mentioned effectiveness would be expected in the ODS process mechanism. GC-MS analysis of [Hnmp][HCOO] and oil phase after ODS of DBT were provided to more clarify the above results. As represented in Fig. 7, DBT and DBTO₂ were found in the PAIL phase after desulfurization that confirmed extraction and oxidation mechanism.

The suggested desulfurization process by PAILs is shown in Fig. 8. In the mixture of PAIL and model oil,

the NMP rings of cations cause the polarization of thiophenic compounds and extraction of them through π - π interaction (step 1) [16,32]. When H₂O₂ is added to the mixture, carbonyl (formyl, acetyl or popanoil) groups of the anions react with H₂O₂ result in the formation of peroxyacid oxidants (step 2). Higher acidic properties of formyl than acetyl and propionyl may involve more peroxy formation with higher oxidation activity from H₂O₂ at a constant H₂O₂/sulfur feeding amount. Finally, the aromatic sulfur compounds oxidized to the corresponding sulfoxides and then sulfones in a same oxidation manner (Step 3). The polar sulfone products were subsequently extracted from oil by the cations (Step 4).

CONCLUSIONS

PAILs of [Hnmp][HCOO], [Hnmp][CH₃COO] and [Hnmp][CH₃CH₂COO] were prepared by neutralization reaction of NMP with formic, acetic and propionic acids verified by FTIR and H-NMR analysis. These PAILs were used in the removal of refractory thiophenic compounds from simulated and real diesel fuels. The attained results could be summarized as follows:

- Based on FTIR and H-NMR results, the stronger formic acid comparing to acetic and propionic acid, resulted in more N-H proton formation from neutralization reaction.

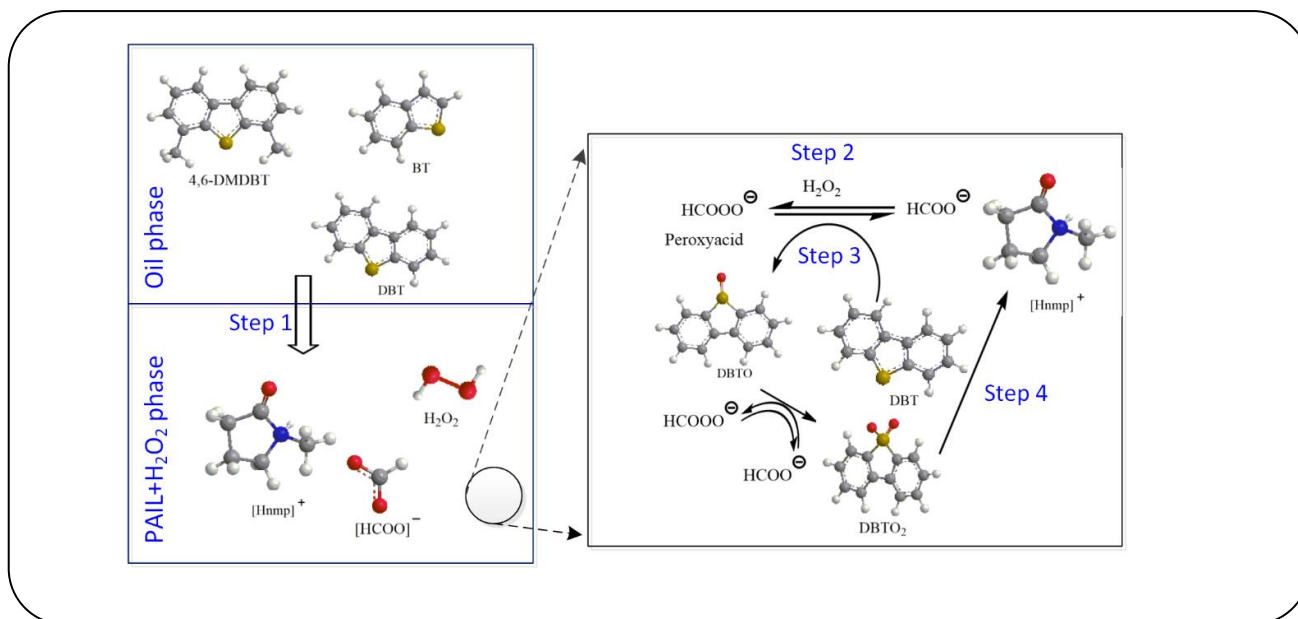


Fig. 8: The overall pathway of ODS by the proposed PAILs.

- The production of peroxyformic acid from [Hnmp][HCOO] could oxidize thiophenic compounds to sulfones with a higher yield comparing to peroxyacetic and peroxypropionic acid formation.

- The effect of main process variables of temperature, $V_{\text{PAIL}}/V_{\text{oil}}$ and $n_{\text{O}}/n_{\text{S}}$ have been examined and discussed.

- The prepared PAILs were efficient in the ODS of real diesel without further extractive solvent and carboxylic acid addition. This could be highly considerable in the future ODS research for deep desulfurization of diesel fuel using a recyclable and easy separable PAIL without using a corrosive carboxylic acid.

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