SYNTHESIS OF MORPHOLINE-BASED IONIC LIQUIDS FOR EXTRACTIVE DESULFURIZATION OF DIESEL FUEL

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Abstract - Extractive desulfurization with ionic liquids has attracted significant attention from a growing number of scientists due to the current environmental restrictions on fuel. Protic ionic liquids (PILs) were synthesized via equimolar neutralization of morpholine and formic-based compounds. The obtained PILs were characterized by Fourier transform infrared and 1H NMR spectroscopy and used as a promoter for the room temperature deep desulfurization of model oil and commercial B0S500 diesel. Extractive desulfurization of the model oil in n-octane showed that the alkyl chain length of the ionic liquid [Nmorph]+[HCOO]− does not enhance the efficiency of dibenzothiophene (DBT) removal. Regardless, the [Morph]+[HCOO]− IL is the most promising candidate for extractive desulfurization. The best results were obtained using multistage extraction (n = 3) and a 1:1 volume ratio, resulting in a 99.44% removal rate of sulfur compounds. For commercial B0S500 diesel, extraction time significantly influenced the removal of sulfur species. For samples with multistage extraction and a 1:1 volume ratio, [Morph]+[HCOO]− removed approximately 47.48% of the sulfur-containing compounds. The recycling study of [Morph]+[HCOO]− suggests that the IL remains active for up to three operating cycles without losing efficiency.

Keywords: Extractive desulfurization; Morpholine; Diesel; Ionic liquid.

INTRODUCTION

Recently implemented global environmental policies have caused a gradual reduction of harmful gas emissions, including CO₂, NOₓ, and SOₓ, generated by burning fossil fuel. These policies have mitigated several negative environmental consequences such as photochemical smog and acid rain, and continue to safeguard public health worldwide by preventing cardiovascular diseases and deterioration of the nervous and immune systems (Balinge et al., 2016; Zhao et al., 2017).

Managing SOₓ emissions from the combustion of petroleum-based fuels has become increasingly important for both the automotive and petrochemical industries (Xu et al., 2017, Raj et al., 2017). It is important to consider the utility of several toxic sulfur-based fuel compounds that contribute to the lubricity of many commercial liquid fuels (Hazrat et al., 2015; Lapuerta et al., 2016).

In this context, hydrodesulfurization (HDS) processes are conventional industrial procedures for removing organosulfurized contaminants from fossil fuels by converting sulfur compounds into hydrogen sulfide (H₂S) and hydrocarbon derivatives (Yu et al., 2016). It is highly selective for the removal of thiols (mercaptans), sulfides, and disulfides, although it has limited extraction efficiency for heterocyclic sulfur and refractory compounds such as thiophene (TF), benzothiophene (BT), dibenzothiophene (DBT), and...
other derivatives (Li et al., 2015; Bui et al., 2017; Moghadam et al., 2017).

Unfortunately, HDS is costly since it requires industrial units operating at high temperatures (>300 °C), pressure (3-10 MPa), and volume of hydrogen gas, with expensive catalysts and low energy efficiency (Kaisy et al., 2016; Jiang et al., 2016; Zaid et al., 2017). Many of these limitations could be solved by developing desulfurization methods involving adsorption (Shah et al., 2016; Mirshra et al., 2017), oxidative desulfurization (Rezvani et al., 2017; Hitam et al., 2018), bio-desulfurization (Martínez et al., 2017; Paixão et al., 2017), microwave assisted desulfurization, ultrasound (Taheri-Shakib et al., 2017; Mozafari and Nasri, 2017), and extractive desulfurization (Safta et al., 2016; Elwan et al., 2017).

Extractive desulfurization (EDS) is a process where a solvent is placed in direct contact with the fuel to remove sulfur compounds by liquid-liquid extraction. Gentle operating conditions in the absence of hydrogen gas and low energy consumption can be inexpensively achieved with this method (Gao et al., 2015). However, EDS efficiency is strongly dependent on the solvent used and its chemical affinity with the sulfur-containing compounds (Ibrahim et al., 2017; Yang et al., 2016).

Thus, by definition EDS solvents must exhibit high chemical and thermal stability, non-toxicity, environmentally safety, and reusability. Because of these requirements, most conventional organic solvents used in liquid-liquid extractions cannot be applied in EDS (Li et al., 2017; Bhutto et al., 2016).

Ionic liquids (ILs), a novel class of green solvents, have recently attracted significant attention for their selective extraction of sulfur-containing compounds from diesel/gasoline (Liu et al., 2017, Julião et al., 2017).

ILs are molten salts with melting points below the boiling point of water due to their small lattice enthalpies and large entropy changes upon melting. ILs are often composed of an unsymmetrical organic cation and an inorganic complex anion, resulting in remarkable properties such as nonvolatility, thermal stability, nonexplosion, high polarity, and temperature-dependent miscibility with water (Jha et al., 2016, Ahmed et al., 2015). A wide variety of anions and cations can be incorporated into ILs, dramatically modifying their physical characteristics for specific applications.

IL-based solvents are often classified as either aprotic ionic liquids (AILs) or protic ionic liquids (PILs). In AILs the ions do not contain any transferable protons and PILs, also called Brønsted salts, are solvents obtained by proton transfer from a Brønsted acid to a Brønsted base (Vafaei-Azadeh and Al inezhad, 2016). It should be noted that PIL solvents often contain protons with higher mobility when compared to the other ILs.

This study aims to synthesize and characterize PILs containing the morpholine cation and to evaluate their efficiency for extractive desulphurization of model oil and commercial BO500 diesel.

**EXPERIMENTAL**

**Materials**

The ILs were synthesized using analytical grade chemicals without further purification: formic acid (Sigma Aldrich, 99%), morpholine (Morph, Sigma Aldrich, 99%), N-methylmorpholine (Nmorph, Sigma Aldrich, 99%), n-octane (Merck, 99%), and dibenzothiophene (DBT, Acros Organics, 98%). Commercial BO500 diesel was purchased from Distribuidora de Combustível Granel Ltda., São Luis, Maranhão (Brazil).

**II. synthesis and characterization**

The [Morph][HCOO] and [Nmorph][HCOO] ionic liquids were prepared according to the methods described by Brigouleix et al. (2010) via the proton transfer reaction between a Brønsted acid (formic acid) and morpholine (Fig. 1a) or N-methylmorpholine (Fig. 1b, Brønsted bases).

A three-necked round bottom flask immersed in an ice bath was connected to a reflux condenser, dropping funnel, and digital thermometer. Each Brønsted base was gently dropped into the formic acid, under constant stirring (600 rpm) and temperature (≈ 5.0 °C). Subsequently, the reaction mixture was isothermally treated ( 25.0 °C) for an additional 4 h under constant stirring. The final product was then recovered and dried under vacuum (12 h at 80 °C) to remove residual water and/or trace reagents.

The obtained ILs were then characterized by Fourier transform infrared (FTIR) and \(^1\text{H}\) NMR spectroscopy. FTIR spectroscopy was performed using an IR prestigie-21 infrared spectrometer (Shimadzu) with KBr as dispersant agent (1:100 wt/wt) and a recording range between 400 and 1000 cm\(^{-1}\). Proton nuclear

![Figure 1. IL synthesis of (a) [Morph][HCOO] and (b) [Nmorph][HCOO].](image-url)
magnetic resonance spectra were recorded using a 400 MHz Bruker DRX spectrometer (Bruker) using CDCl$_3$ as solvent.

The kinematic viscosities were obtained according to the ASTM D445 Standard Test Method using a SCHOTT CT 52 viscometer with a Cannon-Fenske 520 (75) calibrated glass capillary at 40 °C. The water content was determined via Karl-Fischer titration (method TitroLine KF). The samples and solvent were dissolves in methanol and titrated in steps of 0.0025 cm$^3$.

**Model oil preparation**

The model oil was prepared by dissolving 0.5 g of DBT in 1.0 L of n-octane, yielding a blend with 714 ppm sulfur.

**Extractive desulfurization of the model oil**

Two distinct mechanisms were evaluated for the desulfurization of the model oil: single and multiple stage. In the first case, desulfurization was performed in a 50 mL two-necked round bottom flask by mixing the model oil and each IL (volume ratio = 1:1, 1:3, or 1:5) at room temperature (25 °C for 30 min) under vigorous stirring. Conversely, multiple stage desulfurization was performed using the same apparatus and temperature, but three consecutive extractions were performed using volume ratios of 1:1 and 1:2. After 10 min of extraction (representing a single cycle), the immiscible phases were separated by decanting. Subsequently, a fresh aliquot of pure IL was added to the extracted model oil and a new extraction run was initiated.

The sulfur in the model oil layer, before and after desulfurization, was determined using high-performance liquid chromatography (HPLC, Shimadzu) with a UV-SPD20A detector at 280 nm using C18 (CLC - ODS M) 150 mm x 4.6 mm 20 µm columns. A column temperature of 25 °C, mobile phase of methanol:water (90:10 vol/vol) and flow-rate of 1.0 mL.min$^{-1}$ were used in the HPLC runs and each experiment was performed in triplicate.

Finally, sulfur extraction efficiency was estimated according Eq. (1) and the Nernst partition coefficient ($K_N$) was predicted according to Eq. (2):

$$Sulfur\ removal(\%) = \frac{(S_0 - S_f)}{S_0} \times 100$$  \hspace{1cm} (1)

$$K_N = \frac{Sulfur\ concentration_{IL}}{Sulfur\ concentration_{model\ oil}}$$  \hspace{1cm} (2)

where, $S_0$ (ppm) is the initial sulfur concentration and $S_f$ (ppm) is the sulfur concentration after extraction.

**Extractive desulfurization of the commercial B0S500 diesel**

Desulfurization extraction of the commercial B0S500 sample was performed using volume ratios of 1:1 and 1:3 and extraction times of 30 and 60 min in both single and multiple stages. Sulfur in the diesel, before and after desulfurization, was evaluated using a wavelength dispersive X-ray fluorescence (WDXRF) spectrometer (S8 Tiger, Bruker), with a rhodium tube operating at 20 kW/50 mA. The PETRO QUANT® calibration method was performed with XS - 55 detection crystals, 0.46° collimator, helium gas purge, and Prolene® (3.6 µm) film with a container and sample mask of 0.34 mm.

**Regeneration of the IL**

The [Morph]$$^+$$[HCOO]$^-$ IL was regenerated by re-extraction with low-boiling hydrocarbons as previously reported by Gao et al. (2009). The IL was re-extracted twice with hexane (ionic liquid/solvent ratio = 1:1) for 30 min (Figure 2). Subsequently, the IL was heated to 80 °C for 2 h to remove hexane traces and was then used in a new extraction cycle.

**RESULTS AND DISCUSSION**

**Characterization of the ILs**

**FTIR spectroscopy**

The structures of the [Morph]$^+$$^+$[HCOO]$^-$ and [Nmorph]$^+$$^+$[HCOO]$^-$ ILs were investigated by FTIR spectroscopy (Figure 3). The infrared active modes for the cation species were detected at approximately 1442 and 1648 cm$^{-1}$ and were assigned as v(C-N) stretching modes. The v(C-H)$_a$ and v(N-H) stretching modes were observed at 2985-2863 and 1457 cm$^{-1}$, respectively, as previously reported by Ren et al. (2014). The vibration modes at 1372 and 1283 cm$^{-1}$

**Figure 2. Extractive desulfurization mechanism using IL solvents.**
can be attributed to symmetrical deformations of -CH₃ groups. The stretching modes of the ν(O-H) groups were detected at 3457 cm⁻¹ (Kahani et al., 2017; Dharaskar et al., 2016). For the [Morph][HCOO]- sample, the vibration mode detected at 3097 cm⁻¹ was attributed to δ(N-H) axial deformation of the amine groups.

**1H NMR analysis**

The ¹H NMR spectra for both [Morph][HCOO]- and [Nmorph][HCOO]- ILs are shown in Figure 4. The chemical shifts (multiplicity, integration) were as follows for [Morph][HCOO]- ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 3.70 (t, 4H, (1)), 3.66 (t, 4H, (2)), 8.04 (s, 2H, (3)), and 8.06 (s, 1H, (4)). [Nmorph][HCOO]- ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 3.91 (t, 4H, (1)), 2.99 (t, 4H, (2)), 6.41 (s, 2H, (3)), 8.30 (s, 1H, (4)), and 2.65 (s, 3H, (5)). According to the ¹H NMR data, the purities of [Morph][HCOO]- and [Nmorph][HCOO]- ionic liquids were 95.5% and 96.8%, respectively and the water content was estimated to be 61 ppm.

**Desulfurization of the model oil**

Operating parameters such as the extracted and extractor ratio, time of extraction, and extraction cycles can dramatically influence the extraction efficiency in desulfurization. Thus, these factors were evaluated during the extractive desulfurization of both model oil and commercial B0S500 diesel.

Effect of the (V_{IL}/V_{model oil}) ratio on the extractive desulfurization

To enhance the extractive desulfurization efficiency, the ratio of the extracted component and extractor agent was empirically optimized under the following experimental conditions: model oil (714 ppm sulfur); volume ratios (V_{IL}/V_{model oil}) of 1:5, 1:3, and 1:1; and 25 °C. Figure 5 shows the influence of the (V_{IL}/V_{model oil}) ratio on the extractive desulfurization of DBT in model oil for a single stage extraction with both ILs.

According to Figure 5, the extraction efficiency increased with higher IL concentration in the system. Greater sulfur removal was achieved when an (V_{IL}/V_{model oil}) = 1:1 was applied under single extraction conditions (Table 1).
Sulfur compounds with aromatic rings (i.e., BT, DBT, and their derivatives) often reduce π-π interaction (aromatic ring current effect) and enhance CH-π bond interactions and hydrogen bonding effects due to electrophilic attack (Yuan et al., 2016, Anatharaj et al., 2011). In addition, according to Domańska e Wlazio (2014), the extraction efficiency of non-aromatic cation morpholinium-based ILs is significantly influenced by hydrogen bonding of the hetero-atoms of sulfur compounds with the IL cation. In addition, the kinetics are significantly affected by the specific volume and shape of the IL (Zhao et al., 2016).

Although the [Nmorph][HCOO] IL has a longer alkyl group attached to the cation chain compared to [Morph][HCOO], the replacement of the methyl group does not reduce its desulfurization efficiency for the model oil. Similar behavior was reported for a pyridinium-based IL (Rodríguez-Cabo et al., 2014). These results are supported by the lower [Nmorph][HCOO] sulfur partition coefficient ($K_N$), Table 2.

Furthermore, the lower efficiency of [Nmorph][HCOO] may be related to its higher viscosity, which may cause a reduction in the mass transfer potential and consequently lower extraction capacity (Zhang et al., 2017; Mafi et al., 2018) (Table 3).

### Table 2. Sulfur partition coefficients ($K_N$) of the ILs at different volume ratios of IL to model oil.

| ILs            | $K_N$ [mg (S) kg (IL)]/mg (S) kg (oil)] |
|----------------|----------------------------------------|
| [Morph][HCOO] | 2.99/1.28/0.53                          |
| [Nmorph][HCOO] | 0.52/0.12/0.16                          |

### Table 3. Viscosities of the ILs at 25 °C.

| ILs            | Viscosity (mPa·s) |
|----------------|-------------------|
| [Morph][HCOO] | 8.69              |
| [Nmorph][HCOO] | 13.30             |

Multiple stage desulfurization

Although single extraction desulfurization provided good sulfur removal, the final concentration of sulfur in the model oil did not meet the Brazilian Control Agency (ANP) standards of 10 and 50 ppm of sulfur for light- and heavy-weight vehicles, respectively. Thus, multistage extraction (three cycle) was performed (Table 4).

The HPLC data (Figure 6) show that, after three consecutive extraction cycles, the concentration of sulfur compounds in the model oil was reduced from 714 to 4 ppm, (representing a 99.44% removal rate) and 114 ppm (84.03% removal) for the [Morph][HCOO] and [Nmorph][HCOO] ILs, respectively. These results were confirmed by WDXRF spectroscopy, which showed that the multistage extractive desulfurization of DBT with [Morph][HCOO] achieved 99.99% sulfur removal.

### Table 4. Multistage extraction performance for the model oil with different volume ratios of IL to model oil.

| ILs            | S-removal (%) | Final S-content (ppm) |
|----------------|--------------|-----------------------|
| [Morph][HCOO] | 99           | 4                     |
| [Nmorph][HCOO] | 84           | 114                   |

Number of stages = 3, temperature = 25 °C, extraction time = 30 min, ($V_\text{IL}/V_\text{model oil}$) ratio = 1:1 and initial sulfur concentration of model oil = 714 ppm.
should be noted that, in all cases, the final S-content was still higher than the recommended levels, which was attributed to another DBT species in the real diesel media. Analogous results were previously reported by Daraskar et al. (2014), Gao et al. (2009), and Daraskar et al. (2015) with other ILs and multiple extraction processes.

### Regeneration

In industrial processes, large volumes of ILs would be required for extraction desulfurization (Ren et al., 2015). Thus, several regeneration mechanisms have been proposed in the literature (Gao, et al., 2015) and mainly concern the precipitation of sulfur compounds by dilution in water or re-extraction with hydrocarbon solvents. However, when such methods were applied for complex blends, such as commercial diesel/biodiesel, the amount of sulfur compounds retained in the IL was negligible due to dibenzothiophene deactivation mechanisms. Fortunately, some of these limitations can be overcome by re-extraction with low boiling point hydrocarbon solvents such as pentane or hexane (Eßer et al., 2014). Thus, in this study, [Morph]+[HCOO]- was recovered with hexane and its desulfurization efficiency is shown in Figure 7.

As expected, a linear reduction of the desulfurization efficiency was observed with increasing number of cycles as after each stage of the recycling process, some sulfur compounds remained in the IL. However, the [Morph]+[HCOO]- IL remained sufficiently active after three recycling cycles.

### CONCLUSIONS

[Morph]+[HCOO]- and [Nmorph]+[HCOO]- ILs were used as solvents in the extractive desulfurization of model oil and commercial B0S500 diesel via single and multiple cycle extractions. The [Morph]+[HCOO]- IL exhibited high extractive ability for DBT removal in single and multistage extractions with \((V_{IL}/V_{model\text{oil}}) = 1:1\) and an extraction time of 30 min. The highest \(K_N\) value of DBT desulfurization at a volume ratio of 1:1 also indicated that high dosages of ILs are required to achieve optimal desulfurization efficiency. For commercial B0S500 diesel, the removal efficiency of the sulfur compounds was influenced by the extraction time and the type of extraction used in the EDS. Thus, the best results were archived after three multistage extractions (60 min). The recycling study indicated that the [Morph]+[HCOO]- IL remained sufficiently active for extractive desulphurization after three consecutive cycles.

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### Table 5. Desulfurization of diesel using [Morph][HCOO] IL at different times and with different \((V_{IL}/V_{commercial\text{B0S500}})\) ratios.

| Extraction | Time (min) | Volume ratio | S-removal (%) | Final S-content (ppm) |
|------------|------------|--------------|---------------|-----------------------|
| Single     | 30         | 1:1          | 23            | 350                   |
|            | 60         | 1:1          | 35            | 304                   |
| Multistage | 30         | 1:1          | 18            | 376                   |
|            | 60         | 1:1          | 23            | 354                   |

Temperature = 25 °C and initial sulfur concentration of diesel = 500 ppm.
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