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Thiophene Extraction from Liquid Fuel using Ionic Liquid

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Crude petroleum contains numerous sulphurous compounds that cause pollution if not removed from crude oil. Desulphurisation techniques such as hydrodesulphurisation are used to remove these compounds, in which expensive and highly inflammable hydrogen is used. However, this technique is not that efficient for organic non-reacting sulphur compounds like thiophene, dibenzothiophene, alkyl substituted dibenzothiophene, etc. In this study, aqueous solution of an ionic liquid, namely, [BMIM][Cl] has been used to extract thiophene from a model fuel (iso-octane). Various parameters that affect the extractability have been studied. These parameters include contact time, varying thiophene concentration, varying [BMIM][Cl] concentration and temperature. Maximum possible extraction achieved was >99% for a 1000 ppm of thiophene in iso-octane in 1 hr at 40^{O}C, when aqueous [BMIM][Cl] ionic liquid concentration was 1.5 M.

1. Introduction

Diesel and gasoline are the backbone of heavy transportation industry and our day-to-day lives. Diesel engines suffer from particulate emissions in the form of NO_x and SO_x, which are harmful to health. Sulphur is the main contributor of air pollution and reduces the oxidation capabilities of catalytic convertors used in vehicles to avoid air pollution caused due to carbon monoxide emissions. Sulphur present in crude oil needs to be removed to avoid these downstream consequences[1]. Various norms exist to control the sulphur content in fuel. In many European countries, the maximum allowable sulphur content in processed fuel is less than 10 ppm. These fuels are called Ultra Low Sulphur Fuels. In African countries, these norms are quite flexible, where the maximum allowable sulphur content is 500 ppm. In India, the maximum allowable content of sulphur in processed fuel is 50 ppm according to new revised norms[2].

Sulphur exists in the form of organic heterocyclic compounds such as thiophene, dibenzothiophene, alkyl substituted benzothiophenes etc, which are difficult to remove by conventional hydrodesulphurisation technique owing to their aromatic nonreactive nature. On the other hand, sulphur in the form of inorganic sulphur, as thiols, thioethers, mercaptans, etc are quite reactive and can thus be removed efficiently using hydrodesulphurisation technique. Therefore, to meet the stringent norms, an alternative desulphurisation technique is in demand as market demand of deep desulphurised fuels is increasing while the feed quality is declining.

Extractive desulphurisation using ionic liquids is a promising alternative technique. Ionic liquids could be used as an extractant for extracting sulphur compounds from fuel. In this study, 1-butyl 3-methyl imidazolium chloride ([BMIM][Cl]) is synthesised, which is highly miscible in water, hence its aqueous solution was used as an extractant phase. Different parameters affecting extraction were studied and optimized for the given feed concentration.

2. Experimental Section

This was broadly classified into two sections, viz. the synthesis of ionic liquid and the study of the effect of different parameters affecting the extractability of sulphurous compounds. 1-methyl imidazole (>99% w/w) and thiophene (>99% w/w) were procured from Sigma Aldrich and 1-chlorobutane (>98% w/w), ethyl acetate (>99% w/w) and iso-octane (>99% w/w) were procured from S. D. Fine Chemical Pvt. Ltd., India.

2.1 Synthesis of Ionic Liquid

Imidazolium based ionic liquids give better extraction results for aromatics. Long chain is preferable for better separation[3]. Therefore, [BMIM][Cl], i.e. 1-butyl-3-methyl imidazolium chloride was selected as the ionic liquid as sufficient amount of literature is available for its synthesis.

Synthesis Procedure: 1 mol of 1-methyl imidazole was made to react with 1.2 mol of 1-chlorobutane at 75^{O}C for 48 hr under reflux. Speed of overhead agitator was maintained high enough (≈ 1000 rev/min) so that reaction mass is thoroughly mixed. The reaction temperature was maintained at 75^{O}C instead of 60^{O}C[4] and the mole ratio was altered to get the maximum conversion. The following reaction scheme was followed (Figure 1):

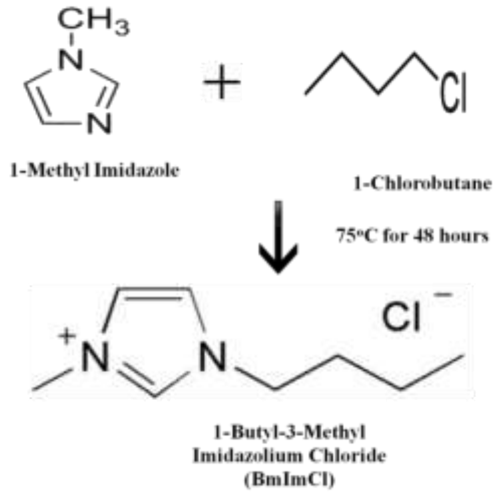

Fig. 1. Synthesis reaction of [BMIM][Cl]

After completion of reaction, two separate phases were observed: one is a semisolid product and other is of unreacted mass. The reaction mass was carefully transferred in hot condition to a large beaker and then agitated at room temperature to get pale yellow coloured crystals of [BMIM][Cl]. The product obtained was not pure as it contained unreacted species. After washing at least 4-5 times with ethyl acetate, the final crystals were dried under vacuum for about 2 hr. As [BMIM][Cl] is highly hygroscopic, it was carefully transferred to an airtight bottle under nitrogen environment. [BMIM][Cl] crystals were always kept in a desiccator to avoid moisture. Practical yield of crystals was >83%.

2.2 Extractive Desulphurization of liquid fuel

The model fuel chosen is iso-octane as it represents fuel with octane number 100. Thiophene is the heterocyclic aromatic compound, which represents the sulphurous impurity in fuel. For extraction of thiophene from iso-octane, a known concentration of thiophene was used. The maximum concentration of thiophene used was 1000 ppm, where 1 ppm is equivalent to 1 mg of thiophene per litre of iso-octane. For extractant, which was a solid ionic liquid, [BMIM][Cl], aqueous solutions of varying molarity were used. Deionised water was used for making aqueous samples of extractant.

Experimental Setup*:* As feed phase and extractant phase were immiscible with each other, in order to provide a better contact between the two phases, a jacketed stirred reactor was used (so as to maintain constant temperature throughout the process) (Figure 2). The stirrer speed in all the experiments were maintained at 1000 rev/min to rule out the agitation effect over the entire system.

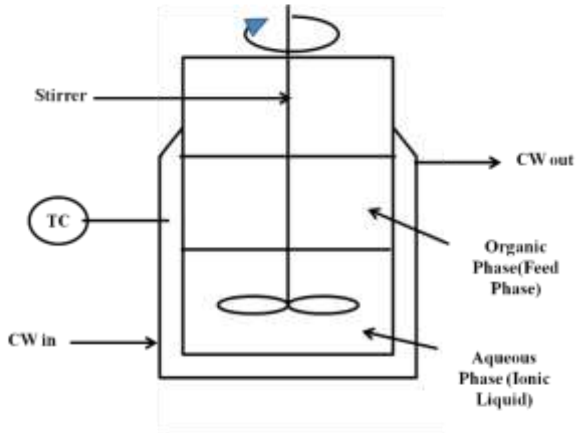

Fig. 2. Schematic experimental setup used for extraction

Mechanism of Extraction*:* Thiophene in iso-octane forms the feed phase, which is the organic one while aqueous solution of [BMIM][Cl] forms the aqueous layer. Thiophene is migrated to aqueous phase by following mechanism shown below (Figure 3):

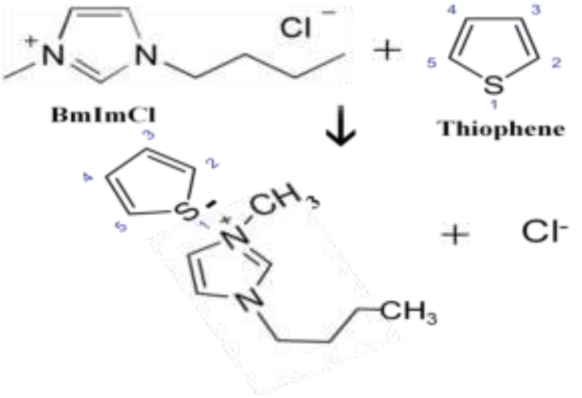

Fig. 3. Extraction mechanism

Analysis: For analysing the sample for thiophene concentration after extraction, a sample was taken from the top layer, (iso-octane + thiophene) and analysed over gas chromatography equipped with FID and SE30 packed column. The following method was developed for analysing thiophene.

Carrier Gas: nitrogen; pressure of carrier: 0.4 bar; gas used for ignition: hydrogen; polarity: positive; injector temperature: 200°C; detector temperature: 280°C.

Temperature Program followed*:* Start with 60°C → hold for 1 min → ramp of 10°C/min up to 70°C → hold for 5 min → ramp of 15°C/min up to 80°C → hold for 1 min → total time 8.4 min.

3. Results and Discussion

3.1 Contact Time Effect

Once the equilibrium is attained, no significant mass transfer is possible under given conditions. To attain this equilibrium system needs some time, which is termed as equilibration time or contact time. Estimation of this time is necessary, as this will become the operational time for further experiments. Mathematically, if we plot thiophene concentration versus time (Figure 4), the time at which slope (dC/dt) ≈ 0 is referred to as equilibrium time.

For pseudo-first order processes or for slow mass transfer controlled processes this equilibrium time is very high[5]. The contact time required for maximum extraction was experimentally found to be in the range of 30-90 min as reported in numerous literatures.

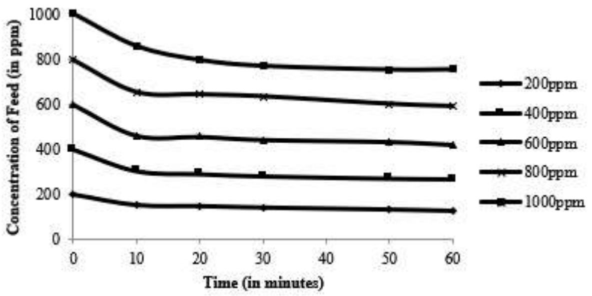

Fig. 4. Concentration profile of thiophene in feed versus time at different feed concentration of thiophene

3.2 Feed Concentration Effect

Extraction is caused by interactions between the solute molecules to be extracted and extractant molecules. If we keep extractant concentration constant and alter the solute concentration, numbers of interactions are also altered and thus extractability changes, this effect is known as feed concentration effect. It is a measure of extractability of extractant when its concentration is kept constant while changing the feed concentration. It gives an idea whether given concentration of extractant is suitable for extracting the entire range of possible feed. A general trend is that as we increase the feed concentration by keeping extractant concentration constant, extraction decreases[6]. A 0.1 M aqueous solution of [BMIM][Cl] was used as extractant and concentration of feed was varied by keeping temperature at 30°C and stirrer speed at 1000 rev/min (Figure 5). Each run was of 60 min as equilibrium (operational) time is set at 60 min.

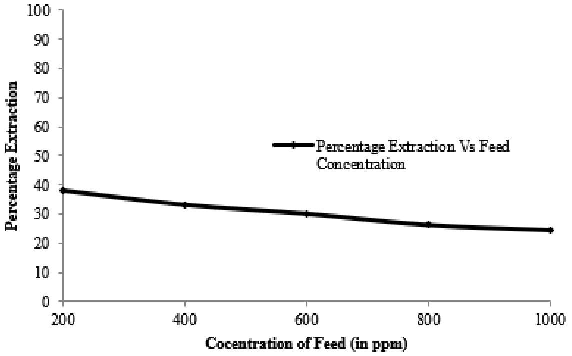

Fig. 5. Percentage extraction of thiophene at different feed concentration for 0.1M [BMIM][Cl] at 30°C

3.3 Extractant concentration effect

Extraction is a mass transfer phenomenon, which is dependent on number of molecular interactions between the chemical species, mobility of ions in case of ionic species involved, surface tension of phases and interfacial mass transfer resistances. As extractant concentration is increased, more and more number of molecules would be available for extraction. Hence, we could conclude that percentage extraction of solute is directly proportional to concentration of extractant. As extractant concentration is increased, viscosity also increases thus declining the rate of mass transfer and therefore percentage extraction decreases[7].

A 1000-ppm feed and contact time of 60 min at 30^{O}C was used for this experiment. Aqueous solutions of 0.1 M, 0.3 M, 0.5 M, 0.7 M, 1 M, 1.5 M [BMIM][Cl] in deionised water were used as extractants. A general trend of increasing percentage extraction with increase in ionic liquid concentration was observed (Figure 6):

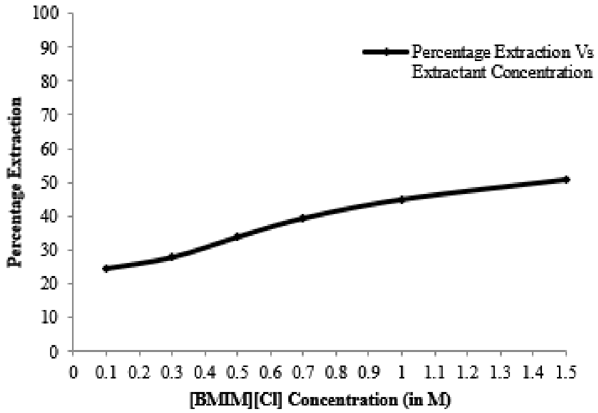

Fig. 6. Percentage extraction of thiophene at different [BMIM][Cl] concentration varying at 30^0C for 1000 ppm feed concentration of thiophene

3.4 Temperature Effect

As temperature increases, the mobility of ions increases, thus promoting random molecular interactions and lowering the surface tension, resulting in high interfacial mass transfer. This in turn increases the extractability of extractant (Figure 7). It is observed that extractive desulphurisation of fuel with ionic liquids is more pronounced when temperature is increased rather than increasing the ionic liquid concentration[7]. Therefore, conclusively we can say that by increasing the temperature we could maximise the extraction, but at elevated temperatures volatile solute might strip, thus resulting in low extraction at elevated temperatures for volatile species.

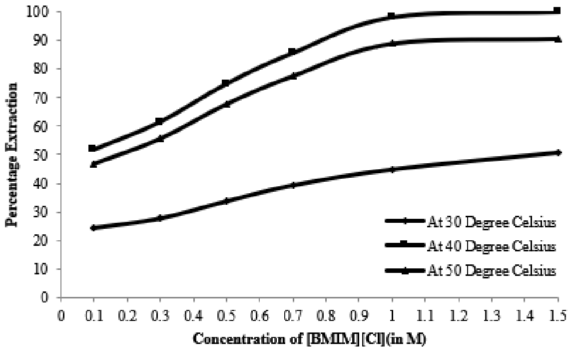

Fig. 7. Percentage extraction of thiophene at different [BMIM][Cl] concentrations at different temperatures

4. Conclusions

- 1-butyl-3-methyl imidazolium chloride ([BMIM][Cl]) was synthesised by modifying the method reported in literature. The total practical yield obtained was >83%.
- More than 99% of thiophene extraction was possible from iso-octane when feed concentration was 1000 ppm, and 1.5 M aqueous solution of [BMIM][Cl] was used as extractant, O:A ratio was set at 1:1 (v/v) at 40^OC.

5. Keywords

Thiophene; iso-octane; desulphurisation; ionic liquid; [BMIM][Cl]

6. Nomenclature

ppm: parts per million

FID: Flame Ionization Detector

SE30: Type of packed column used for Gas Chromatography

[BMIM][Cl]: 1-Butyl-3-Methyl Imidazolium Chloride

NO_x: Oxides of Nitrogen

SO_x: Oxides of Sulphur

TC: Temperature Controller

CW: Cooling Water

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