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Extraction of Dibenzothiophene from N-Dodecane using Ionic Liquids

[1]M. Zulhaziman, [1]M. Salleh, [1]M. Ibrahim, [1]Abd Mutalib and [2]Cecilia Devi Wilfred
[1]Department of Chemical Engineering,
[2]Department of Fundamental and Applied Science, Universiti Teknologi PETRONAS,
Tronoh, Perak, Malaysia

Abstract: Deep desulfurization of fuels has attracted lot of attention from growing number of researchers due to more stringent regulations imposed on sulfur content. There is a great demand to comply the regulation in current technology (hydrodesulfurization) because it requires high pressure, high temperature and high hydrogen consumption. Furthermore, aromatic sulfur compounds are also inefficient to be removed in current technology. Ionic Liquids (ILs), as class of green solvent, actually play important role as a promising alternative for desulfurization of fuels. This study focuses on the selection of potential ILs for extraction of aromatic sulfur compound involving the effect of higher alkyl chain, different cation-anion and nitrile group incorporation.

Key words: Ionic liquid, desulfurization, nitrile, imidazolium, quinolinium

INTRODUCTION

Industrial refinery plant produces more useful petroleum products such as gasoline, diesel, kerosene, heating oil and liquified petroleum gas (Speight, 1999). Removal of sulfur compound is one of the processes involved in petroleum refinery, since sulfur gives negative impact to the environment. With respect to this issue, recently much attention has been given to the desulfurization of fuels such as diesel and gasoline. It is executed because the exhaust gases of these fuels contain sulfur oxide (SO_x) which is responsible for acid rain, air contamination and ozone consumption. For controlling purpose, environmental regulations had been established and progressively modified to only allow the low level of sulfur-containing compounds into the atmosphere. To achieve this target, scientist and engineers have been doing a lot of challenging studies and demanding a newer technology.

Current technology for desulfurization purpose is hydrodesulphurization (HDS) process. However, as time goes by, the regulated sulfur limit in fuels becomes more stringent and this method becomes less reliable. In United States phased from 2004 through 2006, the Environment Protection Agency had lowered the average concentration of sulfur in gasoline more than 90%, which is 30 ppm. The European Union has reduced the sulfur content in gasoline and diesel to maximum 50 ppm in 2005 (Euro IV) and below 10 ppm in 2009 (Euro V). Malaysia has adopted Euro II standard in 2009, where the sulfur content is limited at 500 ppm. In some countries like Sweden and Germany, the majority of fuels is even stricter into S-free (by definition of <10 ppm) (ASCOPE, 2001). However, the enforcement of more stringent regulations in future would result a high demand of sweet fuels which is greatly severe for current technology established in refinery.

HDS is typically effective to eliminate paraffinic compounds like thiols, thioethers and disulfides (Zaczepinski, 1996). However, removal of cyclic especially aromatic sulfur compounds (thiophene, benzothiophene, dibenzothiophene and their alkylated derivatives) is less effective (Kulkarni and Afonso, 2010). In general, dibenzothiophene (DBT) and 4,6-alkyl-substituted DBTs are difficult to be converted into H_2S due to sterically hindered adsorption of these compounds on the catalyst surface (Kwak *et al*., 2000; Shafi and Hutchings, 2000; Ma *et al*., 1994).

A potential solution for this challenge is Ionic Liquids (ILs), which is proved to give more advantages. Ionic liquids recently gains interest in new solvent applications i.e., electrochemistry (Devarajan *et al*., 2009), separation (Han and Row, 2010), synthesis (Dyson and Geldbach, 2007) and catalysis (Parvulescu and Hardacre, 2007). In addition, density, viscosity, melting point and hydrophobicity of IL can be tuned by careful choice of its anions and cations. Common anions used are bromide, chloride, acetate, dicyanamide, hexafluorophosphate, tetrafluoroborate and bis{trifluoromethylsulfonyl}imide. However, IL such as

Corresponding Author: M. Zulhaziman, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Tronoh, Perak, Malaysia

the one containing bis{trifluoromethylsulfonyl}imide has a drawback because of their limited solubilizing ability. A solution to this issue is to use IL with strongly coordinated anion such as bromide and chloride but these ionic liquids typically have high melting point and form solid state at room temperature.

Another method is to use functionalized ionic liquids or Task Specific Ionic Liquids (TSILs). TSILs are ionic liquids which contain functional groups such as $-NH_2$, -OH, $-SO_3H$, $-CO_2H$ and -CN. These ILs show unique properties which make them suitable for specific applications. In this study, the nitrile group was chosen because it has higher stability (Zhang *et al*., 2007; Zhao *et al*., 2004) and is suitable to be used in many applications i.e. as electrolytes for dye-sensitized solar cells (Zhang *et al*., 2007), immobilization of catalyst in carbon-carbon coupling reaction (Zhao *et al*., 2004) and extraction of metal ions (Visser *et al*., 2002). The quinolinium-based ionic liquids were also selected as it demonstrated a promising extraction ability in previous study (Holbrey *et al*., 2008).

METERIALS AND METHODS

Eight ionic liquids had been selected in this study. Six of them were new ILs and the other two were commercially available i.e., [Bmim][SCN] and [Bmim][$N(CN)_2$] as shown in Fig. 1. The synthesis and characterizations for these ILs had been described in our previous study (Zulhaziman *et al*., 2009).

Desulfurization experiment

Preparation of model oil: Model oil containing around 5 (wt%) dibenzothiophene (DBT) was prepared by dissolving 2.5 g of solid dibenzothiophene in 47.5 g of n-dodecane. The 5 (wt%) of DBT in n-dodecane is equivalent to 8701 ppm of sulfur in n-dodecane.

Extraction experiment: Each IL was dried in vacuum oven for at least three hours before being used in extraction. The IL and model oil were mixed at 1:1 weight ratio (3 g), where the mixture in glass bottle was immersed in heating oil for 30 min at 30°C, 500 rpm. Liquids from the oil layer

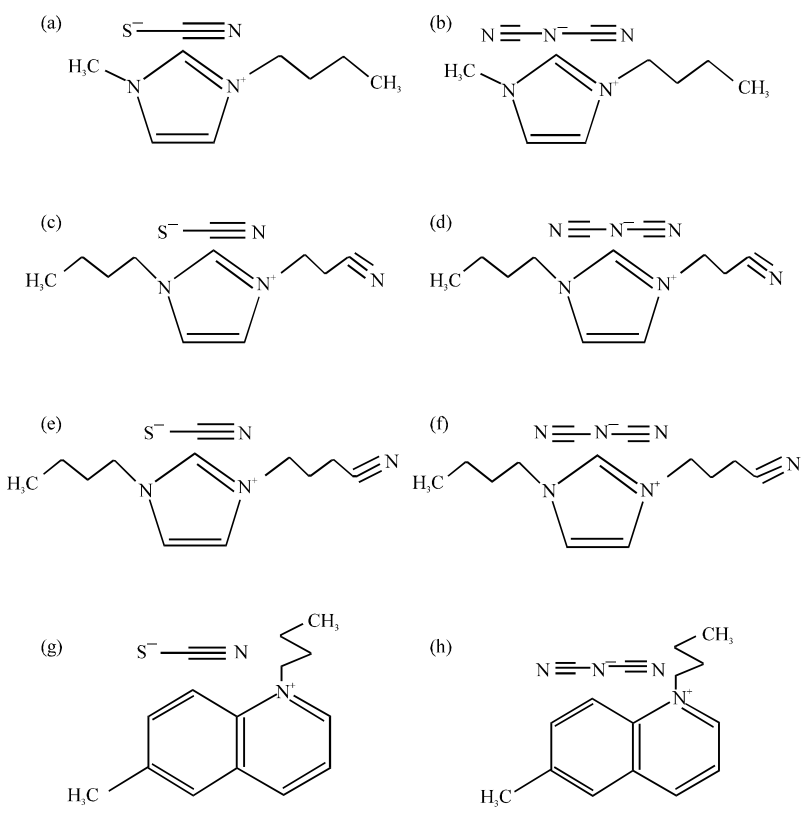

Fig. 1(a-h): Structure of selected ionic liquids, (a) [Bmim][SCN], (b) [Bmim][$N(CN)_2$], (c) [C_2CNbim][SCN], (d) [C_2CNbim][$N(CN)_2$], (e) [C_3CNbim][SCN], (f) [C_3CNbim][$N(CN)_2$], (g) [C_4mquin][SCN] and (h) [C_4mquin][$N(CN)_2$]

and the ionic liquid layer were separated using syringe. The best IL was then used to extract sulfur in real diesels i.e., diesel A (>10000 ppm) and diesel B (500 ppm).

Determination of desulfurization efficiency: GC-SCD was used to determine the sulfur content before and after extraction with injection temperature of 280°C, split ratio 200:1 with helium as carrier gas flowing at 3.5 mL min^{-1}. Oven programme started at 140°C and heated into 250°C with ramping of 20°C min^{-1}. Column used was DBI 30 m×0.32 mm×1 um film.

Computational method: The interaction between sulfur compound and IL was analyzed by using COSMO-RS simulation by comparing the sigma profile and sigma potential of the respective compounds. The calculations were carried out using COSMOt herm software with BP-TZVP C21_0110 parameterization. Data calculations were obtained through Density Functional Theory (DFT), utilizing the Becke Perdew (BP) functional with Resolution of Identity (RI) approximation and a triple valance polarization (TZVP) basis set. All chemical structures have been fully optimized in TURBOMOLE program package, which performed quantum chemical calculations.

RESULT AND DISCUSSION

Figure 2 shows the result of IL screening using model oil of 5% DBT in dodecane. It was observed that $[C_4mquin]^+$ cation demonstrated high DBT removal compared to $[Bmim]^+$ cation, where $[C_4mquin][N(CN)_2]$ performed the highest efficiency (84.1%).

This can be suitably explained by the polarity of each compound. Based on sigma potential curve in Fig. 3, DBT only has a slight attraction with non-polar compound and is highly repulsive with polar character. As seen in Fig. 4, $[C_4mquin]^+$ has higher non-polar area compared to $[Bmim]^+$, hence higher amount of DBT will be attracted to $[C_4mquin]^+$ cation. The non-polarity of $[C_4mquin]^+$ comes from its two aromatic structure of benzene-like and most dominantly attracts with DBT through π-π interaction. Therefore, it is worth noting that the structure similarity of solute and solvent could enhance the desulfurization efficiency. This finding supports the result by Kumar and Banerjee (2009) who found thiophene molecule having five-membered ring was more attached to imidazolium-based cation (five-membered ring) in comparison to pyridinium or quinolinium (six-membered ring) cations.

The types of anion also affected the sulfur removal because each anion has a different polarity. It was observed for each of the same cation, ionic liquid that has $[N(CN)_2]^-$ anion demonstrated higher DBT removal compared to $[SCN]^-$ anion. This is because, $[N(CN)_2]^-$ has more overlapping area with DBT in non-polar region (-1.0-1.0 e nm^{-2}) in Fig. 5 which means more interaction could occur. Adding nitrile functional group decreased the efficiency in [bmim][SCN] and $[bmim][N(CN)_2]$ because nitrile group is a high polarity character (hydrogen bond acceptor) which again reduced the attraction or increased the repulsive behaviour towards DBT.

However, the efficiency still rose up when the alkyl length in cation was increased. This comes from the higher capacity of IL towards DBT after alkyl chain increased as seen in $[C_2CNbim]^+$ and $[C_3CNbim]^+$. The higher capacity value comes from additional methyl group ($-CH_3$) which enhanced the CH-π interaction of cation-DBT, respectively.

In addition, this result can also be explained by the change of density and viscosity. As reported in our previous study, higher alkyl chain resulted in lower density and lower viscosity of IL. Lower density or less packing arrangement could increase the vacant area and

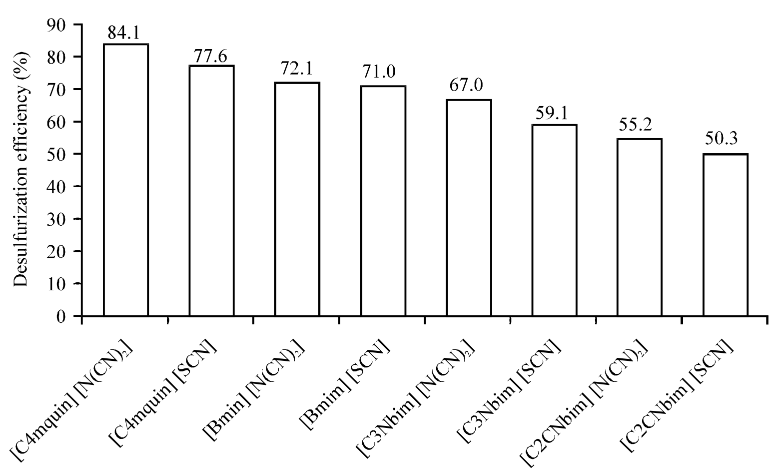

Fig. 2: Desulfurization efficiency of selected ILs

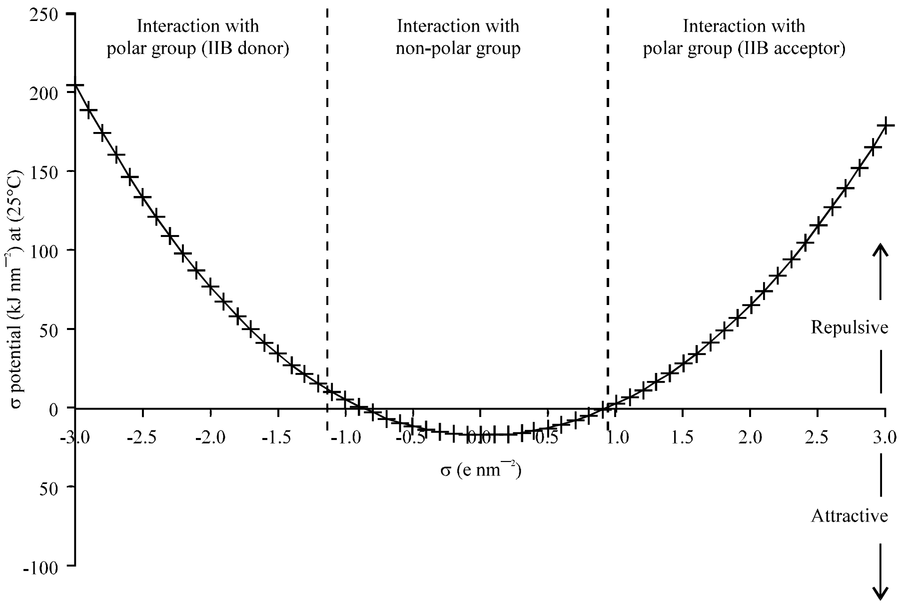

Fig. 3: Sigma potential of DBT

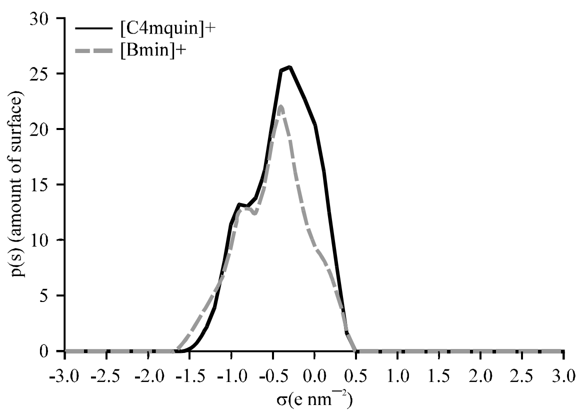

Fig. 4: Sigma profile of $[C_4mquin]^+$ and $[Bmim]^+$

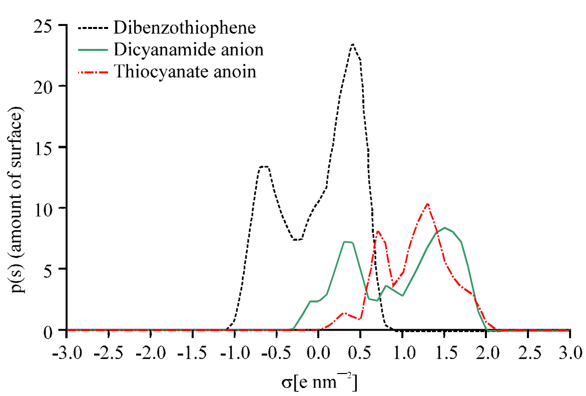

Fig. 5: Sigma profile of $[N(CN)2]^-$, $[SCN]^-$ and DBT

therefore enhance the assignment of DBT within the IL compounds. Furthermore, DBT and IL will also have easier contact and better mass transfer as the viscosity is reduced.

CONCLUSION

The desulfurization efficiency of six new ILs and two commercial ILs were studied. Quinolinium cation showed better aromatic sulfur removal compared to imidazolium, where $[C_4mquin][N(CN)_2]$ shows the best IL as it demostrated the highest desulfurization efficiency. Adding nitrile group into cation reduces the efficiency however, it rises as the alkyl chain increases.

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