Hindawi Publishing Corporation
Journal of Energy
Volume 2013, Article ID 581723, 4 pages
http://dx.doi.org/10.1155/2013/581723

Research Article

Extractive Deep Desulfurization of Liquid Fuels Using Lewis-Based Ionic Liquids

Swapnil A. Dharaskar, Kailas L. Wasewar, Mahesh N. Varma, and Diwakar Z. Shende

Advance Separation and Analytical Laboratory (ASAL), Department of Chemical Engineering, Visvesvaraya National Institute of Technology (VNIT), Nagpur 440010, India

Correspondence should be addressed to Kailas L. Wasewar; k_wasewar@rediffmail.com

Received 21 December 2012; Revised 18 February 2013; Accepted 25 February 2013

Academic Editor: David Kubička

A new class of green solvents, known as ionic liquids (ILs), has recently been the subject of intensive research on the extractive desulfurization of liquid fuels because of the limitation of traditional hydrodesulfurization method. In present work, eleven Lewis acid ionic liquids were synthesized and employed as promising extractants for deep desulfurization of the liquid fuel containing dibenzothiophene (DBT) to test the desulfurization efficiency. [Bmim]Cl/$FeCl_3$ was the most promising ionic liquid and performed the best among studied ionic liquids under the same operating conditions. It can remove dibenzothiophene from the model liquid fuel in the single-stage extraction process with the maximum desulfurization efficiency of 75.6%. It was also found that [Bmim]Cl/$FeCl_3$ may be reused without regeneration with considerable extraction efficiency of 47.3%. Huge saving on energy can be achieved if we make use of this ionic liquids behavior in process design, instead of regenerating ionic liquids after every time of extraction.

1. Introduction

Due to environmental awareness and economic competition, fuel oil standards are more stringent. Sulfur present in transportation fuel leads to sulfur oxide (SO_x) emissions into the atmosphere and causes many environmental problems. It also inhibits the performance of vehicles pollution control equipment. Hence, much recent interest in the deep desulfurization [1, 2] of light oil feedstock is directed. Inconsiderable attention has been given to deep desulfurization of gasoline and liquid fuels due to strict environment regulations on the sulfur limit of fuels [3]. The maximum sulfur content will be limited to 10–50 ppm in 2016, as compared to today's permitted value of 500 ppm in most western countries [4].

In India, the present norms were decided by the Central Pollution Control Board (CPCB); the current value of total sulfur in liquid fuels is limited to 350 ppm which has to be lowered down into possible extent [5]. As a result the deep desulfurization of liquid fuels has fascinated increased attentunity worldwide. In the petroleum industry, low sulfur fuels are often obtained from hydrocracking processes [6].

In petroleum and hydrocarbon industries, various solvents such as ethers, amines, alcohols, and other volatile organic compounds have been used for the processes like extraction, absorption, azeotropic distillation, and so forth [7]. These solvents have their own limitations in terms of environmental issue, recycle ability, and so forth, which can be overcome by the use of ionic liquids as green solvent due to their very low vapour pressure and wide range of application with unique physical and chemical properties [8]. Among these, deep extractive desulfurization is an attractive technology, as it can be carried out at ambient temperature, pressure, and without hydrogen as an catalyst. A good extractant much have the following attributes [9]: good extractive ability for sulfur compounds, free of contamination to the fuels, nontoxicity, environmental benignity, and stability for repetitive use. Ionic liquids have been studied for many possible applications for green chemical processes [10–16].

Ionic liquids (ILs) are usually consisted by various combinations of heterocyclic organic cations, and anions show liquid at room temperature with unique properties such as

nonvolatility, nonflammability, and a wide temperature range for the liquid phase [17–21].

In present work, eleven Lewis acid ionic liquids, [Bmim]Cl/$FeCl_3$ (Bmim: 1-butyl-3-methylimidazolium chloride), [Omim]Cl/$FeCl_3$ (Omim: 1-Octyl-3-methylimidazolium Chloride), T_8Cl/$FeCl_3$ (T_8Cl: Tri-octyl methyl ammonium chloride), T_4Cl/$FeCl_3$ (T_4Cl: Tri-butyl methyl chloride), D_{10}Cl/$FeCl_3$ (D_{10}Cl: didecyl dimethyl ammonium chloride), and [Emim]Cl/$AlCl_3$ (Emim: 1-ethyl-3-methylimidazolium), have been synthesized for desulfurization of liquid fuels. The extent of sulfur removal from the model fuel by the ILs has been used to decide the best ILs. Further the reusability of the IL has been investigated.

2. Experimental

2.1. Materials and Reagents. n-dodecane (AR grade), dibenzothiophene (DBT) (98%), ethyl acetate (99.5%), [Bmim]Cl (98%), [Omim]Cl (99%), [Emim]Cl (98%), anhydrous $FeCl_3$ (99%), anhydrous $ZnCl_2$ min (99%), anhydrous $SnCl_2$(99%), anhydrous $MnCl_2$(99%), and anhydrous $CoCl_2$(99%) are of Acros (USA) available commercially and used as received without further treatment.

2.2. Preparation of Ionic Liquids. [Bmim]Cl/$FeCl_3$ ionic liquid was synthesized as mentioned in the literature [22]. [Omim]Cl/$FeCl_3$, [Bmim]Cl/$AlCl_3$, [Bmim]Cl/$ZnCl_2$, [Bmim]Cl/$SnCl_2$, [Bmim]Cl/$MnCl_2$, [Bmim]Cl/$CoCl_2$, and [Emim]Cl/$AlCl_3$ were prepared by adding the desired amount of chloride to the imidazolium salt. The reaction was carried out with stirring for 2 hours. The synthesis of T_8Cl/$FeCl_3$, T_4Cl/$FeCl_3$, and D_{10}Cl/$FeCl_3$ was followed by a similar procedure [23].

2.3. Preparation of Model Liquid Fuel. A model liquid fuel containing 500 ppm sulfur dibenzothiophene (DBT) (98%) was prepared by dissolving DBT in n-dodecane.

2.4. Extractive Desulfurization of the Model Liquid Fuel. The desulfurization experiments were carried out in a 100 mL two necked flask by mixing of model liquid fuel (10 mL) and specific amount of ionic liquid with the fixed mass ratio between model liquid fuel to ionic liquid as 5/1 at 30°C in a water bath for 30 minutes with vigorous stirring.

On completion of the reaction, the upper phase (model liquid fuel) was withdrawn and analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (Arcos, M/s. Spectro, Germany.), Indian Institute of Technology, Mumbai (M.S.), India, to determine the concentration of sulfur in the model liquid fuels. Then % removal of sulfur can be calculated by the following equation [24]:

% sulfur removal = [DBT] initial − [DBT] final/[DBT] initial × 100.

3. Results and Discussion

3.1. Desulfurization of the Model Liquid Fuel (DBT in n-dodecane) with Various Ionic Liquids. The experiments were carried out to test the feasibility of various ionic liquid for desulfurization of liquid fuels. The results of experiments on the selective extraction of using Lewis acid ionic liquids are given in Table 1.

Table 1: Extractive desulfurization of model liquid fuel (DBT in n-dodecane) using Lewis-acid-based ionic liquids.

Sr. no	Ionic liquid	Sulfur removal (volume %)
1	[Bmim]Cl/$FeCl_3$	75.6
2	[Omim]Cl/$FeCl_3$	70.2
3	T_8Cl/$FeCl_3$	69.5
4	T_4Cl/$FeCl_3$	49.3
5	D_{10}Cl/$FeCl_3$	55.2
6	[Bmim]Cl/$AlCl_3$	68.7
7	[Emim]Cl/$AlCl_3$	60.1
8	[Bmim]Cl/$ZnCl_2$	42.1
9	[Bmim]Cl/$SnCl_2$	50.4
10	[Bmim]Cl/$MnCl_2$	40.1
11	[Bmim]Cl/$CoCl_2$	33.0

Mass ratio of model liquid fuels/ionic liquid = 5/1; extraction time = 30 min; temperature = 30°C; initial sulfur concentration = 500 ppm.

The sulfur removal efficiency of [Bmim]Cl/$FeCl_3$, [Omim]Cl/$FeCl_3$, T_8Cl/$FeCl_3$, T_4Cl/$FeCl_3$, D_{10}Cl/$FeCl_3$, [Bmim]Cl/$AlCl_3$, [Emim]Cl/$AlCl_3$, [Bmim]Cl/$ZnCl_2$, [Bmim]Cl/$SnCl_2$, [Bmim]Cl/$MnCl_2$, and [Bmim]Cl/$CoCl_2$ for model liquid fuel is shown in Table 1. The ionic liquids based on $FeCl_3$ showed the best sulfur removal efficiency among other ionic liquids. This experiment clearly demonstrates that the extraction ability of [Bmim]Cl/$FeCl_3$ is suitable in comparison with the other ionic liquids. It was also found that the extraction process went on quickly, and it could reach extraction equilibrium in little time. (Say 30 minutes). The amount of DBT extracted can be increased with an increased molar ratios of $FeCl_3$/[Bmim]Cl which can be recognized to the increased Lewis acidity of the resulting IL at higher molar ratios of $FeCl_3$/[Bmim]Cl [25]. However the DBT was broadly extracted from the model fuel at the [Bmim]Cl/$FeCl_3$ at higher molar ratios. In general $FeCl_3$ alone exhibited lower extraction ability than the Fe-containing ILs, signifying the important role of [Bmim]Cl [26]. The IL with one or two acidic hydrogen atoms on the imidazolium ring exhibited much lower extraction ability than the ILs containing two or three alkyl groups. The highest DBT extraction was obtained with [Bmim]Cl/$FeCl_3$ that existed as liquids at room temperature. These results may imply that the ability of Fe-based ILs to remove DBT is also affected by the fluidity of the IL. Similar results were reported [26] among the three ionic liquids; [Bmim]Cl/$AlCl_3$ with desulfurization of 45% represents better extraction ability than the other [Emim]Cl; two different chloroaluminate melts suggest a certain influence of the ionic liquids cation as for $[Bmim]^+$ cation containing Lewis acidic ionic liquids, the desulfurization efficiency of different anions expressed different extraction ability. [Bmim]Cl ionic liquid showed

Table 2: Sulfur removal of [Bmim]Cl which was reused for three times in model liquid fuel (n-dodecane + DBT).

Model fuel	Ionic liquid spent	No. of cycle	Sulfur removal (%)
(n-dodecane + DBT)	[Bmim]Cl/$FeCl_3$	I	75.6
(n-dodecane + DBT)	[Bmim]Cl/$FeCl_3$	II	63.2
(n-dodecane + DBT)	[Bmim]Cl/$FeCl_3$	III	47.3

Mass ratio of model fuels/ionic liquid = 5/1; extraction time = 30 min; temperature = 30°C; initial sulfur concentration = 500 ppm.

higher extractive ability than the other ionic liquids [27]. It was also found that [Bmim]Cl/$FeCl_3$ is less viscous than other ionic liquids. However, [Bmim]Cl/$FeCl_3$ is considered as a promising extractive agent in extractive deep desulfurization for the removal of dibenzothiophene (DBT).

3.2. Ionic Liquid Reusability without Regeneration. In order to examine the reusability of the ionic liquid, the spent [Bmim]Cl/$FeCl_3$ was studied. Table 2 shows the desulfurization efficiency of [Bmim]Cl/$FeCl_3$ which was reused for three times without regeneration. It was observed that the spent ionic liquid was able to extract dibenzothiophene from model liquid fuel even without regeneration, however, at a lower efficiency of 47.3% from 75.6% with fresh ionic liquid.

4. Conclusion

Eleven Lewis-acid-based ionic liquids were screened to investigate the desulfurization efficiency. $FeCl_3$-based ILs can be used as effective extractant for removing DBT from liquid fuel. [Bmim]Cl/$FeCl_3$ was found to be the best ionic liquid as a kind of novel extractant for desulfurization of liquid fuel, which exhibits a better extractive performance for dibenzothiophene. The sulfur removal of dibenzothiophene containing model liquid fuel was 75.6% with single-stage extraction process at 30°C in 30 minutes. Lewis acid ionic liquid with long carbon chains can obtain 70.2% with simple extraction. The used ionic liquid was able to extract DBT from model liquid fuel even without regeneration. Furthermore, Fe-based IL system shows considerable promise for providing a technology to meet future needs for low sulfur fuel (less than 50 ppm), that is, clean fuels.

Acknowledgment

The authors gratefully acknowledge, for the financial support, the Council of Scientific Research (CSIR) Grant no. (22(0492)/09/EMR-II), Government of India, India (principal investigator: Dr. K. L. Wasewar).

References

[1] A. Bösmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz, and P. Wasserscheid, "Deep desulfurization of diesel fuel by extraction with ionic liquids," *Chemical Communications*, no. 23, pp. 2494–2495, 2001.

[2] W. Dai, Y. Zhou, S. Wang, W. Su, Y. Sun, and L. Zhou, "Desulfurization of transportation fuels targeting at removal of thiophene/benzothiophene," *Fuel Processing Technology*, vol. 89, no. 8, pp. 749–755, 2008.

[3] X. Chu, Y. Hu, J. Li et al., "Desulfurization of diesel fuel by extraction with [BF4]—based ionic liquids," *Chinese Journal of Chemical Engineering*, vol. 16, no. 6, pp. 881–884, 2008.

[4] G. Parkinson, "Diesel desulfurization puts refiners in a quandary," *Chemical engineering*, vol. 108, pp. 37–41, 2001.

[5] Central Pollution Control Board, "Status of the vehicular pollution control programme in India," Tech. Rep. Probes/136/2010, Central Pollution Control Board, 2010.

[6] C. Kwak, J. J. Lee, J. S. Bae, K. Choi, and S. H. Moon, "Hydrodesulfurization of DBT, 4-MDBT, and 4,6-DMDBT on fluorinated CoMoS/Al_2O_3 catalysts," *Applied Catalysis A*, vol. 200, no. 1, pp. 233–242, 2000.

[7] C. Huang, B. Chen, J. Zhang, Z. Liu, and Y. Li, "Desulfurization of gasoline by extraction with new ionic liquids," *Energy and Fuels*, vol. 18, no. 6, pp. 1862–1864, 2004.

[8] S. Dharaskar, "Ionic liquids (a review): the green solvents for petroleum and hydrocarbon industries," *Research Journal of Chemical Sciences*, vol. 2, no. 8, pp. 80–85, 2012.

[9] X. Jiang, Y. Nie, C. Li, and Z. Wang, "Imidazolium-based alkylphosphate ionic liquids—a potential solvent for extractive desulfurization of fuel," *Fuel*, vol. 87, no. 1, pp. 79–84, 2008.

[10] K. G. Knudsen, B. H. Cooper, and H. Topsoe, "Catalyst and process technology for ultra low sulfur diesel," *Applied Catalysis A*, vol. 189, pp. 205–215, 1999.

[11] A. B. S. H. Salem and H. S. Hamid, "Removal of sulfur compounds from naphtha solutions using solid adsorbents," *Chemical Engineering and Technology*, vol. 20, no. 5, pp. 342–347, 1997.

[12] A. Takahashi, F. H. Yang, and R. T. Yang, "Desulfurization of gasoline by extraction with N-alkyl-pyridinium-based ionic liquids," *Industrial & Engineering Chemistry Research*, vol. 41, pp. 2487–2496, 2002.

[13] M. P. Marszall, M. J. Makuszewski, and R. J. Kaliszan, "Separation of nicotinic acid and its structural isomers using 1-ethyl-3-methylimidazolium ionic liquid as a buffer additive by capillary electrophoresis," *Journal of Pharmaceutical and Biomedical Analysis*, vol. 41, pp. 329–333, 2006.

[14] K. A. Howard, H. L. Mitchell, and R. H. Waghore, US patent 4, 359, pp. 596, 1982.

[15] D. R. Boate and M. J. Zaworotko, "Organic Non–quaternary Clathrate Salts for Petroleum Separation," US patent 5, 220, pp. 106, 1993.

[16] F. G. Sherif, L. Shyu, and C. C. Greco, "Linear alxylbenzene formation using low temperature ionic liquid," US patent 5, 824, pp. 832, 1998.

[17] V. R. Koch, C. Nanjundiah, and R. T. Carlin, US patent 5, 872, pp. 602, 1998.

[18] S. M. Silvu, P. A. Suarcz, Z. de Souza, and R. F. Doupont, "Selective sulfur removal from fuels using ionic liquids at room temperature," *Polymer Bulletin*, vol. 40, pp. 401–405, 1998.

[19] A. J. Carmichael, D. M. Haddlettn, S. A. F. Bon, and K. R. Seddon, "Copper (I) mediated living radical polymerization in

an ionic liquid," *Chemical Communications*, vol. 79, pp. 1237–1238, 2000.

[20] R. T. Carlin and J. S. Wilkes, "Effect of room temperature Ionic Liquids as replacement for volatile organic solvents in free radical polymerization," *Journal of Molecular Catalysis*, vol. 63, pp. 125–129, 1990.

[21] M. Goledzinowski, V. I. Birss, and J. Galuszka, "Oligomerization of low molecular weight olefins in ambient temperature molten salts," *Industrial and Engineering Chemistry Research*, vol. 32, no. 8, pp. 1795–1797, 1993.

[22] G. Yu, J. Zhao, D. Song, C. Asumana, X. Zhang, and X. Chen, "Deep oxidative desulfurization of diesel fuels by acidic ionic liquids," *Industrial & Engineering Chemistry Research*, vol. 50, pp. 11690–11697, 2011.

[23] Y. L. Yang and Y. Kou, "Determination of the Lewis acidity of ionic liquids by means of an IR spectroscopic probe," *Chemical Communications*, vol. 10, no. 2, pp. 226–227, 2004.

[24] X. Sun and S. Zhao, "[bmim]Cl/[$FeCl_3$] ionic liquid as catalyst for alkylation of benzene with 1-octadecene," *Chinese Journal of Chemical Engineering*, vol. 14, no. 3, pp. 289–293, 2006.

[25] N. H. Ko, J. S. Lee, E. S. Huh et al., "Extractive desulfurization using Fe-containing ionic liquids," *Energy and Fuels*, vol. 22, no. 3, pp. 1687–1690, 2008.

[26] D. P. Li, X. L. Hu, Y. M. Zhao, P. Guan, and J. Y. Yu, "Study of green solvents l-butyl-3-methylimidazolium Ionic liquids' structure and properties," in *Proceedings of the IEEE 4th International Conference on Bioinformatics and Biomedical Engineering (ICBBE '10)*, pp. 1–4, June 2010.

[27] H. Li, W. Zhu, Y. Wang, J. Zhang, J. Lu, and Y. Yan, "Deep oxidative desulfurization of fuels in redox ionic liquids based on iron chloride," *Green Chemistry*, vol. 11, pp. 810–815, 2009.