



Extraction of Naphthenic Acid from Highly Acidic Oil Using Hydroxide-Based Ionic Liquids

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S Supporting Information

ABSTRACT: The isolation and recovery of naphthenic acid from highly acidic model oil was performed using hydroxide-based ionic liquids. An extremely low ionic liquid/oil ratio was used to completely deacidify the model oil. Tetraalkylammonium and tetraalkylphosphonium hydroxide ionic liquids were employed in this study. Tetraalkylammonium-based ionic liquids are more efficient than tetraalkylphosphonium-based ionic liquids. The recyclability of the ionic liquids for the extraction of naphthenic acid was also studied. The regeneration of the extracted naphthenic acid was achieved.

1. INTRODUCTION

Naphthenic acids can be defined as a mixture of cyclic, aromatic, and linear monocarboxylic acids present in the crude oil with the general formula $C_nH_{2n+z}O_2$, where n indicates the number of carbon atoms and z indicates the deficiency of hydrogen because of the presence of cyclic or aromatic groups. The value of z can be a negative integer or zero.^{1–4} Pure naphthenic acids are important raw material in the chemical industry. Two-third of the naphthenic acid produced is converted to metal salts for various applications, such as wood preservative, paint driers, lubricants, and fuel additives.⁵ The acidity of crude oil is reflected by the total acid number (TAN) measurement expressed in milligrams of KOH necessary to neutralize 1 g of crude oil. Crude oils with acidity levels above 0.5 mg of KOH/g are considered as potentially corrosive for refinery units.^{6,7} Corrosion problems in refinery equipment arise during the processing of highly acidic crude oils. Corrosion because of naphthenic acids occurs at temperatures between 200 and 400 °C and primarily affects the transfer pipes between the heating furnaces and atmospheric and vacuum distillation units.⁸ Naphthenic acids can also cause corrosion problems in the production equipment and storage and transport facilities, and even they can affect the performance of oil.⁹ In refinery processes, the presence of even small quantities of naphthenic acids in crude oils can cause operational problems, such as foaming in various units and leaching of cations in the desalting process, which, in turn, lead to the deactivation of the catalyst.¹⁰

Presently, the global demand for high acidic crude oil is increasing because of its lower price and greater availability compared to the sweet crude oil. Therefore, a simple method for the effective removal of naphthenic acid is desirable. The problems associated with the presence of naphthenic acids in the crude oil can be avoided by a number of approaches, such as neutralization, solvent extraction, adsorption, thermal decomposition, catalytic decarboxylation, and esterification.

The most common and cost-effective method for isolation of naphthenic acids is the washing of diesel/kerosene fractions

using an aqueous solution of alkali or alkaline earth metals, followed by acidification with mineral acids to recover the insoluble naphthenic acid.⁵ Adsorption and solvent extraction had also been employed for acidity reduction in crude oils.^{11,12} Catalytic or non-catalytic esterification is another efficient method for the deacidification of crude oil.¹³ Decarboxylation is also successfully employed for processing of high-acidity crude oils. Both thermal and catalytic decarboxylation are effective in removing naphthenic acid.^{14,15}

All of the above methods suffer from various shortcomings. For instance, washing with alkali or alkaline earth metals will result in an incomplete removal of naphthenic acid because of its poor water solubility. In addition, the emulsion formed with higher distillate cuts is another drawback associated with caustic wash. The solvent extraction technique lacks environmental viability because of the generation of a significant amount of volatile organic solvent waste, while the adsorption technique is applicable only for low-temperature lighter distillate fractions. As for the decarboxylation process, it requires higher temperatures (>250 °C), which lead to corrosion problems.

Ionic liquids (ILs), a new class of solvents, are usually non-volatile, nonflammable, and thermally stable. In the current decade, ILs have been used in various applications, such as purification, electrochemistry, extraction, and catalysis.^{16–19} IL solution in different organic solvents had also been applied for the naphthenic acid extraction from crude oil. Different organic solvents along with imidazole derivatives were used to remove naphthenic acid. However, only 67% removal efficiency was obtained, and in addition, this process requires a significant amount of different organic solvents.²⁰ Although imidazolium- and pyridinium-based ILs with varying alkyl chain lengths were employed for the removal of naphthenic acid,^{21,22} they were effective only for a model system with a very low TAN (<0.5). It has been reported that naphthenic acid can be removed

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through neutralization using a mixture of sodium hydroxide and hydroxide anion containing ILs.^{23,24} However, this method had not been studied in details, and the regeneration of extracted naphthenic acid has not been addressed. In this study, tetraalkylammonium and tetraalkylphosphonium hydroxide ILs were employed for the complete deacidification and regeneration of naphthenic acid from highly acidic model oil and a continuation of our work on extraction of naphthenic acid using ILs.²⁵ The structure of the ILs used in this study is shown in Figure 1.

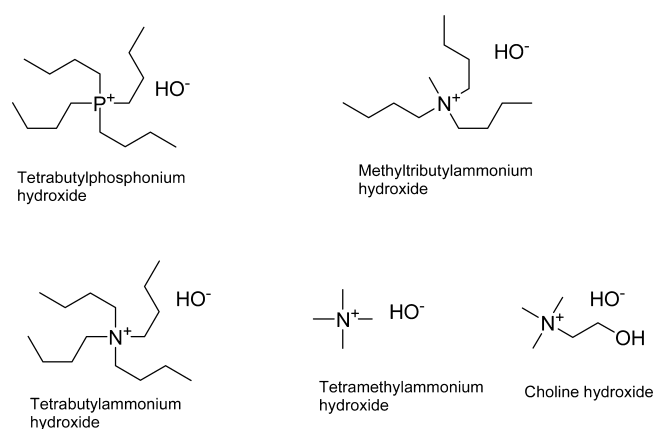


Figure 1. Overview of ILs used in this study.

2. EXPERIMENTAL SECTION

2.1. Materials. Dodecane (synthesis grade, purity of $\geq 99.0\%$) was purchased from Merck (Malaysia). Commercial naphthenic acid technical grade (purity of 90–100%) was purchased from Sigma-Aldrich (Malaysia). Tetramethylammonium hydroxide (25% solution in water) was purchased from Merck (Malaysia). Tetrabutylammonium hydroxide (40% solution in water) was purchased from Acros Organic. Methyltributylammonium hydroxide (20% solution in water), choline hydroxide (20% solution in water), and tetrabutylphosphonium hydroxide (40% solution in water) were purchased from Sigma-Aldrich. No further purification of the chemicals was performed once they were received.

2.2. Preparation of Model Acid Oil. The model acid oil used in this study was prepared by the addition of naphthenic acid to dodecane until the acid number attains a value of 4.74 (± 0.01) mg of KOH/g, which is considered as highly acidic crude oil. Dodecane was used in this study because the majority of commercial naphthenic acids are produced from the kerosene and diesel fraction. Kerosene and diesel can be represented by dodecane. The TAN was calculated using

a Mettler Toledo autotitrator, following the standard method in the oil industry using ASTM D664.

2.3. Deacidification Process. The neutralization of the model oil was carried out by mixing 10 g of dodecane with a set amount of IL in a round-bottom flask with a hot plate, reflux condenser, and magnetic stirrer. The stirring rate was kept at 500 rpm, and the reaction time was 1 h. Several temperature settings were used for the reaction to optimize the process temperature. The reaction mixture was then transferred to a separation funnel and kept for 1 h to enable a clear separation between the IL and the model oil. A total of 5 g of oil was withdrawn from the top of the separation funnel, and the TAN was measured. The reduction in TAN can be converted to the percent naphthenic acid removal using the formula mentioned below

$$\text{percent naphthenic acid removal} = \left(1 - \frac{\text{TAN}_f}{\text{TAN}_i}\right) \times 100$$

where TAN_f and TAN_i refer to final and initial TANs of the oil, respectively. All of the experiments were conducted in triplicate, and the average standard deviation for all of the experiments was of the order of 10^{-3} – 10^{-5} .

3. RESULTS AND DISCUSSION

3.1. Effect of the Reagent/Oil Ratio. The IL/oil ratio is an important parameter in the deacidification process. To investigate the influence of the IL/model oil ratio, different weight ratios were employed and the percent naphthenic acid removal was calculated. The extraction was performed at room temperature for 1 h with a stirring rate of 500 rpm. The separation time was 1 h. The amount of ionic liquids was only considered in calculating the IL/model oil ratio, even though an aqueous solution of ILs was used. It can be calculated from the weight percentage of the IL solution. The influence of the IL/model oil ratio is given in Table 1 and Figure 2.

It can be seen from Table 1 and Figure 2 that the percent naphthenic acid removal increases with an increase in the IL/model oil ratio for all types of ILs. It was found that tetramethylammonium hydroxide, $[\text{N}_{1111}][\text{OH}]$, was the most efficient in naphthenic acid extraction among the ILs used. It may be due to the lower miscibility of the model oil with the ILs, which leads to a complete separation of the model oil and IL layer. The complete removal of naphthenic acid was achieved at a ratio of 0.0075 IL/oil (w/w). From the experimental results, it was clear that tetraalkylammonium-based ILs were more suitable for the extraction of naphthenic acids compared to tetraalkylphosphonium ILs. Tetraalkylammonium hydroxide needed only 0.0075–0.02 IL/model oil ratio for the complete deacidification. On the other hand, a higher reagent/model oil ratio (0.0225) is required for the

Table 1. Effect of the IL/Oil Ratio on Naphthenic Acid Removal^a

IL/oil ratio	percent naphthenic acid removal				
	$[\text{N}_{1111}][\text{OH}]$	$[\text{Ch}][\text{OH}]$	$[\text{N}_{1444}][\text{OH}]$	$[\text{P}_{4444}][\text{OH}]$	$[\text{N}_{4444}][\text{OH}]$
0.0025	40.41	26.545	16	11.63	12.85
0.0050	67.46	50.52	38.47	21.37	24.022
0.0075	100	73.54	56.06	34.43	36.72
0.0100	100	93.58	70.74	46.27	47.99
0.0125	100	100	83.57	59.21	65.87
0.0150	100	100	96.55	70.18	79.79
0.0175	100	100	100	80.83	91.03
0.0200	100	100	100	92.60	100
0.0225	100	100	100	100	100

^aIn the IL/oil ratio, pure IL without water has been considered.

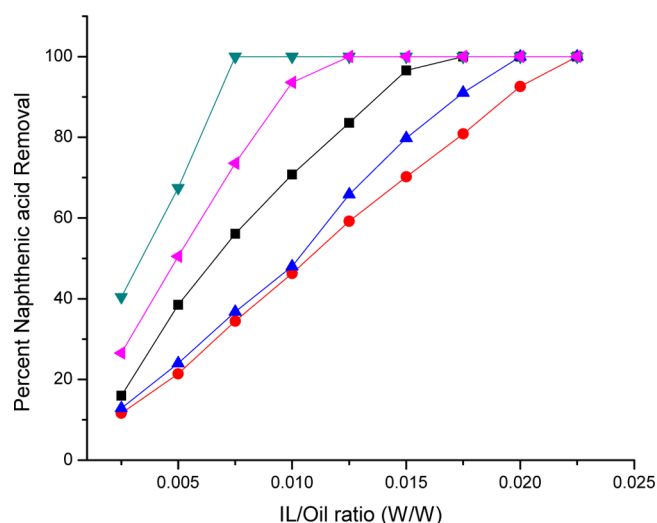


Figure 2. Effect of the IL/oil ratio on percent naphthenic acid removal (teal ▼, $[N_{1111}][OH]$; magenta ◀, $[Ch][OH]$; black ■, $[N_{1444}][OH]$; blue ▲, $[N_{4444}][OH]$; and red ●, $[P_{4444}][OH]$) (stirring rate, 500 rpm; reaction time, 1 h).

complete extraction of naphthenic acid using $[P_{4444}][OH]$. This can be attributed to the higher polarity of the ammonium-based ILs compared to the phosphonium ILs.²⁶ As the polarity increases, the interaction between naphthenic acid and ILs will increase and leads to an enhanced extraction efficiency. The choline hydroxide, $[Ch][OH]$, completely extracted the naphthenic acid at an IL/model oil ratio of 0.0125. The extraction efficiency of the ILs follows the order of $[N_{1111}][OH] > [Ch][OH] > [N_{1444}][OH] > [N_{4444}][OH] > [P_{4444}][OH]$. The longer alkyl groups in the tetraalkylammonium ILs reduce the extraction efficiency. It may be due to the decrease in polarity with an increase in the alkyl chain length. Nuclear magnetic resonance (NMR) spectroscopy was used to study the leaching of the ILs into dodecane. The 1H NMR spectrum of the completely deacidified model oil was recorded (see Figure S1 of the Supporting Information), and no peaks corresponding to the ILs were observed. It indicates that the concentration of ILs in the dodecane layer was below the detection limit of NMR spectroscopy, which shows that leaching of ILs into the dodecane layer was negligibly small. The hydroxide-based ILs showed superior extraction performance compared to the ILs reported in the literature. For example, imidazolium-based ILs with different alkyl chain lengths, such as ethyl, butyl, hexyl, and octyl groups, with imidazolate anions were only able to completely deacidify weakly acidic model oil ($TAN < 0.5$) at an IL/oil ratio ranging from 0.012 to 0.016 with a reaction time of 2 h.²¹ However, hydroxide-based ILs completely extracted naphthenic acid from highly acidic model oil ($TAN > 5$) with a very low IL/oil ratio of 0.0075–0.0125 within 1 h. The pyridinium bromide ILs with a chain length of 2, 4, 6, and 8 carbon atoms needed an IL/oil ratio of more than 0.100 for extracting 93% of naphthenic acid from model oil with a very low TAN .²²

3.2. Effect of the Temperature on Naphthenic Acid Extraction. The effect of the temperature on naphthenic acid removal was investigated to determine the optimum reaction conditions for the extraction at different IL/oil ratios, and the results are shown in Figure 3.

The extraction was performed at a fixed IL/model oil ratio (0.005 wt %). It was observed that the percent naphthenic acid

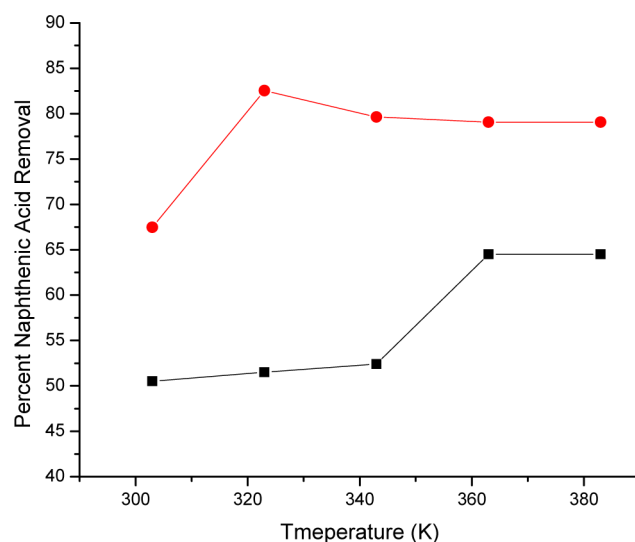


Figure 3. Effect of the temperature on naphthenic acid removal (black ■, $[Ch][OH]$ with 0.005 IL/oil ratio; red ●, $[N_{1111}][OH]$ with 0.005 IL/oil ratio) (stirring rate, 500 rpm; reaction time, 1 h).

removal increases with the extraction temperature up to a certain value for all of the ILs under every IL/oil ratio, beyond which the extraction performance either declined or remained constant. As the temperature increases, the viscosity of the model oil decreases, which enhances the interaction of ILs with the model oil and resulted in an increase of the extraction efficiency of the ILs. The decrease in viscosity lead to an increase in the mass transfer of the solute present in the model oil. In addition, a higher temperature will also increase the solubility of naphthenic acid in ILs. The extraction performance remains constant after a certain temperature because the effect of the temperature on viscosity was smaller at higher temperatures. Similar trends were reported when naphthenic acid extraction was performed using imidazolium- and pyridinium-based ILs with varying alkyl spacer lengths.^{21,22} The optimal extraction temperature for tetramethylammonium hydroxide was found to be 323.15 K, and the highest extraction of naphthenic acid was achieved at that temperature. In the case of choline hydroxide, the maximum efficiency was achieved when the extraction was performed at 363.15 K. The large dissimilarity between the extraction performance of tetramethylammonium hydroxide and choline hydroxide was due to the difference in the alkyl spacer length, which, in turn, affects their physical properties. 1H NMR spectroscopy was used to study the stability of the ILs used in the extraction process. The 1H NMR spectrum (see Figures S2 and S3 of the Supporting Information) of $[N_{1111}]^+$ and $[Ch]^+$ are found to be similar before and after the extraction process. It indicates that the IL cation remains chemically stable during the extraction process. Although the process is more efficient at high temperatures, a low temperature is recommended because of the high cost involved in the heating process in the industrial scale and the difference in extraction efficiency at a higher temperature is not very significant. In the case of $[N_{1111}][OH]$, the extraction performance was increased only about 15% when the temperature was raised from room temperature to 323.15 K, the temperature at which maximum extraction was achieved. $[Ch][OH]$ showed only an increase of less than 15%, and even the temperature was raised to 363.15 K. Moreover, the possibilities of thermal degradation of hydroxide-based ILs

are very high at elevated temperatures because of the high alkalinity of hydroxide anions.

3.3. Repetitive Reaction of ILs. The reusability of two potential ILs was studied at two different temperatures with an IL/oil ratio, which gave maximum extraction in the previous experiments. The ILs were treated with model oil having a TAN of 0.9 mg of KOH/g of oil. After each extraction, the model oil was separated from the mixture and the fresh model oil was introduced into the ILs used in the previous extraction. The above process was repeated until the ILs have lost their efficiency completely. The TAN of the extracted model oil was determined after each cycle. When the experiments were performed at room temperature, the ILs can be recycled up to 5 cycles without losing its activity, and complete deacidification of model oil was achieved in all 5 cycles. After the fifth cycle, the extraction efficiency of the ILs started to decline, and less than 70% activity was shown after 6 cycles. As seen in Figure 4, the temperature has a negative influence on the recyclability of the ILs.

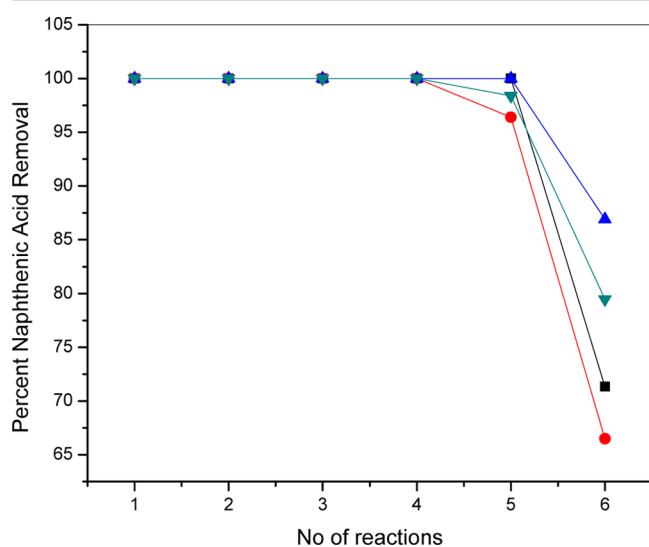


Figure 4. Recyclability study of ILs (black ■, [N₁₁₁₁][OH] with 0.0075 IL/oil ratio at 303 K; red ●, [N₁₁₁₁][OH] with 0.0075 IL/oil ratio at 323 K; blue ▲, [Ch][OH] with 0.0125 IL/oil ratio at 303 K; and teal ▼, [Ch][OH] with 0.0125 IL/oil ratio at 363 K) (stirring rate, 500 rpm; reaction time, 1 h).

The efficiency of [Ch][OH] declines after 5 cycles of extraction when the extraction was carried out at 303.15 K. The IL was, nevertheless, still extracting more than 85% naphthenic acid after 6 cycles. When the extraction temperature was increased to 363.15 K, the extraction capacity of [Ch][OH] drops after 4 cycles. A similar trend was observed in the case of [N₁₁₁₁][OH]. However, the percentage of naphthenic acid extraction has significantly reduced at both temperatures after the fifth cycle of extraction. At 303.15 K, [Ch][OH] extracted more than 85% naphthenic acid in the sixth cycle of extraction. However, [N₁₁₁₁][OH] extracted less than 80% naphthenic acid at the same temperature. The difference in the extraction performance of [Ch][OH] and [N₁₁₁₁][OH] was more evident when the extraction was performed at optimum temperature, which was found to be 323 K for [N₁₁₁₁][OH] and 363 K in the case of [Ch][OH]. More than 77% naphthenic acid was extracted by [Ch][OH] at 363.15 K, while [N₁₁₁₁][OH] extracted less than 70% naphthenic acid at 323 K. The loss of

efficiency at a higher temperature can be explained by the decomposition of the ILs because of the prolonged heating (1 h for each cycle) during the extraction process. The ILs are prone to thermal decomposition in the presence of a base at an elevated temperature because of Hoffman elimination.²⁷ The recyclability experiments with ILs showed that they can be reused up to 5 cycles without losing their efficiency.

3.4. Effect of the Different TANs of Oil. The effect of different TANs of oil on the extraction efficiency of ILs was studied by preparing the model oil with different TAN strengths, and the results are shown in Figure 5.

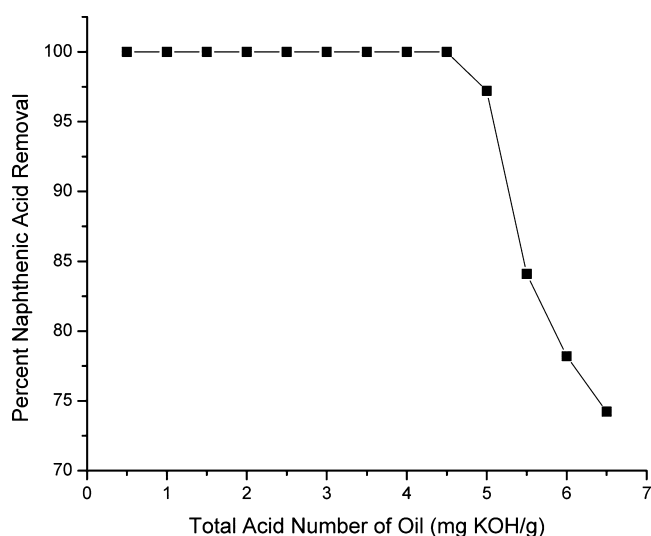


Figure 5. Effect of the increase in TAN on extraction efficiency of naphthenic acid (black ■, [N₁₁₁₁][OH] with IL/oil ratio of 0.0075) (stirring rate, 500 rpm; reaction time, 1 h).

Tetramethylammonium hydroxide was used as the model system because of its higher extraction efficiency among all of the ILs under study. The IL/oil ratio was kept constant, and all of the reactions were carried out at room temperature for 1 h. [N₁₁₁₁][OH] completely deacidified the model oil with a TAN up to 4.74 mg of KOH/g with an IL/oil ratio of 0.0075. [N₁₁₁₁][OH] was able to extract more than 72% naphthenic acid, even when the TAN of the model oil was increased to 6.73 mg of KOH/g. This result clearly indicates that hydroxide-based ILs have the potential to completely deacidify the high TAN model oil with an extremely low IL/oil ratio.

3.5. Recovery of Naphthenic Acid. After the complete extraction of naphthenic acid from model oil, attempts were made to recover the extracted naphthenic acid from the IL. The plausible mechanism of extraction and recovery of naphthenic acid is given in Figure 6. The picture of extraction and recovery of naphthenic acid is shown in Figure S4 of the Supporting Information.

The hydroxide anions in the ILs abstract the carboxylic acid proton in the naphthenic acid to form a tetraalkylammonium/tetraalkylphosphonium/cholinium naphthenate salt (compound II; Figure 6) and form a separate layer with dodecane (see the lower layer in Figure S4a of the Supporting Information). The highly basic hydroxide anion (OH⁻) from IL can easily abstract the carboxylic acid proton from naphthenic acid because of its acidic nature. All other hydrogen atoms in the naphthenic acid remain unaffected because of their non-acidic nature. The extracted naphthenic acid was recovered by

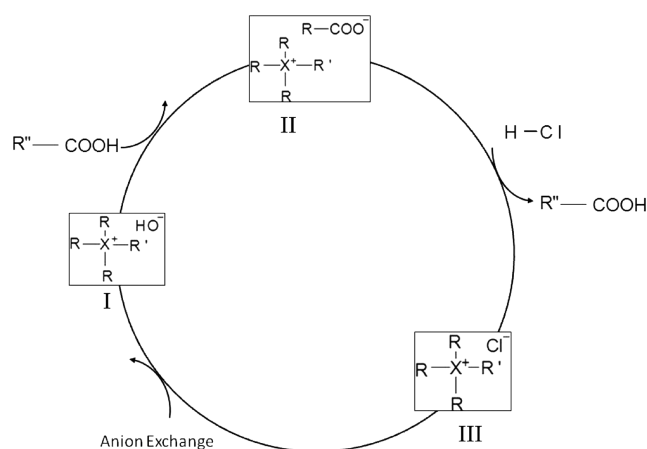


Figure 6. Plausible mechanism for deacidification of naphthenic acid (X, N/P; R, alkyl group; R', $\text{CH}_2\text{--CH}_2\text{--OH}$ or alkyl group; and R'', aliphatic, aromatic, or cyclic hydrocarbon).

the addition of an aqueous solution of a mineral acid to the naphthenate salt of the ILs. When the mineral oil was added to IL naphthenate salt, the naphthenate anion (RCOO^-) will abstract the H^+ ion from the mineral acid and result in the regeneration of naphthenic acid (RCOOH). On the other hand, the cationic part (tetraalkylammonium/tetraalkylphosphonium/cholinium) will coordinate with the halide anion (Cl^-/Br^-) to form the corresponding halide precursor ILs (compound III; Figure 6). Because of the high solubility of halide precursor ILs in water, they would not leach into water-insoluble naphthenic acid. Model oil was removed before adding the mineral acid solution. Two layers are formed because of the very low solubility of naphthenic acid in water (see Figure 4b of the Supporting Information). The upper layer was naphthenic acid, and the lower layer was the aqueous halide salt of the corresponding ILs. Naphthenic acid thus formed was isolated by simple extraction with diethyl ether and the evaporation of the solvent under vacuum (see Figure 4c of the Supporting Information). The halide salt of the tetraalkylammonium/tetraalkylphosphonium or choline cation was recovered by evaporating the water under vacuum. The Fourier transform infrared (FTIR) spectra for pure and regenerated naphthenic acids are shown in Figure 7.

From Figure 7, it is clear that the FTIR spectra for both the pure and regenerated naphthenic acids were similar. It indicates that the regeneration of naphthenic acid has been successful. The broad peak at 2956 cm^{-1} corresponds to the C–H stretch for alkanes. The strong peak at 1698 cm^{-1} indicates the presence of the carbonyl group (C=O) in carboxylic acid. The absorption at 1463 cm^{-1} is due to the C–H bend in alkanes. Another strong peak at 1258 cm^{-1} represents the C–O stretch in carboxylic acid. More than 95% naphthenic acid was recovered after the extraction with ILs. Of 100 mg of naphthenic acid extracted by $[\text{N}_{1111}][\text{OH}]$ from model oil [100 mg of naphthenic acid was added to model oil to obtain a TAN of $4.74 (\pm 0.01)$ mg of KOH/g], 95 mg of naphthenic acid was recovered by treating with mineral acids.

The halide salt of the tetraalkylammonium/tetraalkylphosphonium/choline formed during the regeneration of naphthenic acid can be converted to hydroxide ILs by anion-exchange resin²⁸ or treating with sodium or potassium hydroxide²⁹ and can be used for the next cycle of extraction. The current process is highly viable at a large scale compared to

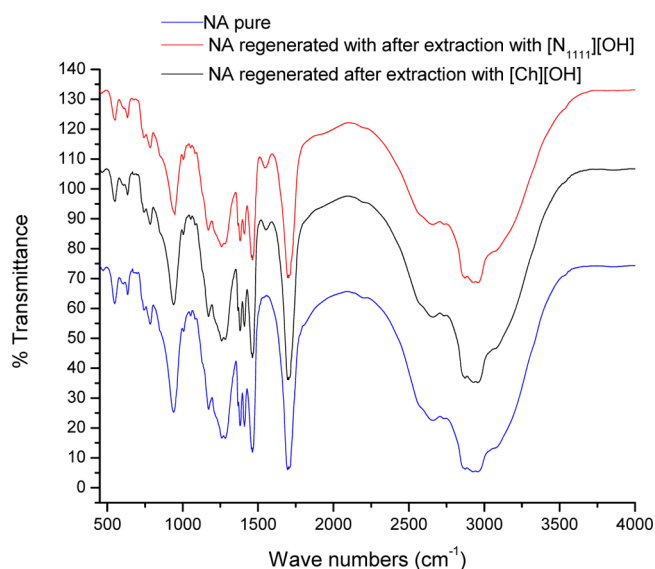


Figure 7. FTIR spectra of pure and regenerated naphthenic acids after extraction with $[\text{N}_{1111}][\text{OH}]$ and $[\text{Ch}][\text{OH}]$.

the conventional process because of its high extraction performance, the possibility of recyclability of the ILs used, and the simple procedure for the recovery of extracted naphthenic acid. For instance, the fiber film contactor⁵ (commercial process for production of naphthenic acid) requires 10 L of sodium hydroxide solution for the extraction of 1 L of crude naphthenic acid. The sodium sulfate brine solution formed after the extraction and regeneration of naphthenic acid (by addition of H_2SO_4) contains phenolic compounds, and their disposal is an environmental problem. In the current method, the ILs can be recycled for many cycles without compromising their extraction efficiency. In addition, the recovered naphthenic acid had a TAN in the range of refined naphthenic acids (225–310 mg of KOH/g). One of the problems associated with the use of ILs in the industrial process is their high viscosity. However, the current process has no such shortcomings because of the low viscosity of the aqueous solution of the ILs used. In terms of economic aspects, although the cost of ILs is high compared to the conventional solvents, the ILs used in this study showed 100% extraction efficiency for the first 5 cycles, they can be regenerated and reused, and recovered naphthenic acid is a value-added product. Hence, the current process is economically viable as well.

4. CONCLUSION

The hydroxide-anion-based tetraalkylammonium and tetraalkylphosphonium ILs are very effective in the complete deacidification of high TAN model oil. Only a very low IL/oil ratio is necessary for the complete extraction of naphthenic acid. When the alkyl spacer length on the cation increases, the extraction performance of the hydroxide-based ILs decreases. The plausible mechanism of extraction is the formation of naphthalenate salt of the tetraalkylammonium or tetraalkylphosphonium cation, resulting from the reaction between naphthenic acid and the hydroxide anion of ILs. The extracted naphthenic acid can be regenerated by the addition of an aqueous solution of a mineral acid. The hydroxide IL can be used several times for the extraction process without losing its activity. The results revealed that this method has the potential

to extract and regenerate naphthenic acids from high TAN crude oil.

■ ASSOCIATED CONTENT

■ Supporting Information

¹H NMR spectra of the completely deacidified model oil (Figure S1), [N₁₁₁₁]⁺ cation (before and after reaction with model oil; Figure S2), and [Ch]⁺ cation (before and after reaction with model oil; Figure S3), isolation and regeneration of naphthenic acid (Figure S4), and FTIR spectra of pure naphthenic acid (Figure S5) and naphthenic acid regenerated from [Ch][OH] (Figure S6) and [N₁₁₁₁][OH] (Figure S7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Fan, T. P. Characterization of naphthenic acids in petroleum by fast atom bombardment mass spectrometry. *Energy Fuels* **1991**, *5*, 371–375.
- (2) Schmitter, J.; Arpino, P.; Guiochon, G. Investigation of high-molecular-weight carboxylic acids in petroleum by different combinations of chromatography (gas and liquid) and mass spectrometry (electron impact and chemical ionization). *J. Chromatogr. A* **1978**, *167*, 149–158.
- (3) Hsu, C. S.; Dechert, G.; Robbins, W.; Fukuda, E. Naphthenic acids in crude oils characterized by mass spectrometry. *Energy Fuels* **2000**, *14*, 217–223.
- (4) Rudzinski, W. E.; Oehlers, L.; Zhang, Y.; Najera, B. Tandem mass spectrometric characterization of commercial naphthenic acids and a Maya crude oil. *Energy Fuels* **2002**, *16*, 1178–1185.
- (5) Briant, J. A.; Wessner, P. J.; Doyle, M. N. Naphthenic acids. *Kirk-Othmer Encyclopedia of Chemical Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, 1995.
- (6) Dettman, H. D.; Li, N.; Luo, J. Refinery corrosion organic acid structure and Athabasca bitumen. *CORROSION* **2009**; Atlanta, GA, March 22–26, 2009.
- (7) Alvisi, P. P.; Lins, V. F. C. An overview of naphthenic acid corrosion in a vacuum distillation plant. *Eng. Failure Anal.* **2011**, *18*, 1403–1406.
- (8) Qu, D.; Zheng, Y.; Jing, H.; Yao, Z.; Ke, W. High temperature naphthenic acid corrosion and sulphidic corrosion of Q235 and 5Cr1/2Mo steels in synthetic refining media. *Corros. Sci.* **2006**, *48*, 1960–1985.
- (9) Varadaraj, R.; Brons, C. Molecular origins of crude oil interfacial activity part 3: Characterization of the complex fluid rag layer formed at crude oil–water interfaces. *Energy Fuels* **2007**, *21*, 1617–1621.
- (10) Jones, D.; Watson, J.; Meredith, W.; Chen, M.; Bennett, B. Determination of naphthenic acids in crude oils using nonaqueous ion exchange solid-phase extraction. *Anal. Chem.* **2001**, *73*, 703–707.
- (11) Wang, Y.; Chu, Z.; Qiu, B.; Liu, C.; Zhang, Y. Removal of naphthenic acids from a vacuum fraction oil with an ammonia solution of ethylene glycol. *Fuel* **2006**, *85*, 2489–2493.
- (12) Gaikar, V.; Maiti, D. Adsorptive recovery of naphthenic acids using ion-exchange resins. *React. Funct. Polym.* **1996**, *31*, 155–164.
- (13) Wang, Y. Z.; Sun, X. Y.; Liu, Y. P.; Liu, C. G. Removal of naphthenic acids from a diesel fuel by esterification. *Energy Fuels* **2007**, *21*, 941–943.
- (14) Zhang, A.; Ma, Q.; Wang, K.; Liu, X.; Shuler, P.; Tang, Y. Naphthenic acid removal from crude oil through catalytic decarboxylation on magnesium oxide. *Appl. Catal., A* **2006**, *303*, 103–109.
- (15) Ding, L.; Rahimi, P.; Hawkins, R.; Bhatt, S.; Shi, Y. Naphthenic acid removal from heavy oils on alkaline earth-metal oxides and ZnO catalysts. *Appl. Catal., A* **2009**, *371*, 121–130.
- (16) Huddleston, J.; Rogers, R. Room temperature ionic liquids as novel media for ‘clean’ liquid–liquid extraction. *Chem. Commun.* **1998**, 1765–1766.
- (17) Ohno, H. *Electrochemical Aspects of Ionic Liquids*; John Wiley & Sons, Inc.: Hoboken, NJ, 2011.
- (18) Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- (19) Welton, T. Ionic liquids in catalysis. *Coord. Chem. Rev.* **2004**, *248*, 2459–2477.
- (20) Shi, L. J.; Shen, B. X.; Wang, G. Q. Removal of naphthenic acids from Beijiing crude oil by forming ionic liquids. *Energy Fuels* **2008**, *22*, 4177–4181.
- (21) Sun, Y.; Shi, L. Basic ionic liquids with imidazole anion: New reagents to remove naphthenic acids from crude oil with high total acid number. *Fuel* **2012**, *99*, 83–87.
- (22) Duan, J.; Sun, Y.; Shi, L. Three different types of heterocycle of nitrogen-containing alkaline ionic liquids treatment of acid oil to remove naphthenic acids. *Catal. Today* **2013**, *212*, 180–185.
- (23) Ballinger, B. H.; Sartori, G.; Savage, D. W. Process for neutralization of petroleum acids using overbased detergents. U.S. Patent 6,054,042 A, 1996.
- (24) Ries, D. G.; Roof, G. L. Choline for neutralizing naphthenic acid in fuel and lubricating oils. U.S. Patent 4,600,518 A, 1985.
- (25) Shah, S. N.; Mutalib, M. I. A.; Pilus, R. B. M.; Lethesh, K. C. Separation of naphthenic acid using hydroxide based ionic liquids. *Appl. Mech. Mater.* **2014**, *625*, 570–573.
- (26) Carvalho, P. J.; Ventura, S. P.; Batista, M. L.; Schröder, B.; Gonçalves, F.; Esperança, J.; Mutelet, F.; Coutinho, J. A. Understanding the impact of the central atom on the ionic liquid behavior: Phosphonium vs ammonium cations. *J. Chem. Phys.* **2014**, *140*, 064505.
- (27) Cope, A. C.; Trumbull, E. R. Olefins from amines: The Hofmann elimination reaction and amine oxide pyrolysis. *Org. React.* **2011**, *11*, 317–493.
- (28) Fukumoto, K.; Yoshizawa, M.; Ohno, H. Room temperature ionic liquids from 20 natural amino acids. *J. Am. Chem. Soc.* **2005**, *127*, 2398–2399.
- (29) Ranu, B. C.; Jana, R. Ionic liquid as catalyst and reaction medium—A simple, efficient and green procedure for Knoevenagel condensation of aliphatic and aromatic carbonyl compounds using a task-specific basic ionic liquid. *Eur. J. Org. Chem.* **2006**, 3767–3770.