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Nickel Tetraphenylporphine Extraction from Model Heavy Oil Using Ionic Liquids

Pradip Chandra Mandal

Abstract

Heavy metals containing compounds present in heavy oils create particular problems on their upgradation and refinement processes. The aim of this work is to extract nickel (II) tetraphenylporphine (NiTPP) from model heavy oils using ionic liquids (ILs). Exploring open literature, four different ILs such as 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM]TFSI), 1-ethyl-3-methylimidazolium octyl sulfate ([EMIM]OS), 1-butyl-3-methylimidazolium octyl sulfate ([BMIM]OS), and 1-methyl-3-octylimidazolium tetrafluoroborate ([OMIM]BF₄) were utilized in this study. Potential experiments were conducted in a batch-type extractor (design temperature of 250°C and pressure of 6 MPa) at temperatures of 0–180°C. The extracted samples were analyzed using UV-visible spectrophotometer to determine the concentration of metallic compounds. The results show that NiTPP extraction was increasing with increasing temperature and treatment time and approximately 63% NiTPP was extracted in [BMIM]OS at a temperature of 100°C and a treatment time of 40 min. It is also observed that NiTPP extraction was decreasing above temperature 100°C. The extraction kinetics followed first-order kinetics with respective activation energy and pre-exponential factor of 1.24 kcal per mol and $2.156 \times 10^{-3} \text{ s}^{-1}$. Therefore, the IL, [BMIM]OS, is capable to extract NiTPP from model heavy oils at temperatures below 100°C indicating the effectiveness of this IL to extract NiTPP from heavy oils.

Keywords: heavy oil, heavy metal, ionic liquid, extraction kinetics, activation energy

1. Introduction

1.1 Heavy oil

Crude oil is a naturally occurring unrefined petroleum product that contains hydrocarbons 50–97%, nitrogen, oxygen, and sulfur-containing organic compounds which typically make up between 6 and 10%, while metals such as copper, nickel, vanadium, and iron account for less than 1% of the total composition. According to Koliander [1], some of the metals found originated from the crude itself, while others were added during production and transportation and migration of metals into the crude oil due to corrosion of pipelines, and tasks could also explain the existence of heavy metal in heavy oil. According to the API gravity (degree API = 141.5/specific gravity = 131.5), crude oil can be classified as follows:

Light crude oil: API gravity higher than 31.1.

Medium crude oil: API gravity from 31.1 to 22.3.

Heavy crude oil: API gravity from 22.3 to 10.

Extra-heavy crude oil: API gravity below 10.

Heavy oil is a crude oil having a viscosity generally greater than 10 cP and gravity below 22.3° API [2]. It contains high-molecular-weight hydrocarbons having more than 15 carbon atoms in its chain [3] and hence has low hydrogen-to-carbon ratios. In addition, it has elevated levels of heteroatom-containing compounds such as sulfur, nitrogen, oxygen, and metals. Moreover, it is highly acidic. The presence of heavy metal in heavy oil has been identified throughout the years, and although it only accounts for 1% of the total composition, accumulation of these metals over a long period of time could hinder the upgrading and the refinery process.

1.2 Heavy metal removal processes

Heavy oil generally needs to undergo several processes before it can be sold to the consumers to meet their specification. Metal removal process is one of the processes involved in the refinery stage where the hydrocarbons are treated to remove heavy metal before delivering into the downstream process to increase its market value. The presence of heavy metals, such as nickel and vanadium in the heavy oil, could lead to serious problems during any of the heavy oil refinement and upgradation processes. Hence, oil and gas companies of the world are interested in finding ways to remove the heavy metals from the heavy oil. Some of the problems caused by these metallic compounds are discussed below:

- a. *Environmental effects:* Vanadium is the most common metal found in heavy oil. It produces vanadium pentoxide when it burns during the combustion process [4, 5]. Vanadium pentoxide is a toxic material and is harmful to the environment. In addition, less volatile metals and metal compounds can be found in great amount in the ashes of heating oil, which also disperse into the environment which could lead to a serious environmental problem [1]. Due to the hazardous and carcinogenic nature of heavy metal, it could have caused serious health issues, such as nervous system damage, cancer, and, in extreme cases, death.
- b. *Industrial damages:* When heavy metal-containing heavy oil is burned during combustion process, the existing heavy metals would be stored in ashes which will result in the corrosion of the container. If heavy oil is used in power generation, it can lead to the corrosion of the turbine which will eventually lead to operational failure. Apart from this, once crude oil is produced, it will then be transported to a place where it will be processed. However, corrosion in pipelines could occur if there is a presence of heavy metal. In addition, the effective diameter of the pipeline could also be reduced due to the deposition of metal-containing compounds in the pipeline. In the oil industry, removal of the heavy metal is necessary to prolong the lives of catalysts in the fluid catalytic cracking [1].
- c. *Cost:* As a result of decreasing amount of light hydrocarbon worldwide, oil and gas companies have taken interest in developing heavy oil into useful products. Generally, oil and gas companies invest a huge amount of money especially in terms of CAPEX (capital expenditure) and OPEX (operating expenditure). The presence of heavy metals in the heavy oil however causes spoilage to the

equipment, hence resulting in further increment of the operating and maintenance costs. Thus, removal of heavy metal is a vital stage in upgrading the heavy oil.

Nowadays, there are various methods available in removing heavy metals from the heavy oils and its fractions which can be divided into several categories: physical, chemical, electrochemical, and catalytic hydro-treatment. Some of the methods in the category are chemical precipitation, adsorption process, membrane filtration, electrodialysis, and photocatalysis. These heavy metal removal processes come with its pros and cons with some of it being high in terms of operational costs, and other methods such as photocatalysis have a long processing time with very limited applications to the industry. The advantages and disadvantages of conventional heavy metal removal processes are summarized in **Table 1**.

Removal of heavy metals especially nickel (Ni) and vanadium (V) has been investigated in the recent years as more and more companies have taken the interest in upgrading heavy crude oil. Researchers all over the world have developed many metal removal methods and have published their findings in open literature. Although some of the methods have been proved to be efficient, unfortunately others have not shown a significant result within a specified amount of time. Therefore, further studies are essential to investigate the best way on removing heavy metal present in heavy oil. **Table 2** shows the experiments that have been done in removing heavy metal present in heavy oil under different sets of operating conditions.

Limited research works on the removal of heavy metal in heavy oil using ionic liquid (IL) are available in open literature. Most of the written papers are focusing on the removal of metal in wastewater or industrial effluent rather than in heavy oil.

1.3 History of IL

Ionic liquids (ILs) are chemical compounds of ion structure which have the melting point below 100°C or even at room temperature [16]. An IL contains positively

Treatment method	Advantages	Disadvantages	References
Photocatalysis	Less harmful and toxic by-products Simultaneous removal of both metals and organic pollutants	Limited applications Long removal time	[6, 7]
Chemical precipitation	Low initial cost Simple operation	Sludge generation requires additional operational cost for its disposal	[8]
Adsorption	Low cost Wide pH range Simple operating conditions	Production of waste products requires additional operation cost Low selectivity	[9, 10]
Membrane filtration	High separation selectivity Small space requirement	Requires frequent membrane replacement due to membrane fouling	[8]
Electrodialysis	High separation selectivity	Increased operational cost due to membrane fouling and high energy consumption	[11]

Table 1.
Advantages and disadvantages of conventional heavy metal removal processes.

Experiment	Operating conditions	Removal	References
Microwave-assisted nickel and vanadium removal from crude oil	Microwave power = 600–800 W Irradiation time = 3 min Dosage methane sulfonic acid = 2 wt%	Ni = 76.8% V = 83.2%	[12]
Using supercritical water (SCW) to remove nickel from Ni-EP	T = 450–490°C P = 25–45 MPa Time = 180 min	Ni = 90.64%	[13]
Mixed solvent (SCW) and toluene without the addition of any catalyst to remove vanadium	T = 410–490°C P = 25MPa Time = 180 min	V = 80.26%	[4]
Removing nickel from NiTPP using SCW in the presence of toluene	T = 450–490°C P = 25–35 MPa Time = 90 min	Ni = 65.65%	[14]
Effect of cationic starch on removal of Ni and V from crude oils under microwave irradiation	Microwave power = 300 W Irradiation time = 5 min T = 60°C	Iran crude oil Ni = 50%, V = 76% Shengli crude oil Ni = 60%, V = 79%	[15]

Table 2.
Methods in removing heavy metal from heavy oil.

charged cation and negatively charged anion. The commonly used cations are based on ammonium, sulfonium, phosphonium, imidazolium, pyridinium, picolinium, pyrrolidinium, etc. with different substitutes. The generally used anions are halogen (first-generation ILs), organic ($[\text{CH}_3\text{COO}]^-$, $[\text{CF}_3\text{CO}_2]^-$, $[\text{PhCOO}]^-$, etc.) or inorganic ($[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{AlCl}_4]^-$, etc.). Though the properties of ILs depend on mutual fit of cation and anion, size, geometry, and charge distribution, they well fit in the assumptions of green chemistry. In 1998, Anastas and Warner have formulated 12 principles of green chemistry [17]. ILs meet three pillars of these principles—safer solvents (principle no. 5), provision of energy efficiency (principle no. 6), and usage in catalytic reactions (principle no. 9) [16]. **Figure 1** represents a simplified model of an irregular system of ions present in the IL structure.

IL precursors are quaternary ammonium halide salts that are known from the 1890s. But these salts are widely used and tested in the twentieth century for different applications such as synthesis, disinfection, fabric softener, wood preservation, and so on. These salts are used as IL from 1996.

A low-melting organic salt has been observed as red oil in the mid-nineteenth century for the first time. This oil was produced as a by-product in the Friedel-Crafts reaction of benzene alkylation with aluminum chloride as a catalyst. The red oil known as chloroaluminate, σ -complex, was structured after the popularization of nuclear magnetic resonance technique as shown in **Figure 2**.

Gabriel and Weiner produced ethanolanmonium nitrate with the melting point (MP) of 52°C in 1888. Paul Walden [18–20] in 1914 produced ethylammonium nitrate with the MP of 12°C. This compound is considered as the first IL by many researchers [20], and Walden is known as the father of ILs. But this compound has no use due to its high reactivity.

In 1934, US patent no. 1943176 has claimed that the cellulose has dissolved in 1-benzylpyridinium chloride, 1-ethylpyridinium chloride, and so on at the temperature above 100°C. In 1948, just after World War II, 1-ethylpyridinium bromide has appeared in another US patent [19] for the electrodeposition of aluminum

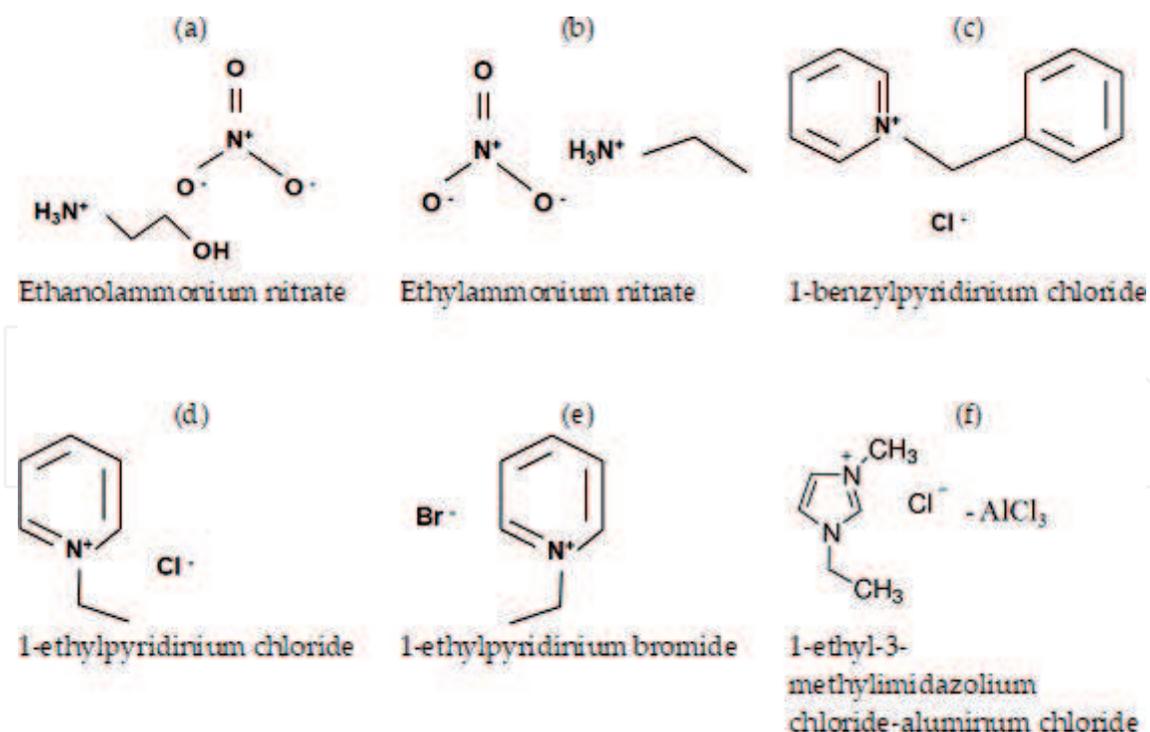


Figure 1.
 Structure of historic ILs (ILs developed in the 20th century).

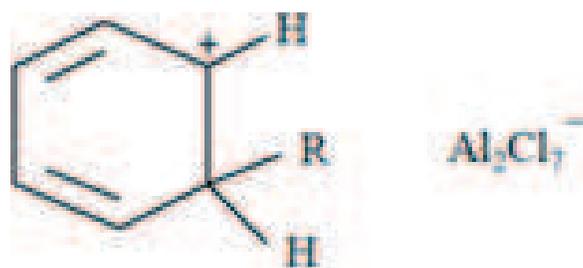


Figure 2.
 Chloroaluminate, σ -complex, in the Friedel-Crafts reaction.

from aluminum (III) chloride. At that time, they were unable to investigate the IL because of the complex mixture of bromide and chloride salts. Later, in 1975, the physical and chemical properties of this IL were investigated by Osteryoung group aided by Bernard Gilbert [19]. The IL attracted the international researchers in the 1970s as aluminum chloride-based molten salts were used in the 1940s for the formation of nuclear warhead batteries. Wilkes in 1970 has tried to develop better batteries for nuclear warheads and space probes as they needed molten salts to operate [18]. Wilkes and Hussey have discovered an IL system which is liquid at room temperature known as 1-ethyl-3-methylimidazolium chloride-aluminum chloride ([EMIM]Cl-AlCl₃). This was the first appropriate example of IL system [19]. ILs emerged as solvents in the late 1990s.

ILs are interesting compounds due to their variable properties such as they are not all noncorrosive, but they can be designed to be noncorrosive [21]. Generally, ILs have negligible vapor pressure, high thermal and chemical stability, nonflammability, and numerous potential applications, such as microwave-assisted organic synthesis, catalysis, biocatalysis, separation, extraction, electrochemistry, nanomaterial synthesis, polymerization reactions, and corrosion inhibitors [22]. They have potential efforts to replace and optimize the existing petroleum-based technologies and processes.

This chapter explores the capability of ILs to extract NiTPP from model heavy oil that is not disclosed previously in open literatures.

2. Materials and methods

2.1 Materials

Based on literature survey, four specific ILs as stated in **Table 3** were utilized to extract nickel tetraphenylporphyrin (NiTPP) from model heavy oil. These ILs were purchased from Sigma-Aldrich and used without any modification. The heavy metal-containing compound, NiTPP, and the solvent, toluene, were also purchased from Sigma-Aldrich and used without further treatment.

2.2 Model heavy oil preparation

Model heavy oil was prepared by dissolving NiTPP in toluene. For producing 250 mL 0.06 M model heavy oil solution, exactly 0.015 g of NiTPP was taken in a beaker. Then required volume of toluene was added in the beaker at least three occasions at a volume of 50 mL in each occasion to ensure complete and stable mixing. The beaker was then placed on a hot plate, and the solution was stirred using a magnetic stirrer at a temperature of 50°C and a speed of 200 rpm. After the completion of mixing, the resultant solution was transferred into 250 mL volumetric flask, and toluene was added up to the mark to make a 250 mL solution.

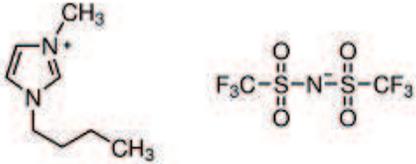
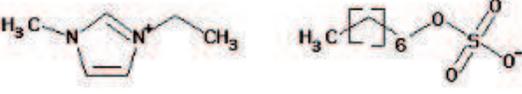
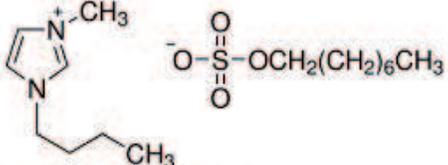
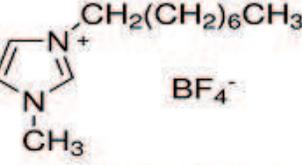
<p style="text-align: center;">(a)</p> <p>Name: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide Synonym: [BMIM]TFSI Empirical Formula: $C_{12}H_{15}F_6N_3O_4S_2$ Molecular weight: 419.36 g/mol Structural Formula:</p>  <p>Signal word: Danger Target organ: Nervous system</p>	<p style="text-align: center;">(b)</p> <p>Name: 1-ethyl-3-methylimidazolium octyl sulfate Synonym: [EMIM]OS Empirical Formula: $C_{14}H_{22}N_2O_4S$ Molecular weight: 320.45 g/mol Structural Formula:</p>  <p>Melting point: -9 degC Density: 1.095 g/cc (20 degC)</p>
<p style="text-align: center;">(c)</p> <p>Name: 1-butyl-3-methylimidazolium octyl sulfate Synonym: [BMIM]OS Empirical Formula: $C_{14}H_{22}N_2O_4S$ Molecular weight: 348.50 g/mol Structural Formula:</p>  <p>Signal word: Warning</p>	<p style="text-align: center;">(d)</p> <p>Name: 1-methyl-3-octylimidazolium tetrafluoroborate Synonym: [OMIM]BF₄ Empirical Formula: $C_{12}H_{23}BF_4N_2$ Molecular weight: 282.13 g/mol Structural Formula:</p>  <p>Density: 1.12 g/cc (20 degC)</p>

Table 3.
General information of four used ILs.

2.3 Experimental method

The ILs and model heavy oil were taken in an autoclave reactor at a ratio of 1:10 (v/v). Then the reactor was loaded into an oven which was preheated to the planned temperatures of 0–180°C. The reactor was removed from the oven after a specific treatment time of 10–40 min. and kept under a water bath to cool the reactor up to room temperature. The samples were then collected into the separating funnel by washing the reactor interior at least three times with toluene. Two layers were formed after allowing sufficient time—the top is NiTPP solution portion, and the bottom is NiTPP-extracted IL portion. The top portion was separated and made ready for analysis.

2.4 Analytical method

Out of two layers, the separated top layer was analyzed using UV-visible spectrophotometer (UV-VIS), Perkin Elmer Lambda 26 model, to find out the concentration of NiTPP. A cuvette, size of 12.5 × 12.5 × 45 mm, was used to place the samples in the UV-VIS. Toluene is used as the reference solvent.

A calibration curve, a plot of the concentration of NiTPP vs. absorbance, was plotted using five known samples of NiTPP at the beginning of experiments. The best-fit curve was a straight line almost passing through the origin. After analyzing the treated samples, the concentration of NiTPP in the samples was calculated using the aforesaid calibration curve. The following term is used in this study.

NiTPP extraction was calculated using Eq. (1):

$$\text{NiTPP extraction (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of NiTPP in the toluene solution and C_t is the concentration of NiTPP in the toluene solution at treatment time, t .

The experiments were carried out three times. The error margin of the achieved data was less than 5 with 96% confidence level.

3. NiTPP extraction using ILs

3.1 Effect of ILs on NiTPP extraction

Four toluene (boiling point 110.6°C at 0.01 MPa and critical point 318.64°C at 4.109 MPa) insoluble imidazolium-based ILs such as [BMIM]TFSI, [EMIM]OS, [BMIM]OS, and [OMIM]BF₄ were utilized in this study to extract NiTPP from model heavy oil as they have a capability to extract some metals. Hildebrand's solubility parameter (HSP) of different solvents and ILs are displayed in **Table 4**. NiTPP is a purple solid crystal. Mandal et al. in 2011 [14] have disclosed that this compound is soluble in toluene (HSP = 18.3) and xylene (HSP = 18.20) but insoluble in water (HSP = 48.00) indicating that the HSP of this compound is close to 18.00. The toluene-soluble NiTPP was purple in color and had intensive absorption peaks in the visible region.

The IL, [BMIM]TFSI was not dissolved in toluene and water at room temperature. It was not capable of extracting NiTPP at this temperature. Hamidova et al. in 2015 [25] have disclosed that [BMIM]TFSI IL has a density of 1436.76 and 1385.21 kg/m³ at 25 and 80°C. When NiTPP solution was treated with [BMIM]TFSI at a temperature of 75°C and a treatment time of 30 min, the color of [BMIM]TFSI did not change (**Figure 3a**) at all, indicating that it was not able to extract NiTPP

Name of solvent or ILs	Hildebrand's solubility parameter (HSP) (MPa ^{0.5}) [23, 24]
[BMIM]TFSI	26.70 at 25°C
[EMIM]OS	30.20 at 25°C
[BMIM]OS	22.83 at 25°C, 23.25 at 55°C
[OMIM]BF ₄	22.50 at 25°C
Toluene	18.30 at 25°C
Xylene	18.20 at 25°C
Water	48.00 at 25°C

Table 4.
HSP of different solvents and ILs.

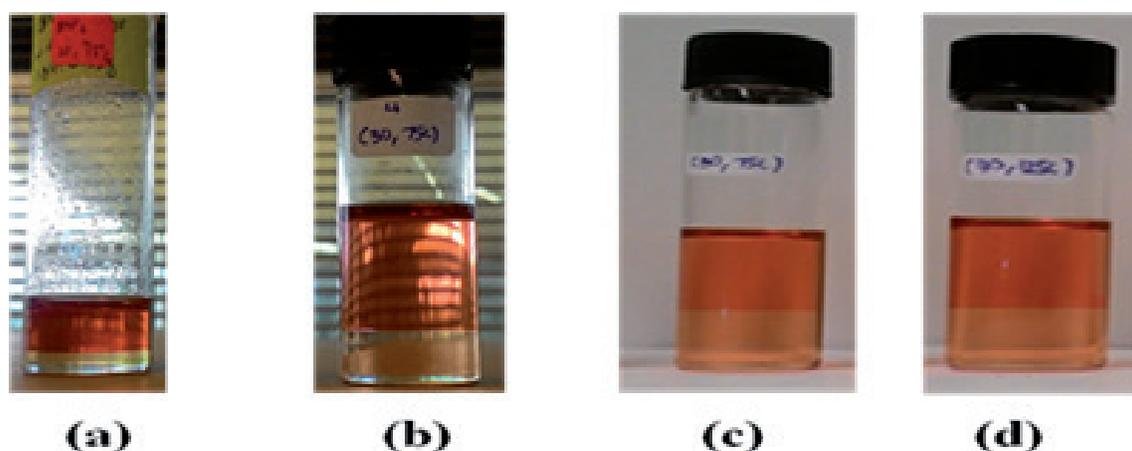


Figure 3.
Effect of ILs on NiTPP extraction at a temperature of 75°C and a treatment time of 30 min: NiTPP extraction using (a) [BMIM]TFSI, (b) [EMIM]OS, (c) [BMIM]OS and (d) [OMIM]BF₄.

though the density of this IL was reduced with the increase of temperature. This was probably due to the unequal HSP of NiTPP and [BMIM]TFSI.

Similarly, the IL, [EMIM]OS (density = 1095 kg/m³) was not dissolved in toluene at room temperature. It is lighter than [BMIM]TFSI. When NiTPP solution was treated with [EMIM]OS at a temperature of 75°C and a treatment time of 30 min., the color of [EMIM]OS slightly changed (**Figure 3b**) due to some of the NiTPP being extracted into this IL. The IL, [BMIM]OS, is insoluble in toluene. When the NiTPP solution was treated with [BMIM]OS at a temperature of 75°C and a treatment time of 30 min., the color of [BMIM]OS was darker than the color of [EMIM]OS (**Figure 3c**). The IL, [OMIM]BF₄ (density = 1120 kg/m³), is insoluble in toluene at room temperature. When the NiTPP solution was treated with [OMIM]BF₄ at a temperature of 75°C and a treatment time of 30 min, the color of [OMIM]BF₄ was darker than the color of [EMIM]OS (**Figure 3d**) but very close to [BMIM]OS. This means that [BMIM]OS and [OMIM]BF₄ are more efficient in order to extract NiTPP from the NiTPP solution. For the next studies, [BMIM]OS is used due to its availability and cheapness.

3.2 Effect of temperature of [BMIM]OS on NiTPP extraction

Variation of NiTPP extraction in [BMIM]OS as a function of temperature is shown in **Figure 4**. It is observed that NiTPP extraction was increasing with temperature up to 100°C, and after that, NiTPP extraction was decreasing with increasing

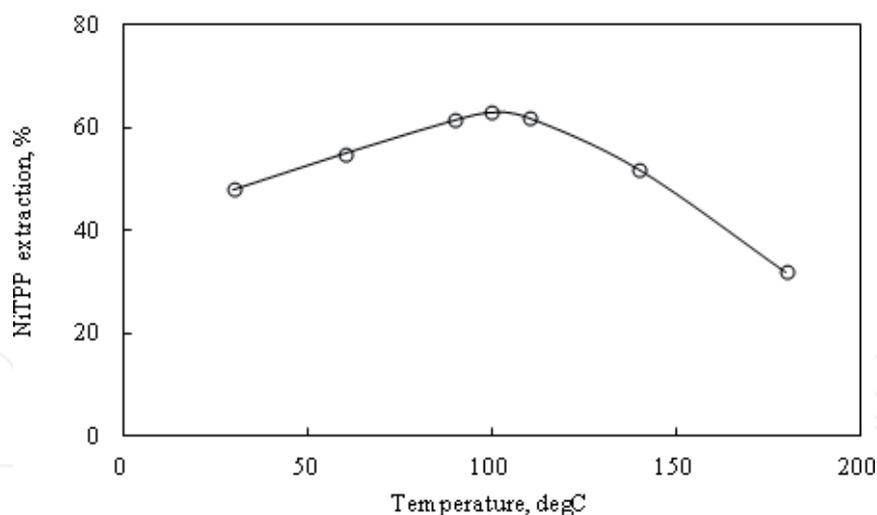


Figure 4.
Variation of NiTTP extraction in [BMIM]OS at a function of temperature.

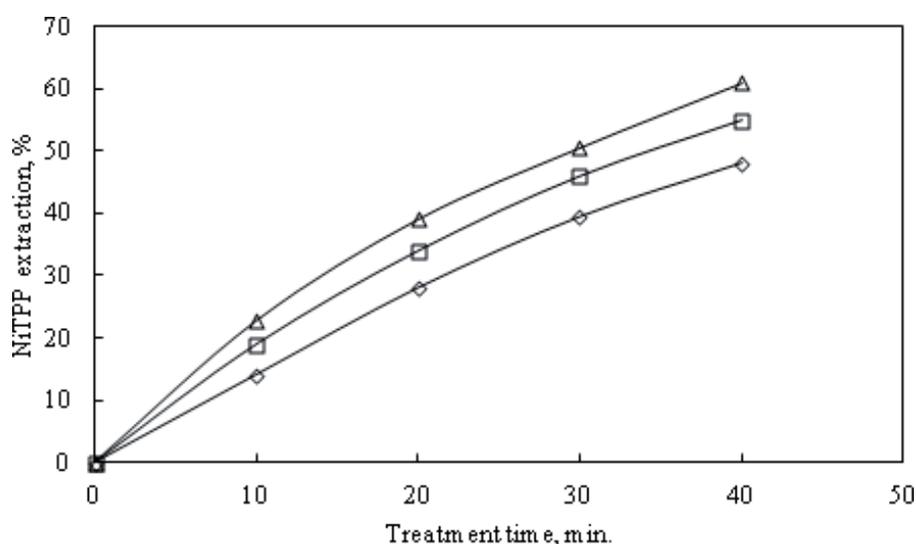


Figure 5.
Variation of NiTTP extraction at a function of temperature and treatment time (symbol: \diamond , at temperature of 30°C; \square , at temperature of 60°C; and Δ , at temperature of 90°C).

temperature. Maximum 63% NiTTP was extracted at a temperature of 100°C and a reaction time of 40 min. Thus, [BMIM]OS was effective to extract NiTTP at temperatures below 100°C. The reason is that viscosity of IL normally reduces gradually with the increase of temperature. Hence, NiTTP mixed well with IL by increasing the collisions between them. Such viscosity-temperature criteria no longer exist after a temperature exceeding 100°C for the case of IL [BMIM]OS because this IL decomposed at a temperature exceeding 100°C. Therefore, low temperature was favorable to extract NiTTP using this IL.

3.3 NiTTP extraction at temperatures below 100°C

Figure 5 shows that NiTTP extraction increased with increasing reaction temperature and time. Approximately 61% NiTTP was extracted at a temperature of 90°C and a treatment time of 40 min. One reason for this is that NiTTP and IL mix properly with increasing temperature, increasing their respective collisions events and thus increasing treatment rate. Mandal et al. in 2015 [26] have disclosed

that IL molecules themselves could form cage structure through specific chemical bonds with the increase of treatment time. In this cage, the objective molecules would be captured through the formation of liquid clathrate due to the π - π interaction between ILs and objective molecules. This was the reason of increasing NiTPP extraction with the increase of treatment time.

3.4 NiTPP extraction kinetics

Extraction kinetics is important for good extractor design. To determine the extraction order, a kinetic plot of $\ln(1-X)$, where X denotes fraction of NiTPP extraction, versus reaction time (t , min) is constructed (Figure 6). The NiTPP extraction was close to zero at zero treatment time. Each set of data gives a straight line obtained with the least square method that passes almost exactly through the origin indicating first-order kinetics with respect to NiTPP extraction, and it follows the kinetics equation [Eq. (2)]:

$$\ln(1 - X) = kt \tag{2}$$

where k is rate constant in time^{-1} .

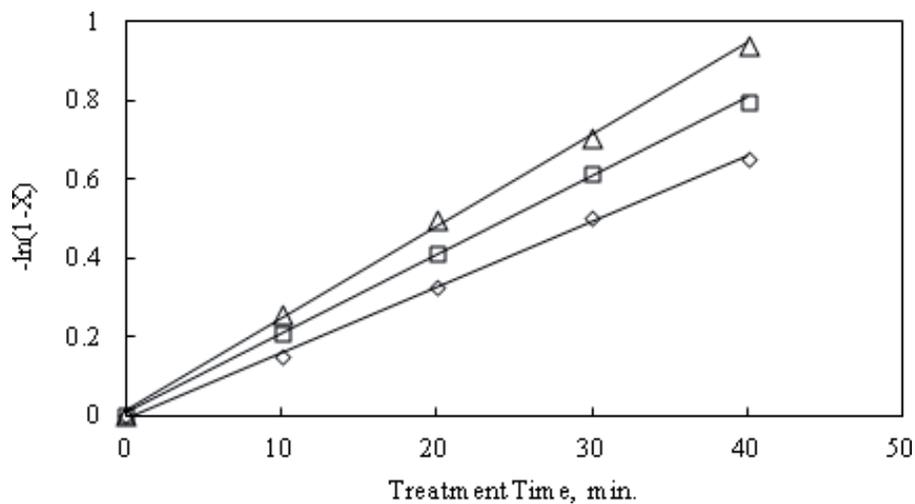


Figure 6. NiTPP extraction kinetics plot (symbol: ◇, at temperature of 30°C; ◻, at temperature of 60°C; and △, at temperature of 90°C).

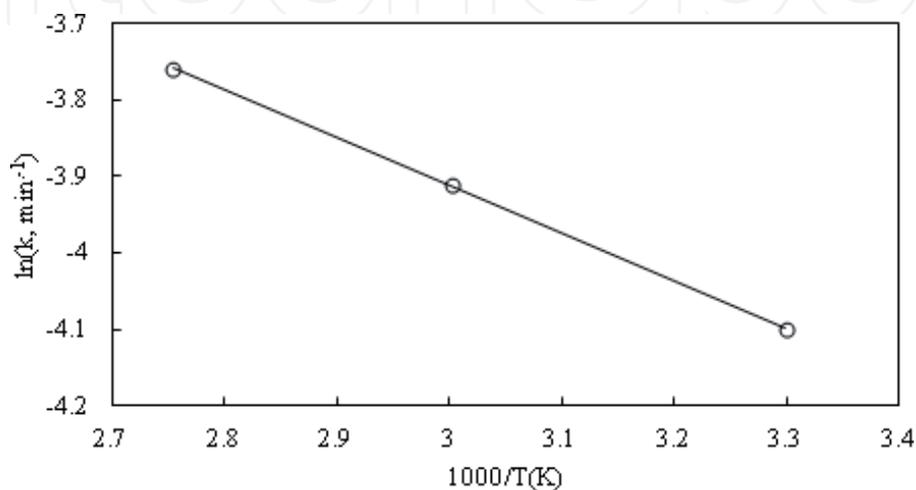


Figure 7. Arrhenius plot.

Reaction kinetics analyses of this study were tested and evaluated to a maximum of 61% NiTPP extraction as kinetics data were more compatible with first-order kinetics at this extent [27]. From the slope of the straight lines of **Figure 6**, the respective rate constant was determined, and an Arrhenius-type temperature dependency acidity removal rate constant plot was then plotted (**Figure 7**). By exploring this plot, activation energy and pre-exponential factor of the said extraction process were estimated with respective values of 1.24 kcal per mol and $2.156 \times 10^{-3} \text{ s}^{-1}$. Thus, the Arrhenius equation for NiTPP extraction can be rewritten as shown in Eq. (3):

$$k_{\text{NiTPP extraction}} = 2.156 \times 10^{-3} e^{-\frac{1.24}{RT}}, \text{ temperature below } 100^\circ \text{C} \quad (3)$$

4. Conclusions

The IL-based metal extraction from heavy oil process is presented in this study. The IL, [BMIM]OS, is capable to extract NiTPP from model heavy oil, and approximately 63% NiTPP was extracted at a temperature of 100°C and a treatment time of 40 min. The extraction is dependent on temperature and treatment time at temperatures below 100°C. The time dependency extraction kinetics follows first-order kinetics with activation energy of 1.24 kcal per mol and pre-exponential factor of $2.156 \times 10^{-3} \text{ s}^{-1}$. Therefore, IL-based metal extraction processes can attract the researcher's attention due to their greenness and separability tendency after using.

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