Fundamental studies on extraction of vanadyl oxide tetraphenyl porphyrin (VO TPP) presence in heavy oil model using toluene assisted ionic liquids

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Abstract. The demand on petroleum resources are increasing in recent years but the production of conventional oil is depleted. Hence, the unconventional oil seem to be an alternative. Unfortunately, the value of heavy oils are lower than conventional oils because of the content of contaminants such as heavy metals. These heavy metals cause problems during the upgrading process. It tends to accumulate during distillation, poisoning the catalyst and will cause injurious to the wall of furnace. The aim for this work is to remove Vanadyl Oxide Tetraphenyl Porphyrin (VO TPP) from heavy oil model using toluene-assisted ionic liquids (ILs). Temperatures used are 30˚C, 60˚C, and 90˚C at mixing time of 30 minutes, 60 minutes, and 90 minutes. Result shows 1-ethyl-3-methylimidazolium octyl sulfate (EMIM OS) have higher efficiency of VO TPP removal compared to 1-butyl-3-methylimidazolium octyl sulfate (BMIM OS). Although EMIM OS removed VO TPP higher than BMIM OS but the removal was decreased at 90˚C. The optimum extraction achieved when using EMIM OS is about 45 % removal at 30˚C and 30 minutes. Thus, EMIM OS is suggested to be used as it capable to remove VO TPP at minimal temperature and lowest mixing time which low operating cost.

1. Introduction

The amount of conventional oil is depleting day by day with increasing market demand. Study shows that world conventional production after 2025 is likely to be quite flat and the gap between the production and demand is large and need to be replace by unconventional oil as alternative [1]. Heavy oil resources from around the world are mostly located Venezuela, Canada, United State, Middle East and Russia [2]. Unfortunately, heavy crude oil has low value in market price due to its contaminants, high viscosity and density which make the production process more difficult [3]. Heavy oil is unconventional oil with American Petroleum Institute (API) gravity 10˚ and 20˚ [4].

In global, the heavy oil and bitumen resources is estimated around 6.2 trillion barrels, according to The World Energy Outlook from International Energy Agency. However, this heavy oil is not well commercialized as it having high amount of impurities such as heavy metals. Heavy metals found in heavy
oil are chromium, copper, nickel and vanadium. The most abundant and undesired heavy metals are nickel and vanadium [5]. Mandal et al, stated that the most abundant trace elements in heavy oil are vanadium and nickel which identified at level ranging up to 200 ppm to 2000 ppm [6]. Approximately, 2% to 54% of vanadium and 1% to 47% of nickel in crude oil occur as extractable metalloporphyrins (MPs) [6]. Previously, several technologies have been used to remove the heavy metals in heavy crude oil. Hydro treatment process which is the alternative for delayed coking gave disadvantages in removing heavy metals [7]. This costly method only able to produce 50-60% of useful residual oil, and the remainder contain high sulphur fuel oil. Same goes to vis-breaking and solvent deasphalting where both of these methods are inefficient and costly [7]. Due to uneconomical and unpractical existence methods, researchers still exploring new method to develop green technology to remove heavy metals from crude oil.

Ikyerene et al. reports on removing metal ions such as nickel, vanadium, and sulphur from heavy oil using natural zeolite. The result revealed that zeolite is good to remove a specific metal ion from the crude oil. However, this method is ineffective as zeolites deactivated due to deposition of heavy compounds in crude oil besides having low efficiency of metal ion removal [8]. In 2012, Ameur et al. proposed salting out separation method to remove metal ions from heavy crude oil. The result shows that 10 % (vol) of NaCl provided the best window for separation at 100 ppm heavy oil, while 20 vol % was needed for 1000 and 2000 ppm heavy oil. The advantage of this technique was able to extract highly charged molecules. The downside of this technique is it consumes high cost and the efficiency of removal is low [9]. Wang et al. was using a series of cationic starches with different degrees of substitution synthesized on removal of nickel and vanadium from Iranian and Shengli crude oils by a microwave-dry process. As the result, they found that the optimum conditions were 200 mg/L of CS4, 300 W microwave power and 5 minutes microwave time. Under these conditions, the removal efficiencies of nickel and vanadium were approximately 60 % and 80 % respectively. The disadvantage of this technique are it costly as it consumed high energy, and the temperature control is very difficult [10].

The objectives of this study is VO TPP extraction from model heavy using toluene-assisted ionic liquids (ILs). The molecular structure of VO TPP can be found in Figure 1. Subcritical toluene is a condition where the temperature of toluene is between boiling point temperature (110 °C) and critical point temperature (318.64 °C). The use of toluene is because it is highly diffusive and a good solvent to asphaltene where most organometallic species in heavy oil are agglomerated. ILs get attention among researchers and widely used in industry nowadays as it is known as green solvent. The uniqueness of ILs are it is environmentally friendly, good solubility, thermally stable, negligible vapor pressure and noncorrosive [11]. Earlier studies show that ILs has been applied in many areas. There are electrochemistry [12], chemical engineering [13], and extraction purpose such as glycerin extraction from palm oil based biodiesel [3].

![Figure 1. Molecular structure of vanadyl oxide tetraphenyl porphyrin](image)
2. Methodology

2.1. Material and Apparatus
Vanadyl Oxide Tetraphenyl Porphyrin (VO TPP), 1-ethyl-3-methylimidazolium Octyl Sulfate (EMIM OS), and 1-butyl-3-methylimidazolium Octyl Sulfate (BMIM OS) were purchased from Avantis Laboratory Supply, Malaysia. The other chemical being used was toluene. The chemicals were used without further treatment. VO TPP is purple crystal with empirical formula C_{44}H_{24}N_{4}VO and molecular weight of 679.66 g/mol, EMIM OS having molecular weight of 320.45 g/mol and BMIM OS having molecular weight of 348.502 g/mol. Toluene was used as a solvent.

2.2. Equipment used
The experiments were performed in 25 mL autoclave reactor invented by Shanghai Yanzheng Experiment Instrument Co., Ltd., China, and designed for maximum temperature of 230°C and pressure of 3 MPa (gauge). The reactor is made of stainless steel, which is durable, and gas-tight. Meanwhile, inner chamber of the reactor is polytetrafluoroethylene (PTFE) structure to minimize corrosion.

The analysis was carried out on UV-visible spectrophotometer Perkin Elmer Lambda 25 model. 12.5 mm × 12.5 mm × 45 mm cuvette was used and the reference used was toluene. Lambert-Beer Law was applied in order to compute the concentration of porphyrin and its hydrogenated intermediate compounds.

2.3. Generating Calibration Curve
Metal compound solution was prepared by dissolving 0.015 g of VO TPP crystal in 50ml of toluene at the temperature of 50°C with 200 rpm. 150 ml of toluene was further added in three occasions, 50 ml each occasion over certain period. Once VO TPP was completely dissolved in toluene, the solution was transferred into 250ml volumetric flask.

For construction of the calibration curve, five standard solutions were prepared. 0.5 ml, 1.0 ml, 1.5 ml, 2.0 ml and 2.5 ml was measured from the metal compound solution and transferred into different 25 ml volumetric flask. Toluene was added into the volumetric flask up to the 25ml mark. All the standard solutions are analyze using UV-Visible Spectrophotometer (UV-Vis) to determine the concentration of porphyrinic reactant as well as the reactant intermediate in the samples. The analysis was carried out on UV-Visible spectrophotometer Perkin Elmer Lambda 25 model with 200 – 700 range of wavelength. 12.5 × 12.5 × 45 mm cuvette was used, and the reference used was toluene. Lambert-Beer Law was applied to compute the concentration of porphyrin and its hydrogenated intermediate compounds. The graph of absorbance against wavelength was shown in Figure 2.

2.4. Experimental Procedure
0.5 ml of ionic liquid and 5 ml of heavy oil model was loaded into the reactor. The reactor was placed on top of hot plate and the experiment condition is set. Once the parameter was set, the reactor is left on the hot plate for few minutes to equalize the temperature. After that, IL and heavy oil model were mixed for a certain period of time at 150 rpm. After reaction, the sample was cool at room temperature. Then, sample was sent for analysis. Percentage of VO TPP removal were determined using the following equation.

\[ \text{Removal} \, (\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \] (1)

where \( C_0 \) is initial VO TPP concentration (0.06 g/L). Meanwhile, \( C_t \) is concentration of VO TPP after extraction.
3. Results and Discussion

3.1. Calibration Curve

Figure 2. Absorption peak of five different samples with different concentrations for calibration curve.

Figure 2 shows the absorbance value of five different samples with different concentration. From this absorbance, a straight line graph of calibration curve was plotted. The graph obtained is linear with the value of $R^2 = 0.9995$. The equation obtained from the graph is $y = 40.417x - 0.0011$. From this equation, the final concentration for each sample can be calculated through its absorbance value.

The porphyrin macrocycle is greatly conjugated, and a number of resonance forms can be recognized using UV-visible spectrum. Soret band ($S$ band) and several $Q$ bands are the most significant characteristics of electrons in UV-Vis absorption spectrum as stated by Mandal et al. [6]. Soret band at approximately 400 nm refer to all type of free-metal porphyrins while $Q$ bands refer to particular MPs complex when the metal replaced two hydrogen atoms in the centre of the porphyrin ring. Different MPs has different value of absorbance for $Q$ band as stated in previous studies. Mandal et al. [14] stated the wavelength of Ni-TPP found using UV-visible spectrum is at 527.5 nm. In another report, Mandal et al. [15] stated the characteristic absorption peak for nickel etioporphyrion (Ni-EP) is at peak of 550 nm. Meanwhile, Mandal et al. [16] carried out another study on vanadyl etioporphyrin (VO EP). For this experiment, the Soret band obtained from Figure 2 is at 420 nm. Meanwhile $Q$ band formed for VO TPP is at wavelength of 548 nm when nickel was replaced the two hydrogen atoms at the center of the tetraporphyrin ring. In a study reported by Mandal et al. [6], the absorption wavelength of Soret band is at 422 nm meanwhile VO TPP is at 548 nm which close to the result obtained.

3.2. VO TPP Removal

Figure 3. Effect of temperature and mixing time on VO TPP removal using EMIM OS

Figure 4. Effect of temperature and mixing time on VO TPP removal using BMIM OS
The experiment was conducted at different temperature which are 30°C, 60°C and 90°C to study the effect of temperature on efficiency of VO TPP removal using two ILs, BMIM OS and EMIM OS. Based on the results obtained in Figure 3 and Figure 4, EMIM OS and BMIM OS show opposite trends to each other. In Figure 3, at mixing time of 30 minutes (mins), VO TPP removal is increased up to 57 % as temperature increased from 30°C to 90°C by using EMIM OS. While, at 60 mins and 90 mins, the removal of VO TPP increased from 50 % to 55 % when temperature at 30 °C and 60 °C but it drastically declines below 35 % to 20 % when the temperature reached 90 °C. The possible reason for the result is that when increasing the temperature, the EMIM OS becomes more miscible with toluene. Then, decreasing its selectivity, thus made EMIM OS extract more toluene instead of vanadium.

In the other hand for BMIM OS, as the temperature increase from 30°C to 90°C, the removal of VO TPP using BMIM OS gradually increases. Based on Figure 4, it shows that when the temperature increased, the removal of VO TPP can be reach up to 25 %, 40 % and 55 % at mixing time 30 mins, 60 mins and 90 mins respectively. This clearly shows that increase in temperature can enhance the removal of VO TPP when BMIM OS was used. This is because at high temperature, the metal ion transfer becomes faster as stated by Germani et al. At low temperature, the high viscosity of BMIM OS reduces the rate of mass transfer between the two phases during liquid-liquid extraction. By increasing the temperature, the viscosity of BMIM OS decreases and the frequency of collision between ionic liquid and heavy oil model increases, thus increasing the extraction rate.

A study on the removal of vanadium from crude oil at temperature of 50°C and extraction time of two hours was reported in 2013 [17]. The ILs used were 1-ethyl-3-methylimidazolium (EMIM) and 1-butyl-3-methylimidazolium (BMIM) as cation with several anions. The results revealed that only EMIM bis(trifluoromethylsulfonyl)imide was capable to remove vanadium at 7.3 %. Besides, they also carried out another experiment to remove vanadium from residue [18]. They used BMIM hexafluorophosphate, BMIM bromide, and EMIM ethyl sulphate at 150°C and was mixed overnight. As the result, 40 % of vanadium was removed by BMIM hexafluorophosphate, 11 % of vanadium was removed by BMIM bromide and 23 % of vanadium was removed by EMIM ethyl sulfate. They did another set of experiment were done using EMIM trifluoroacetate and EMIM chloride at 120°C for 2 hours of mixing time [19]. It was revealed that both ILs capable to remove vanadium for approximately 22% From these previous studies, BMIM cation-based and EMIM cation-based ILs have the capability to remove vanadium but their performance depends on source of petroleum fraction likes vacuum gas oil, crude oil and residue.

3.3. Effect of Mixing Time on Percentage of VO TPP Removal

Effect of mixing time was examined at 30 minutes (mins), 60 mins and 90 mins at respective temperature and stirred at 150 rpm. Figure 3 and Figure 4 illustrates the efficiency of VOTPP removal as the mixing time increased. Result shows that when mixing time increases, the percentage of VO TPP removal increases by using BMIM-OS. At temperature of 30°C, the removal of VO TPP increased to 30 %. Meanwhile at 60°C and 90°C, the removal increased to 45 % and 54 % respectively. The performance of EMIM OS to remove VO TPP are not as good as BMIM OS. When mixing time increased, the removal increased only for temperature of 30°C and 60°C. When the temperature was extended to 90°C, the removal dropped drastically from 50% to 20% at mixing time of 30 mins to 90 mins. Even though the extraction efficiency seems to increase with time, the increase in efficiency was not very significant. It can be concluded that mixing time influence the extraction efficiency on selectivity of the ions. Further study on mechanism should be accomplishing to have deep understanding on the metal ions transfer process as ILs consists of both anion and cation.

Messadi et al. [19] studied the extraction mechanism of cation exchange and ion-pair extraction for task-specific ionic liquids with coordinating anion for heavy metal ions extraction. In their studies, they generated a cationic ester derivative of glycine betaine with bis(trifluoroethylsulfonyl)imide and dicyanamide anions in order to extract copper ions from water and the experiment was done at room
temperature. They reported that the extraction process involved both cation exchange and ion-pairing. It was found that the transfer extent was determined by hydrophobicity of organic cation of IL phase through the cationic exchange process together with ion-pairing extraction mode. The elongation of the alkyl chain on the imidazolium moiety from 5 to 10 carbon atoms encourages a gradual change from cationic exchange to ion-pairing transfer mode and caused progressive decrease of the extraction yields.

3.4. Capability of Ionic Liquids

![Figure 5. 3D graph of factor time and temperature toward VO TPP removal using EMIM OS](image)

![Figure 6. 3D graph of factor time and temperature toward VO TPP removal using BMIM OS](image)

![Figure 7. Color indicator for 3D graph of VO TPP removal](image)

**Table 1. ANOVA Table.**

| Source | Sum of Squares | DF | Mean Square | F value | Prob > F |
|--------|----------------|----|-------------|---------|----------|
| Model  | 3017.882       | 6  | 502.980     | 6.906   | 0.0031   |
| A      | 51.834         | 1  | 51.834      | 0.712   | 0.4168   |
| B      | 245.346        | 1  | 245.346     | 3.369   | 0.0936   |
| C      | 1036.339       | 1  | 1036.339    | 14.230  | 0.0031   |
| AB     | 118.349        | 1  | 118.349     | 1.625   | 0.2287   |
| AC     | 704.107        | 1  | 704.107     | 9.668   | 0.0099   |
| BC     | 861.908        | 1  | 861.908     | 11.835  | 0.0055   |
| Residual | 801.1034      | 11 | 72.828      |         |          |
| Cor Total | 3818.985      | 17 |             |         |          |

Based on Figure 5 and Figure 6 represent 3D graph of VO TPP removal for BMIM OS and EMIM OS with the factors of temperature and mixing time. Meanwhile Figure 7 shows the colour indicator for the 3D graph found in Figure 5 and Figure 6. In Figure 7, the colour range from blue to green then to red indicated the increasing of VO TPP removal. Based on Figure 5 and Figure 6, it shows that there were interactions between the ionic liquid and heavy oil thus allow extraction process to occur Figure 5 shows
maximum removal of VO TPP by EMIM OS is at 30°C with almost 50% removal meanwhile Figure 6 shows maximum removal of VO TPP by BMIM OS for almost 50% at temperature of 90°C. In the other hand, for mixing time factors, EMIM OS extracted almost 32% of VO TPP at 90 minutes while BMIM OS extracted almost 32% of VO TPP at 30 minutes. Due to that, BMIM OS is suggested to be used for extraction process as it gave optimum extraction of VO TPP with only minimal energy required and lowest mixing time, which require low operating cost. Other than that, BMIM OS is has good potential for VO TPP extraction because of the alkyl group length. According to Meindersma et al. [20], the shorter alkyl group length leads to higher toluene selectivity. Since the extraction is non-selective, EMIM OS ionic liquid tends to extract more toluene compare to VO TPP.

Based on Table 1, the Prob > F value of the model possess less than 0.05 which mean the model is significant. In this experiment, the parameters effecting the removal of VO TPP in decreasing order are type of ILs (C), mixing time (B) and temperature (A). It can be seen in Table 1 that the sum of squares for type of ILs is the highest value which is 1036.339 followed by mixing time with 245.346 and lastly temperature with 51.834 of sum of squares. From Table 1, it shows that when type of ILs interacted with time (BC) and temperature (AC) possess less than 0.05 of P value. These interaction can be seen in 3D surface graph in Figure 5 and Figure 6. Figure 5 shows the 3D surface graph of VO TPP removal using EMIM OS. From the graph, it concluded that when treatment time increased from 30 minutes to 90 minutes, the removal of VO TPP decreased. Meanwhile, when temperature increased from 30 °C to 90 °C, the removal of VO TPP was increased. 3D surface graph of BMIM OS can be found in Figure 6. It shows that when temperature increased from 30°C to 90°C and treatment time increased from 30 minutes to 90 minutes, the VO TPP removal decreased. But when time interacted with temperature without type of liquids (AB), the P value is more than significant value which means that type of ionic liquid plays an important in removing VO TPP in this experiment. The optimized condition obtained through this model is using EMIM OS at temperature of 30 °C and mixing time of 30 mins. Equations generated to predict the respond at any given mixing time and temperature, as shown in equation below:

\[
\text{EMIM OS: Removal} \% = 48.92 + (0.12 \times t) + (0.07 \times T) - (4.27 \times 10^{-3} \times t \times T)
\]

\[
\text{BMIM OS: Removal} \% = -30.79 + (0.69 \times t) + (0.58 \times T) - (4.27 \times 10^{-3} \times t \times T)
\]

where \(t\) is mixing time (minutes) and \(T\) is temperature (°C).

4. Conclusion

In conclusion, the project was able to study the capability of EMIM OS and BMIM OS to remove vanadium from heavy oil model. Somehow, the extraction was non-selective as both toluene and VO TPP are being extracted by IL. Further analysis should be done to confirm the behaviour of the extraction. Besides that, it shows that extraction temperature and mixing time can affect the extraction efficiency of vanadium. For optimization, it is preferable to use EMIM OS to extract VO TPP with only minimal temperature and lowest mixing time. This can provide good extraction efficiency at low operating cost.

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