

## Application of ILs as carbonate scales dissolver

Muhammad Suhaimi Man <sup>a,c</sup>, Hanida Abdul Aziz <sup>b</sup>, Syamsul B. Abdullah <sup>a,\*</sup>

<sup>a</sup> Faculty of Process and Chemical Engineering Technology, Universiti Malaysia Pahang, Gambang Campus, Lebuhraya Tun Razak, 26300, Kuantan, Pahang, Malaysia

<sup>b</sup> Faculty of Science and Technology, Universiti Malaysia Pahang, Gambang Campus, Lebuhraya Tun Razak, 26300, Kuantan, Pahang, Malaysia

<sup>c</sup> Setegap Ventures Petroleum Sdn. Bhd. No.68, Jalan Metro Pudu 2, Fraser Business Park, 55200 Kuala Lumpur, Malaysia



### ARTICLE INFO

#### Keywords:

Calcium carbonate  
Scale dissolver  
Ionic liquid  
Dissolution

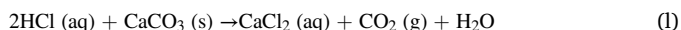
### ABSTRACT

The scale formation was a crucial problem in the petroleum industry. Among the scales, calcium carbonate (CaCO<sub>3</sub>) was the predominant scale produced. Thus, a suitable alternative solution is needed to be identified to overcome the effect of hydrochloric acid (HCl), which is usually used to dissolve CaCO<sub>3</sub>. This study introduced ionic liquid (ILs) for scales dissolver due to their unique properties, likely known as a green solvent. This ILs N-pyrindinium chloride ([NPy][Cl]) was studied experimentally in order to know the performance during the dissolution of scale toward some parameters. The parameters tested in this study are carbonates scales, the concentration of ILs, stirring speed, pH and temperatures. In order to get better efficiency of the performance on actual condition, [NPy][Cl] was tested with model crude oil, salinity, corrosion evaluation and regeneration of the used ILs. The finding shows that the [Npy][Cl] is suitable for replacing HCl as a carbonate scale dissolver due to its ability to dissolve carbonate scales. Furthermore, the performance of [NPy][Cl] in the dissolution rate of carbonate scales was maintained, although inaccurate condition testing. This finding will enhance crude oil production by using solvent-based ILs in this application.

### 1. Introduction

Scale formation is a critical issue and is recognized as one of the significant flow assurance problems affecting production in the oil and gas industry [1]. Scales formation causes oil production decline, costing the oil industry millions of dollars annually in inhibition, including removal and lost revenue from deferred production [2]. Calcium carbonate is one of the most frequently occurring scales in the oil field [3]. Stimulation of carbonate rocks usually involves a reaction between an acid and the minerals calcium carbonate (CaCO<sub>3</sub>) or dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> [4].

Acids are crucial in boosting production or increasing injectivity in oil and gas fields. Hydrochloric acid (HCl) is commonly used in acid treatment for the carbonate scales [5]. The use of HCl gives a better result, but they are also very corrosive, although it is cheaper than other scale removals. It dissolves carbonate scale but also damages the metal surface. Hence, corrosion inhibitors are required along with such acids and indirectly cause an increase in the cost of operation. Hydrochloric acid reacts with calcium carbonate to give the water-soluble product as per the following equation [1–6].



Ionic liquids (ILs) have received great environmental and technological attention as a potential alternative to traditional organic solvents [6]. ILs are gaining widespread recognition as novel solvents in chemistry. Compared to classical organic solvents, ILs generally consist of bulky, nonsymmetrical organic cations such as imidazolium, pyrrolidinium, pyridinium, ammonium, or phosphonium, and numerous different inorganic or organic anions such as tetrafluoroborate and bromide anions. The unique properties of ILs, such as negligible vapor pressure, good thermal stability, tunable viscosity, miscibility with water and organic solvents and good extractability for various organic compounds and metal ions, mainly depend on their tailored structures. Replacing organic solvents currently used in different extraction processes with ILs can be considered a “hot” research. The non-flammable, non-volatile nature of ILs makes them an excellent choice for the development of safer processes. Furthermore, their polarity, hydrophobicity, viscosity and other chemical and physical properties can be selected by choosing the cationic or the anionic constituent. ILs are regarded as “designer solvents” because of their tunable nature, which increases their potential applications [7].

A brief review of the literature shows there is no alternative to HCl as a scale dissolver toward the carbonate scale problem and HCl is preferable for calcium carbonate. Surprisingly, there is no work to study the application of ILs in the dissolution of inorganic scale although, ILs have

\* Corresponding author.

E-mail address: [syamsul@ump.edu.my](mailto:syamsul@ump.edu.my) (S.B. Abdullah).

<https://doi.org/10.1016/j.crgsc.2022.100277>

Received 19 December 2021; Received in revised form 11 January 2022; Accepted 15 January 2022

Available online 20 January 2022

2666-0865/© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

**Abbreviation**

CaCO <sub>3</sub>	Calcium carbonate
CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dolomite
HCl	Hydrochloric acid
CaCl <sub>2</sub>	Calcium chloride
CO <sub>2</sub>	Carbon dioxide
H <sub>2</sub> O	Water
ILs	Ionic liquids
N <sub>2</sub>	Nitrogen gas
ICP-MS	Inductively coupled plasma mass spectrometry
HNO <sub>3</sub>	Nitric acid
H <sub>2</sub> O <sub>2</sub>	Hydrogen peroxide
OFAT	One factor at a time
NaCl	Sodium chloride
AAS	Atomic absorption spectrometry
[NPy][Cl]	N-pyridinium chloride

the unique properties and ability to form interaction with ILs. For this purpose, ILs were introduced as a scale dissolver toward the carbonate scale, which is the new application of ILs.

## 2. Experimental

### 2.1. Preparation of ILs

Equal molar amounts of N-pyridine and acid were added to a three-necked, round bottom flask equipped with a reflux condenser, a magnetic stirrer, and an inlet and outlet for N<sub>2</sub> gas. The reaction mixture was cooled under N<sub>2</sub> atmosphere at  $T = (278.15\text{--}283.15)$  K depending on starting materials, with continuous stirring for 3 h. The resulting viscous liquid was distilled under a vacuum to dissolve any unreacted materials to form solid pure [NPy][Cl].

### 2.2. Dissolution of CaCO<sub>3</sub> in [NPy][Cl]

The [Npy][Cl]/calcium carbonate mixtures (10:1 w/w) were prepared by the addition of calcium carbonate powder ( $0.1 \pm 0.01$  g) to a sample of the [Npy][Cl] ( $10.00 \pm 0.01$  g) in a 100 ml beaker glass containing a magnetic stirrer bar. The beaker was then partially submerged into an oil bath with an integrated thermostat, set at a constant temperature of 30 °C, and maintained, with stirring, for 24 h. The apparatus was positioned behind a protective blast screen as a safety precaution. The same procedure undergoes for CaMg(CO<sub>3</sub>)<sub>2</sub> sample as well.

### 2.3. Quantification method for (CaCO<sub>3</sub>) and (CaMg(CO<sub>3</sub>)<sub>2</sub>) after dissolution process using Inductive couple plasma mass spectroscopy (ICP-MS)

ICP-MS measurement was carried out to determine some inorganic elements present in ILs after the dissolution of the carbonate scale. The measurement was conducted using ICP-MS (Agilent ICP-MS 7500 series). The dried samples (0.5 g) were digested using 6 ml of 65% wt nitric acid (HNO<sub>3</sub>) and 2 ml of 30% wt hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a microwave digester. The digested solution was diluted in a 50 ml volumetric flask with 2% wt HNO<sub>3</sub> before being analyzed in ICP-MS.

### 2.4. Experimental study based on one-factor-at-a-time (OFAT)

The screening study of the dissolution carbonate scales using ILs was carried out. The parameter studied in this section included types of carbonate scale, the concentration of ILs, stirring speed, pH, and temperature. These parameters were studied in one-factor-at-a-time (OFAT)

to determine the effect of each parameter on the dissolution rate of the carbonate scale, and the analysis was done in triplicates. At the end of the OFAT process, the time of dissolution of carbonate scales and weight of carbonate scales was used to assess the degree of dissolution rate. A reaction volume a 10 ml of ILs was maintained in the OFAT study. The OFAT study on the dissolution of carbonates scales was detailed in the following subsections.

#### 2.4.1. Type of carbonates

The effect of types of carbonates scales against dissolution rate was studied. Types of carbonates scale used in this experiment are calcium carbonate, dolomite, barium carbonate and potassium carbonate. The amount of carbonate scale was weighed 0.1g and 10 ml ILs of was measured using a measuring cylinder. The ILs and the carbonate scales were mixed in the beaker. The duration was recorded until the dissolution of the carbonate scales finished.

#### 2.4.2. Effect of concentration

The effect of the concentration of ILs on the dissolution of carbonate scales was studied. The concentration of ILs was diluted with water using ratios 70:30, 50:50, 30:70, 20:80, 10:90 wt (%). Then, 10 ml ILs of each concentration were measured using a measuring cylinder. The ILs and the carbonate scales were mixed in a beaker. The duration was recorded until the dissolution of the carbonate scales finished.

#### 2.4.3. Stirring speed

The effect of stirring speed on dissolution rate was investigated. The stirring speed was fixed to be 0 rpm, 300 rpm, 600 rpm, 900 rpm, 1200 rpm and 1500 rpm. Then, the amount of carbonate scale was weighed 0.1g and 10 ml ionic liquid was measured using a measuring cylinder. The ILs and the carbonate scales were mixed in a beaker using stirring speed. The duration was recorded until the dissolution of the carbonate scales finished.

#### 2.4.4. pH

The experiment was set in different pH values. The ILs with different pH were adjusted by diluting sodium chloride (NaCl) in the ILs. The pH value was set to be 1, 2, 3 and 4. Then, the amount of carbonate scale was weighed 0.1g and 10 mL ILs of each pH was measured using a measuring cylinder. The ILs and the carbonate scales were mixed in a beaker. The duration was recorded until the dissolution of the carbonate scales finished.

#### 2.4.5. Temperature

The effect of the temperature was set using one set of experiments in different temperatures. The temperature was varied 25 °C, 40 °C, 60 °C and 80 °C. The amount of carbonate scale was weighed 0.1g and 10 ml ILs of was measured using a measuring cylinder. The ILs and the carbonate scales were mixed in a beaker. The duration was recorded until the dissolution of the carbonate scales finished.

#### 2.4.6. Dissolution of scale on model crude oil

Dissolution scales in the oil field include several types of a compound like crude oil. According to Ref. [8]; the highest oil compositions are toluene and n-dodecane. Toluene and dodecane represent aromatic compounds and aliphatic compounds, respectively. Model oil consisting of toluene and n-dodecane was used to replace crude oil to avoid the influence of impurities (gelatin, asphaltene and other uncertain matters) in the mixtures [9]. 10 ml of ionic liquid and model crude was mixed in the beaker. The duration was recorded until the dissolution of the carbonate scales finished.

#### 2.4.7. Concentration of salinity

Effect on the concentration of salinity toward dissolution rate was studied. The ILs were diluted with sodium chloride solution. The salinity concentration was varied to be 11000 ppm, 13000 ppm, 15000 ppm,

17000 ppm and 19000 ppm [10]. Then, the amount of carbonate scale was weighed 0.1g and 10 ml ionic liquid with each concentration of sodium chloride was measured using a measuring cylinder. The ionic liquid and the carbonate scales were mixed in a beaker. The duration was recorded until the dissolution of the carbonate scales finished.

## 2.5. Corrosion study

Carbon steel metal was used in this corrosion test. A rectangular plate of carbon steel was used for weight loss studies. The metal pieces were initially cleaned using abrasive paper to dissolve steel oxide and the weight of the steel plate sample was recorded.

The weight loss experiments were carried out under total immersion conditions in HCl and [Npy][Cl] solution at room temperature. The experiments were carried out in which the plate metal was placed in a corrosion study kit with supply air in seven days. Then the weight loss was determined by a sensitive analytical balance after three, five and seven days. The experiment setup is shown in Fig. 1.

## 2.6. Regeneration of ionic liquid

Due to the production costs of ILs, recycling ILs potentially reduces total operating costs. ILs have an excellent solubility with organic materials and inorganic salts. They can be miscible with a variety of compounds. ILs are usually recycled using a more straightforward method.

Firstly, the mixture solution that contained ILs and the carbonate scale were mixed with the cold acetone. Then this solution was soaked for a while. Finally, acetone in the mixture was removed using a rotary evaporator for more than 3 h. The recovered ILs can be re-used.

## 3. Result and discussion

### 3.1. ICP-MS analysis

ICP-MS measurements were carried out to determine the existing inorganic elements. Table 1 and Table 2 show the ICP-MS result for selected inorganic elements in ILs after the dissolution of calcium carbonate and dolomite scales. The content of scales ions such as Calcium (Ca) and Magnesium (Mg) was relatively higher in ILs. According to Table 1, the calcium concentration is high, which is 17550 ppm compared to the other elements. This result proves the existence of the

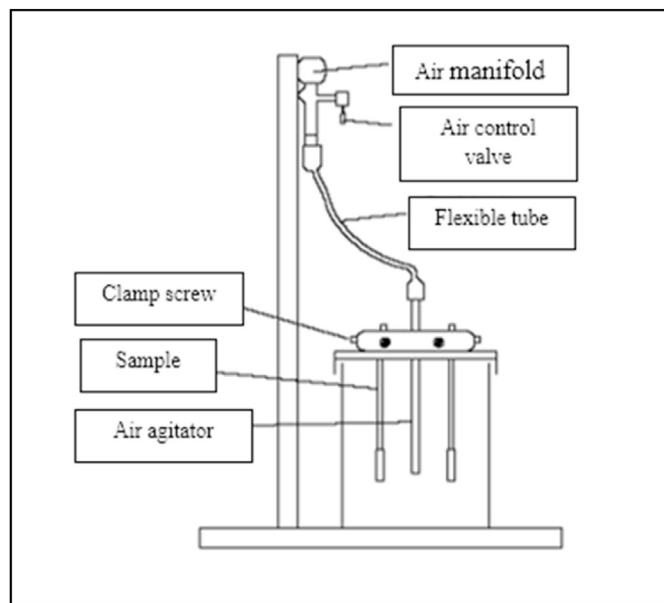


Fig. 1. Experimental corrosion schematic diagram.

**Table 1**  
ICP-MS result for validation test of mixture ILs with calcium carbonate.

Parameter	Result	Unit
Calcium (Ca)	17550.9	ppm
Sodium (Na)	N. A	ppm
Potassium (K)	N. A	ppm
Aluminium (Al)	N. A	ppb
Vanadium (V)	N. A	ppb

**Table 2**  
ICP-MS result for validation test of mixture ILs with dolomite.

Parameter	Result	Unit
Magnesium (Mg)	7152	ppm
Calcium (Ca)	6661.9	ppm
Sodium (Na)	N. A	ppm
Potassium (K)	N. A	ppm
Aluminium (Al)	N. A	ppb
Vanadium (V)	N. A	ppb

calcium element in the ILs solution after the dissolution of calcium carbonate. Then the result in Table 2 shows the concentration of Ca and Mg in the sample after the dissolution of dolomite. It is because the main metal element in dolomite is calcium and magnesium. Atomic absorption spectrometry (AAS) has been used to reconfirm the existence of those two metals in the solution.

From the quantification confirmation of [Npy][Cl] through AAS and ICP-MS, the result for both analyses show confirmation that the carbonate scale dissolves in [Npy][Cl] with the presence of calcium and magnesium ion in [Npy][Cl].

### 3.2. Types of carbonate scale

Fig. 2 depicts the effect of types carbonate scales on dissolution rate using [Npy][Cl]. Five types of carbonate scales were screened in dissolving using [Npy][Cl], which are calcium carbonate, potassium carbonate, barium carbonate, magnesium carbonate and dolomite.

The highest dissolution rate is potassium carbonate which is 2.27 mg/s, followed by barium carbonate and magnesium carbonate with 2.08 mg/s and 1.72 mg/s accordingly. Calcium carbonate and dolomite have the lowest dissolution rate compared to the others, 1.62 mg/s and 1.1 mg/s, respectively. All scales used in the experiment were basically from the carbonate scales. So, mostly oilfield carbonate scale can dissolve in [Npy][Cl] solution.

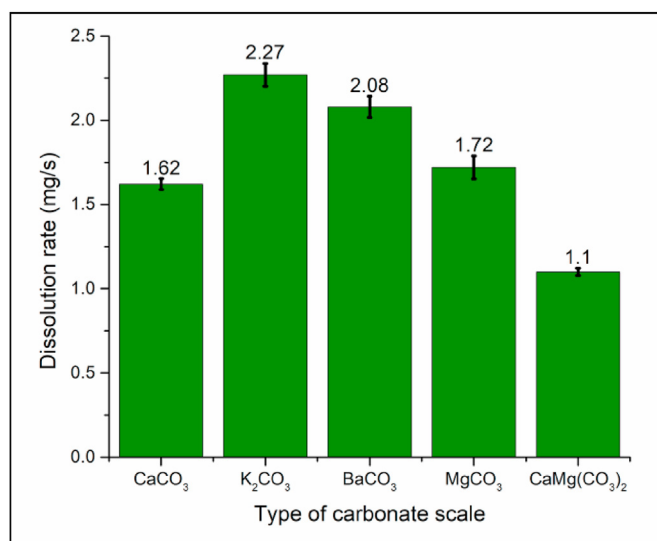


Fig. 2. The effect of type of carbonate scale on dissolution rate.

Besides calcium carbonate and dolomite, the most common carbonate scales found in oilfield scale, potassium carbonate, barium carbonate and magnesium carbonate, are formed when forming water associated with crude oil. Formation water contains a large concentration of potassium ion, barium ion and magnesium ion beside calcium and chloride ion. These carbonate scales are formed when there is a pressure drop in the reservoir, leading to the supersaturation of carbonate scale precipitation.

According to Ref. [11]; the production of scale including this carbonate scale near the wellbore, will cause a further reduction in pressure and more precipitation. This scale can entirely create an impermeable wall between borehole and reservoir completely shutting down production within a few days.

Therefore, several carbonate scales need to be evaluated using [Npy][Cl] solution. The result shows that [Npy][Cl] is suitable for dissolving carbonate scales. This result also matches the finding by Ref. [12], where the ILs can act as a ligand to form metal complexes during the dissolution of carbonate scales.

According to Fig. 2 above, different carbonate scales have different metal ions in the compound. This different type of metal ion gives different results in the dissolution rate of carbonate scales. This metal ion will act with a ligand to form metal complexes during the dissolution process.

The result shows that the  $K^+$  ion in potassium carbonate as a metal has the highest dissolution rate than other ions, followed by  $Ba^{2+}$  ion in barium carbonate,  $Mg^{2+}$  ion in magnesium carbonate and  $Ca^{2+}$  ion in calcium carbonate, respectively. The metal (M) oxidized produced cation  $M^{x+}$ , will interact with one or more types of ligand in solution to form a metal complex. The solubility of the complex will depend upon the solvation and the overall charge of the complex species, where the latter can vary for an ion-ligand-combination depending on the coordination number [13].

Every metal ion has its characteristics and behavior during the dissolution process, to form a metal complex with various ligands. In the [Npy][Cl] solution, water also can act as a ligand to form  $H_2O$ ,  $OH^-$ ,  $O^{2-}$  besides the ion from the ILs itself. According to Abbot et al., the rate of the dissolution process will depend upon the activity of the ligand and in most cases the viscosity of the ILs.

### 3.3. Concentration effect

Fig. 3 shows the effect of concentration [Npy][Cl] on dissolution rate of calcium carbonate and dolomite. The concentration of [Npy][Cl] was diluted to water using ratio 70:30 [8.12 M], 50:50 [5.80 M], 30:70 [3.48 M]

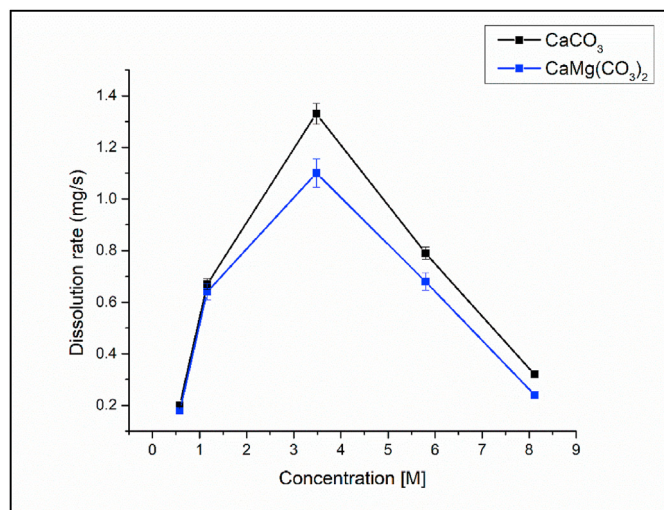


Fig. 3. The effect of concentration [Npy][Cl] on dissolution rate of calcium carbonate and dolomite.

[M], 20:80 [1.16 M], 10:90 [0.58 M] wt. (%).

As can be seen from the graph, there was an initial increase in the dissolution rate from concentration 0.58 M–3.48 M of [Npy][Cl] solution. However, when the concentration increases from 3.48 M to 8.12 M, there is an apparent decrease in the dissolution rate for calcium carbonate and dolomite scales.

Concentration is one of the significant parameters in the dissolution of scales. The optimum dissolution rates for calcium carbonate and dolomite were at concentration 3.48 M (30:70 wt%), which is 30% of [Npy][Cl] and 70% of water.

Based on the result above, the concentration of all ligands plays a vital role in the dissolution rate. The ligands in the system are  $Py^+$  and  $Cl^-$  ion from ILs and  $H_2O$ ,  $OH^-$  and  $O^{2-}$  from the water. According to [13], ligands concentration is strongly affected by metal complex formation. All the ligands can affect the overall charge of the complex.

The dissolution rate was decreased at a high concentration, i.e., 8.12 M due to the [Npy][Cl] solution at this concentration being viscous compared to others. According to Ref. [13]; the rate of dissolution process will depend upon the activity of the ligand and the viscosity of the ILs. The dissolution rate increased when [Npy][Cl] was diluted in water until the concentration of ILs was 3.48 M. Diluted [Npy][Cl] means the ligand from water molecule also increase. This ligand from the water promotes the dissolution rate during the dissolution process [14]. also stated that the water promoted the dissolution rate during the dissolution process.

### 3.4. Stirring speed effect

Fig. 4 above shows the effect of stirring speed on the dissolution rate of calcium carbonate and dolomite in [Npy][Cl]. Six different stirring speeds from 0 to 1500 rpm were applied to determine the condition for maximum dissolution rate.

Fig. 4 shows that the dissolution rate significantly increases when the stirring speed increases from 0 to 1500 for both scales. However, the dissolution rate becomes slowly from 1200 to 1500 rpm for both scales.

[14] suggested dependencies on stirring speed for the overall dissolution rate process. In that research, the author studied the effect of stirring velocity toward the dissolution rate of calcium carbonate and dolomite in a batch reactor. The finding shows that the dissolution rate increases when the stirring speed increases.

The stirring effect has a massive effect on the reaction between ligands in [Npy][Cl] solution with calcium carbonate and dolomite scale. This stirring speed factor will increase the dissolution process and speed

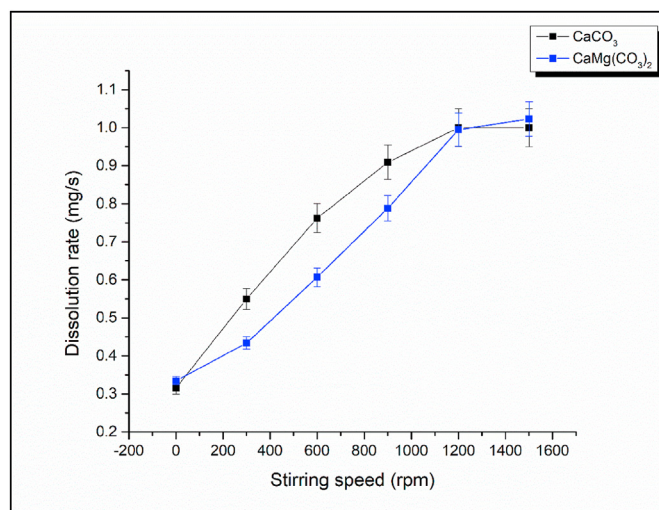


Fig. 4. The effect of stirring speed on dissolution rate of calcium carbonate and dolomite.



up the metal complex formation between ligands and metal ions from the scales.

### 3.5. pH effect

Fig. 5 shows the effect of pH on the dissolution rate of calcium carbonate and dolomite. The pH varies from 0.7 to 4 which is in an acidic medium.

The dissolution of scales is dependent on the pH of the medium because the scales generally have a specific pH range in which they are most active. Fig. 5 above also shows a robust relationship of the dissolution rate to the pH of the medium.

The dissolution rate is increased when the pH value decreases. According to Ref. [15]; fast dissolution of carbonate scale when the pH is low [14]. also stated that when the pH is below 4, it is more likely that the fluid pH is the main parameter controlling carbonate mineral dissolution. It was believed that hydrogen bonding is involved in forming ligand of the carbonate during the dissolution process.

### 3.6. Temperature

Fig. 6 shows the effect of temperature on the dissolution rate of calcium carbonate and dolomite. The effect of temperature was studied at four (4) different temperatures ( $25 \pm 3$  °C, RT), 40 °C, 60 °C and 80 °C.

The result depicted in Fig. 6 above; the dissolution rate increases for both scales when the temperature increases. The optimum dissolution rate was at a temperature of 80 °C, 4.32 mg/s for calcium carbonate and 1.42 mg/s for dolomite.

According to Ref. [13]; when the temperature increase, the dissolution rate also will increase due to the lower viscosity of the solution. When the degree of solubility increment of metal salt at a higher temperature, the formation of different solid phases, or the increased diffusion of the ligand due to viscosity decrement of the solution. The dissolution rate also will increase when the temperature increases due to increasing the diffusion of ligand to form metal complex formation rapidly.

### 3.7. Dissolution of carbonates scale on model crude oil

Fig. 7 shows the data on the dissolution rate of carbonate scales when dissolving in [Npy][Cl] solution with model crude oil. The data show that the dissolution rate does not change too much when mixing with the model crude, like n-dodecane represents saturated and toluene represent the aromatic compound. The unchanged effect relies on the ILs and the model crude which is immiscible.

In the dissolution process, ligands will play a vital role in dissolving the carbonate scale and the condition of the system will enhance the dissolution rate. Nevertheless, the presence of model crude in the system does not affect the ligand in the ILs or change the ligand concentration in the ILs solution due to immiscibility.

This result shows the ability of [Npy][Cl] to be used in oilfield applications, especially in dissolving carbonate scales.

### 3.8. Salinity effect

Fig. 8 shows the effect of salinity on the dissolution rate of calcium carbonate and dolomite. The effect of salinity was investigated to explore the actual condition of operation when these ILs applied in the oil field, which involves the seawater.

As shown in Fig. 8, the dissolution rate decreases when the NaCl concentration is applied for both types of scales. The salinity was tested for five different concentration points and the result shows the dissolution rate is constant, although the concentration of salinity increased.

The salinity test showed the dissolution rate decreased when NaCl was mixed in the ILs solution; however, the concentration of the NaCl does not affect to dissolution rate of the carbonate scales. These results

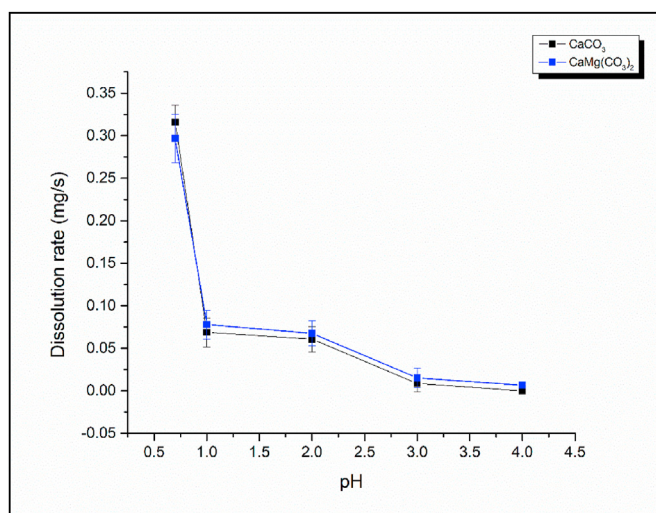


Fig. 5. The effect of pH on dissolution rate of calcium carbonate and dolomite.

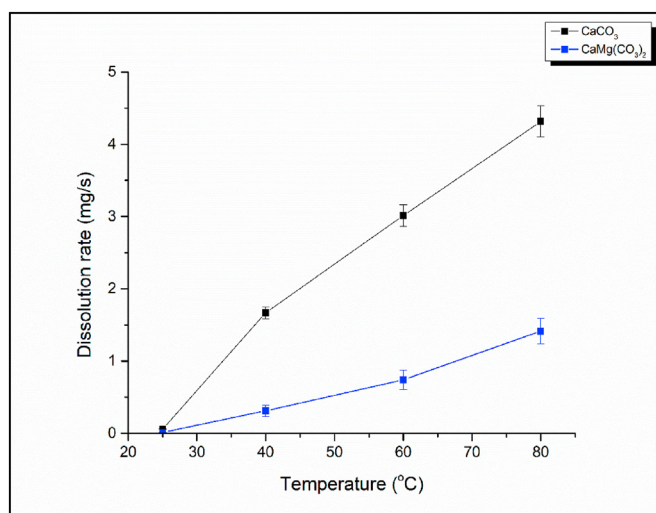


Fig. 6. The effect of temperature on dissolution rate of calcium carbonate and dolomite.

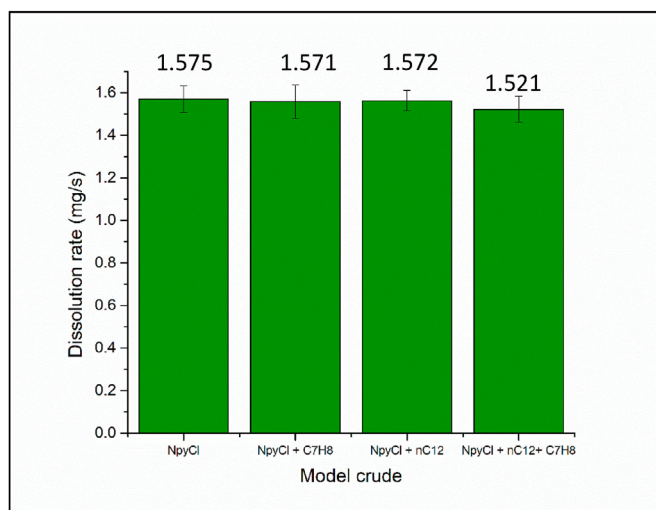


Fig. 7. Dissolution rate of scales on model crude oil.

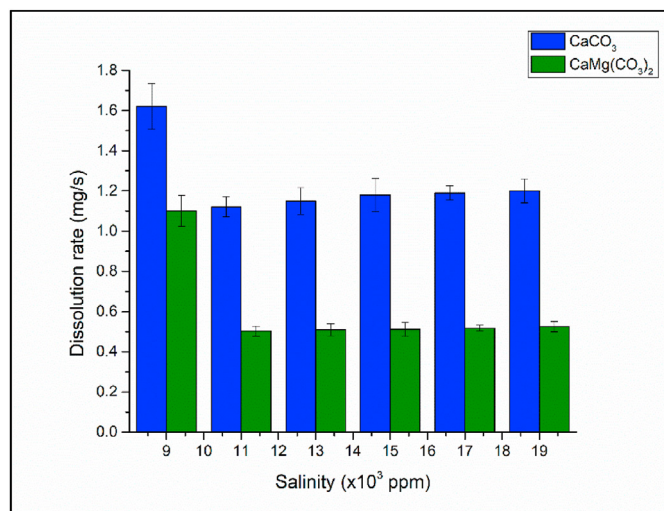


Fig. 8. The effect of salinity on dissolution rate of calcium carbonate and dolomite.

are similar to the finding done by Refs. [14,15]. The effect of an organic ligand like NaCl on the carbonate dissolution rate is feeble and does not produce a significant variation. The concentration of NaCl does not affect the dissolution rate of the carbonate scale, but the existence of NaCl in ILS solution gives the effect compared to pure ILS solution. This is because of the change of viscosity of the ILS solution before and after NaCl was applied. The viscosity of the solution gives the effect on the dissolution rate on the carbonate scale.

### 3.9. Corrosion study of [Npy][Cl]

Table 3 and Fig. 9 show the result of weight losses for carbon steel immersed in hydrochloric and [Npy][Cl] solution. The carbon steels were immersed in the solution within 3–7 days. Table 3 below shows the figure of carbon steels after being immersed in hydrochloric solution and ILS.

The data was recorded from the experiment of corrosion. The figure

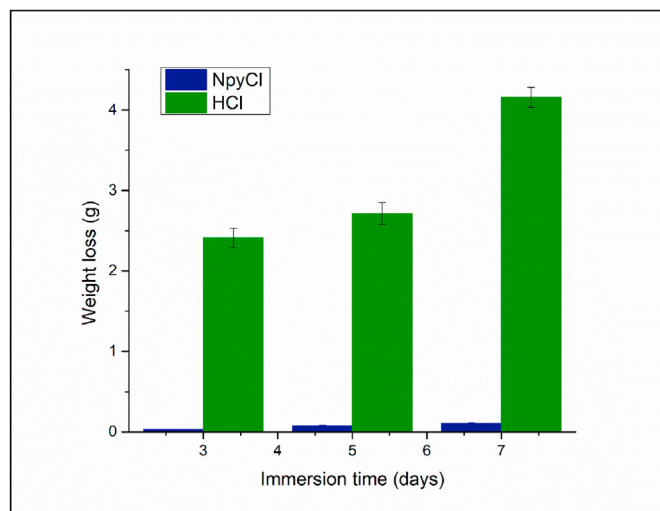


Fig. 9. Weight loss of steel plate on immersion time in HCl solution and [Npy][Cl].

shows that HCl solution gave the highest weight loss of carbon steel at room temperature compared to ILS solution. This shows that the highest corrosion rate is in the HCl solution medium compared to the ILS solution.

From Table 3 and Fig. 9, the percentage of weight loss increased when the immersion time was increased. HCl solution showed the highest weight loss percentage compared to [Npy][Cl] solution. [Npy][Cl] solution showed less than 1% weight loss from 3 to 7 days of immersion time. Although the initial pH and chloride element (Cl) are almost the same between HCl and [Npy][Cl] solution, the percentage of weight loss between these two solutions a way big differ (see Table 4).

From this result, [Npy][Cl] expected has characteristic of inhibitor or anti-corrosion substances. According to Refs. [16,17]; the compound containing nitrogen was an efficient corrosion inhibitor and has been used to control the corrosion of the steel.

Table 3

Comparison of corrosion effect on HCl solutions and [Npy][Cl].

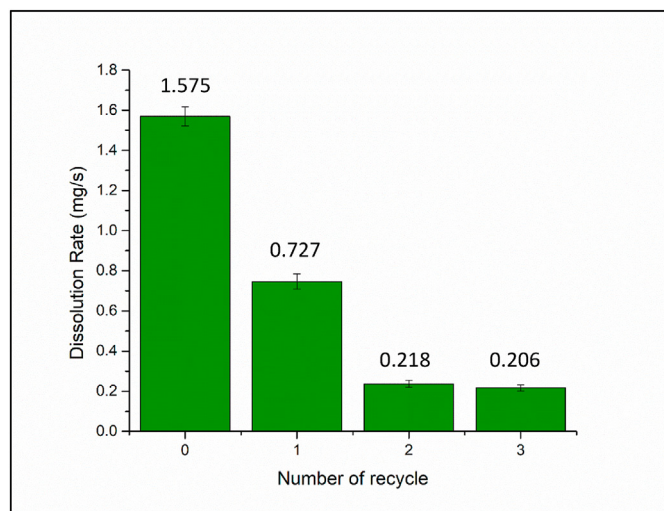
Type of solution	Description
HCl	Carbon steel after 7 days. The corrosion cause HCl solution turn to dark color and thin the carbon steel.
[Npy][Cl]	The [Npy][Cl] change a little bit to yellowish color and no corrosin observed on carbon steel after 7 days.



**Table 4**

Percentage of weight loss between HCl solution and [Npy][Cl] on immersion time.

Immersion time (Days)	Weight loss %	
	HCl	[Npy][Cl]
3	12.13	0.13
5	16.07	0.38
7	22.15	0.63



**Fig. 10.** Dissolution rate of scales on recycles of [Npy][Cl].

The used organic compound containing oxygen (O), sulphur (S) and nitrogen (N) to reduce corrosion attack on steel has been studied. According to Ref. [18]; O, S and N are the active center for the process of adsorption on the metal surface. Availability of lone pair in this element facilitates electron transfer to the metal steel. The strength of the bond depends upon the electron density of the donor atom of the functional group. The electron density in the metal at the point attachment changed, resulting in the retardation of the cathodic or anodic reactions. Electrons are consumed at the cathode and are furnished at the anode. Thus, corrosion is retarded.

### 3.10. Regeneration of [Npy][Cl]

Fig. 10 above shows the effect of recycling [Npy][Cl] on the dissolution rate. The recycle [Npy][Cl] was applied to calcium carbonate scales. The graph above shows that the dissolution rate significantly decreased when the number of recycling increased. For the first recycling time, the dissolution rate was dropped in half compared to the dissolution rate using pure of [Npy][Cl]. The second recycle of [Npy][Cl] also decreases in dissolution rate and the result is also the same for the third recycle.

The significant decrease of dissolution rate is because of the viscosity of [Npy][Cl] solution increase. After the dissolution process, the [Npy][Cl] was washed using solvent and purified using the distillation process to remove the impurities. During the distillation process, the concentration of water in the [Npy][Cl] solution also decrease caused by this process. So, the viscosity of [Npy][Cl] was different before and after the recycling process. This result shows that water's vital concentration as a ligand promotes the dissolution rate during the dissolution process. This finding also will minimize the cost when this product is ready to be used in oilfield applications.

## 4. Conclusion

The proposed ILs [Npy][Cl] has successfully been evaluated as a new scale dissolver through efficiently dissolving calcium carbonate. Experimental showed the performance of [Npy][Cl] in dissolving calcium carbonate scale through dissolution rate. This finding will give the alternative to the carbonate scale problem as a new scale dissolver that is more environmentally friendly due to the unique properties of ILs.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgment

The authors would like to thank the Ministry of Higher Education Malaysia under the Fundamental Research Grant Scheme (FRGS/1/2021/TKO/UMP/02/83 – RDU 210157) and UTP-UMP-UTM-UNIMAP Collaborative Research Grant (CRG UTP – RDU 213202) for the financial research support.

## References

- [1] M.D. Garba, M.S. Sulaiman, Oilfield scales treatment and managerial measures in the fight for sustainable production, *Petrol. Technol. Dev. J.* 2 (2014) 19–37.
- [2] M.I. Refaei, I.A.K. Alkandari, Oil Fields Scale Deposition Prediction Methodology, SPE International Formation Damage Control Symposium and Proceeding, 2009, pp. 14–16.
- [3] S. Kumar, T.K. Naiya, T. Kumar, Developments in oilfield scale handling towards green technology: a review, *J. Petrol. Sci. Eng.* 169 (2018) 428–444.
- [4] L.B. Smith Jr., G.R. Davies, Structurally controlled hydrothermal alteration of carbonate reservoirs: introduction, *AAPG (Am. Assoc. Pet. Geol.) Bull.* 90 (2006) 1635–1640.
- [5] L. Li, A. Texas, F.F. Chang, T. Lindvig, Reaction of simple organic acids and chelating agents with calcium carbonate, *Int. Petrol. Technol. Conf.* (2008) 12886.
- [6] M.B. Dahbag, A. AlQuraishi, M. Benzagouta, Efficiency of ionic liquids for chemical enhanced oil recovery, *J. Petrol. Explor. Prod. Technol.* 5 (2015) 353–361.
- [7] D. Han, K.H. Row, Recent applications of ionic liquids in separation technology, *Molecules* (2010) 2405–2426.
- [8] M. Mahmoud, M. Attia, H. Alhashim, EDTA chelating agent/seawater solution as enhanced oil recovery fluid for sandstone reservoirs, *J. Petrol. Sci. Eng.* 152 (2017) 275–283.
- [9] H. Jia, X. Leng, M. Hu, Y. Song, H. Wu, P. Lian, Y. Liang, Y. Zhu, J. Liu, H. Zhou, Systematic investigation of the effects of mixed cationic/anionic surfactants on the interfacial tension of a water/model oil system and their application to enhance crude oil recovery, *Colloids Surf. A Physicochem. Eng. Asp.* 529 (2017) 621–627.
- [10] M.H. Sorour, H.A. Hani, H.F. Shaalan, M.M.H. Elsayed, Experimental screening of some chelating agents for calcium and magnesium removal from saline solutions, *Desalination Water Treat.* 57 (2016) 22799–22808.
- [11] M. Crabtree, D. Eslinger, P. Fletcher, M. Miller, A. Johnson, G. King, Fighting scale — removal and prevention, *Oilfield Rev.* (1999) 30–45.
- [12] O. Bortolini, C. Chiappe, T. Ghilardi, A. Massi, C.S. Pomelli, Dissolution of metal salts in bis(tri fluoromethylsulfonyl)imide-based ionic liquids: studying the affinity of metal cations toward a “ weakly coordinating ” anion, *J. Phys. Chem.* (2014) 1–10.
- [13] A.P. Abbott, G. Frisch, J. Hartley, W.O. Karim, K.S. Ryder, Anodic dissolution of metals in ionic liquids, *Prog. Nat. Sci.: Mater. Int.* 25 (2015) 595–602.
- [14] S.V. Golubev, J.T. Schott, O.S. Pokrovsky, Dissolution kinetics of calcium carbonate, dolomite and magnesite at 25 °C and 0 to 50 atm pCO<sub>2</sub>, *Chem. Geol.* 217 (2005) 239–255.
- [15] O.S. Pokrovsky, S.V. Golubev, G. Jordan, Effect of organic and inorganic ligands on calcium carbonate and magnesite dissolution rates at 60° C and 30 atm pCO<sub>2</sub>, *Chem. Geol.* 265 (2009) 33–43.
- [16] M.P. Chakravarthy, K.N. Mohana, Adsorption and Corrosion Inhibition Characteristics of Some Nicotinamide Derivatives on Mild Steel in Hydrochloric Acid Solution, *ISRN Corrosion*, 2014, pp. 1–13.
- [17] E. Ituen, A. James, O. Akaranta, S. Sun, Eco-friendly corrosion inhibitor from pennisetum purpureum biomass and synergistic intensifiers for mild steel, *Chin. J. Chem. Eng.* 24 (2016) 1442–1447.
- [18] B.E.A. Rani, B.B.J. Basu, Green inhibitors for corrosion protection of metals and alloys : an overview, *Int. J. Corrosion* (2012) 1–15.