Molecular Interaction Study on a New Application of Ionic Liquids as Dissolver Toward Carbonate Scale

(Kajian Interaksi Molekul terhadap Aplikasi Baharu Cecair Ion sebagai Pelarut kepada Skala Kalsium Karbonat)

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ABSTRACT

Latest advances of ionic liquids (ILs) have allowed to a new application on the dissolution of calcium carbonate (CaCO₃) scales where the CaCO₃ scale deposition have seriously severe threat in the petroleum field. In this study, the molecular interaction between CaCO₃ and ILs n-pyridinium chloride [NPy][Cl] was studied experimentally in order to get a better understanding during the dissolution of scale. NMR and FTIR spectroscopy was used to study the molecular interaction between CaCO₃ and [NPy][Cl] solution during the dissolution process. To further evaluate the result, the simulation study using Gaussian software was utilized to predict in detail the molecular interaction between [Npy][Cl] and CaCO₃. The finding from this study showed that the metal complex was formed via ligand after dissolution scale process. Based on the findings, it can be clinched that [Npy][Cl] has potential to be used as a scale dissolver in the oilfield, especially in dissolving calcium carbonate scales.

Keywords: Calcium carbonate; dissolution; ionic liquids; molecular interaction

INTRODUCTION

The petroleum production growth in oil field varies depending on geological factor and operational challenges faced in the oil and gas sector. Scale formation is the critical issue and known as one of the main flow assurance obstacles which influencing production in the oil and gas industry. Scales formation mainly causes the declination of oil production, increasing the oil production...
cost more than millions of dollars annually for scale inhibition specifically, including removal as well as lost in revenue consequences from deferred production (Garba & Sulaiman 2014; Refaei & Al-Kandari 2009).

The oilfield scale can be divided into two types which are organic and inorganic scales. The organic and inorganic scales can take place in various parts of the oilfield system, including reservoir structure, well perforations, artificial lifting equipment, and production lines. Paraffin wax and asphaltenes are the most often encountered organic scales in the oil industry. For inorganic scales, the most common oilfield scales are sulfate scales such as calcium sulfate (anhydrite, gypsum), barium sulfate (barite), strontium sulfate (celestite) and calcium carbonate (calcite) (Moghadasi et al. 2003; Ramones et al. 2015). Owing on their relatively high in stability and low of insolubility, the process to eliminate or remove these inorganic scales is limited.

Inorganic scaling can cultivate in the formation of pores close by the wellbore, prominent to reduction establishment porosity and permeability. These scales also able to block of fluid flow in pipeline through the formation of dense lining in the production line whereby it able to coat and harm down holes' completion equipment. This makes the fluid flow to become inferior, lessening its ability and excellent performance, thus leading to plugging of tubing, valves, transport facilities, and surface equipment.

Chemical scale removal is currently cost-effective and efficaciously treat scale problem. It is more efficient when the scale is deposited in unreachable spaces to operate mechanically, so chemical approach shall be the only method which is currently eligible to remove this scale. Based on that, various classes of chemical compounds such as acids, chelating agents, and blended chemicals have been implemented (Kumar et al. 2018).

The use of chelating agents is a more efficient method in removing inorganic scale generally. Chelating agents are substances that able to form complexes with free metal ions and thus get rid of that metal ions which accessible to counter within their structures. The conventional chelating agents used are ethylene diamine tetra-acetic acid (EDTA) and diethylene tri-amine penta-acetic acid (DTPA). Some of the significant advantages to using chelating agents are reduced corrosion, precipitation control, no clay sensitivity, biodegradability, and thermal stability. However, for carbonate scales removal such as calcium carbonate whereas acid treatment is the most widely used to treat it. Hydrochloric acid (HCl) is commonly used in scales treatment especially for the carbonate scales. The use of HCl gives superior result, but in nature they are very corrosive, nevertheless it is cheaper as compares to others scale treatment currently. HCL able to eradicate carbonate scale but unfortunately at the same time harms the surface of the pipeline metal. Hence, corrosion inhibitors along with such acids are needed and indirectly cause the cost increment in operation. HCl retiates with calcium carbonate to give water-soluble product by following stoichiometric equation (Kumar et al. 2018; Li et al. 2008).

\[2\text{HCl(aq)} + \text{CaCO}_3(s) \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O}\] (1)

The implementation of ILs in separation processes has drawn increasing scientific attention for their distinctive characteristics, i.e. trivial toward vapor pressure, elevated heat stability, non-flammability, and structural tun-ability. ILs are therefore, is likely preferences to conventional organic solvents that may cause ecological and operational issues. Extractive distillation, gas separation, and liquid extraction are three distinctive separation methods with high solvent usage in most chemical-related industries. To further apply ILs in these processes, its thermodynamics properties essentially need to be known first. In recent decades, many studies concentrated on the bench-scale experimental and modeling thermodynamic data for systems comprising ILs.

Based on the succinct review on literature, currently there is no alternative to replace HCl as a carbonate scale dissolver and yet HCl is preferable for other scales treatment including sulphate. Surprisingly, neither work nor studies was conducted on the application of ILs for inorganic scale dissolution although ILs have the unique properties in which the possibility to react or interact with ILs. In order to further clarify this for the first time at the molecular level, the reaction/interaction was studied between ILs and carbonate scale to get a better understanding for clear justification in the application.

**Materials and Methods**

**Preparation of ILs**

Equal molar quantities of N-pyridine and chloride-based acid was put into a three-necked round bottom flask fitted by a reflux condenser, a magnetic stirrer, and together with an inlet and outlet for \( \text{N}_2 \) gas flows. The reaction mixture was inerted under \( \text{N}_2 \) at atmospheric condition reliant on raw materials with continuous stirring for 3 h. Figure 1 shows the setup for ILs synthesis. The resulting viscous
liquid later was heated in vacuo at 70 °C to remove any unreacted materials using rotary evaporator apparatus equipped with vacuum pump for purification process, as shown in Figure 2. The resulting viscous liquid was then cooled to room temperature and washed with acetone for three times and the remaining acetone was removed at 75 °C in vacuo again to produce 99% purity of [NPy][Cl] yellowish viscous liquid in colour. Besides NMR and FTIR chemical structure confirmation and analysis, both CHNS and ICP-MS analysis were also taking place in order to quantified the purity of synthesized ILs, whereby impurities content should be below than 100 ppm during considering 99% purity.
Dissolution in [Npy][Cl]

[Npy][Cl]/CaCO₃ mixtures (100:1 wt/wt) were prepared by the addition of CaCO₃ powder (0.1 ± 0.01 g) to a sample of the [Npy][Cl] (10.00 ± 0.01 g) in a 100 mL beaker containing a magnetic stirrer bar. CaCO₃ was obtained from Sigma-Aldrich and synthesized [Npy] [Cl] were used which both having purity with 99.0%, respectively. The beaker was then partially submerged in an integrated thermostat oil bath, set at a constant temperature of 30 °C and kept at this temperature for 24 h with continuous stirring. The experimental setup (as shown in Figure 3) was placed behind a protective blast screen for safety precaution. Afterward, the mixture was collected and was examined by ¹H NMR, ¹³C NMR, and FTIR spectroscopy. Same procedure was adapted to [Npy][Cl]/dolomite mixture where dolomite was obtained from Sigma-Aldrich with 99.0% purity.

NMR and FTIR

NMR spectra were recorded on 500 MHz Bruker, where ¹H and ¹³C spectra logged at 500 and 125 MHz, respectively. All the spectra were assimilated and analyzed with Bruker Top Spin version 3.0 on a Windows PC. ILs samples in approximately amount of 5 mg were diffused in 500 µL of DMSO-d₆ while ILs solution (dissolved carbonate scale) samples were diffused in 500 µL of 0.03% (wt/v) TMS/DMSO-d₆. Each solution was held in a 5 mm NMR glass tube. The sample temperatures were increased up to 363 K for the samples in DMSO-d₆ and TMS/DMSO-d₆, respectively.

Steady-state and time-resolved FTIR spectra were acquired by means of an Attenuated Total Reflectance (ATR) procedure based on Nicolet iS50 spectrometer (Thermo Fisher Scientific, Waltham, USA). All measurements were taken on the built-in diamond ATR crystal in standard room conditions. Steady-state FTIR spectra were registered at 4 cm⁻¹ resolutions over the range 4000-400 cm⁻¹ and signified an average of 128 scans.

GAS CHROMATOGRAPHY FOR CARBON DIOXIDE DETECTION

Agilent 6890 series gas chromatography equipped with thermal conductivity detector and capillary column (HP-MOLSIVE) (30.0 m × 530 µm × 40.0 µm) was used for gaseous product analysis. The column was operated at 353 K with Helium as a carrier gas, while the temperature was maintained at 393 K. For gas chromatography calibration the standard gas with known composition was injected for the five time to achieve calibration curve. Additionally, the experimental data obtained during reaction are compared to the result of the standard gas analysis and calibration curve. The standard carbon dioxide (CO₂) gas information including composition 19.98% and retention time from the GC analysis is 10.07 min.

GAUSSIAN PROCEDURES

Density Functional Theory (DFT) calculations were executed by Gaussian 09W program package, using three parameterizations generalized-gradient approximation corrected correlation (B3LYP) hybrid functional, together with Los Alamos effective core potential plus double-ζ quality (LanL2DZ) basis sets, to optimize the complex structure to a minimum energy structure. This method of DFT calculations which mostly suggested by several researchers were able to simulate optimized geometries and binding energies very well at low computational cost (Becke 1993; Fischer et al. 2012; Frisch et al. 2010; Hay & Wadt 1985; Lee et al. 1988; Muzakir et al. 2013).
RESULTS AND DISCUSSION

Molecular interaction between carbonate scales and [Npy][Cl] was investigated during the dissolution process. Further characterization analysis with spectroscopic methods such as Proton and Carbon Nuclear Magnetic Resonance (NMR) spectroscopy, Attenuated Total Reflectance-Fourier Transform Infrared (FTIR) spectroscopy, Gas Chromatography (GC) and assisted by Gaussian software to simulate the possible structure of carbonate scale and [Npy][Cl] interaction. The result may vary depending on the purity of analyzed substances.

CARBON-CARBON BONDS EVALUATION USING C-NMR

$^{13}$C NMR spectroscopy is a suitable approach to identify of carbon-carbon bonds in explanation of pyridine ring. The experiment was carried out in the spectrum range of 0-175 ppm and two patterns were recorded; (a) before and; (b) after the carbonate scale dissolve in [Npy][Cl]. However, analysis on shift signals from carbons on the pyridine ring only at 125-150 ppm is more revealing as shown in Figures 1 and 2 for calcium carbonate and dolomite (CaMg(CO$_3$)$_2$), respectively.

Figures 1 and 2 show the spectrum $^{13}$C NMR of pure [Npy][Cl] Figure 4(a) and Figure 5(a) and mixture of [Npy][Cl] with calcium carbonate and dolomite scales Figure 4(b) and Figure 5(b), respectively. The spectrum was in aromatic ring range which is between 110-155 ppm. There are three peaks in the graph (i), (ii) and (iii) which is each of peaks refer to the location of carbon in the pyridine ring structure as depicted in Figures 4 and 5, respectively. The location of the peak was differing based on the location of carbon in the ring.

Based on the $^{13}$C NMR spectra above, there is a change in a chemical shift which is moved downfield toward three peaks after the dissolution of scales with [Npy][Cl]. The changes in chemical shift show the interaction between [Npy][Cl] and carbonate scales was occurred and change the pyridine ring structure in the [Npy][Cl] solution.

The change in the chemical shift was influenced by the distribution of electron in the pyridine ring. This shifting can be used as an indicator of the substituent attached to the ring after the dissolution process. They are sensitive to changes in electron distribution, especially those induced by the involvement of the nitrogen lone pair of electrons in chemical processes such as the formation of coordination bond. The electronegativity of the substituent will give the effect to the chemical shift.

There is a possible pyridine act as a ligand where will be attached to the metal ion and cause change to electron density in the ring. The effect on changing in electron density due to electronegativity of the substituent and tend to draw electron density toward themselves and de-shields from the nucleus. This electronegativity of the substituent gives the effect on the chemical shift toward NMR spectrum.

On the other hand, accordance to COSMO-RS principle whereby rely on the quantum chemical continuum solvation model, which extends of the basic quantum chemical method to the liquid phases and provides a virtual conductor environment for the quantum chemical calculations. COSMO-RS’ ability to estimate the chemical potential of an arbitrary solute in any pure or blended solvent at variable temperatures that allows thermodynamic properties including a degree of solute solubility to be predicted. In simple words, through the chemical structure of molecules alone, the charge density, σ profile, σ potential, activity coefficient, and another parameter can be predictably calculated using COSMO-RS approach. This signifies through COSMO-RS which not necessitate any of functional group parameter or any experimental data for prediction. As a result, it is able to practically investigate all ILs and their mixtures, even the uncommon and complex combinations (Grabda et al. 2014; Han et al. 2018; Khan et al. 2016a, 2016b).

![FIGURE 4. $^{13}$C NMR chemical shifts of the spectrum of (a) pure [Npy][Cl] before dissolution and (b) after dissolution with calcium carbonate](image-url)
HYDROGEN BONDS EVALUATION USING H-NMR

Proton nuclear magnetic resonance spectroscopy gives the spectrum of hydrogen environments in each molecule. This spectroscopy method depends on the magnetic field produced by a spinning nucleus containing protons. The dissolution of carbonates scales in ILs, it was found that the molecular interaction in term of hydrogen bonding is occurring in the complex formation between carbonate scales and [Npy][Cl]. Thus, H-NMR spectroscopy was used to analyze the difference in chemical shift of protons attached to a carbon in pyridine ring.

H-NMR provides information involving the hydrogen environment in the mixture of [Npy][Cl] and carbonate scale. The signals of hydrogen in H-NMR spectra can be identified easily as they are produced a doublet and triplet due to the location of hydrogen-bonded in pyridine ring. The H-NMR spectrum of the molecule is used to validate the presence of interaction involving the hydrogen molecules. Kaur and Prakash (2016) has also evaluated the presence of molecular interaction by studying the chemical shift in the hydrogen molecules from the H-NMR spectra. Figures 6 and 7 show the comparison between the chemical shifts observed in H-NMR spectra for pure [Npy][Cl] and the mixture of [Npy][Cl] and carbonate scales.

The comparison of the H-NMR spectra for two types of carbonate scales with [Npy][Cl] follows similar behavior. All the hydrogen environment present in the pure [Npy][Cl] molecules are also present in the mixture of [Npy][Cl] and carbonate scales. This factor proves that there is no formation of any other new functional groups occur at pyridine ring involving −H molecules at pyridine ring. Nevertheless, the interaction cannot be seen clearly just by comparing the peaks representing the hydrogen environment of the components. The presence of interaction needs to be further validated with analysis of chemical shift values of these hydrogen environments.

In this study, only the chemical shift values of hydrogen environment were taken into consideration. This is because the variation in chemical shift values of hydrogen spectra may indicate the strength of the interaction. Kaur and Prakash (2016) mentioned that lower field strength is needed for inducing resonance when there is a strong interaction between the bonds. They have said that in the strong association between the molecules, the hydrogen bonding influences the reduction in electron density around the proton, which results for the chemical shift to lower values.

A chemical shift of hydrogen spectra value was observed after the dissolution process occurs. The shifting hydrogen spectra (ppm) to lower values further confirms the presence of interaction in the mixtures compared to pure [Npy][Cl].

MD simulations produce information at the microscopic level, including atomic positions and velocities. This method is useful in visualizing and inferring the interactions that present between both the ions of an ILs and any dissolved solutes and between the ions themselves. For instance, the mechanism of LCST phase partitioning of mixed ILs in the present of water had been studied by Zhao et al. (2016) using this computational approach. The sequences of all-atom using MD simulations were performed on the ternary mixtures comprising of two different ILs and water for targeted

FIGURE 5. $^{13}$C NMR chemical shifts of the spectrum (a) pure [Npy][Cl] before dissolution and (b) after dissolution with dolomite.
temperatures. The numerous interaction energies and radial distribution functions (RDFs) were simulated and analyzed for these various systems. It was discovered that –NH₂ or –COOH functional group of anions for amino-acid based ILs could possibly have a hydrogen bonding interaction with –COO⁻ ion of another anion. Due to temperature increase, this type of hydrogen bonding interaction amongst anions was reinforced and then the anion–H₂O electrostatic interaction was deteriorated, leading to the phase partitioning of the mixed ILs in water (Kohno & Ohno 2012; Maginn 2009; Tomé et al. 2012; Zhao et al. 2016).

![FIGURE 6. Comparison of H-NMR spectrum for (a) pure [Npy][Cl] and (b) the mixture of ILs with dissolved calcium carbonate scale](image)

![FIGURE 7. Comparison of H-NMR spectrum for (a) pure [Npy][Cl] and (b) the mixture of ILs with dissolved dolomite scale](image)

**FUNCTIONAL GROUP EVALUATION USING FTIR**

FTIR provides a reliable indicator presence of molecular interactions during the dissolution of scale. Each of the bonds in the molecule has its own vibrational frequency which results from the change in dipole moment. The presence of interaction can be studied in terms of shifting in-band or peak intensity of the pure [Npy][Cl] and the mixture of [Npy][Cl] with carbonate scales. This has
been proven by several previous studies conducted to evident the presence of molecular interaction in mixtures (Majstorović et al. 2016; Qiao et al. 2017; Rahul et al; 2015; Silverstein et al. 2006).

The detailed ATR-FTIR spectrum of pure [Npy][Cl] and a mixture of [Npy][Cl] was studied. The comparison of ATR-FTIR spectrum of the mixture ILs with their respective ILs pure components is shown in Figures 8 and 9. Figures 8 and 9 illustrate the stretching frequency responsible for the functional groups of crucial the components studied in this work. A detailed analysis of the band shifts and interestingly new peak was detected present in each of the systems. The dissolution of carbonate scales may induce the self-association behavior of the [Npy][Cl] molecules. Thus, enabling the molecular interaction between molecules of scale and [Npy][Cl].

Besides that, the presence of interaction can also be studied in terms of shifting in a band. Molecular interaction is observed between the -OH group from water toward carbonate scales and ILs mainly due to hydrogen bonding and complex formation. Thus, the presence of interaction between [Npy][Cl] and scale molecules can be identified from the vibrations in the frequency of -OH group. Figure 10 shows the frequencies of -OH group in the pure [Npy][Cl] and the mixture [Npy][Cl] with scales. If there is interaction involving -OH group, it can be observed from the band shift of -OH group between the [Npy][Cl] pure and after the dissolution of carbonate scales.

It can be evidenced from Figure 10 that there is shifting in the frequency of stretching of -OH group between [Npy][Cl] pure and after the dissolution of carbonate scales. Silverstein et al. (2006) have stated that the presence of molecular bonded -OH is identified from the shift in frequency and sharpness of the peak. For the mixtures of [Npy][Cl] and calcium carbonate scales, it was observed the stretching frequency of -OH is 3353 cm⁻¹ whereas for pure [Npy][Cl] the stretching frequency is at 3361 cm⁻¹. It was noted that the stretching frequency of -OH in mixtures of [Npy][Cl] and calcium carbonate scales shift to a lower frequency from the pure ILs. The -OH peak observed from Figure 10 for the mixtures of [Npy][Cl] with calcium carbonate/dolomite scales appears broader than -OH peak of pure [Npy][Cl].

Figure 11 shows that the new peak appears in the FTIR spectrum after the dissolution process. The new peak was detected at band 1442 cm⁻¹ for both scales calcium carbonate and dolomite. Molecular interaction is observed between [Npy][Cl] and carbonate scales when a new peak appears in the spectrum. Based on Ammawath et al. (2004), the new peak appears in this range of wavelength corresponds to an aromatic ring. The appearance of the new peak at 1442 cm⁻¹ shows the existing molecular interaction between [Npy][Cl] and carbonate scales mostly happened at aromatic pyridine ring.

![Figure 8](image-url)  
**FIGURE 8.** Functional groups frequency and comparison between FTIR spectrum of (a) pure [Npy][Cl] and (b) mixture of [Npy][Cl] with calcium carbonate scale.
FIGURE 9. Functional groups frequency and comparison between FTIR spectrum of (a) pure [Npy][Cl] and (b) mixture of [Npy][Cl] with dolomite scale.

FIGURE 10. Chemical shift in FTIR spectrum after dissolution of (a) calcium carbonate and (b) dolomite with [Npy][Cl].
CO$_2$ DETECTION USING GAS CHROMATOGRAPHY (GC)

During the experiment, the bubble was identified and released from the dissolution process. This bubble has resulted from reaction occurred between [Npy][Cl] and both carbonate scales. In order to recognize the gas release, gas chromatography analysis was used. Figure 12 shows the types of gas release during the reaction. There was only one peak in the GC spectrum, which is at 10.65 min retention time whereby H$_2$ peak was noted at 12.95 min retention time that was used as a gas carrier. The peak at retention time 10.65 min indicate CO$_2$ gas which was confirmed the released gas as a CO$_2$. After finished the molecular interaction study through FTIR, C-NMR, H-NMR, and GC, the simulation study is needed to evaluate further the result of molecular interaction which relied on upon through experimental data.
REALISTIC MODELLING OF LIGAND FORM COMPLEX STRUCTURE

Figure 13(a) and 13(b) shows propose ligand in the optimized model for calcium and magnesium complex using Gaussian software. The models were hitherto proofed experimentally through FTIR where the appearance of a new peak at 1442 cm⁻¹ shows possible chemisorption between [Npy][Cl] and carbonate scales which mostly happened at pyridine aromatic ring (based on NMR observations) in the previous section. The existing molecular interaction between pyridine aromatic rings with calcium/magnesium as a complex structure through ligand binding. This model also coincides with the NMR result, which is forming the ligand between pyridine and calcium/magnesium will cause the chemical shift via electronegativity of the calcium/magnesium.

![Proposed ligand model](image)

FIGURE 13. Proposed ligand model in (a) calcium and; (b) magnesium (for dolomite) complex whereas; green represent for Cl, blue for N, red for O, yellow for Ca/Mg, grey for C and white for H

MECHANISTIC OF DISSOLUTION CARBONATE SCALES

The mechanistic model was proposed based on the result of FTIR, NMR, GC, and simulation study by Gaussian. Briefly, the metal complex was formed between calcium ion of the carbonate scale and ligand from [Npy][Cl] solution. The FTIR result shows the existing new peak appears in the spectrum where the range of wavelength has corresponded to an aromatic ring. This result indicates the existing molecular interaction between [Npy][Cl] and carbonate scales at pyridine aromatic ring. The NMR result shows the chemical shift change that occurs in HNMR and CNMR was affect by substituent attached to pyridine ring. The electronegativity of the calcium metal as substituent change the electron density in pyridine ring that will cause the change in a chemical shift in NMR spectra. The GC result was confirmed the gas released
during the dissolution process was CO₂ gas. Finally, the proposed metal complex by Gaussian software was matched well with the experimental result. A promising mechanistic of the dissolution carbonate scales were proposed as illustrated in Figure 14.

\[ \text{CaCO}_3 + 2 \text{Npy} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{Npy} \cdot \text{Ca} \cdot \text{Cl}_2 \]

**FIGURE 14. Proposed mechanistic of dissolution carbonate scales**

**CONCLUSION**

The molecular interaction between proposed ILs [Npy] [Cl] as a new carbonates scale dissolver was confirmed through this study. The experimental analysis showed the proposed ILs was formed metal complex after the dissolution process. The metal complex was formed through a ligand of pyridine ring. This finding will give the alternative to carbonate scale problem as a new scale dissolver which is more environmentally friendly due to unique properties of ILs.

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