Intermolecular Interaction of Carboxylic Group with Calcium Ions and Dissolution of Solid Scales in Bmim-PF6 and Tba-NfO Ionic Liquid Solution

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Abstract

Understanding the mechanism of solid scale dissolution at a molecular level is important to formulate a new chemical dissolver. A molecular dynamics simulation between glutamic acid diacetic acid (GLDA) with calcite was performed to understand the intermolecular interaction between the carboxylic groups with calcium ions (Ca) during the dissolution process at 90 °C. Two solid scales obtained from oil wells were characterised using a scanning electron microscope (SEM) and energy dispersing x-ray (EDX). The dissolutions test of the solid scales were conducted using two ionic liquids solutions; 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim-PF$_6$) and tetrabutylammonium nonafluorobutane sulfonate (Tba-NfO) to evaluate the ionic liquids for solid scales dissolution. Hydroxyls (-OH) in the carboxylic groups of GLDA have strong intermolecular interactions with Ca that plays a role in the chelation process. Two of the carboxylic groups close to amine have the strongest interactions with calcium ions in calcite. Characterisations result shows that the two solid scales are silica-based and barite based. Barite scales have kink-terrace-step crystal surface. Dissolutions test shows that both ionic liquids solutions can dissolve the silica solid scale up to 2700 ppm.

Keywords: solid scale dissolution, molecular dynamic simulation, chelate agent, ionic liquids

Introduction

Well flow may be reduced or stopped due to several factors including a reduction in the well pressure, blocking of reservoir pores near the drainage areas and scale formations in a wellbore that blocks the flow of the fluid [1]. This problem is contributed by solid deposition comes from the inside of the reservoir itself [2]. In oil and gas production, precipitation or deposition of dissolved solid scale which is commonly inorganic salt from aqueous solution in well tubular will cause the formation of scales [3]. Oilfield scale might contain several minerals, sand, organic precipitates, wax as well as the corrosive materials [4-7]. Over time, the depositions or crystallisations of solid scale will grow to form a scale lining on the tubular surface, thereby reduce the flow and eventually block it completely [2].

Chemical treatment such as acid is used to dissolve solid scale often conducted to recover the oil flow [5, 8]. A less corrosive chemical such as chelate agent is utilised to dissolve and prevent the reprecipitation of the solid scale [9-11]. Glutamic acid diacetic acid (GLDA) is one of the chelating agents developed for low corrosivity for calcite scale dissolution in an oil well [12]. GLDA is an amino polycarboxylic group with four carboxylic groups synthesised from glutamic acid [11, 13]. The intermolecular interactions of these functional groups with the metals ions in solid scales is of interest to study due to their roles in the chelation process. Understanding intermolecular interaction in the dissolution process between the main functional group in a solvent and metals ion in the solid scale will improve the dissolution of solid scales at a molecular scale.

Ionic liquid (IL) is also a potential solvent that can be used for solid scale treatment. IL is salt in liquid phase at temperature below 100 °C [14]. Application of IL in oil and gas is still at early stage of laboratory study. The unique properties of IL can be promising to be used in a various process stage in petroleum industries. Several laboratory studies have successfully utilised ionic liquid 1-ethyl-3-methyl- imidazolium tetrafluoroborate ([Emim][BF4], to recover bitumen from oil sand [15, 16]. IL has been proved to be able to dissolve metals ions for mining application [17-19]. Study on the potential of ionic liquid for solid scale dissolution is still at early stage [20, 21]. In this study, two solid scales sample from South East Asia oil fields were conducted a dissolution test using two different ionic liquid solutions to determine the capability of IL in dissolving the scales.

Materials and Methods

Molecular Dynamic Simulation

In this study, intermolecular interactions were simulated using molecular dynamic simulation (MD) and condensed phase optimised the molecular potential for atomic simulation study (COMPASS) forcefield [14, 15]. In this force field, molecular classes are parameterized by incorporating the most common organic and polymer materials [16, 17]. This has allowed for broader application such as intermolecular interaction [18, 19], solubility study [19-21], and molecular recognition [22]. Application of COMPASS for carboxylic group intermolecular interaction with metal ions has been simulated and shows a good result indicating the suitability of COMPASS to be used in this study [23, 24]. MD simulation was conducted using Material Studio version 5.5 (Acceryls Inc, San Diego, USA). The molecular structure was downloaded from the ChemSpider website and optimised using Smart Algorithm and COMPASS force field with an atom-based summation method for electrostatic and van der Waals interactions. The naming scheme for the molecules in GLDA and $CaCO_3$ are shown in Fig. 1. The carboxylic

groups were numbered from 1 to 4. The respective hydroxyl groups were labelled as Hydroxyl 1, Hydroxyl 2, Hydroxyl 3 and Hydroxyl 4. Carbonyl groups were labelled as Carbonyl 1, Carbonyl 2, Carbonyl 3 and Carbonyl 4. Calcium atoms in calcite were labelled as Ca. The intermolecular interaction was interpreted using radial distribution function between oxygen of carbonyl and oxygen of hydroxyl from carboxylic group (-COOH) with calcium ions in $CaCO_3$.

The simulation box was constructed using the Amorphous Cell module in the Material Studio. The box consists of the 30 molecules of glutamic acid diacetic acid (GLDA), 60 molecules of calcite ($CaCO_3$), and 270 molecules of water. The number of molecules was selected based on experimental data by LePage et al. [12] and Mahmoud et al. [11] in which one GLDa may chelate maximum of two calcium ions. It is also within the range recommended by van Gunsteran and Berendsen [22] in which 10^3 to 2×10^4 total atom numbers in the system for liquids. The system was then minimized using a 10,000-steps (fine) Smart Minimizer (Conjugate Gradient method) [23, 24]. Fig. 2 shows the system box consist of GLDA, calcite and water molecules. The simulations were performed with Ewald [25] based summation method for electrostatic and van der Waals interactions. The Ewald accuracy was set at 0.0001kcal/mol/Å. The MD simulation was first conducted using a microcanonical ensemble (NVE) for 3000 ps, beginning with a smaller time steps of 0.02 fs and gradually increasing the timesteps at the early stage of simulation to 1 fs. NVE ensemble was performed to equilibrate the energy of the system prior to isothermal-isobaric (NPT) ensemble simulation [23, 26]. NPT ensemble is to simulate the conditions in a well reservoir at 136 atm and temperature of 90 °C for an additional 3000 ps with a timestep of 1 fs. The Nosé [27] thermostat and Berendsen [28, 29] barostat were used for temperature and pressure control, respectively. The intermolecular interactions were calculated as radial distribution functions (RDF).

Understanding the intermolecular interaction between functional group that play a role in dissolution process will allow us to obtain an insight at molecular level possibilities of functional groups that play a role in solid scale dissolution. Ionic liquid is a class of solvent that can be designed to be incorporated with desired functional group to suit the end purpose. However, study on IL application in well intervention generally and solid scale dissolution specifically is still limited and at early phase [14, 30]. This dissolution study proved that the potential of sulfonate and phosphate to be a functional group that play a role in the dissolution process of solid scale. A future study will involve the incorporation of carboxylic group into the new amino acid based ionic liquid.
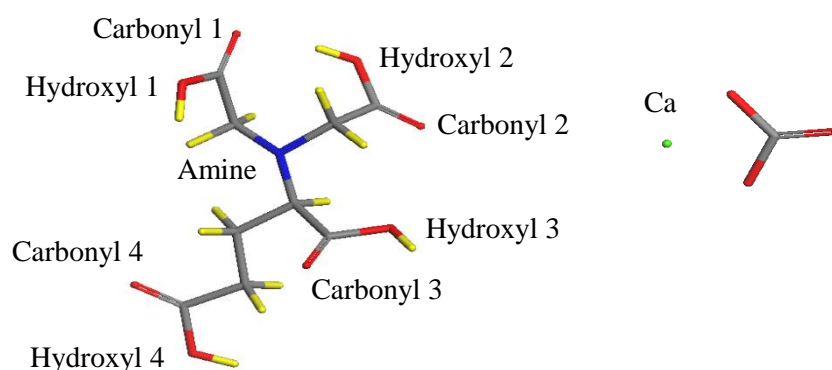

Figure 1. Labelling scheme for glutamic acid diacetic acid (GLDA) and calcite (CaCO₃). Oxygen coloured red, hydrogen coloured white, amine coloured blue, carbon coloured blue, and calcium coloured green.
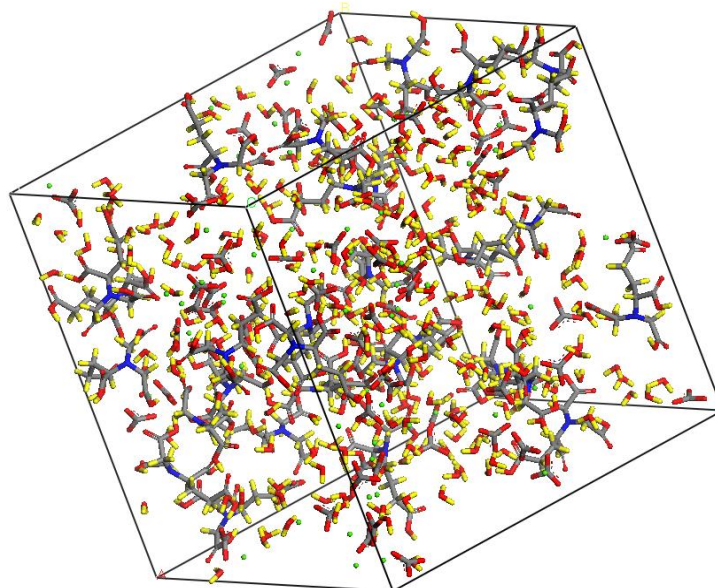
Figure 2. Simulation box consisting of GLDA, CaCO₃ and water system

Surface Analysis

Surface analysis of the solid scales was conducted using a Hitachi Tabletop Microscope TM3030 Plus (Japan) scanning electron microscope. The samples were first dried in an oven at 60 °C until a constant weight was achieved. The analysis was done for 1000x, and 3000x magnification scales.

Elemental Analysis

Energy-dispersive X-ray spectroscopy was used to determine the elemental compositions of the solid scales. Hitachi Tabletop Microscope TM3030Plus (Japan) that was equipped with Energy Dispersive X-ray Spectrometer (EDX). The EDX analysis was conducted for several points and area to get the average of the elemental percentage.

Dissolution Test

The dissolution tests were conducted using the gravimetric method. In this method, the initial and final weight of the solid scales were measured to determine the weight difference. Prior to the dissolution test, the solid scales were crushed and dried in an oven at 60 °C for minimum of 24 hours until a constant mass was obtained. 4 % v/v of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim-PF$_6$) was prepared in 10% v/v of acetone in water solution. Acetone function as a solvent is to allow the ionic liquids to dissolve in the water. About 1 g of Scale 1 and 1 g of Scale 2 were prepared in separate tube for dissolution test in 10 mL of ionic liquid solution at 60 °C for 24 hours. After the test, the scale was filtered from the solution using filter paper, dried and weighted for its final mass. The procedure was repeated for 4% v/v tetrabutylammonium nonafluorobutanesulfonate (Tba-Nfo) solution. The filtered solutions were analysed for the concentration of metals ion using Perkin Elmer Optima 8000 (United State) inductively coupled plasma optical emission spectrometry (ICP-OES). The final concentration of metal ions was determined in ppm. The molecular structure of the two ionic liquids are shown in Fig. 3. Bmim-PF$_6$ contains phosphonium hexafluorophosphate anion

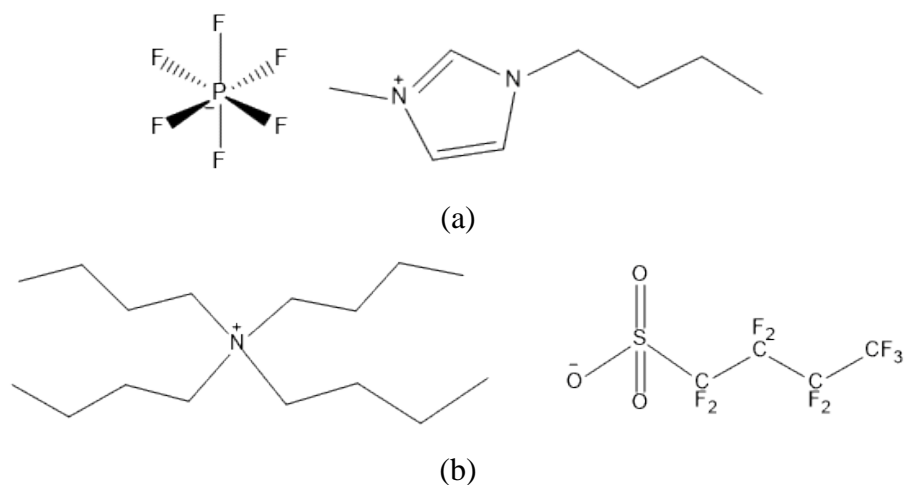and Tba-Nfo contains sulfonate anion which are of interest functional group in the dissolution test.

(a)

(b)

Figure 3. The molecular structure of ionic liquids (a) 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim-PF$_6$) [31] and (b) tetrabutylammonium nonafluorobutanesulfonate (Tba-Nfo) [32]

Results and Discussion

Intermolecular Interaction of Calcite with GLDA

The intermolecular interaction was expressed in radial distribution function (RDF) between the main functional group in the chelating agent and metals ions in calcite. The RDF value, *g(r)*, gives the probability of finding an atom or molecule at a distance *r* from another atom or molecule compared to an ideal gas distribution; *g(r)* is dimensionless [33]. A closer interatomic distance (*r*) and higher peak (*g(r)*) can be interpreted to indicate a stronger interaction [34]. Fig. 4 shows the RDF of intermolecular interaction between the oxygen in hydroxyl groups of GLDA and calcium ions in calcite. The strongest interaction was observed at the radius (r) 3.75 Å with g(r) of 1.42 for Hydroxyl 1 representing the first neighbouring atom. The first neighbouring atom was observed at (r) 4.25 Å with g(r) 1.52 for Hydroxyl 3 and 1.35 for Hydroxyl 4. Hydroxyl 2 shows poor interaction at (r) 3.75 Å with g(r) of only 1.04 for the first neighbouring atom. Fig. 5 shows the intermolecular interaction between the carbonyl group in GLDA with calcium ions in calcite. The Carbonyl 1 and Carbonyl 2 were observed with interaction at the radius (r) 4.75 Å with g(r) of 1.25. However, this interaction was significantly weaker compared to their respective hydroxyl pair. Carbonyl 4 and Carbonyl 2 interaction with calcium ions occurs at the radius (r) 4.75 Å with g(r) value of 1.16 and 0.96 respectively. All carboxylic group of GLDA shows strong intermolecular interaction with calcite with exception of carboxylic group 2 (Hydroxyl 2 and Carbonyl 2). For chelation to occurs, the carboxylic group need to be deprotonated to form carboxylate ions, occurs when GLDA was dissolved in water [35]. The presence of intramolecular hydrogen bonding between amine and hydrogen in carboxylic group 2 will reduce the probability of hydroxyls to deprotonate and cause the weak intermolecular interaction between the carboxylic group and calcite [36]. From the RDF, hydroxyls have stronger intermolecular interaction compare to carbonyl due to its tendency to deproteinized and forming a bond with calcium ions.
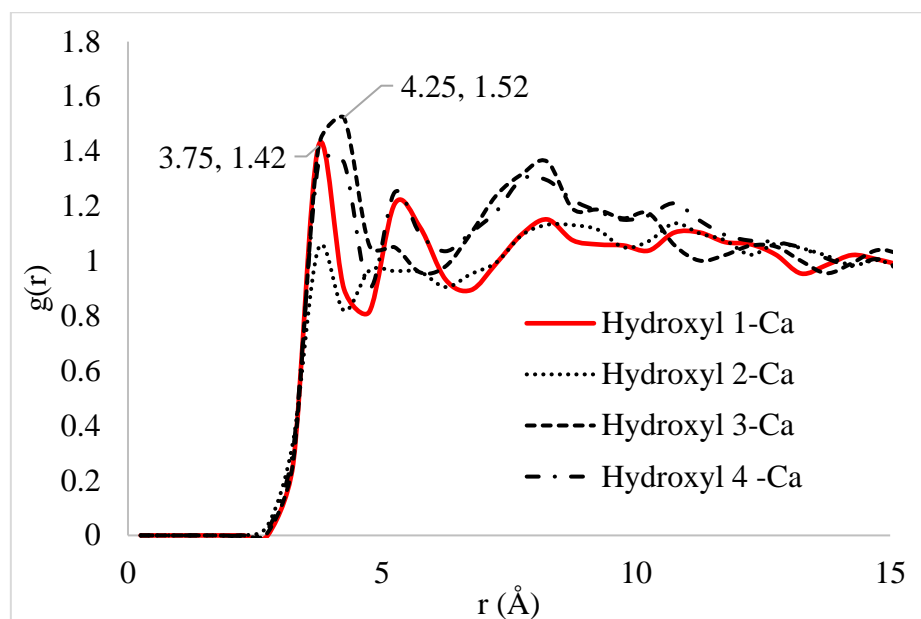
Figure 4: Radial Distribution function of intermolecular interaction between hydroxyl group in GLDA with calcium ions in calcite.
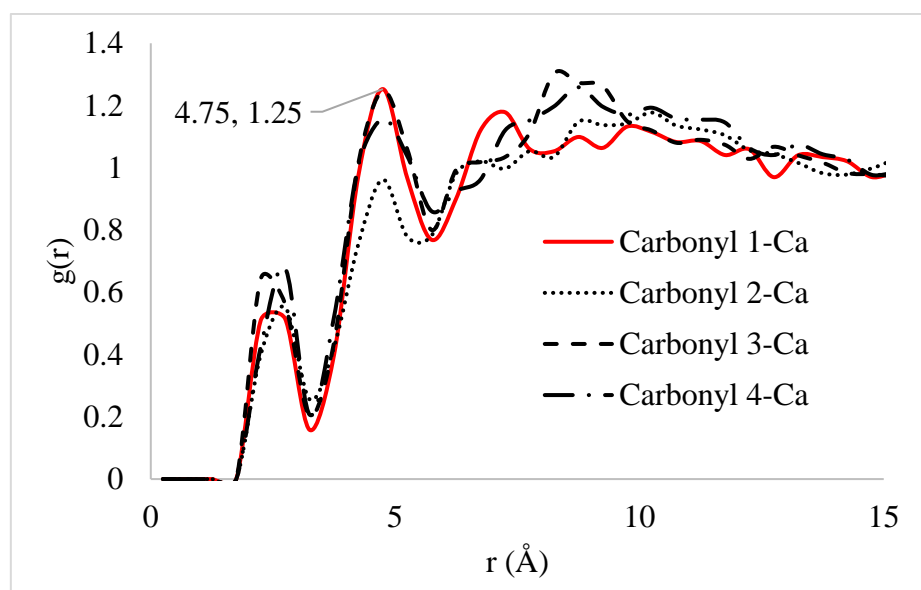

Figure 5: Radial distribution function of intermolecular interaction between the carbonyl group in GLDA with calcium ions in calcite.

Characterisation of Oil Well Solid Scale

Two solid scales were labelled as Scale 1 and Scale 2 respectively. Scale 1 has a yellowish or light brown colour with layered structure. Scale 2 has a dark greyish colour with a white patch. Scale 2 is more brittle compared to Scale 1. EDX result gives the composition of elements available in the solid scale. Table 1 shows the composition of Scale 1 form EDX analysis. EDX analysis shows that Scale 1 consist of mainly barium (43.12 %), oxygen (30.86 %), sulphur (9.57 %) carbon (14.42 %) and strontium (1.37%) with other trace of chemical elements. Based on this composition, the minerals that might present in Scale 1 are barium

sulphate ($BaSO_4$), barium oxide (BaO) and strontium oxide (SrO). Fig.6 shows surface image of Scale 1 at (a) 1000x magnification and (b) 3000x magnification. The SEM image of Scale 1 solid scale shows a crystalline surface; steps, kink, and edge vacancies that can be associated with crystallisation of barium sulphate. Barium might form when incompatible water containing barium and sulphate mixes together, caused the nucleation of barium sulphate crystal that will grow becoming a solid scale crystal [2, 37]. Due to the presence of minerals other than barium sulphate, microcrack and porous space can be observed at 3000x magnification in Fig. 6 (b). Porosity and microcrack can increase mass transfer of chemical absorption for scale dissolution. However, $BaSO_4$ is considered the most difficult solid scale to be removed [38-40]. This is caused by the high purity of the barium sulphate scale during crystallisation that creates a layer of very low porosity and impervious to chemical treatment [2].

Table 1: Composition of Scale 1 solid scale from EDX analysis

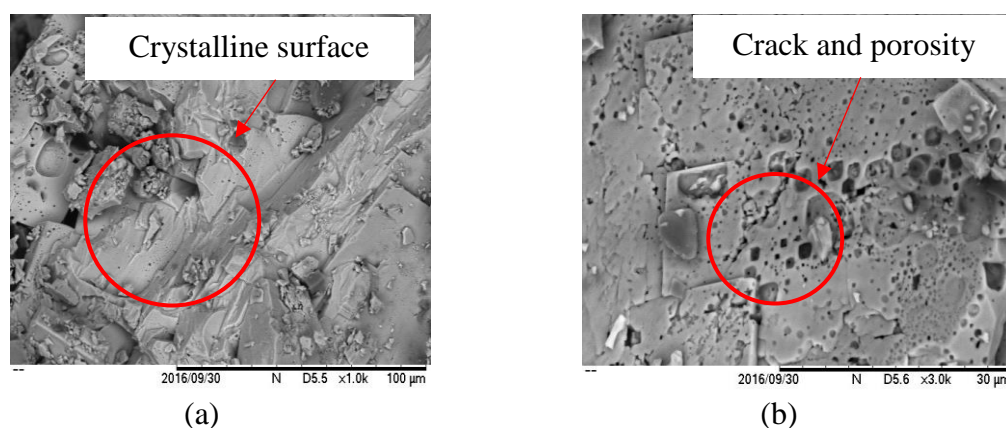| Elements	Weight % (%)
Ba	43.12 ± 0.424
O	30.86 ± 0.379
S	9.57 ± 0.152
C	14.42 ± 0.486
Sr	1.37 ± 0.424

(a)   (b)

Figure 6: Surface image of SCALE 1 solid scale at a) 1000x magnification and b) 3000x magnification using SEM.

Table 2 shows the composition of Scale 2 obtained from EDX analysis. The main composition of Scale 2 is oxygen and silicon at 55.77 % and 23.52 % respectively. Other elements present are aluminium (10.65 %), potassium (3.84 %), iron (2.60 %), calcium (1.54 %) and magnesium (1.02%). Based on this composition, Scale 1 consist of silica (SiO_2) either in its amorphous or crystalline (quartz) form. The presence of aluminium and carbon indicate the possibility of aluminium silicate minerals (andalusite, sillimanite and kaolinite) and a possible trace of calcium carbonate ($CaCO_3$). The high amount of silica indicated that Scale 2 might originate from clay, dissolved sand or very fine sand agglomerated to form a scale [6, 41, 42]. Silica scale formation mechanism likely starts with the dissolution of silica (SiO_2) during matrix acidizing or alkaline flood. When this dissolved silica meets neutral pH water, it

will start to form colloidal silica. The presence of metals such as magnesium will bond this colloidal silica and from the amorphous structure eventually grow to become silicate solid scale [43].

Fig. 7 shows the surface image of Scale 2 at (a) 500x magnification, (b) 1000x magnification and (c) 3000x magnification using SEM. The image shows a surface with microcrack and deposition of fine particles. Although quartz is expected to the presence in Scale 2, crystal structure could not be observed on the surface of Scale 2. This indicate that Scale 2 is a deposition of clay or precipitation of dissolved sand from the oil well. Quartz or sand particles do not easily dissolve. However, dissolved silica in alkaline condition can form silicate solid scale [6, 43].

Table 2. Details composition of Scale 2 solid scale from EDX analysis

Elements	Weight Percent (%)
Si	23.52 ± 0.663
O	55.77 ± 1.434
Al	10.65 ± 0.307
Fe	2.60 ± 0.208
K	3.84 ± 0.148
Ca	1.54 ± 0.104
Mg	1.02 ± 0.208

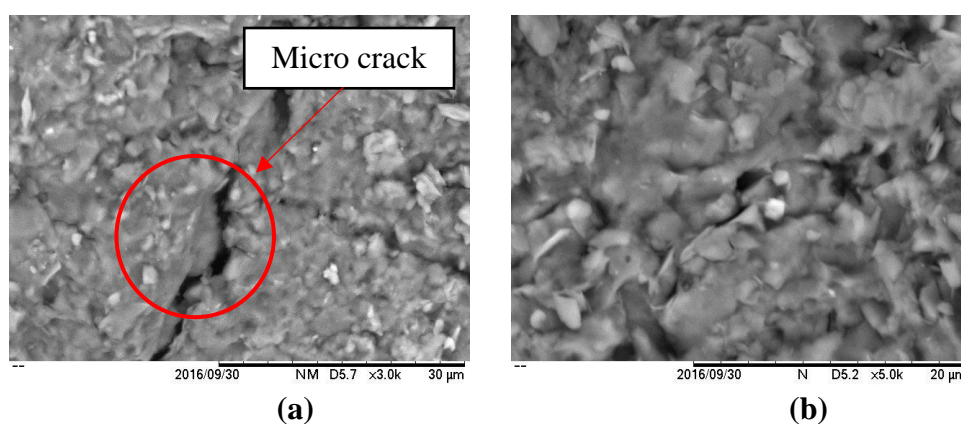(a)   (b)

Figure 7: Surface image of Scale 2 solid scale at (a) 1000x magnification and (b) 3000x magnification using SEM.

Dissolution of Solid Scale in Ionic Liquid Bmim-PF$_6$ and Tba-NfO Solution

Table 3 shows the dissolution test result for the dissolution of Scale 1 and Scale 2. The reduction in mass after the dissolution test for Scale 1 is about 1% in both Bmim-PF$_6$ and Tba-NfO solution. The mass reduction for Scale 2 in Bmim-PF$_6$ is about 2 % and 1.2% in Tba-NfO solution. Analysis using ICP-OES shows that barium ion was not detected in both ionic liquids after the dissolution of Scale 1. This is in agreement with the small reduction in mass of the solid scale after the dissolution. The small reduction may be contributed by the dissolution of other metals such as strontium which present in Scale 1.

For Scale 2, 1622 ppm and 2754 ppm of silicon were detected in both ionic liquid Bmim-PF$_6$ and Tba-NfO respectively. Silica scale is a difficult and challenging solid scales to be dissolved. Acid such as hydrofluoric acid was used to dissolve silica [8, 44]. The mechanism of the dissolution of Scale 2 in IL solutions occurs on other metals present in the solid scale such as magnesium and aluminium that bind the silica fine particles [41, 42]. These metals are easier to dissolve in IL compare to silica [45]. Tba-NfO is better in dissolving silica scale compare to Bmim-PF$_6$. This can be associated with the strong electronegativity of the anion in Tba-NfO compared to Bmim-PF$_6$.

Table 3. Dissolution test result of Scale 1 and Scale 2 in ionic liquid solution of Bmim-PF6 and Tba-NfO

Analysed Element	Solid Scale + Solvent	Percentage Reduction (%)	Metals ion Concentration (ppm)
Barium (Ba)	Scale 1+ Bmin-PF$_6$	1.08	Not Detected
	Scale 1 + Tba-NfO	0.75	Not Detected
Silicon (Si)	Scale 2 + Bmim-PF$_6$	1.94	1622±200
	Scale 2 + Tba-NfO	1.26	2754±94

Conclusion

Hydroxyls from carboxylic group show stronger intermolecular interaction with calcium ions compared to the carbonyl in GLDA. RDF from MD simulations shows that two of the carboxylic group closer to amine in GLDA molecules have intermolecular interaction with calcium ions. The scales obtained from oil field determine to be barite and silica solid scale. SEM analysis shows that the barite scale has crystalline surface; steps, kink, and edge vacancies from crystallised barium sulphate. Silica scale shows surface with microcrack and deposition of fine particles. It was demonstrated that the ionic liquid solution can be utilised as the solid scale dissolver for oil well application. 1-butyl-3-methylimidazolium hexafluorophosphate (Bmim-PF$_6$) can dissolve up to 1622 ppm of silicon from silica solid scale. Tetrabutylammonium nonafluorobutanesulfonate (Tba-Nfo) can dissolve up to 2754 ppm of silicon from silica scale at a concentration of 4% v/v, 24 hours at 60 ºC respectively. A further study on the utilisation of ionic liquid as solid scale dissolver should be conducted to determine the best functional group that can be incorporated in the ionic liquid for better dissolution performance.

Acknowledgement

Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards

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