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Molecular Interaction of Carboxylic and Amine Group with Calcium and Iron for Solid Scale Dissolution

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EXTENDED ABSTRACT

Calcium carbonate is one of the common solid scale in oil and gas upstream production occurred along with other type of scale such as iron (II) sulphide. Commonly, acid is used for dissolution of solid scale however acid is corrosive and dangerous to handle [1]. Non-acidic dissolution technology such as chelating agent form complexes with metals ions and highly depends on pH [2]. The agent may contain carboxylic and amine as the main functional group that plays a role in solid scale dissolution. This paper aims to study the molecular interaction between carboxylic and amine group with metal ions in calcium carbonate ($CaCO_3$) and iron (II) sulphide (FeS).

The interaction was studied through molecular dynamic (MD) simulation using Material Studio 7.0. There are two steps of dynamic simulation applied to simulate the dissolution of solid scale. The first step is the equilibration calculation to ensure the system is stable with energy conservation. It was done under a constant number of molecules, volumes and total energy (NVE) assemble for 3 nanoseconds with random initial velocity and 1fs time step. The second step was conducted at a constant number of molecules, pressure and temperature (NPT) to simulate the condition in the well reservoir at 136 atm assemble for another 3 nanoseconds. After dynamic simulation, trajectory output analysis was analysed using radial distribution function (RDF). Atom based summation method was used for geometry optimisation, Ewald summation for equilibrium and production stage dynamic calculation and condensed-phase optimised molecular potentials for atomistic simulation studies (COMPASS) force field for energy interatomic potential calculation. The selected compounds selected for MD are glutamic acid diacetic acid (GLDA) and ethylenediaminetetraacetic acid (EDTA) with $CaCO_3$ and FeS. Meanwhile an experimental work involve dissolution of $CaCO_3$ and FeS with EDTA and monosodium glutamate (MSG) at several pH values. Atomic absorption spectroscopy (AAS) were used to measure the concentration of Ca and Fe in the solution after the dissolution. Fourier-transform infra-red spectroscopy (FTIR) were used to detect the change in functional group of EDTA and MSG after the dissolution as a validation for simulation result.

Fig. 1 illustrates the partial naming of selected molecules in every functional group of GLDA. On-GLDA represent oxygen atom in hydroxyl, On=GLDA represent carbonyl group and N-GLDA represent tertiary amine in GLDA. Fig. 2 shows the radial distribution function graph of molecular interaction On=GLDA with Fe ions in FeS. The smaller the radius (r) and higher the probability g(r) shows the stronger the interaction. All the strongest interaction observed from the RDF occurs at radius 0.225 nm. The strongest interaction with Fe ions is for O4=GLDA at probability of 6.84 followed by O3=GLDA with probability of interaction at 6.24. O2=GLDA have probability of interaction with Fe ions at 5.87 and O1=GLDA have probability at 5.30. Based on the RDF, overall interaction of oxygen atom in carbonyl group of GLDA with Fe ions is considered very strong. At low pH, dissolution of $CaCO_3$ in EDTA and MSG solution is expected to be high. At pH lower than 5, EDTA and MSG will initially behave like acid to dissolve $CaCO_3$ before forming a

complex with Ca^{2+} or Fe^{2+} [3]. Once the complex was formed, the chelate should remain stable and analysed using FTIR for differences in spectrum for -OH bond in carboxyl group.
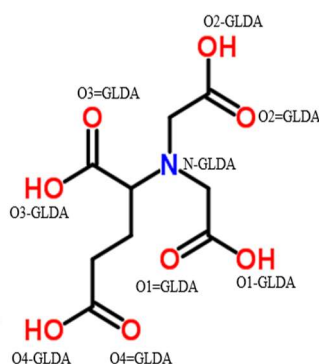

Fig. 1: Partial naming of molecular structure of important molecules in glutamic acid diacetic acid (GLDA) in molecular dynamic simulation for radial distribution function analysis.
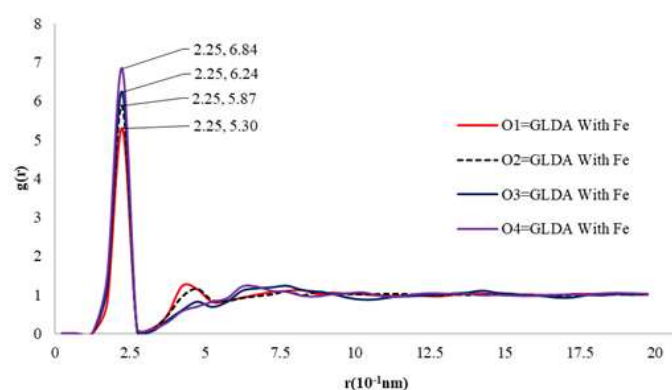

Fig. 2: Radial distribution function of molecular interaction between On-GLDA with calcium ions (Ca) in calcium carbonate (CaCO$_3$).

Keywords: Molecular interaction; Molecular dynamic simulation; Solid scale dissolution; Chelating agent.

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