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EFFECT OF ADSORPTION ON SATURATED SANDSTONE WITHIN ELECTRIC DOUBLE LAYER ON SOLID/LIQUID INTER-PHASE

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Abstract

The formation of the porous medium is based on solid mineral grains, including quartz's, carbonate, and oxides. Many studies have been conducted only for silica; the adsorption behavior of crude oil on sandstone has not been explored. This research work considered the different concentrations of NaCl electrolytes in molecular dynamics simulation to determine interaction of ionic adsorption on sandstone. Obtained results show that the adsorption capability of NaCl electrolyte at higher concentration indicates the interaction between components of oil and sandstone surface in which the penetration of water film and adsorption with ionic molecules improves the adsorption capability. The adsorption values in obtained result are -23.91, -27.69, -29.32, -32.89/ -34.65 and -45.89 kcal/mole for concentration of 3000 ppm, 5000 ppm,7000 ppm 9000 ppm, 11000 ppm and 11000 ppm with copper-oxide respectively. Obtained results also reveal the adsorption process of oil components formation in the reservoir gives guidance to oil detaching agent in reservoir exploration. It also shows, the adsorption components alter the wettability from oil-wet to water-wet that provides a repaid distribution of fluids flow and sweep efficiency.

Keywords: *Ions, Electrolyte, Porous media, Adsorption, Electric double layer, Sandstone, Molecular dynamics.*

1. Introduction

The interface between sandstone with other media is normally charged, and these can be classified into the water interfaces, oil, or solid-water interface that include clay, ions, oxide or polymers [2-5]. The magnitude and sign of the surface density play a role in multiple applications as well as adsorption of particular ions from the solution [4]. Once a porous medium is formed because of mineral solid grains such as quartz's, carbonate, oxides [6-7]. The surface charge repels to ion in the electrolyte whose charges have the same sign as the surface charge, and it is known as cations. It attracts ions because of opposite charge and known as cations [6]. These occur in the vicinity of the electrolyte in sandstone interface due to clay contents present. The Electrical double layer (EDL), which comprise of the Stern layer and diffuse layer, stern layers are the first internal layers that form at a charged surface in an ionic solution, and the ion is immobile because of the charge opposite to the surface. While the diffuse layer is the ionic structure that explained the variation of electric potential near the charged surface which is mostly clay, which is more negative surface charges.

The electric potential distribution, as well as ions within the diffuse layer, is governed by the Poisson Boltzmann (PB) equation is used to balance between electrostatic and thermal diffusion forces [7]. The diffuse layer is the closest plane to the solid surface at which floe occurs, and it is termed shear plane or the slipping plane. The electrical potential at this plane is called zeta potential (ζ). This play significant role in determines the degree of coupling between the electric flow and the fluid flow in porous media. It has been recorded that most

reservoir rocks are negative charges when in contact with liquids [8-9]. The adsorption mechanism of oil in the reservoir with the use of electrolytes should be well known so that the displacing agent of oil desorbed from the rock can be designed. Moreover, in the oil reservoir formation, adsorption of oil can change the wettability of the reservoir from oil-wet to water-wet on the mineral surface. And this will make a proper distribution of fluid in the reservoir [1,10,11]. From the experiment, the adsorption of crude oil on the surface of mineral has been studied but not extended to the adsorption of ions at different concentrations on sandstone. Once a surface of solid grains is in contact with a liquid, it will try to attain surface electric charge, In comparison to the cations, the anions usually adsorb more strongly to the neutral surfaces, and resultant many surfaces are negatively charged. The clay minerals acquire their charge using isomorphous substitution of silicon and aluminum atoms by metal ions of lower charge, and it leads to charge the crystal negatively [12]. The mineral particles of the clay are made of stacked layers and space in-between two adjacent layers. This space is named as the interlayer space particles that typically consist of 5 to 20 stacked layers [13]. In this study, the molecular dynamics simulation on material studio has been implemented and investigated to the adsorption of crude oil interaction between the ionic electrolyte at different concentrations using NaCl and copper-oxide nanoparticles on sandstone reservoir to reveal their adsorption mechanism.

2. Materials and methods

2.1. Adsorption simulation using material studio

The simulation mode is based on the adsorption with different concentrations of NaCl electrolyte solution. The sandstone was built with all reservoir sandstone composition were imported from material studio software library. The geometry optimizations of each material were calculated to optimize the molecules using forcite modules. In the molecular dynamics simulation (MSD), the force-filed is one the major parameters for better calculation of the energy. COMPASS force field with a unified molecular force field used in both organic and inorganic molecules, polymers, some metal ions, metal oxides, and metals, so it is widely used in molecular dynamics simulation. For the electrostatic force and van der Waals interaction between different particles Ewald and atom based were chosen respectively. To calculate bond angle bending energy, bond torsion energy, bond angle and mutual coupling energy between them include Van der Waals energy and Coulomb by using equation 1 to 3

$$E_{pot} = E_{bond} + E_{ij} + E_{elec} \quad (1)$$

$$E_{ij} = \sum_{ij} \varepsilon_{ij} \left[2\left(\frac{r_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{r_{ij}}{r_{ij}}\right)^6 \right] \quad (2)$$

$$E_{elec} = \sum_{ij} \frac{q_i q_j}{r_{ij}} \quad (3)$$

where r_{ij} is the distance between atoms; i anc j are the energy length parameters, respectively. These parameters are determined for given molecules. Similarly, q_i and q_j are the atom charges of the atoms i anc j, ε dielectric constant of the material.

In this research, the molecular dynamics (MD) simulation method has been used to investigate the molecular interactions of sandstone reservoir at microscopic level behavior in the presence of electrolytes with percentages. The movement of grouped ion particles (e.g., atoms) is obtained by solving the classical equations of motion that give the information on system dynamics at atomic scale. The adsorption of molecular dynamics in simulation has been performed with sandstone at different concentrations of NaCl electrolytes using material studio software. The setting parameters in proposed simulation, the force field module is used from COMPASS. This module assigned charge force field with fine quality summation method for electrostatic and van der Waals forces. That is Ewald and atom based respectively for (geometry optimization). The construction of amorphous cell COMPASS force field has been used, and sandstone information was imported, including kaolinite, albite, SiO_2 quartz, H_2O and oil C_8 H_{18} into simulation environment. In order to comprise the reservoir environment,

the energy interaction potential, time integrator algorithm calculation, COMPASS force field are need be optimized molecular potential for the atomic simulation studies. In polymers, the organic and inorganic gas molecules' COMPASS force field is suitable [15]. Prior to carrying out the adsorption, some steps are needed to take place. Initially, it is required to sketch or import the molecular structures from the library to form the sandstone reservoir environments. The kaolinite, albite, quartz, oil and water molecular structures were built, and then geometry optimization calculation was carried out for each molecule to ensure their stabilities using force fields. Complete interaction parameters were carried out through a suitable force field, and then MD simulation started with replicating the structure of accurate molecules. The amorphous cell model's calculation was constructed to combine all the molecules with one boundary. The cubic periodic boundary condition ensures the surface effects are overcome, and the size of the simulation depends on the amounts of the molecules that are involved [16-17]. Adsorption energy locator was calculated suing the COMPASS force filed with the summation methods of electrostatics group and van der Waals force of atom. The quality chooses for the simulation is tuned with low energy configurations of fixed energy window of 10kcal/mol and maximum energy of 10kcal/mol. The properties used for the simulation were energy destruction, low energy configuration, density field and energy field with a temperature of 298k and cutoff distance of 12.5A.

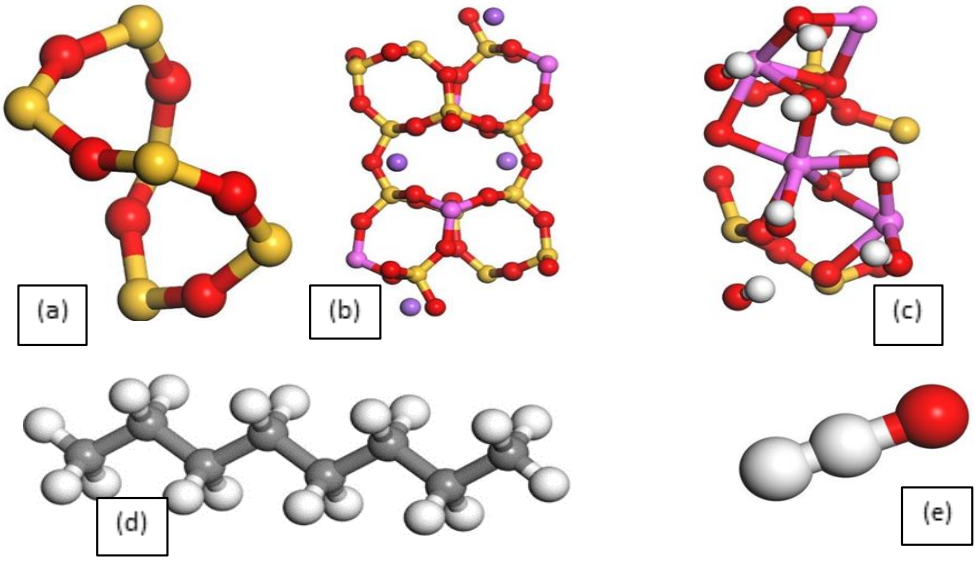


Fig. 1. Molecular structure of (a) SiO_2-quartz, (b) Albite, (c) kaolinite, (d) Oil (C_8H_{18}) and (e) water (H_2O) used molecular dynamic simulation

3. Result and discussion

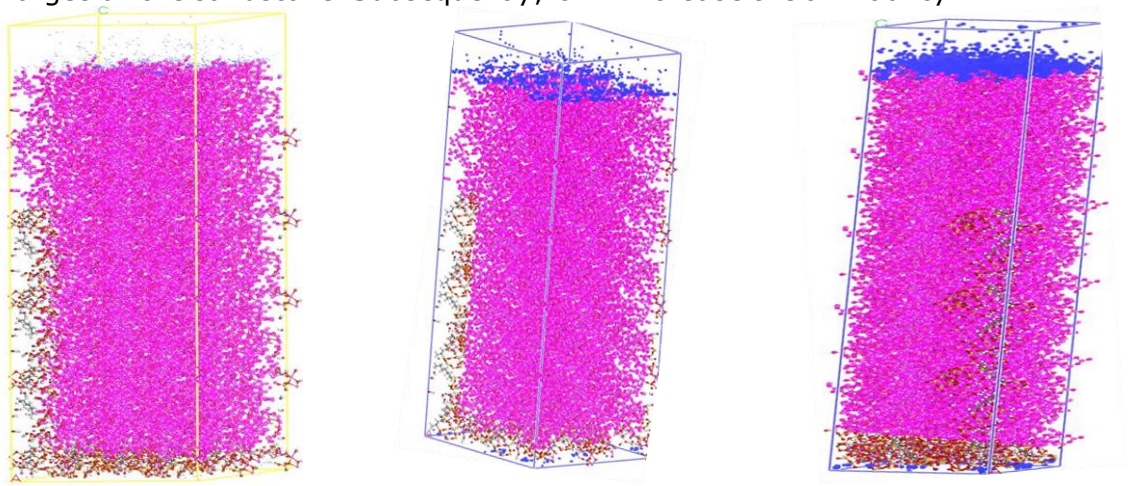
The adsorption energy of NaCl electrolyte on sandstone for different concentration provides more understanding of the distribution of the ion on sandstone. This relation can mathematical expressed as,

$$E_{ads} = E_{Sur-Oil} - E_{Sur} + E_{Oil} \quad (4)$$

where $E_{Sur-Oil}$, E_{Sur} and E_{Oil} are single point energies of sandstone, oil, and electrolyte, respectively.

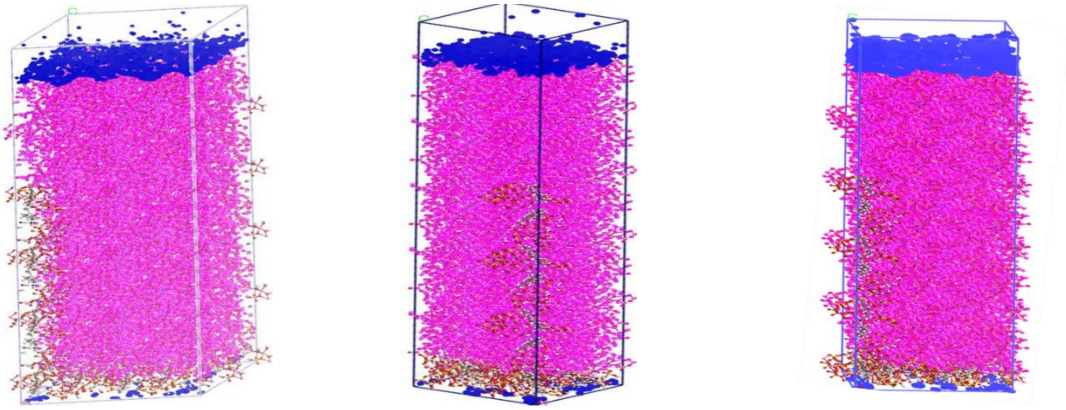
The higher the adsorption, the more the displacement of the oil molecules in the porous media and the stronger adsorption interaction of the entering ions on the sandstone. This relation will detach the oil molecules from the sandstone and alter the wettability of the reservoir for more oil mobility. The increase in concentration of NaCl electrolyte has significant improvement in adsorption energy that shows the electrolyte have positive effect on the displacement of oil molecules. The different ionic content on the sandstone provides more interaction between the injected ions content from the NaCl solutions. Obtained results show that when the concentration of NaCl raised to 11000ppm (see Figure 3b), then resultant adsorption

energy increased drastically to (-34.65kcal/mol), and this value falls under the chemisorption that shows higher binding energies between the chemical bond of the electrolyte and the sandstones. This is because of charge transfer or charge distribution involved on the surface and the adsorbate. Furthermore, it also shows that the internal molecular bond between the pore spaces and sandstone is broken because of interaction between NaCl electrolytes and charges on the sandstone. Subsequently, it will increase the oil mobility.



(a) (b) (c)

Fig. 2. (a) adsorption configuration of sandstone reservoir with 3000ppm of NaCl solutions, (b) adsorption configuration of sandstone reservoir with 5000ppm of NaCl solutions and (c) adsorption configuration of sandstone reservoir with 7000ppm of NaCl solutions



(a) (b) (c)

Fig. 3. (a) adsorption configuration of sandstone reservoir with 9000ppm of NaCl solutions, (b) adsorption configuration of sandstone reservoir with 11000ppm of NaCl solutions and (c) adsorption configuration of sandstone reservoir with 11000ppm of NaCl solution and copper-oxide nanoparticles

Table 1. Adsorption energy of sandstone reservoir in the presence of a different concentration of NaCl electrolyte

Percentage of NaCl electrolyte	Adsorption energy (kcal/mol)	Total energy (kcal/mol)
3000 ppm	-23.91	-24.01
5000 ppm	-27.69	-29.62
7000 ppm	-29.32	-32.37
9000 ppm	-32.89	-34.23
11000 ppm	-34.65	-36.89
11000ppm with copper oxide	-45.89	-49.45

Material studio Accelry 8.1 modules were used to determine the adsorption energies; the desired molecular structures were constructed and then geometrically optimized by using forcite module. These molecules were then added sequentially to a built vacuum slab enclosing a SiO_2 quartz (111), C_8H_{18} (111), albite (111), kaolinite (111), NaCl (111), H2O (111) and CuO (111) with cleaved surface of specific dimensions at distance of 5Å and thickness of 15Å. The total energy is defined as the sum of the adsorbate components energies, the rigid adsorption energy, and the deformation energy adsorption energy in kcal/mol reports energy released (or required) when the relaxed adsorbate components. From Figures 3b and 3c, it was observed that there is high adsorption on the sandstone. Also, all adsorption energy values are negative, which indicates that the adsorption of ions on solid interface surface is spontaneous

Adsorption of energy that refers to the change in material is total energy before and after the adsorption. Table 1 shows that the adsorbing conditions of the sandstone reservoir with reaction of oil and electrolytes are observed abundantly on the surface. Since the adsorption process is exothermic, the adsorption of different adsorbed is negative. Figure 2(a), 2(b), and 2(c) show that the adsorption of sandstone reservoir NaCl electrolytes at 3000ppm, 5000ppm, and 7000ppm and their respective adsorption energy is -23.92, -27.69 and 29.32kcal/mol. Figure 3 shows that the result of the adsorption configuration of sandstone reservoir with 9000ppm and 11000ppm of NaCl electrolytes have adsorption value of -32.89 and 34.65kcal/mol. It indicates strong adsorption with 11000 ppm of NaCl, and when copper-oxide nanoparticles were introduced, the increase in adsorption energy occurred that ranges from 34.65 kcal/mol to 45.89 kcal/mol. This is because of the stable properties of CuO. The observation based on obtained results shows that there is strong adsorption on the solid surface of the sandstone, which basically falls to chemisorption. Table 1 shows that the value of the adsorption energy indicates the binding energy is more ionized by the crystal surface. The values of adsorption of ions were inadequately high due to excess of the ions adsorbed on the solid phase of sandstone. Subsequently, it has more oil displacement.

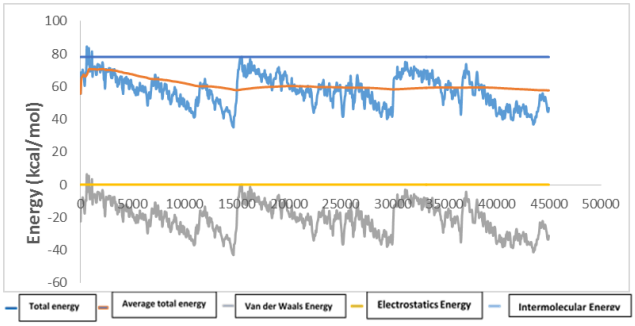


Fig. 4. Total energy distribution, Van der Waals energy, electrostatics energy and intermolecular energy of sandstone with 3000ppm of NaCl electrolyte obtained by adsorption locator module during the energy optimization process

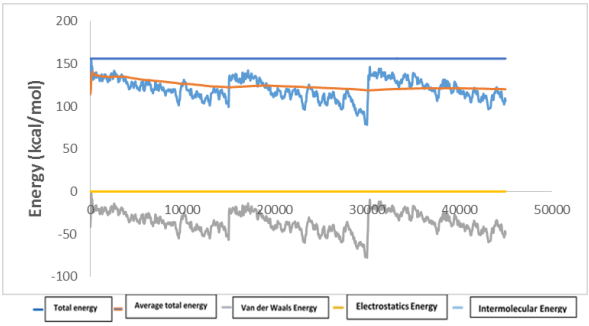


Fig. 5. Total energy distribution, Van der Waals energy, electrostatics energy and intermolecular energy of sandstone 5000ppm of NaCl electrolyte obtained by adsorption locator module during the energy optimization process

The study used MD simulation to determine the behavior of adsorption on the sandstone reservoir with different electrolyte concentrations, from Figure 4 to Figure 7. It shows that the graph of the total energy, Van der Waals energy, average total energy, electrostatics energy, and intermolecular energy for the system under the study of solid/liquid interface are calculated by optimizing the whole structures. The most stable adsorption configuration of the electrolyte is adsorbed onto the sandstone which was observed on Figure 8 and Figure 9 respectively also the adsorption of NaCl electrolyte on the sandstone which shows that there is strong interaction between the adsorbate and the substrate

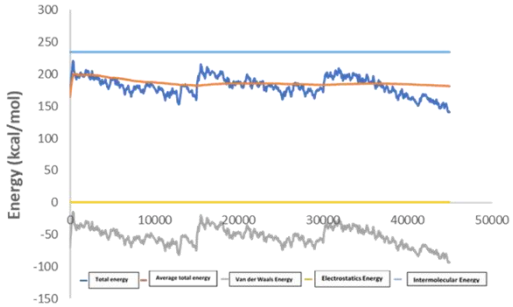


Fig. 6. Total energy distribution, Van der Waals energy, electrostatics energy and intermolecular energy of sandstone with 7000ppm of NaCl electrolyte obtained by adsorption locator module during the energy optimization process

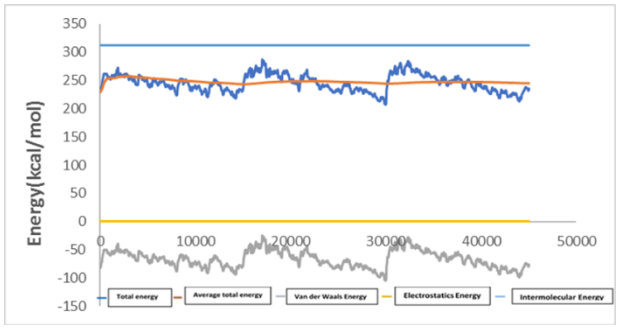


Fig. 7. Total energy distribution, Van der Waals energy, electrostatics energy and intermolecular energy of sandstone with 9000ppm of NaCl electrolyte obtained by adsorption locator module during the energy optimization process

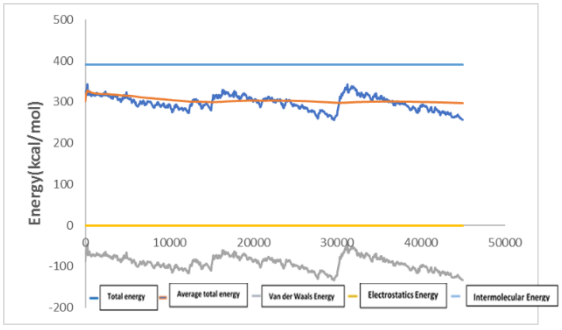


Fig. 8. Total energy distribution, Van der Waals energy, electrostatics energy and intermolecular energy of sandstone with 1100ppm of NaCl electrolyte obtained by adsorption locator module during the energy optimization process

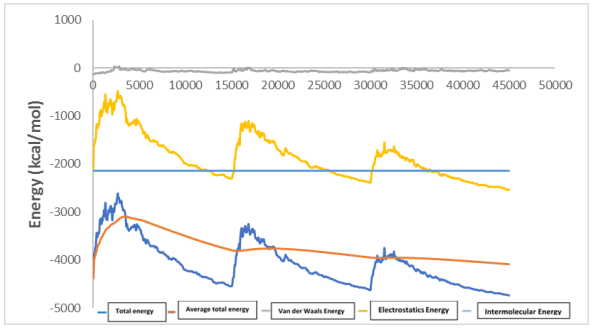


Fig. 9. Total energy distribution, Van der Waals energy, electrostatics energy and intermolecular energy of sandstone with 1100ppm of NaCl electrolyte with copper-oxide nanoparticles obtained by adsorption locator module during the energy optimization process

4. Conclusion

Molecular dynamics simulation is used to investigate the adsorption of ionic molecules on sandstone reservoir with different concentration of NaCl electrolyte. The highest absorption energy was achieved at the solid (rock)/brine/oil interphase with the injection of copper-oxide nanoparticles. However, this can be inferred that chemical interactions between quartz's, brine, crude oil, and nanoparticles contribute more adsorption to the rock surface due to intermolecular energy and Van der Waals energy interaction between them.

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