DPD Simulation of Surface Wettability Alteration by Added Water-Soluble Surfactant in the Presence of Indigenous Oil-Soluble Surfactant

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The effect of a surfactant on wettability alteration and emulsion inversion is studied using Dissipative Particle Dynamics (DPD) modeling. The DPD model contains 1200 oil molecules, 4800 water molecules, 400 oil soluble (indigenous to the oil) surfactants with a head-tail configuration and 400 water soluble molecules to mimic a surface active chemical/ion in the water. Results show that surfactant migrates to the fluid-fluid interface in general, where its potential energy is minimal. However, thermal kinetic energy can lead to a "tunneling" through the interface and into the other phase with a small probability. The same effect lead to migration of the oil soluble surfactant from the oil phase onto the water wet surface, and caused wetting alternation from a water-wet to a surfactant coated effectively oil-wetting surface. The water soluble surface active molecule suppressed this effect when added. Additional emulsion inversion studies confirmed the "Bancroft rule": oil-in-water emulsions were induced by water soluble surfactant, and water-in-oil emulsions were induced for oil soluble surfactant. The explored cases were characterized by high interfacial curvature. For cases in which the surfactant is just as soluble in water as in oil, the interface had a minimal curvature; i.e., a flat interface or a more geometrically complex gyroid interface with a minimal average curvature. Results demonstrate that DPD represents a suitable numerical laboratory to investigate the macroscopic behavior (topology and morphology) of an oil/water/surface system as function of the molecular parameters such as solubility.

1. Introduction

Surfactants play a fundamental role to alter the oil/water wetting properties in the reservoir for enhanced oil recovery purposes (Español et al, 1995). A surfactant is usually used as a chemical compound to reduce interfacial tension, promote emulsification and induce emulsion inversion (Español et al, 1995) and/or to alter the wetting properties of the fluid towards a substrate (solid wall) (Li et al, 2009). Understanding the physics of these phenomena is a fundamental challenge which is addressed in this paper using Dissipative Particle Dynamics (DPD) modeling. DPD is a stochastic, classical Newtonian–Lagrangian approach introduced by Hoogebrugge and Koelman (Hoogerbrugge, 1992). Each DPD particle (bead) represents a segment of a real molecule. The beads repulse each other via inter-particle forces, and the magnitudes of these forces are controlled through interaction parameters. Simulations were carried out changing the number of time-steps until a statistically converged solution was obtained.

2. Wettability alteration

Sodium dodecylbenzenesulfonate (SDBS) surfactant has been chosen for this case study. This surfactant has the following molecule formula: $C_{18}H_{29}NaO_3S$ (Encyclopædia Britannica, 2017). From its chemical and physical properties, it could be assumed that this type of surfactant with its long hydrocarbon chain is more soluble in oil than in water. Indeed, some references state that SDBS is 20% soluble in water (Chemical Book, 2016). In DPD, SDBS has a simple head-tail configuration (see Figure 1). The interaction/parameters are presented in matrix format (Tables 1, 2) and control the way surfactant, oil, water and the surface (surface is

wall in our code) behave. The numbers represent the strengths or magnitudes of the repulsive DPD-forces, which occur between the beads. W stands for Water, O stands for Oil, T stands for Tail, H stands for Head and S stands for Substrate (Wall) parameters for all the instances. Tail and Head refer to the surfactant parameter. There is, also, unknown column (fourth column) marked as a simple dot, which is not used in this type of simulation. This column is important if another surfactant is added for the simulation. Otherwise, it can be neglected. All interaction parameters were calculated via consideration of mixing energies and Flory-Huggins interaction parameters, which were gained through simulations based on Monte Carlo techniques (Li et al, 2009).
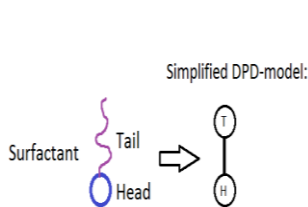

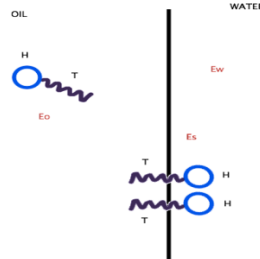Figure 1 Surfactant configuration

Figure 2 Oil-water-surfactant interaction

Our DPD model uses one bead for the head, and one for the tail. The matrix is symmetrical, and the numbers are normalized. Mainly, the bigger the input parameters, the more repulsion between beads will occur. For example, the TW interaction is more than HW interaction (67>32). Overall, we have implemented 4 different settings for both oil and water wet substrates.

2.1 Case 1: "Water wet to oil wet surface induced by oil soluble surfactant"

Wettability of the surface is a crucial characteristic, which describes the relative ability of a fluid to spread over the surface. This feature of the fluid could be identified through the contact angle, where two fluids form an interfacial angle, which might be less or more than 90^0. If a contact angle is small ($< 90^0$), then a surface has a high wettability, if a contact angle is big ($> 90^0$), then the surface has a low wettability to a particular fluid (Skartlien, 2016). In this simulation, we would like to observe changes in the wettability by adding surfactants. Apparently, the surface of the fluid could be altered from low-wettable to high wettable surface and vice versa. First, we carried out the same type of simulations as reported by Li, Liu, Tang et al. (2009). The simulation itself was separated into two cases (1A and 1B) in order to see the effect of the surfactant. A water-wetting surface was prescribed at the beginning of the simulation for the case 1A. Second, adding the particular type of oil soluble surfactant, the surface wettability changed to oil-wetting for case 1B. Also, the solubility can be observed from Tables 1 and 2: TW = 67, TO = 32, HW = 32, and HO = 47. Graphically, it can be seen from Figure 2(Black line represents the interface between oil and water; E_O, E_W, E_S represent potential mixing energies for oil, water and surfactant and can be estimated via interaction. Values of relevant parameters are: $E_O = a_{HO} + a_{TO} = 32 + 47 = 79$; $E_W = a_{HW} + a_{TW} = 32 + 67 = 99$; $E_S = a_{TO} + a_{HW} = 32 + 32 = 64$; $E_S < E_O < E_W$ (for a_{ij}, a is an interaction parameter between two particles – i and j). The surfactant appears on the interface, where chemical potential has the lowest value, which corresponds to the oil-water interface. A fraction of surfactant is positioned in oil as well, because it is oil soluble ($E_O < E_W$). Small amount of surfactant is located in water since the potential energy is the highest there.

2.1.1. Case 1A: "Water wet surface, no surfactant"
In this case, the matrix in Table 1 is used.

Table 1 Matrix of the water-wetting surface

W	O	T	H	.	S	
30	62	67	32	0	35	W
	30	32	47	0	55	O
		30	48	0	40	T
			30	0	10	H
				0	0	.
					0	S

Table 2 Matrix of the oil-wetting surface

W	O	T	H	.	S	
30	62	67	32	0	55	W
	30	32	47	0	35	O
		30	48	0	10	T
			30	0	40	H
				0	0	.
					0	S

Table 3 Matrix of VI case simulation

	W	O	T	H	H^{II}	S	
W	30	62	67	32	0	55	W
O		30	32	47	0	35	O
T			30	48	0	10	T
H				30	0	40	H
.					0	0	.
S						0	S

We have water-wetting surface identified through the interaction of the following parameters – SW and SO. If the corresponding number in the matrix is bigger than the other one in comparison, then the bigger value shows more repulsion between molecular beads. In case 1A, we see that the surface is water-wetting, since 35 < 55 (SW< OW). This can be observed from the Figure 3a. The surface appears water-wet, because the oil formed three droplets on the surface without spreading on the wall. In this paper, the direct visual inspection is used for all the cases (at 15000 time steps. Red beads represent oil beads, grey thin layer represent very dense wall, and rest of the space is covered by water beads, not presented in 3D picture due to overlap with other beads).
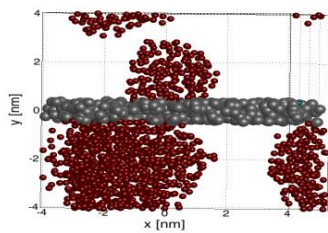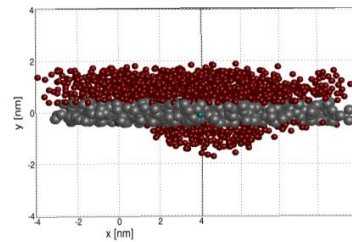

Figure 3 a) Water-wetting surface

Figure 3 b) Oil-wetting surface

2.1.2. Case 1B: "Oil wet surface caused by surfactants"
This case uses the same matrix as in case 1A, except that, 400 surfactants are added. Impact of those surfactants is noticeable in Figures 3a and 4a (Alterations at 15000 time steps. Green and turquoise beads represent surfactant, which has a Head and Tail configuration. Water beads are not presented here)
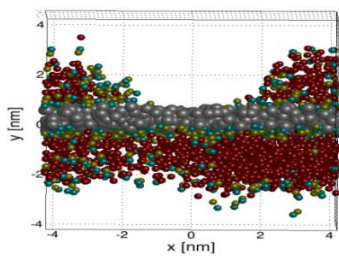

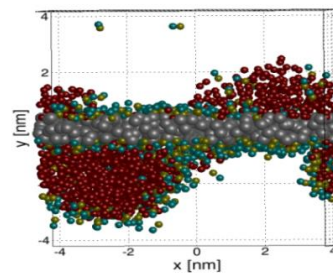Figure 4a) Water-wetting surface to oil-wetting surface.

Figure 4b) Oil-wetting surface to water-wetting surface

Once thermodynamic equilibrium is reached in the system, the surfactants prefer to reside on the wall and the interface between oil and water. The surfactants are oil soluble. Observing the matrix of parameters, the interaction between ST and SH differs. ST > SH (40 > 10), which shows that the heads of the surfactants are most likely to stick to the wall. The surfactant migrates out on the surface and the oil is effectively attracted towards the tails. Sometimes, surfactants reach the wall sooner from the water-oil mixture before the system is in equilibrium or prominent phase separation occurs. The whole route of alteration could be observed in Figure 5a.
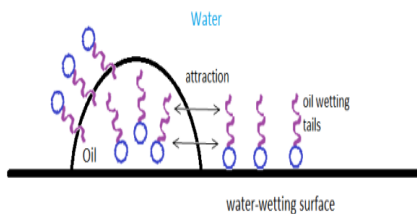

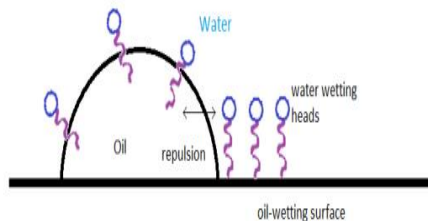Figure 5 a)Water-wet to oil-wet alteration process induced by surfactants

Figure 5 b) Oil-wet to water-wet alteration process induced by surfactants
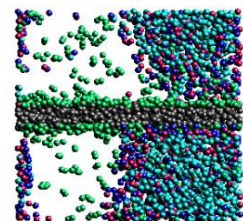

Figure 6 at 15000 t-s(time-step)

2.2 Case 2: "Oil wet to water wet by oil soluble surfactant"

This arrangement has an oil-wetting surface for option A which is altered for a water-wet surface for the option B after adding surfactants. The wall is oil-wetting, because interaction between SW=55 and OW=35(see Table 2 and Figure 3b). OW has less repulsion forces between molecules in comparison with SW, and therefore it is an oil-wetting surface.

2.2.1   Case 2A: "Oil wet surface, no surfactant"

Figure 3b shows how oil spreads out on the wall as a thin layer at the top and forms a spherical droplet at the bottom. The contact angle between oil and surface is about 150^0; i.e., the surface is oil-wettable.

2.2.2   Case 2B: "Water wet surface, surfactants are added"

The following case has 400 additional surfactants, which will change the surface from oil-wetting to water-wetting surface after some time. This could be observed in Figures 3b and 4b. The same oil-soluble surfactant is used here according to Table 2. Figures 4b and 5b show that surface tends to be water-wetting after adding particular surfactants. Oil is formed as a droplet since it is squeezed up on the water-wetting surface. Strong repulsion between oil and the water-wetting heads of the surfactants is evident, which leads to the wettability alteration. The main conclusion is that any oil-based indigenous surfactant may not only lead to an oil-wet surface. Migration of surfactants from oil phase onto the surface might cause alternations from water-wet to oil-wet or oil-wet to water-wet surfaces.

3. Improved oil recovery(IOR): wetting alteration by inserting water soluble chemicals

In order to prevent the effect of the alteration described above by the oil soluble surfactant, further simulations were required. The goal was to block the oil droplets from spreading out on the oil-wetting surface in case 1, when alternating from water-wet to oil-wet surfaces. Primarily, the surface was oil wet due to migration of the oil soluble surfactant, which represents indigenous surfactant. Next, a new type of molecule was embedded into the system in order to obtain the blocking effect. This type of molecule keeps the system properties stable preventing the water-wetting property of the surface despite the oil-soluble surfactant, which represents indigenous surfactant. Finally, it is assumed this molecule is water-based to deal with the task of mechanical blocking in IOR - applications. It could be any polar solvent or mineral molecule. For example, $Al(OH)_3$ or particles of sodium sulphate. However, further research is required in order to implement a specific mineral or compound. For now, we can call it a *green molecule* or *chemical* (because of its green color in simulations). The basic principle of the simulation will stay the same, except that the forth column in the matrix is included to accommodate the green molecule. Now, it will have a name as H^{II}, which refers to the new DPD-bead. This new bead might participate in various configurations (e.g., head-tail, head-head, head-head-tail) (Refer to Figure 6). After several progressions of time-steps, we could notice that the most efficient configurations of this chemical is of the polar, water soluble type, with no hydrocarbon tail: H-H^{II} or H^{II}- H^{II}. These configurations show the best blocking effect. The newly placed H^{II} is always water soluble, and it repels the oil-soluble surfactant both head and tail in order to prevent the surfactant migration effect. Implicitly, this water-based chemical cannot be soluble in the surfactant's head parts (H) either, but it would still have to be soluble in water. The matrix could be seen in Table 3.

4. Chemical potential energy of the "green molecule"

Four options are considered in order to calculate the potential energy of the green molecule: 1) Energy of water soluble chemical on wall and in oil: a_{SH} + $a_{SH^{II}}$ + a_{OH} +$a_{OH^{II}}$ = 10+10+47+47=114; 2) Energy of water soluble chemical in oil: a_{OH} + $a_{OH^{II}}$ + a_{OH} + $a_{OH^{II}}$ = 47+47+47+47=188; 3) Energy of water soluble chemical in water: a_{WH} + $a_{WH^{II}}$ + a_{WH} + $a_{WH^{II}}$ = 32+32+32+32 = 128; 4) Energy in water and on wall: a_{SH} + $a_{SH^{II}}$ + a_{WH} + $a_{WH^{II}}$ = 10+10+32+32 = 84**.** The following results for all the interaction energies were obtained:

$$[\text{On wall + in water}] < [\text{On wall + in oil}] < [\text{In water}] < [\text{In oil}]$$
$$84 < 114 < 128 < 188$$

The wall-interaction was replaced by water-interaction when the molecule is situated in pure water or oil.

It is seen that the potential energy is the highest when the chemical interacts with oil, and therefore repulses it markedly more. The potential energy is the lowest on the wall, therefore all the parts of water-soluble chemical prefer the wall surface in water. However, some polar molecules are found in the water and fewer of them appear in a domain with a high potential energy, since this appears with lower probability.

4.1 VI case: H^{II}- H^{II}, increased oil repulsion for H^{II}

The water-soluble surfactant has head II–head II (H^{II} - H^{II}) configuration (see Table 3 and Figure 6). The $H^{II}O$ value is 70, which shows that this molecule will resist oil very strongly. Here, the oil is almost pulled out from the wall and formed droplets in the water surrounded by oil-soluble surfactant. This is one of the best configurations for the newly embedded molecule.

4.2 Preliminary remarks and observations

The green molecule should not have a tail structure in addition to the head part configuration, like H^{II}-H^{II}-T. Any configuration with tails attracts T-part of the surfactant (H-T) and oil prevents a mechanical blocking. It should be water soluble. It is preferable to have adhesion effect between the wall and green molecule. It provides mechanical blocking. The exact molecular structure of the newly embedded chemical is unknown for now. This requires more research and a calibration of the interaction parameters by coarse graining a "real molecule". Water-soluble molecule has to repel the oil-soluble surfactant either partially or fully in order to get a mechanical blocking effect.

5. Emulsion inversion with surfactant

For all simulations the number of surfactant beads is less than the number of oil and water beads. As a simulation proceeds, the surfactants have a preference to situate on the interface. For oil-in-water emulsions the surfactant is water soluble, and for water-in-oil emulsions the surfactant is oil soluble (as it should). This case is characterized by high interfacial curvature. If the surfactant is just as soluble in water as it is in the oil, the interface has a minimal curvature, for example a flat interface, or a more geometrically complex interface with a minimal average curvature. For various soluble cases, different type of curvature corresponds. For example, oil soluble case obtains a positive curvature, water soluble case obtains a negative curvature, and the "neutrally soluble" case (where the matrix is symmetrical) gets zero curvature. In the simulations, the curvature is partially controlled by the bending energy of the interface via the H-H and T-T forces. The solubility of the surfactant is mainly controlled by the H-W, T-W, H-O, T-O forces. We have chosen to run three independent simulations for each case due to the stochastic nature of the system (the initial condition is random) as shown in next sub-sections.

5.1 Oil soluble cases: water drops in oil

The surfactant is oil soluble rather than water soluble due to its input parameters (Refer to Figure 7): TO = 15, HW = 25. Hence, the tail in water represents less energy than head in water: TO < HW. The equality TW = HO = 80 does not affect the surfactant solubility.
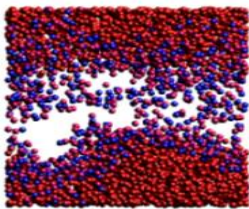

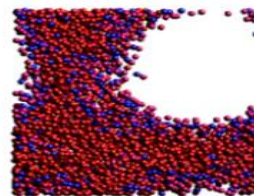*Figure 7 Oil soluble case15000 t-s*   *Figure 8 Water soluble case at 15000 t-s*

Oil-soluble surfactants acquire the positive curvature. The positive bending shows that surfactant prefers to be oil-soluble rather than water-soluble.

5.2 Water soluble cases: oil drops in water

In the second case(TO = 25, HW = 15; TO > HW), it is clear that oil is formed as a sphere and surrounded with water soluble surfactants, with curvature in the opposite (negative) way (Refer to Figure 8).

5.3 Neutrally soluble cases

The neutral soluble case (TO=HW=25) has the same amount of surfactant in oil and water. In case 3A (Refer to Figure 9), the structure corresponds to the *minimal surface gyroid* (a liquid matrix geometry), which has a surface curvature of zero. The interfacial area of the gyroid is larger than for a flat interface: $A_{gyroid} > A_{flat\ surface}$, giving a larger surface energy of the gyroid as well. With surfactant, the surface concentration is smaller for the gyroid $G_{gyroid} < G_{flat\ surface}$ due to depletion of the surfactant, which will further increase the surface energy of the gyroid. Therefore the surface energy of the gyroid is larger than for the flat surface, and it is therefore, a

lower probability of obtaining the gyroid structure. In cases 3B(Refer to Figure 10) and 3C(Refer to Figure 11) a "flat" interface, with waves is obtained. Sometimes, a liquid bridge is established through the other phase. This bridge did not dissipate easily, to form fully separated layers of water and oil. However, we still get a flat surface on the average which corresponds to zero curvature. It is interesting to note that bridges have relevance to a coalescence process where pore holes can develop through the thin liquid film that separates the emulsion droplets.
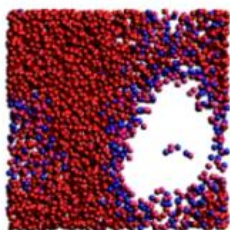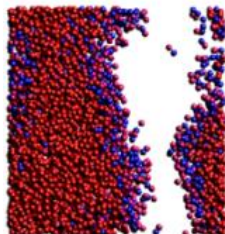

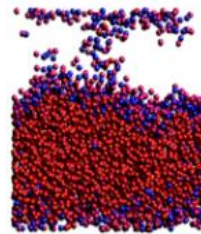*Figure 9 A-case at 15000 t-s*   *Figure 10 B-case at 15000 t-s*   *Figure 11 C-case at 15000 t-s*

6. Applications

In many oilfield applications, wettability is crucial, because the rock is either water-wet or oil-wet. If a rock is a water-wet, then the porous medium is saturated with water and likely to have a water layer on the mineral, rather than oil. The same principle works with the oil-wet surface. Depending on the wettability of the surface, a particular surfactant could be used to alter the wettability of the rock to obtain enhanced recovery (Skartlien, 2017).

7. Concluding remarks

DPD is a suitable tool to study wetting and emulsion behavior in an oil/water system as function of surfactant molecular structure. The addition of surfactant or other water soluble species can be studied for an oil/water system that contains indigenous surfactant in the oil, similar to an improved oil recovery setting. We confirmed that the tail-tail and head-head interaction of the surfactant dictates the curvature outcome in an emulsion. The average curvature of the Water/Oil interface matches the solubility behavior of the surfactant in line with the Bancroft rule for emulsions. The results are however sensitive to the domain size, as droplets can then interact easily with its "ghost" neighbor due to the periodic boundary conditions. The neutrally soluble case acquired zero curvature as expected, and a minimal-surface energy complex gyroid interface.

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