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Competitive effects of interfacial interactions on ion-tuned wettability by atomic simulations

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ABSTRACT

The dependence of wettability on brine ionic composition in organic-brine-mineral systems, which is denoted as ion-tuned wettability in this paper, has important industrial applications but is still not well understood. The dominant mechanisms and their relative importance are still under debate. This paper uses molecular dynamics to study three possible mechanisms of ion-tuned wettability in an oil-brine-quartz system, including electrical double layer (EDL) repulsion, cation bridging, and hydration repulsion. We compare the contact angle and COO⁻ distribution of the molecular system under different interface charging conditions and the contact angle predicted by EDL repulsion theory. The results indicate the existence of Ca²⁺ bridging and K⁺ bridging, and that medium ionic strength favors the form of K⁺ bridging most. The three mechanisms are all proved to have impact on wettability, of which Ca²⁺ bridging is the strongest, EDL repulsion and hydration repulsion the weaker, K⁺ bridging the weakest. Based on the results, we suggest that all the three mechanisms should be evaluated to predict the ion-tuned wettability, and conclude several possible brine-modifying strategies to make sandstone reservoir more water-wet.

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1. Introduction

Wettability plays a critical role in various transport problems in organic-brine-mineral systems [1–5]. For instance, it can influence the generation of droplets in microfluidics [6]; the remediation of organic-contaminated soil and water [7,8]; the biofouling control of marine vehicles [9]; the efficiency of waterflooding [10,11] and CO₂ sequestration [12] in oil fields; and so on. Recently, it has attracted increasing attention that the wettability is dependent on brine ionic composition [13–16], which is denoted as ion-tuned wettability in this paper. Especially, people find that if the brine is multi-component natural brine such as seawater and formation water, usually the oil-brine-sandstone system can become more water-wet by diluting the brine to less than 5000 ppm [17–21], which may be used to increase the waterflooding efficiency to recovery oil. However, the mechanism of this low-salinity effect is still not clear. It is important to understand ion-tuned wettability in order to direct waterflooding and inspire wettability-altering strategies in other fields [22–24].

Oil-brine and brine-silica interfaces are usually spontaneously negatively charged due to mechanisms like ionization of surface

groups and specific ion adsorption [25–27], which can induce interface interactions that may explain ion-tuned wettability. On the one hand, a charged interface attracts the counter-ions and repels the co-ions in brine to balance its own charge; on the other hand, ions tend to diffuse to eliminate the concentration gradient. The balance of the above Coulombic force and osmotic force promotes the form of electrical double layer (EDL) with finite thickness proportional to the square root of brine ionic strength [28]. Near the contact line, the EDLs near oil-brine interface and brine-silica interface can get overlapped, which causes EDL repulsion between the two interfaces. The increase of interface charge by increasing pH or the increase of EDL thickness by decreasing ionic strength can enhance the EDL repulsion, which tends to make the OBS system more water-wet [11,27,29–31]. Secondly, the multivalent cations can screen the two negatively charged interfaces simultaneously and thus connect the oil to the silica surface, which mechanism is called cation bridging [29,32]. If cation bridging dominates ion-tuned wettability, the OBS system tends to be more water-wet as multivalent cations get removed. Thirdly, at high ionic strength, lots of half-hydrated cations are closely attracted to the charged interface, forming a hydration layer near the interface. The overlap of the hydration layers near contact line can induce a strong repulsive force, which is called hydration repulsion [11,27,31,33,34]. For interfaces whose charged groups do not extrude significantly into the brine phase, hydration repulsion is brine-dependent. Its strength enhances as ionic strength and cation

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valance increases, and its kick-in salinity usually increases as cation valence increases. There is a debate on whether the breaking of cation bridging or the enhanced EDL repulsion dominates the water-wetness enhancement by dilution of multi-component brine [32,35,36], but the role of hydration force is usually less emphasized.

Continuum theory and experiments have provided some evidence for the existence of the above interactions. The classical DLVO (Derjaguin-Landau-Verwey-Overbeek) theory can be used to calculate EDL interaction energy, and a detailed discussion of its application in ion-tuned wettability problem has been recently published [22]. However, the theory is incapable to calculate the wettability alteration by non-continuum effects like hydration repulsion and cation bridging. On the other, it has been experimentally proved that usually very high (>0.1 M) or low concentration (<0.001 M) and high pH can make the oil-NaCl (aq)-silica/silicate system more water-wet [27,33,37,38], which may indicate the co-effect of EDL repulsion and hydration repulsion. Experiments also have proved that CaCl_2 solution can make the system more oil-wet compared with similarly-concentrated NaCl solution [18], which is consistent with the characteristics of cation bridging. In addition, it has been found that the contact angle variation with ionic composition is correlated with surface charge variation, which may indirectly prove the role of EDL repulsion in ion-tuned wettability [20,21]. Nevertheless, experiments show too large contact angle variance to compare with theory, and cannot directly observe ion and charge distribution near interface, and thus are difficult to differentiate the contribution of EDL repulsion, hydration repulsion and cation bridging to ion-tuned wettability. Molecular dynamics (MD) simulation can capture the three mechanisms, and provide repeatable contact angle and details of ion and charge distribution near interface, thus should be important supplements to above methods to help understand ion-tuned wettability [22].

Up to our knowledge, MD studies on ion-tuned wettability are still limited. The previous studies Underwood et al. [39], Greathouse, et al. [40], Kobayashi et al. [41] used MD simulation to observe Ca^{2+} bridging and prove its important role in ion-tuned wettability. Especially, it was found that K^+ can also form cation bridging Kobayashi et al. [41], but the principles of this unusual monovalent cation bridging were not fully discussed, like its dependence on ionic composition. In addition, MD simulations Zhang et al. [42], Kobayashi et al. [41] have been used to prove that the mineral charge can repel uncharged oil from the mineral surface, and attributed this to water bridging, though EDL repulsion can also explain this. To conclude, the above works all ignored or denied the role of EDL repulsion, lacked the discussion of monovalent cation bridging, did not compare the relative impact of the EDL repulsion, cation bridging, and hydration repulsion on ion-tuned wettability, and did not present wettability by contact angle which is more direct to experimenters. A recent paper of our group [43] simulated an oil drop-KCl (aq)-quartz system, validated its contact angle with experiments and EDL theory, and proved the role of EDL repulsion in wettability alteration if quartz but not oil is charged. Based on that work, this paper also considers multivalent cations and oil surface charge to analyze the role of EDL repulsion, cation bridging, and hydration repulsion cohesively.

This paper aims to use MD simulation, to (1) identify the three mechanisms and their effect on wettability, especially the rules of monovalent cation bridging, (2) compare the relative strength of these three mechanisms to alter wettability, and (3) suggest some brine-modifying strategies to make OBS system more water-wet. This paper is organized as below. We will first introduce how we model the MD system and analyze the results, then present the MD results and make a detailed discussion towards the three aims of this paper, and finally give the conclusion.

2. Method

A scheme for the model system is shown in Fig. 1. We use the OPLSaa force field for oil [44], the SPC/Fw model for water [45], the force field from Ref. Beglov and Roux [46] for ions, and the force field from Ref. Cruz-Chu, et al. [47] for quartz. The oil drop is composed of 263 $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ and 20 $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ or 20 $\text{CH}_3(\text{CH}_2)_8\text{COO}^-$. The brine is KCl solution or CaCl_2 solution and its bulk ionic strength I_{real} is estimated from MD results according to Boltzmann distribution [31]:

$$I_{real} = \left\langle \left(\langle c_K \rangle_{\Delta t} \langle c_{Cl} \rangle_{\Delta t} \right)^{1/2} \right\rangle_{\Omega} \text{ or } \left\langle 3 \left(\langle c_{Ca} \rangle_{\Delta t} \langle c_{Cl} \rangle_{\Delta t}^2 / 4 \right)^{1/3} \right\rangle_{\Omega} \quad (1)$$

where $\langle \rangle_{\Delta t}$ means time average in the sampling time period Δt , and $\langle \rangle_{\Omega}$ means volume average in interface-excluded brine volume Ω [43]. The α -quartz is placed with crystal orientation [100] parallel with x axis and [001] parallel with y axis, and has five layers of unit cells in z direction. The upper most oxygen atoms of α -quartz are set at $z = -0.2003$ nm. Since the sum of OH bond length (0.096 nm [31]) and van der Waals radius of hydrogen in OH (0.11 nm [31]) is about 0.2 nm, we assume the brine-quartz interface is approximately located at $z = 0$. The lower part of α -quartz ($z < -0.6$ nm) is fixed to avoid wall drift. The top vacuum region with thickness $H' = 1$ nm is used to release internal pressure, and the system is set large enough to avoid EDL overlap between images of the oil drop and that between oil and vapor.

Since the classical force field that we use does not allow modeling of kinetic chemical reactions, this work simulates four series of cases with different fixed interface charge: both oil and quartz are charged (COCQ), oil is charged while quartz is uncharged (COUQ), quartz is charged while oil is uncharged (UOCQ), and neither oil nor quartz is charged (UOUQ). The oil is uncharged or charged by mixing 20 $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ or 20 $\text{CH}_3(\text{CH}_2)_8\text{COO}^-$ with $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$. The averaged surface charge density of charged oil is about -0.06 C m^{-2} . When α -quartz is charged, one hydroxyl of every nine brine-contacting unit cells is deprotonated (corresponding to -0.067 C m^{-2}), as shown in Fig. S1. The UOUQ systems correspond to real OBS systems at $\text{pH} \approx 2-3$, while the COCQ systems at $\text{pH} \approx 6-9$. In COCQ cases, EDL repulsion, hydration repulsion, and cation bridging may exist; in UOCQ cases, cation bridging cannot exist; in UOUQ cases, none of the three mechanisms should exist. We will compare the COO^- distribution near quartz surface between COUQ and COCQ cases, and combine with VMD [48] videos to analyze the existence

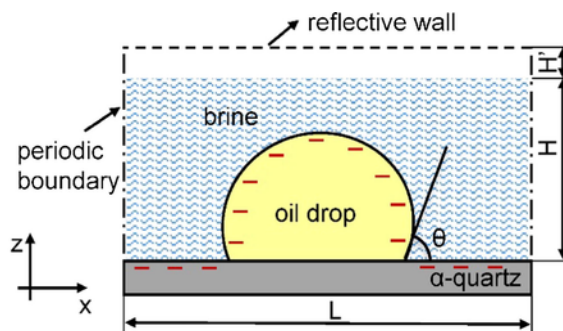


Fig. 1. A scheme of the simulation system for MD. The length in the third dimension, the y direction, of the system is W .

of cation bridging. Then we will compare the contact angle of the UOUQ, UOCQ, COCQ cases and EDL repulsion theory to analyze the impact of the three mechanisms on ion-tuned wettability.

We use LAMMPS package [49] to run MD simulations. For all the cases, *NVT* assemble is applied ($T=300\text{K}$), time step is 1 fs, and data of the last 40 ns is used for analysis. The contact angle θ is calculated from the height of the mass center z_m , and the 90% confidential interval of θ is estimated using the standard error of the mean (SEM) [50,51], with 2 ns for one sampling. The validation of the contact angle estimating method and more detailed discussion of the MD framework can be referred to Ref. [43], and a summary of all the simulated cases presented in this paper, including the detailed information of system size, interface charging, number of ions and water molecules, bulk ionic strength, and running procedures, is presented in Table S1. Except for the six cases published before [43], all the other 34 cases are presented for the first time in this paper.

Below we will briefly introduce the classical theory to predict the contact angle variation due to EDL repulsion [11,31] for UOCQ cases. The Poisson-Boltzmann (PB) equation is used to model the EDL

$$\frac{d^2\phi}{dz^2} = -\frac{eN_A}{\epsilon_0\epsilon_r} \sum_i z_i c_i^\infty \exp(-z_i e\phi/k_b T) \quad (2)$$

where ϕ is the electrical potential, ϵ_0 the vacuum permittivity, ϵ_r the relative permittivity, e the electron charge, N_A the Avogadro number, z_i and c_i^∞ respectively the valence and bulk concentration of the i -th ion, k_b the Boltzmann constant, and T the temperature. The boundary conditions for Eq. (2) are $\phi(z=0) = \phi_{0,qz}$ and $\phi(z=h) = 0$. We assume constant charge boundary and contact value theorem [31] to calculate EDL repulsion energy,

$$w_{EDL} = \int_{h_{eq}}^{\infty} N_A k_b T \left[\sum_i c_i^\infty \exp(-z_i e\phi_{0,qz}(h)/k_b T) - \sum_i c_i^\infty \exp(-z_i e\phi_{0,qz}(\infty)/k_b T) \right] dh \quad (3)$$

where the function $\phi_{0,qz}(h)$ can be obtained from the PB equation

with the Gauss Law and constant charge assumption. $h^{eq} = 0.03\text{ nm}$ is assumed to calculate w_{EDL} . We can get the linear relation between contact angle θ_0 and ionic strength of UOUQ cases (where $w_{EDL} = 0$) by fitting the MD data, and apply the Young-Dupr e's equation [11,52,53] to predict the contact angle θ of UOCQ cases

$$\theta = \cos^{-1}(\cos\theta_0 + w_{EDL}/\gamma_{ob}) \quad (4)$$

where γ_{ob} is the surface tension of the oil-brine interface, and is approximately 55 mN m^{-1} and not sensitive to ionic composition or surface charge for our modeled system (see the supporting information).

3. Results and discussion

3.1. Cation bridging observation

Firstly, the COO^- distribution near quartz surface for COUQ and COCQ cases will be compared to indicate the existence of cation bridging, as shown in Fig. 2 and Fig. 3. Fig. 2 counts the time-averaged COO^- number in five layers respectively defined by $z < 0\text{ nm}$, $0\text{ nm} \leq z < 0.1\text{ nm}$, $0.1\text{ nm} \leq z < 0.2\text{ nm}$, $0.2\text{ nm} \leq z < 0.3\text{ nm}$, and $0.3\text{ nm} \leq z < 0.4\text{ nm}$, since almost no COO^- exists in the region $z < -0.1\text{ nm}$ and the number of COO^- is almost irrelevant with ionic strength and charging conditions for $z > 0.4\text{ nm}$. Besides, Fig. 3 shows the VMD captures of COO^- adsorption mechanisms.

We will first clarify the COO^- adsorption mechanisms for COUQ cases. The blue lines in Fig. 2 indicate that when quartz is not charged, COO^- is highly concentrated at low I_{real} in the layer $z < 0\text{ nm}$, which should be explained by the attraction between COO^- and hydroxyls on quartz surface, as shown in Fig. 3(a) and Movie S1. At high I_{real} , this attraction should be weakened because COO^- tends to be screened by cations.

When quartz is charged, the COO^- adsorption mechanism will change to cation bridging. In CaCl_2 solution, Fig. 2(b) shows the significant increase of COO^- in the layer $0\text{ nm} \leq z < 0.3\text{ nm}$, which combines with the VMD snapshots (Fig. 3(b) and Movie S2) to support the existence of Ca^{2+} bridging. Since calcium ions are bigger than hydrogen atoms, the adsorbed COO^- due to Ca^{2+} bridging locates farther away from quartz surface than those due to COO^- -OH connection. Besides, Ca^{2+} bridging proves to exist for all the studied ionic strength, which indicates that the break of Ca^{2+} bridging re-

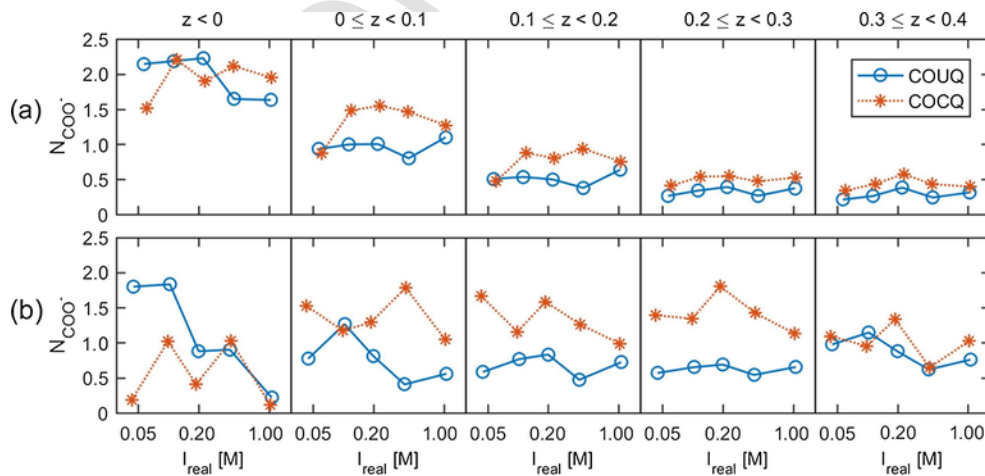


Fig. 2. The adsorption of COO^- onto quartz from MD results, for cases with (a) KCl solution, or (b) CaCl_2 solution as the brine phase. Each column shows the number of COO^- in a layer defined by z coordinate (unit: nm). COUQ represents the charging condition of charged oil and uncharged quartz, and COCQ charged oil and charged quartz.

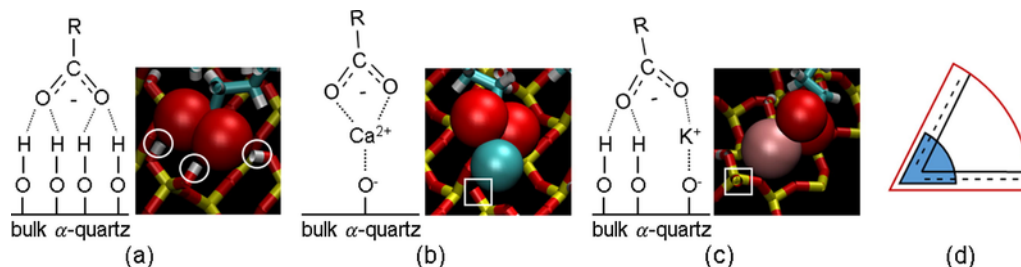


Fig. 3. Schemes and snapshots from VMD videos (Movie S1, S2, S3) for three main COO^- adsorption mechanisms on quartz surface, respectively (a) COO^- -hydroxyl connection, (b) Ca^{2+} bridging, and (c) K^+ bridging, and a scheme (d) to help analyze what concentration favors K^+ bridging most. In the VMD snapshots, the red, cyan, and pink balls respectively represent O in COO^- , Ca^{2+} , and K^+ ; water molecules and anions are not shown; and other H, C, O, Si atoms are represented by dynamic bonds and colored by white, cyan, red, yellow. The white circles and squares respectively mark the visible OH and O^- on quartz surface connected to the COO^- . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

quires lower Ca^{2+} concentration. In KCl solution, Fig. 2(a) shows the significant increase of COO^- in the region $0 \text{ nm} \leq z < 0.2 \text{ nm}$ at medium I_{real} , which combines with the VMD snapshots (Fig. 3(c) and Movie S3) to prove the existence of K^+ bridging between oil and rock. We explain the dependence of K^+ bridging on ionic strength as below. Note that K^+ bridging carries one negative charge, while Ca^{2+} bridging is charge neutral. This makes their preference for ionic strength totally different. It can be speculated that K^+ bridging can form only in the condition that the brine charge is almost half of total interface charge near contact line (shown as the blue fan in Fig. 3(d)). At very high I_{real} , K^+ ions tend to screen oil and quartz charge respectively, so there are too many K^+ ions near contact line to favor the form of K^+ bridging; at very low I_{real} , K^+ ions tend to diffuse into bulk solution, so there are not enough K^+ ions to favor the form of K^+ bridging. Therefore, K^+ bridging only forms at some medium ionic strength. Compared with Ca^{2+} bridging, K^+ bridging attracts COO^- more closely to the surface since the COO^- is also attracted by OH on quartz surface; and K^+ bridging is weaker and less stable due to the smaller charge of K^+ .

3.2. Ion effects on wettability

Next, contact angle for different charging conditions and ionic composition from MD simulation and EDL theory will be compared to see the impact of EDL repulsion, hydration repulsion, and cation bridging on wettability, as shown in Fig. 4.

When neither oil nor quartz is charged, the contact angle does not show strong dependence on ionic composition. As the quartz gets charged, the contact angle decreases in both KCl and CaCl_2 solution at all the ionic strength. Since cation bridging does not exist in these cases, the contact angle decrease should be caused by EDL repulsion or hydration repulsion or both. To differentiate the contribution of these two mechanisms, we calculate the contact angles of UOCQ cases by EDL repulsion theory described in Section 2, and plot them in Fig. 4. The contact angle drop induced by EDL repulsion decreases as ionic strength and cation valence increases. The predicted contact angle is well consistent with MD results when ionic strength is smaller than 1M, which indicates that EDL repulsion dominates ion-tuned wettability for these UOCQ cases. When ionic strength is 1M, the contact angle predicated by EDL repulsion theory is slightly larger for KCl solution, and much larger for CaCl_2 solution. This difference is probably induced by hydration repulsion, which theoretically should be enhanced by multivalent counter-ions and high ionic

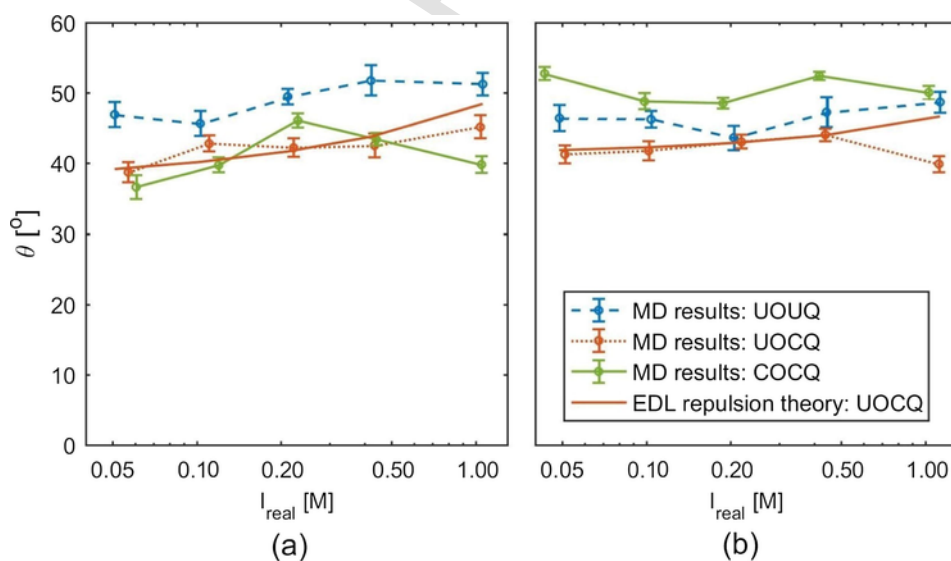


Fig. 4. The contact angle from MD results and EDL repulsion theory for cases with (a) KCl solution, or (b) CaCl_2 solution as the brine phase. UOUQ means the charging condition of uncharged oil and uncharged quartz, UOCQ uncharged oil and charged quartz, and COCQ charged oil and charged quartz. The error bars give the 90% confidence intervals.

strength, and make the system more water-wet. However, more concrete demonstration of hydration repulsion is required in future works.

When both oil and quartz are charged, which condition mostly occurs in real OBS systems, the MD results indicate that very concentrated or diluted KCl solution makes the system most water-wet, and CaCl₂ solution makes the system most oil-wet, which is qualitatively consistent with previous experiment results [17,18,20,21,27,33,37,54]. What's more, the relative strength of the three mechanisms can be indicated by comparison of all the UOUQ, UOCQ, COUQ, and COCQ cases. For KCl solution, at high and low ionic strength, the contact angles of COCQ cases are lower than those of UOCQ cases; at medium ionic strength, the contact angles of COCQ cases are between those of UOUQ and UOCQ cases. Combined with above discussion on K⁺ bridging, we speculate that hydration repulsion and EDL repulsion should dominate respectively at high and low concentration, and K⁺ bridging offsets part of repulsive force at medium concentration. For CaCl₂ solution, at all the studied concentrations, the contact angles of COCQ cases are higher than those of UOUQ and UOCQ cases, which indicates that Ca²⁺ bridging should overwhelm other repulsive forces. To conclude, all the three mechanisms can influence wettability, and Ca²⁺ bridging has the strongest impact, EDL repulsion and hydration repulsion the weaker, and K⁺ bridging the weakest.

3.3. Brine-modifying strategies

Finally, based on previous analysis, we suggest that all the three mechanisms should be evaluated to optimize brine composition for waterflooding, and conclude several effective brine-modifying strategies for sandstone reservoirs. The formation brine usually has a high salinity. If it contains plentiful multivalent ions, multivalent cation bridging should overwhelm EDL repulsion and hydration repulsion in original sandstone reservoirs. Therefore, diluting the brine down than a critical salinity favors the break of cation bridging and the enhancement of EDL repulsion, and thus makes the system more water-wet. Other than by diluting, the water-wetness can also be enhanced by removing multivalent ions, which favors the break of cation bridging and makes hydration repulsion dominate wettability. If the brine contains few multivalent ions, then diluting does not necessarily make the system more water-wet, because the enhancement of EDL repulsion is accompanied by the attenuation of hydration repulsion. In this case, the elevation of surface charge by increasing pH should enhance both EDL repulsion and hydration repulsion, thus effectively makes the system more water-wet.

4. Conclusions

This paper uses MD simulation to identify and compare the impact of EDL repulsion, hydration repulsion, and cation bridging on ion-tuned wettability in oil-brine-quartz system. It is the first work to directly observe those possible mechanisms on a molecular scale [19,22,35], and analyze the relation between them based on microscopic details. Firstly, both Ca²⁺ bridging and K⁺ bridging are observed, and especially, K⁺ bridging is proved to form at some medium ionic strength. Secondly, cation bridging is found to enhance oil-wetness while EDL repulsion and hydration repulsion are found to enhance water-wetness, and Ca²⁺ bridging performs the strongest impact, EDL repulsion and hydration repulsion the weaker, and K⁺ bridging the weakest. Finally, we summarize that the three mecha-

nisms should be evaluated together to optimize wettability for specific oil-brine-rock system. For instance, if the original brine contains plentiful multivalent cations, we suggest diluting brine or removing multivalent cations to break cation bridging, otherwise we suggest elevating pH to enhance EDL repulsion and hydration repulsion, in order to make the sandstone reservoir more water-wet. Our framework can be applied to more complex systems to investigate more intricate mechanisms for further study.

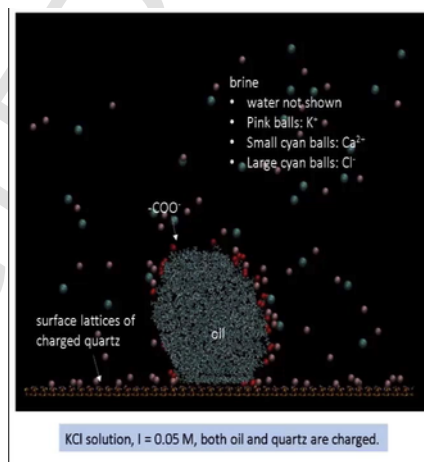
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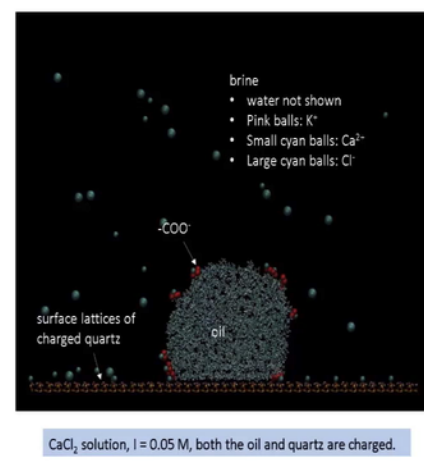
Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2018.12.108>.

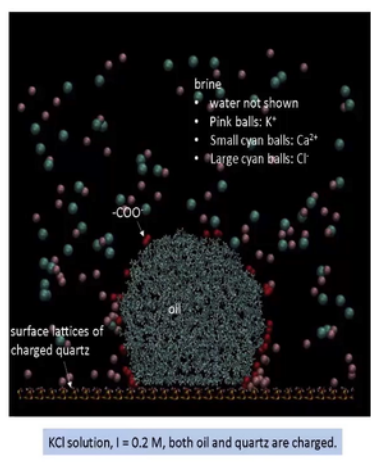
Movie S1



Movie S2



Movie S3



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