Wettability Alteration During Low Salinity Waterflooding: Effect Oil Composition and Divalent Cations*

Jie Yang[1], Zhaoxia Dong[1], Zihao Yang[1], Meiqin Lin[1], Juan Zhang[1], and Chen Chen[1]

[1]China University of Petroleum, Changping, Beijing, China (yangjie_cup@163.com)

Abstract

Laboratory and field tests have shown that reducing the overall salinity especially the concentration of divalent ions of the injected water can markedly improve the oil recovery. However, no mechanisms have been widely accepted as the main reason for the enhanced oil recovery by low saline water. As wettability alteration toward be more water-wet has been observed in many promising cases, desorption of polar oil components from the rock surfaces should occur during low salinity waterflooding. In this paper, the influence of solution cations (Ca^{2+} and Na^+) of initial water on initial wettability of sandstone cores and the reduction of salinity of imbibing water on wettability alteration was examined by spontaneous imbibition, and the adsorption/desorption of acidic polar compounds of crude oil onto clays were investigated by static adsorption experiments, thereby provide a better understanding of possible relations of microscopic desorption of acidic polar compounds from mineral surface to the macroscopic wettability alteration during low saline water flood and the relevance of divalent ions (Ca^{2+}) in this process. Spontaneous imbibition experiments showed that Ca^{2+} in initial water can largely bring about the retention of polar oil components onto mineral resulting in the initial wettability alteration of cores toward more oil-wet conditions in comparison to Na^+, and lowering salinity of imbibing brine can improve oil recovery of cores aged by Ca^{2+} solutions, whereas no obvious enhanced oil recovery (EOR) was observed for cores saturated with Na^+ solutions. This indicated that oil components like carboxylate can retain on rock surface mainly by calcium-bridging to alter the wettability toward more oil-wet condition, and the reduction of salinity of imbibing brine can break the calcium bridges due to increased electric repulsive forces between oil and rock to change the wettability to be more water-wet, as a result, EOR occur. This is in accordance with the adsorption/desorption of acidic polar compounds experiments. The presence of background electrolyte Ca^{2+} can largely enhance the adsorption of acidic polar compounds (benzoic acid) onto clays (kaolinite and illite) in contrast with Na^+, and reducing the salinity can lead to the desorption of acidic polar compounds pre-adsorbed onto clays. In conclusion, breaking calcium bridges between oil and rock due to increased repulsion forces can contribute a lot to EOR during low-salinity waterflooding.

Introduction

Laboratory and field tests have shown that lowering salinity especially the concentration of divalent ions of the injected water can yield significant incremental oil (Tang and Morrow, 1999; Alotaibi et. al, 2011). Wettability alteration caused by the interaction of polar oil

constitutes, mineral surface and the ions in brine was widely believed to be an important factor behind low salinity waterflooding (Agbalaka et. al, 2009). Laboratory results have shown that the divalent cations (i.e. Ca^{2+}) in formation water are necessary for wettability modification by low saline water Tang and Morrow, 1999; Skrettingland et. al, 2011). It has also been found that the adsorption of polar oil components onto sandstone relied on both the ions in brine and the components of the crude oil, i. e. the retention of oil components were dominated by bonding of carboxylic groups to mineral surfaces through calcium bridges (Fjelde et. al, 2014).

A possible explanation of this observation may be that over geological time scales, the intrinsically hydrophilic reservoir mineral was altered to be hydrophobic due to the adsorption of polar compounds from the crude oil (Morrow, et. al, 1973; Buckley et. al, 1998; Liu et. al, 2003). Consequently, the mineral surface altered to be more oil-wet. During this process, the multivalent ions like Ca^{2+} and Mg^{2+} are supposed to play a role, since these can bind negatively charged polar end such as carboxylate group from the oil to negatively charged sites on the surface via an ion bridging mechanism. Lowering salinity of injection water can make the interface of oil/brine and brine/mineral more negatively charged, resulting in enhanced repulsive forces between the interfaces, and then wettability alteration occurred (Hassenkam et. al, 2011).

In this work, we performed spontaneous imbibition experiments, static adsorption/desorption of benzoic acid onto clays and interficial tension (IFT) to investigate the effect of bivalent cations (Ca^{2+}) in brine on the macroscopic wettability variation and microscopic adsorption/desorption, thereby provide a better understanding of the mechanism behind the EOR by low salinity water.

Experimental Section

Materials: Porous media. Six Berea sandstones, labeled B1-B6, were selected. The core data are as follows: length≈14cm, diameter 3.8cm, permeability to water 70-100mD, porosity ≈20% and total clay content about 10% wt%.

Crude Oil. Properties of crude oils are listed in Table 1.

Chemicals and Solutions. The brines were artificially made by dissolving desired amounts of salts in deionized water (Table 2).

Particles. Clay (<45 μm) used for static sorption was obtained from the national mineral company.

Sample Preparation and Test Procedure

Spontaneous Imbibitions. The dry core was evacuated and saturated by synthetic brine. Porosity and pore volume were calculated from weight difference between wet and dry core. Then the core was mounted in a core holder in an oven at 60°C and at least 10 PV of the same synthetic brine was injected into the core until getting a stabilized pH at the outlet, a same ions composition and a constant pressure drop across the core, which was used to calculate the permeability. The initial water saturation was established by injecting four PV oil in both directions at 60°C. All the injection rates were four ml/h. Then the core holder was kept in oven at 60°C for two weeks. After that, spontaneous imbibitions were performed at 60°C. The volumes of produced oil were recorded at intervals, and the oil recovery factor was calculated as the percent of original oil in place (%OOIP).

Adsorption/Desorption of BA on Clays. Prior to experiment, kaolinite and illite were washed by deionized water for three times, and then freeze-dried to remove contamination. Benzoic acid sorption to clays was conducted with batch experiments under different ionic strengths (0~0.35 M), solution cations (Na^+, Ca^{2+}) and temperatures (40°C, 60°C). Four gram clays were rotated and equilibrated with 40 ml brine in polyethylene bottles for 1h before addition of 40 ml benzoic acid solution (0.1g/l), and then rotated (300 rpm) and equilibrated for another 24h (preliminary tests showed that equilibrium was reached before this time) at the fixed temperature. During equilibration, the pH of solution was always controlled at 9.5 with NaOH in order to deprotonate substantial benzoic acid molecules in solution. After that, samples were placed into polyethylene centrifuge tubes and centrifuged (3500 rpm for 20 min). The supernatant containing the remaining benzoic acid was decanted and retained in a polyethylene centrifuge bottle for TOC (TOC-LCPH) analysis. This procedure was repeated three times for each solution. A calibration curve using known concentrations of benzoic acid was used to determine the benzoic acid concentration in the supernatant. Adsorption is reported as mg acid adsorbed per gram of quartz, and it is plotted versus the ionic strength of solution. Desorption was performed for the organo-clay previously formed in the 12,500 ppm $CaCl_2$ solution. It was attempted by removing parts of the supernatant and replacing it with deionized water. The samples were rotated for 24h to re-establish equilibrium prior to the analysis.

Results and Discussion

The effect of bivalent cations (Ca^{2+}) in brine on the macroscopic wettability variation. Spontaneous imbibition was used to investigate the influence of cation type of initial water on the initial wettability of sandstones (Ber 1-6) and the wettability modification by reducing salinity of imbibing brine. The process of spontaneous imbibition is shown in Table 3.

We can see from Figure 1 that during imbibition 1, the oil recovery and imbibition rate of core 1-3 aged by $CaCl_2$ brine were generally lower than that of core 4-6 saturated with NaCl brine. The oil recovery by HS-1 decreased with the increase of concentration of $CaCl_2$ in initial water (core 1, 2 and 3). On the other hand, core 4-6 had like oil recovery and rate although their salinity of initial water was different (Table 3). The results exhibit that the Ca^{2+} of initial water can change the initial wettability to be more oil-wet while initial wet state is independent on the concentration of Na^+. We infer that the increased salinity of the thin film of water between oil and mineral results in less negative brine/rock and brine/oil interfaces, then leading to closer approach of polar oil components to rock surface. However, the calcium bridges are much stronger and more effective than sodium bridges or Van der Waals to bind negatively charged acidic group from the crude oil to negatively charged sites on the mineral surfaces, then the adsorption of acidic components onto surface occurred, therefore, the rock surface changed to be more oil-wet.

Lowering salinity of imbibing water can improve oil recovery of cores aged by $CaCl_2$ brine compared to Ber 4-6 (imbibition 2). This is because the reduction of salinity can lead to less cations existing between negatively charged mineral/brine and brine/oil interfaces and then electrostatic repulsive forces between acidic group and mineral surface increase to break the calcium bridges. So the acidic components desorbed from rock surface to change the wettability to be less hydrophobic. However, when the LS-1 was turned to LS-2 with the same ionic strength, no improved oil recovery was observed. These results tell us that the simple cations (Na^+) of imbibing brine are not able to exchange the cations bridges, suggesting that the multicomponent ionic exchange (MIE) is not the main mechanism of low salinity water effect.

<u>Effect of Cation Valence and Ionic Strength of Solution on Sorption/Desorption of Acidic Component onto Clays</u>. The sorption/desorption of benzoic acid onto clays (kaolinite and illite) were used to prove the mechanisms of macroscopic wettability alteration. In all cases, the solution pH was adjusted to 9.5 by adding NaOH solution to ensure that the carboxylic acid groups are largely deprotonated so that the mechanism of adsorption/desorption of dissociative carboxyl can be analyzed.

Figure 2 shows that the background electrolyte Ca^{2+} can markedly enhance sorption of benzoic acid onto kaolinite and illite in comparison to Na^+. For instance, the adsorption of benzoic acid onto kaolinite in the presence of $CaCl_2$ solution was about six times greater than that in NaCl solution with the same ionic strength, and the adsorption of benzoic acid onto illite in the presence of $CaCl_2$ solution was about five times greater than that in NaCl solution with the same ionic strength. The results suggest that the Ca^{2+} is more effective than Na^+ and van der Waals forces to combine the negatively charged mineral surfaces and anionic functional groups of benzoic acid, which is consistent with previous results (Feng et. al, 2005; Theng, 1982).

For both kaolinite and illite, lowering the concentration of $CaCl_2$ was able to make the benzoic acid desorb from organo-clay previously formed in the 12500 ppm $CaCl_2$ solution (Figure 3). When the salinity decreased to 1562 ppm $CaCl_2$, substantial pre-adsorbed BA desorbed. We attribute this to the break of calcium bridges due to enhanced electrostatic repulsive forces between negatively charged acidic groups and clays.

Conclusion

(1) The initial wettability of Berea sandstone became more oil-wet with the increase in Ca^{2+} in initial water, while increasing the concentration of Na^+ cannot change the initial wettability. Lowering salinity of imbibing brine is able to improve oil recovery of cores aged by $CaCl_2$ brine compared with cores aged with NaCl brine. We propose that this is because the calcium bridges rather than sodium bridges or Van der Waals forces can effectively compress the electric layers between negatively charged carboxylic acid groups of crude oil and clay surface, leading to the combination of acid groups and mineral surface to make the rock surface hydrophobic. When decreasing the salinity of solution, the repulsive forces between negative rock surface and acidic components increase, resulting in wettability alteration toward less oil-wet.

(2) The presence of Ca^{2+} ions can notably enhance the adsorption of benzoic acid onto clays (kaolinite and illite) in comparison with Na^+, which demonstrates that calcium bridges are more effective than sodium bridges and Van der Waals forces to combine BA with clays. The reduction of salinity can break the calcium bridges between benzoic acid and clays and make them desorb.

Acknowledgement

References Cited

Agbalaka, C.C., A.Y. Dandekar, and S.L. Patil, 2009, Coreflooding studies to evaluate the impact of salinity and wettability on oil recovery efficiency: Transport in Porous Media, v. 76/1, p. 77–94.

Alotaibi, M.B., R.A. Nasralla, and H.A. Nasr-El-Din, 2011, Wettability studies using low salinity water in sandstone reservoirs: SPE Reservoir Evaluation & Engineering, v. 14/6, p. 713-725.

Buckley, J.S., Y. Liu, and S. Monsterleet, 1998, Mechanisms of wetting alteration by crude oils: SPE Journal, v. 3/1, p. 54-61.

Feng, X.J., A.J. Simpson, and M.J. Simpson, 2005, Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces: Organic Geochemistry, v. 36/11, p. 1553-1566.

Fjelde I., A.V. Omekeh, and Y.A. Sokama-Neuyam, 2014, Low salinity water flooding: effect of crude oil composition: Proceedings of the 2010 Society of Petroleum Engineering (SPE) Improved Oil Recovery Symposium; Tulsa, OK, April 12-16, 2014; SPE Paper 169090.

Hassenkam, T., C.S. Pedersen, K. Dalby, T. Austad, and S.L.S. Stipp, 2011, Pore scale observation of low salinity effects on outcrop and oil reservoir sandstone: Colloids Surf., v. 390/1, p. 179-188.

Liu, K., P. Eadington, and D. Coghlan, 2003, Fluorescence evidence of polar hydrocarbon interaction on mineral surfaces and implications to alteration of reservoir wettability: J. Pet. Sci. Eng., v. 39/3, p. 275-285.

Morrow, N.R., P.J. Cram, and F.G. McCaffery, 1973, Displacement studies in dolomite with wettability control by octanoic acid: SPE Journal, v. 13/4, p. 221-232.

Skrettingland, K., T. Holt, M.T. Tweheyo, and I. Skjevrak, 2011, Snorre low-salinity-water injection-coreflooding experiments and single-well field pilot: SPE Reservoir Evaluation & Engineering, v. 14/2, p. 182-192.

Tang, G.-Q., and N.R. Morrow, 1999, Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery: J. Pet. Sci. Eng., v. 24/2, p. 99-111.

Theng, B.K.G., 1982, Clay-polymer interactions: summary and perspectives: Clays and Clay Minerals, v. 30/1, p. 1-10.
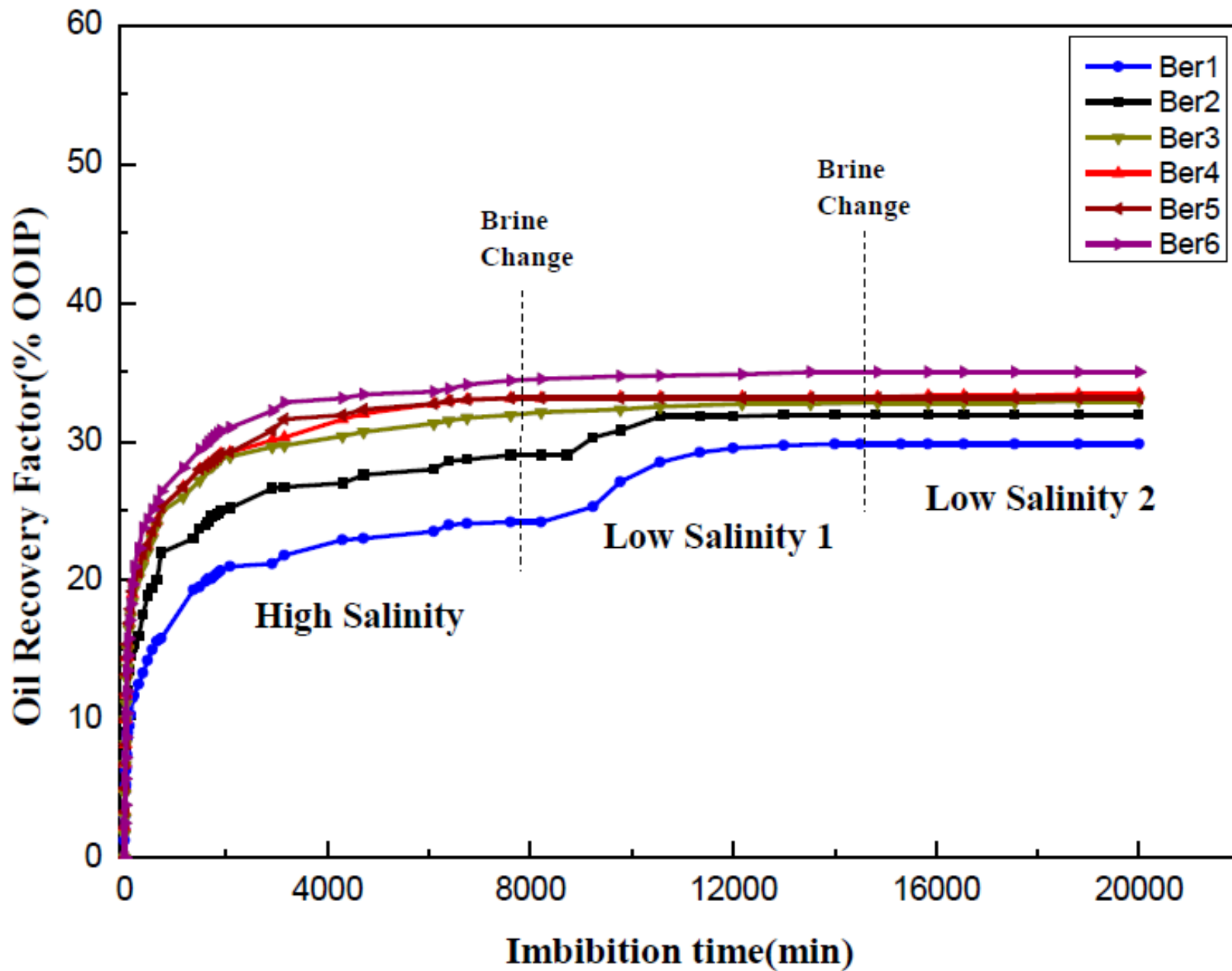
Figure 1. Effect of cation type and ionic strength of initial water on initial wettability and the wettability alteration by low saline water.
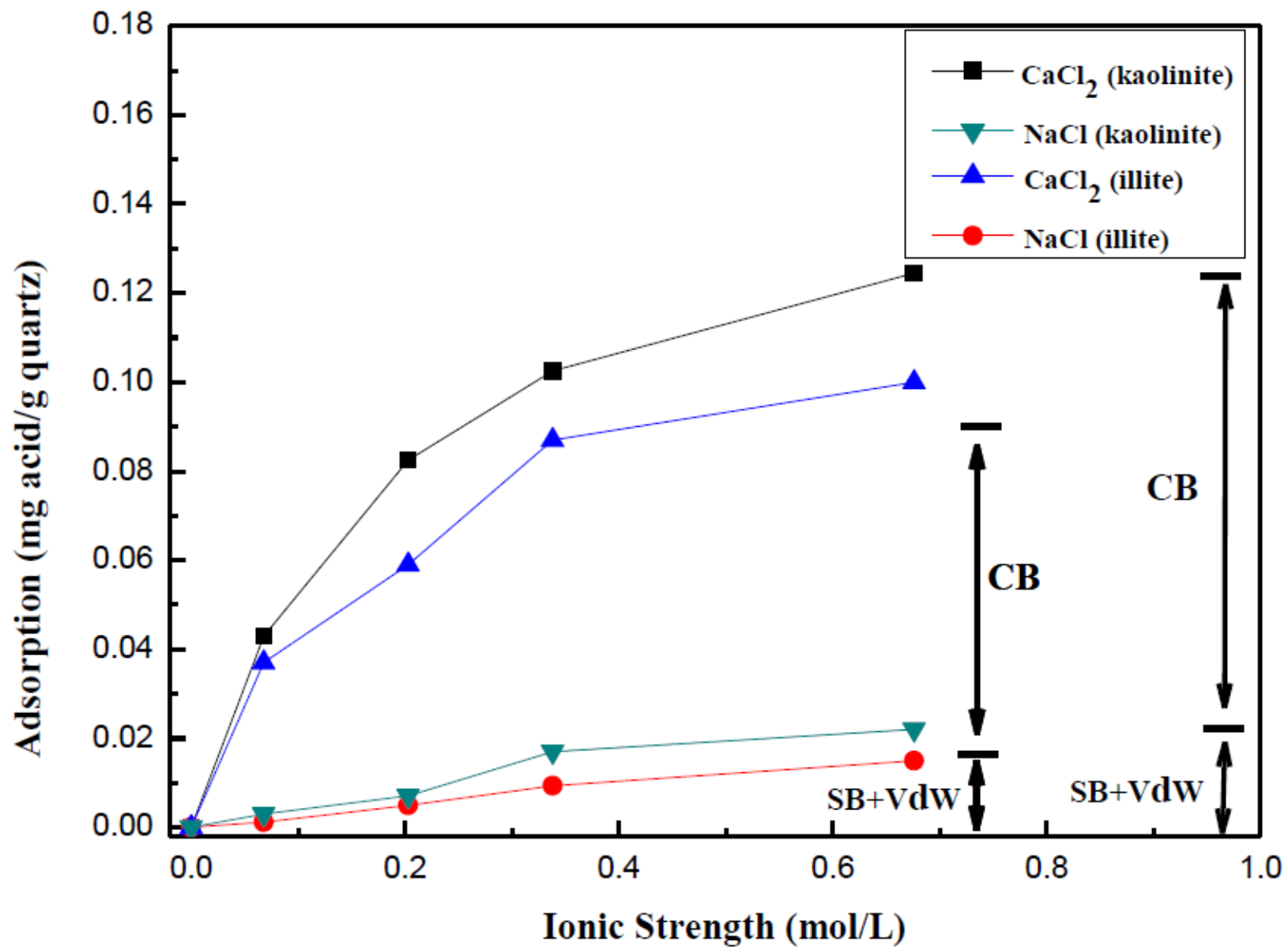
Figure 2. Effect of cation valence and ionic strength on the adsorption of benzoic acid onto kaolinite and illite. The arrows show the involved adsorption mechanism, with ionic strength 0.676 mol/L used as an example. CB = calcium bridging; SB = sodium bridging; VdW = Van der Waals.
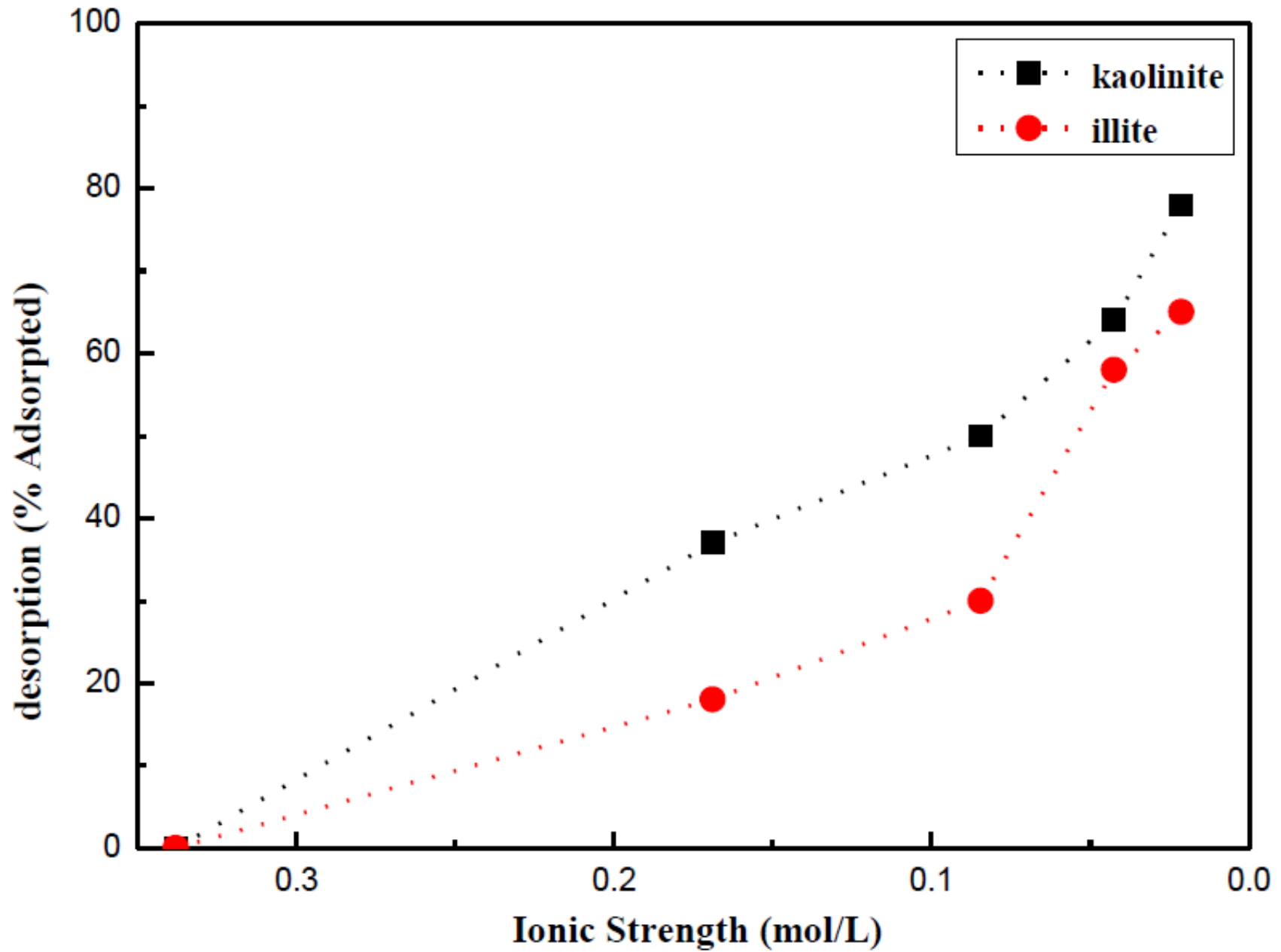
Figure 3. Effect of lowering ionic strength on the desorption of benzoic acid from kaolinite and illite.

Oil Type	Density@20°C ,g/cm^3	Saturates ,wt%	Aromatics ,wt%	Resins ,wt%	Asphaltenes ,wt%	Total Acid Number ,mg KOH/g	Viscosity@60°C ,mPa·s
Baken Oil	0.801	45.5	16	3.5	1.9	1.3	2

Table 1. Properties of crude oil.

	CaCl$_2$ (mol/L)	NaCl (mol/L)	Salinity (ppm)	Ionic strength (mole/L)
HS-1	0.225	0.0	25000	0.676
MS-1	0.045	0.0	5000	0.135
LS-1	0.009	0.0	1000	0.027
HS-2	0.0	0.676	39500	0.676
MS-2	0.0	0.135	7900	0.135
LS-2	0.0	0.027	1580	0.027

Table 2. Brine solutions.

Plug	Initial Water	Imbibition 1	Imbibition 2	Imbibition 3
Ber-1	HS-1	HS-1	LS-1	LS-2
Ber-2	MS-1	HS-1	LS-1	LS-2
Ber-3	LS-1	HS-1	LS-1	LS-2
Ber-4	HS-2	HS-1	LS-1	LS-2
Ber-5	MS-2	HS-1	LS-1	LS-2
Ber-6	LS-2	HS-1	LS-1	LS-2

Table 3. Cores for spontaneous imbibition.