

INVESTIGATION OF ELECTRICAL SURFACE CHARGES AND WETTABILITY ALTERATION BY IONS MATCHING WATERFLOODING

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ABSTRACT

In recent years, Ions Matching Waterflooding has been a promising technique to recover oil in sandstone reservoirs. However, the optimum conditions to improve oil recovery by Ions Matching Waterflooding are still not clear because of the lack of understanding of oil/brine and rock/brine interface interaction mechanisms. In this study, rock surface chemistry and wettability alteration studies were conducted to explain the mechanisms involved for improving oil recovery in low permeability sandstone reservoirs. Zeta potential was measured for solutions of oil/brine, and solid/brine; solids used were kaolinite, illite, chlorite, montmorillonite and quartz. Contact angle was tested with different concentrations of NaCl, CaCl₂, MgCl₂, Na₂SO₄ and one crude oil sample from Changqing Oil Field. Zeta potential results indicated that NaCl and Na₂SO₄ change electrical charge at both oil/brine and rock/brine interfaces to highly negative charge. The results of the contact angle measurement also showed that NaCl and Na₂SO₄ solutions changed wettability significantly compared to CaCl₂ and MgCl₂. Results demonstrate that the types of ions in the injection water have a more dominant influence on the recovery factor than the salinity. These findings can help in Ions Matching Waterflooding to obtain higher potential to recover oil.

INTRODUCTION

From the literature we know a Log-Inject-Log test (LIL) conducted in the Middle

East et al. [1] evaluated low salinity benefits indicated a 25 to 50% reduction in Sorw as waterflooding with low salinity brine and single well chemical tracer tests performed in Alaska resulted in reductions in remaining oil saturation of 6 to 12% OOIP which increased waterflood recovery by 8 to 19% [1]. But low salinity water might not be efficient in certain cases when the rock wettability characteristics and conditions are favorable as seawater injection is already efficient according to the literature [2-4]. The application conditions of low salinity waterflooding on field and core scale are still uncertain due to the lack of understanding of the underlying mechanisms by which oil recovery improved even though low salinity water effect showed great success in most of the laboratory experiment and field trials.

Tang *et al.* [5] indicated that potentially mobile fine particles play a key role in the sensitivity of oil recovery. McGuire *et al.* [1] investigated that the mechanism of low salinity waterflooding to enhance oil recovery is the same as alkaline waterflooding. Soraya *et al.* [6] showed that the hypothesis of alkaline waterflooding and fines release/flow diversion are not deemed to be the cause of the additional oil recovery observed by low salinity injection, and these phenomena have to be considered as consequences rather than causes although they might play a positive role as they occur. Lager *et al.* [7] suggested that multi-component ionic exchange (MIE) between the mineral surfaces and the invading brine is the major mechanism enhancing oil recovery. They assume that oil polar compounds are bonded to clay surfaces with negative charges either through multivalent cations in the case of carboxylate functions or adsorbed onto the mineral surface directly in the case of cation exchange [6]. Ligthelm *et al.* [8] and Sandengen *et al.* [9] attributed the main mechanisms of wettability alteration to cation exchange and expansion of the electrical double layer. Rock wettability is dependent on the stability of the water film between the surface of the rock and the crude oil. However, the thickness of the water film which dominates its stability may still depend on the mineral-surface charges and on the charges of water/oil interface [10]. Repulsive electrostatic force will occur which keeps the disjoining pressure high and maintains a thick water film to generate a water-wet rock surface if the solid/water and water/oil interfaces have similar charges [11].

Ionic composition of injection water dominates the wettability alternation of the reservoir which is closely related to the oil recovery factor. Therefore, the primary objectives of this paper are to investigate the impact of cation and anion type and concentration in the injection water on the zeta potential of oil/brine and solid/brine interfaces. Since the content of clay in Changqing Oil Fields is more than 20% as can be seen from Table 2, and the magnitude of specific surface area in low permeability reservoirs is much larger than that in the reservoirs with high

permeability. Kaolinite, illite, chlorite, montmorillonite, quartz and the natural core plugs extracted from Changqing Oil Field were used in the experiments, and the contact angle was tested with different concentrations of NaCl, CaCl₂, MgCl₂, Na₂SO₄ and one crude oil sample from Changqing Oil Field.

EXPERIMENTAL STUDIES

Materials

The oil sample used in the experiment to measure the zeta potential of the brine/oil interfaces was degassed crude oil from the well head of the well in Changqing Oilfield. The density of oil sample was 0.81g/cm³ at a temperature of 65 degrees Celsius. The viscosity of the experimental oil was tested using a capillary viscometer at the temperature of 65 degrees Celsius. The oil sample viscosity is 9.0cp, and the composition of the oil used in the experiment can be seen from Table 1. To prevent solid particles in the crude oil from influencing the zeta potential and wettability results, the oil sample was centrifuged at 5000rpm. Zeta potential and contact angle measurement were conducted with synthetic solutions of NaCl, CaCl₂, MgCl₂ and Na₂SO₄ with different concentration and de-ionized water. The solutions used in the experiment were vacuumed filter through two layers of filter paper to avoid impurity. The filter size used for solutions is from 1.5-2.5micro-meter.

Zeta Potential (ζ): Surface Chemistry Study

Zeta potential of oil/brine and solid/brine interfaces were measured through a Zetasizer Nano ZS manufactured by Malvern in Britain, and the zeta potential and electrophoretic mobility measure using Laser Doppler Microelectrophoresis. The measurement principle of zeta potential was Electrophoretic Light Scattering. All the measurements were conducted at 25 degrees Celsius and the error for zeta potential is $\pm 5\%$. The core plug extracted from the Chang 8 Formation of Changqing Oilfield was crushed into very fine powder, with the diameter at 100nm-20micron tested by the Zetasizer Nano ZS, which can satisfy the zeta potential measurement range. The mineralogy of the core plug used in the zeta potential test is given in Table 2.

The powders of kaolinite, illite, and chlorite, montmorillonite, quartz and natural core was put in the oven at 105 degrees Celsius for more than 12 hours until the weight was constant. The size of the clays range from 0.90-1.10 micro-meter. Samples of oil/brine and solid/brine were prepared using to the procedure proposed by Zhang [13]. The solutions of oil/brine were prepared at a volume ratio of 1:8 and with the oil from the Changqing Oilfield. The solid/brine samples were prepared by putting 2wt% of solids powder into the brine. The fluids used in the experiment included NaCl, CaCl₂, MgCl₂ and Na₂SO₄ at concentrations of 0.1, 1 and 5%wt and

de-ionized water. The powders was added to the solutions and stirred by a mixing rod to make sure that the powders were well-distributed. Then the supernatant fluid was extracted by syringe to be put into the measurement cell after the majority of solids particles were deposited at the bottom of the test-tube since the particles with big diameter would cause inaccurate results. Before the zeta potential testing, the measurement cell was flushed through with ethanol to facilitate wetting. With a full syringe in one of the sample ports on the cell and an empty syringe into the other, the capillary were flushed with the experimental fluid into the empty syringe back and forth between the syringes for at least 5 times to make sure that the capillary was clean.

Contact Angle Measurement

The method of 'Drop Shape Analysis' (DSA) was applied to measure the contact angle, which is a technique to determine contact angles from the shape of axisymmetric menisci [14]. The contact angle of the sample oil on the quartz glass was tested using the solutions with different concentration and ion types at the temperature of 25 degrees Celsius. The effect of high pressure on the contact angle was not considered during the experiment. The measurement device consists of a testing cell, a quartz glass holder, a capillary needle to introduce the oil droplet, an oil accumulator, a heating jacket and a temperature controller, a digital camera and computer to record and analyze the contact angle images. A diagram of the contact angle measurement device is given in the Fig.1. The contact angle between the baseline and the tangent at the drop boundary was determined by software. The error for contact angle is $\pm 5\%$. The surface of the quartz plates used in the experiment was smooth and homogeneous to ensure the precision of the experimental measurements [15, 16]. Each piece of the quartz plate was used in the experiment once to avoid surface wettability alternation.

A piece of dry quartz glass was placed inside of the measurement cell and the experimental solution was injected into the chamber through the capillary needle until the quartz glass was submerged in the solution to make sure all of the air bubbles were excluded. Then, the measurement cell was put inside of the heating jacket which was controlled by a temperature controller and the temperature at 25°C was set up. To be certain that the adsorption equilibrium condition between the quartz glass and the brine was reached, the quartz glass was left in the solutions for at least 30 minutes. An oil drop was introduced to the surface of the quartz glass using a capillary tube with the volume of about 0.5ml. The digital camera captured the shape of the oil drop on the quartz glass surface to determine the advancing contact angle. The oil drop was left on the surface of the quartz glass for at least one hour to achieve the adsorption balance.

RESULTS AND DISCUSSION

Zeta Potential (ζ)

Zeta potential technique and contact angle analysis were applied to understand the relation between electric double layer and wettability regarding the charges at interfaces of oil/brine and solids/brine. Rock wettability is extremely closely related to the water film between rock surface and crude oil which depends on the electrical double layer repulsion and Van der Waals force [10, 17]. Wettability of the rock will be determined by the stability of the water film which is bounded by the interfaces of oil/brine and solid/brine [5, 10]. An unstable water film, or thin water film, may cause the wettability preferential to be oil-wet. Therefore, injection water with different ions types and concentration would trigger the alternation of the surface charges of the both interfaces – oil/brine and solids/brine. Then, oil film may detach from the pore wall by the increase of electrical double layer repulsion and the oil recovery will be improved.

Experimental oil sample from Changqing Oilfield and the solutions of NaCl, CaCl₂, MgCl₂ and Na₂SO₄ with different concentration, 5%, 1% and 0.1wt% were deployed for zeta potential measurement at the interface of oil/brine. The solutions' pHs are closely related to zeta potential and was listed in Table 3. The error for pH measurement is $\pm 5\%$. Zeta potential at the interface of crude oil/brine is shown in Fig.2. The results indicated that surface charge at oil/brine interface is negative for all solutions except 5wt% CaCl₂ which is the same as the experimental results investigated by Nasralla [12]. Obviously, the ion types and concentration have the huge impact on the zeta potential. Particularly, the zeta potential of the interface of oil/NaCl solution is more negative than that of CaCl₂, MgCl₂ solutions at all concentrations. This phenomenon becomes much more apparent at the low concentration. Nevertheless, zeta potential of oil/Na₂SO₄ solution at the concentration of 1%, -30.8mV, is more negative than NaCl at all of the experimental concentrations. However, zeta potential at oil/Na₂SO₄ decreased to -17.0mV as the concentration reached 5wt% which was less negative compared to the concentration at 1%. The primary electrostatic bonds to link oil to most sandstone are oil-COO⁻ and oil-NH⁺, Sulfate-rich floods can eliminate oil-NH⁺ through sulphate sorption. Additionally, the high concentration of Na⁺ can neutralize the negative charge from the oil-COO⁻. Adsorption balance may exist with Na⁺ and SO₄²⁻ at the surface of oil/brine. Furthermore, the zeta potential at oil/de-ionized water was -34.3mV which was more negative than Na₂SO₄ at the concentration of 1wt%. Overall, charge at the surface of oil/brine will tend to become more negative by lowering the concentration of the brines except for the Na₂SO₄ solution. Consequently, charges at the surface of oil/brine not only depend on salinity, but also on the cations and anion types.

Zeta potential at the surface of solids/brine was tested for clay minerals and quartz with different brines and the results are given in Fig. 3 and Fig.4. Apparently, the zeta potential of the brine/clays is strongly dependent on the cations types and concentration and is similar to oil/brine. It is indicated that sodium chloride solutions with clay minerals showed strong negative charges compared to calcium chloride and magnesium chloride. The highest negatively surface charge was obtained by 0.1wt% NaCl when compared to CaCl₂ and MgCl₂ at all the concentrations. Na₂SO₄ at the concentration of 0.1wt% caused negative charge with higher magnitude than 0.1wt% of CaCl₂ and MgCl₂ with all types of clays. Fig.3 and Fig.4 shows that the anion types and concentrations are a strong influence on the charge and the magnitude of the zeta potential.

Moreover, it is demonstrated that the type of the mineral clay affects the zeta potential significantly. For example, the zeta potential of montmorillonite for all the solutions was negatively charged, while the other clays had zeta potentials with both positive and negative charges. The surface charge of kaolinite with the CaCl₂, and MgCl₂ solutions at concentration of 1wt% and 5wt% were positive. Surface charge of illite was almost zero with 1wt% concentration of MgCl₂ solution and the surface charge of chlorite was positive with the 5wt% CaCl₂ and MgCl₂ solution. The interesting thing is that the concentration of Na₂SO₄ solution was not sensitive to the zeta potential with different types of clays except for illite which resulted in the highest negative magnitude of the surface charge at the concentration of 0.1wt%. Zeta potential at surface of clay/de-ionized water was higher negative magnitude compared to that of clay/brine excluding NaCl and Na₂SO₄ solution at the concentration of 0.1wt% for the illite and kaolinite. It is demonstrated again that zeta potential is not only dependent on salinity level, but also strongly dependent on the ion types. Zeta potential was measured for the core which was crushed to very fine powder and mixed with brines, shown in Fig.4. The sandstone sample from the reservoir was cleaned by benzene and ethyl alcohol with the ratio 3:1 before all the measurements. It is very clear that ion types and concentration have a strong influence on the magnitude and charge of the zeta potential at the surface of sandstone/brines and this recognition is the same as the standpoint proposed by Nasralla [12]. Surface charge of sandstone with CaCl₂ and MgCl₂ with 1wt% and 5wt% are positive. Zeta potential of sandstone with Na₂SO₄ is still negative with all of the concentration the same as other minerals in this study. Additionally, the zeta potential for 1% Na₂SO₄ is still higher than the 5% solution which is same as oil/Na₂SO₄. The primary electrostatic bonds to link oil to most sandstone are clay-Al-O-Ca⁺, clay-Si-O-Ca⁺ and clay-Al-O⁻ and clay-Si-O⁻, Sulfate-rich floods can eliminate positive charge through sulphate sorption. Moreover, the high concentration of Na⁺ can neutralize the negative charge from the clay-Al-O⁻ and clay-Si-O⁻. Adsorption balance may be existent regarding Na⁺ and SO₄²⁻ at the

surface of reservoir rock/brine. Nevertheless, the surface charge of de-ionized water with the sandstone is just -10.5mV which is less than the interface of the mineral with NaCl at the concentration of 0.1wt%. Overall, the results indicated that the types of the mineral and ion dominate the magnitude of the zeta potential.

It is acknowledged that pH of the solutions affect the magnitude of the zeta potential at the surface of solids/brine significantly, and more positive charge will be obtained with the decrease of solution pH[10, 16]. However, the de-ionized water/solids and water/oil interfaces have the large negative charge magnitude except for the interface for brines with illite, quartz and sandstone, even though the pH of the de-ionized water with solids and oil is lower than that of other brines. Therefore, this demonstrates that pH is a result of chemical reactions between the solutions and the minerals and it is not the factor that alters the electric charge[12]. The additives that determine solution pH are responsible for changing the electrokinetic charge because of the dominant charges they carry such as acid and alkali which make the solution positively and negatively charged, respectively [4].

Contact Angle Wettability

The contact angle, θ , was measured through the aqueous phase, which was determined by extrapolating the meniscus shape through the thin-film region to the solid surface given by Fig.5. Contact angle for crude oil with the different brines and de-ionized water on quartz were tested and the results are given in Fig.5. The wettability measurement was conducted at room temperature of 25°C and standard atmosphere. The objective of the contact angle tests was to investigate the impact of the ion types and concentration on the wettability alternation to enhance the understanding to improve oil recovery during Ions Matching Waterflooding in low permeability sandstone.

The oil drop was left on the surface of the quartz glass for at least one hour to achieve the adsorption balance according to the contact angle measurement conducted by Nasralla [4]. The average angle between the right and left angles was tested at least three times and then, the average value was drawn in Fig.5. It is apparent that the ion types and concentration have a large impact on the wettability. The surface of the quartz tends to water-wetting with the decrease of the solution concentration except Na₂SO₄. NaCl solution makes the surface preferential to water-wet compared to the CaCl₂ and MgCl₂ solutions at the same concentration, which is compatible to the measurement of the zeta potential at the surface of brine/oil shown in Fig.2. It is demonstrated that water-wetting can be created by the high negative surface charge. Moreover, the contact angle was 38° for the Na₂SO₄

at the concentration of 1wt%, and which was the lowest magnitude compared to other solutions except de-ionized water. This outcome matches the zeta potential measurement from Fig.2. It is acknowledged again that the zeta potential at the surface of the brine/oil closely related to the wettability, and NaCl and Na₂SO₄ can make the zeta potential become much more negative than CaCl₂ and MgCl₂. De-ionized water may cause fine particles migration that will damage the formation since it will cause clay swelling even though it can trigger low zeta potential and more water-wet.

Rock wettability is a function of the magnitude of electric charge at the surface of brine/oil and brine/rock since the repulsion is determined by the electrical double layer and the attractive pressure dominated by London-van der Waals force and structure force. Rock tends to water wet as the zeta potential at the surface of brine/oil and brine/rock are of highly negative charge which cause electrical double layer expanding and the water film becomes thick and stable [10]. Zeta potential at the surface of formation brine/oil under formation temperature and pressure are usually negative[7], and the surface charge of the brine and rock in-situ is either positive or negative which depends on the composition of the brine and rock as shown in Fig.2 to Fig.4. Water-wet interfaces can be formed with increase of the zeta potential at both interfaces towards high negative charge since the disjoining pressure can be increased by the increase of the electrical double layer force. Disjoining pressure is the sum of the electrical double layer, the London-van der Waals and the structural forces[10]. The London-van der Waals force between the two similar materials is usually attractive. The structural forces are short-range interactions at a distance of less than 5nm, whereas the London-van der Waals and electrical double layer forces are long-range interactions compared to the structural forces. Consequently, the main objective to change the wettability is to alter the surface charge to highly negative charge at the interface of brine/rock. It was demonstrated that the contact angle created by NaCl, Na₂SO₄ at the concentration of 0.1wt% and 1wt%, respectively, and de-ionized water was lower than other solutions. This wettability measurement results are consistent with the zeta potential test.

CONCLUSIONS

In this study, the effect of ion types and concentration on the zeta potential and contact angle were investigated to understand the mechanism of Ions Matching Waterflooding to enhance oil recovery. Several observations have been made during this study:

- Zeta potential results indicated that NaCl and Na₂SO₄ changes electrical charge at both oil/brine and rock/brine interfaces to highly negative charge which causes the increase of rejoining pressure between two interfaces.

- The results of the contact angle measurement also showed that NaCl and Na₂SO₄ solutions at the concentration of 0.1wt% changed wettability significantly compared to CaCl₂ and MgCl₂.
- Water-wet interface can be formed with an increase of the zeta potential at both interfaces towards highly negative charge since the disjoining pressure can be increased by the increase of the electrical double layer force.
- The types and concentration of cations and dianions in the injection water brine and the minerals have a more dominant influence on the wettability than the salinity. These findings can help in Ions Matching Waterflooding to improve potential to recover additional oil.

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Table 1: Ingredients of the oil sample from Changqing Oilfield

Ingredients	Saturated hydrocarbon	Aromatic hydrocarbon	Non-hydrocarbon	Asphaltic bitumen
wt%	65.05	23.3	6.68	4.97

Table 2: Mineralogy of core plug using in the zeta potential test

Mineral	Concentration, wt%
Quartz	45.50
Potassium feldspar	9.10
Sodium feldspar	24.40
Illite	1.89
Chlorite	10.08
Kaolinite	1.05
Illite/Montmorillonite	7.98

Table 3: pH of oil/brine solutions at 25°C

Brine		Kaolinite	Illite	Montmorillonite	Chlorite	Sandstone	Oil
		pH					
NaCl	5%	5.3	8.1	8.2	9.9	8.7	6.5
	1%	5.1	7.5	7.6	9.9	8.7	6.2
	0.1%	4.9	7.1	7.4	9.7	8.3	6.3
CaCl ₂	5%	4.3	7.6	7.4	9.2	8.2	6.3
	1%	4.2	7.1	7.1	9.2	7.8	5.9
	0.1%	4.3	6.9	6.9	8.7	7.3	5.8
MgCl ₂	5%	4.7	7.9	7.6	9.5	9.0	6.2
	1%	4.2	7.5	7.3	9.2	8.5	5.4
	0.1%	4.5	7.1	7.0	8.7	8.0	5.0
Na ₂ SO ₄	5%	5.7	8.3	7.8	9.9	8.7	6.0
	1%	5.4	7.6	7.6	10.2	9.0	7.0
	0.1%	5.3	7.4	7.3	10.1	8.6	6.3
De-ionized water		5.1	8.0	7.3	7.2	7.6	5.8

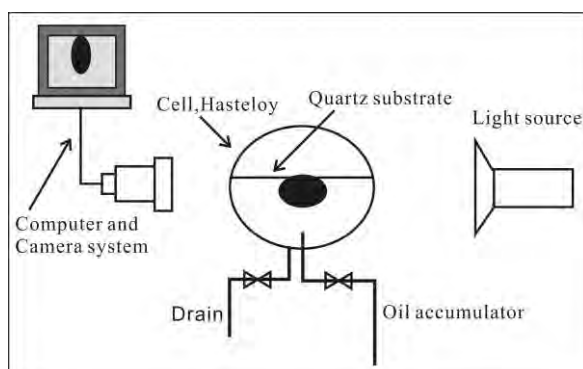


Fig.1: The schematic diagram of contact angle test

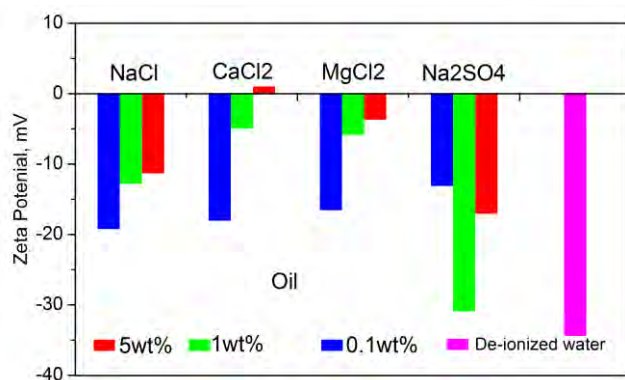


Fig.2: Effect of ion types and concentration on zeta potential at oil/brine

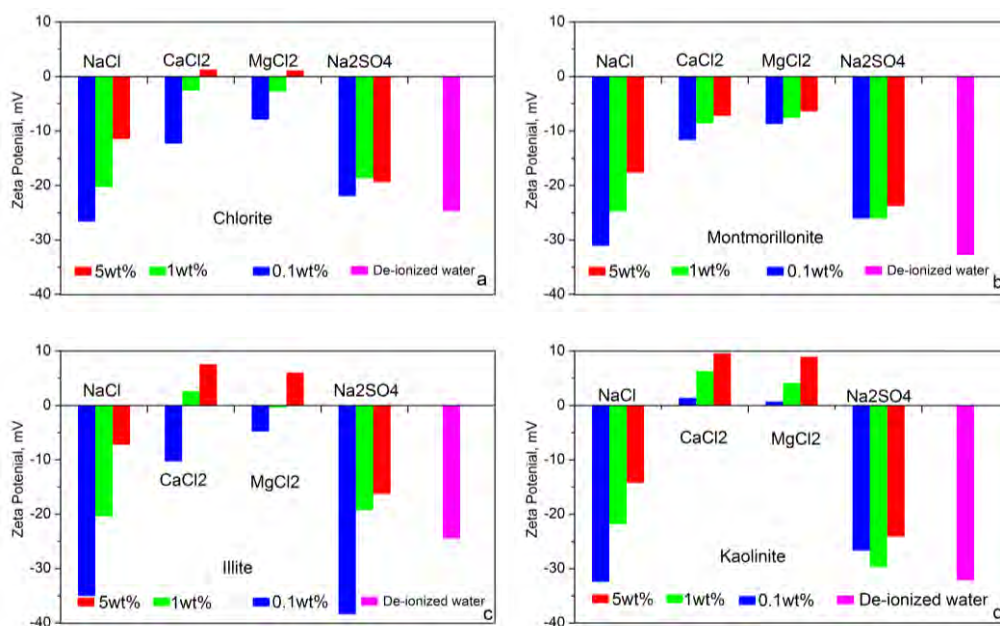


Fig. 3 Effect of ion types and concentration on zeta potential at brine/clay minerals (From a to d)

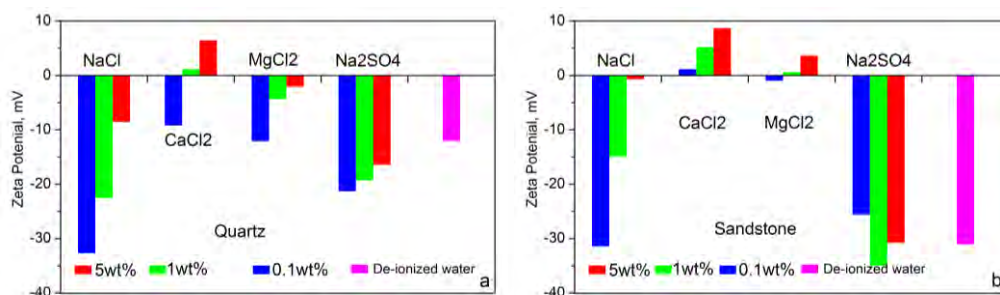


Fig. 4 Effect of ion types and concentration on zeta potential at brine/quartz and brine/sandstone

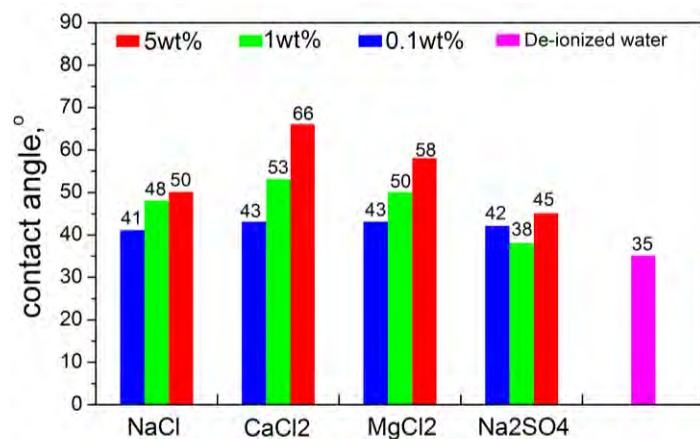


Fig. 5 Effect of ion types and concentration on contact angle at brine/oil