PRIMARY MECHANISM OF IMPROVED OIL RECOVERY BY IONS-TUNING WATERFLOODING: DOUBLE LAYER EXPANSION OR MULTICOMPONENT IONIC EXCHANGE?

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ABSTRACT

Ions-tuning waterflooding (ITW) has recently become a promising improved oil recovery (IOR) technique for sandstone reservoirs. However, the major contributor to wettability alteration is still uncertain despite a decade-long investigation. This paper investigates the major mechanisms of ITW in the process of IOR. The pHs and zeta potential of the brines/reservoir rock and brines/crude oil systems were tested under the reservoir temperature at 65℃. Coreflood experiments were conducted using six Changqing reservoir cores with 1 in. diameter; five brines with TDS variation from 0.2 to 10% were injected under reservoir temperature. Zeta potential results show that decreasing divalent cation and salinity makes the electrical charges at both oil/brine and brine/rock interfaces strongly negative. Different coreflood experiments showed that ITW (0.5569%) with 0.023% divalent cation as secondary (starting at Swi) and tertiary (starting at Sorw) mode recovered 15.6% and 13.3% OOIP, respectively. Injecting brine (0.2%NaCl) as tertiary mode recovered 10.3% OOIP with the original brine 5.8% NaCl solution. It demonstrates that the ITW can improve oil recovery in secondary and tertiary mode even though there is no multi-component ions exchange. Furthermore, 10% NaCl as tertiary mode only recovered 3.3% OOIP with the original brine-formation brine. It proved that the multi-component ions exchange is not dominant to recover additional recovery without double layer expansion. In conclusion, double layer expansion caused by highly negative zeta potential as a result of lower salinity and divalent cation plays a major role in recovering additional oil.

INTRODUCTION

The general agreement among researchers is that Ions-tuning waterflooding (ITW) causes reservoirs to become more water-wet [1-3]. Even though different mechanisms have been proposed to explain the wettability alternation, the primary mechanisms are still uncertain. Lager *et al.* [4] suggested that multi-component ionic exchange (MIE) between the mineral surface and the invading brine is the major mechanism to improve oil recovery. They assume that oil polar compounds are bonded to clay surfaces with negative charges; either through multivalent cation association in the case of carboxylate functions, or directly adsorbed onto the mineral surface in case of cation exchange [3]. Nasralla *et al*[5]. proposed wettability alteration due to change of electrical charge at water/oil and water/rock interfaces by ITW which is one of the dominant mechanisms of improving oil recovery by manipulating injected water chemistry as there is a match between electrical surface charge experiment results and improvement of oil recovery by coreflood experiment. However, what is the major cause to improve the wettability among the electrical double layer expansion, multi-component exchange? Therefore, the main objective of this paper is to investigate the fundamental mechanism to enhance oil recovery of the ITW with the combination of surface chemistry, contact angle tests and coreflood experiments.

Experimental Preparation

Zeta potential of oil/brine and solid/brine interfaces was measured through Zetasizer Nano ZS manufactured by Malvern, Zeta potential and electrophoretic mobility using Laser Doppler Microelectrophoresis. The measurement principle of zeta potential is Electrophoretic Light Scattering. All the measurements were conducted at 65 degree Celsius. The core plug extracted from the Chang 8 Formation of Changqing Oilfield was crushed to a very fine powder with diameters at 100nm-100micron before zetapotential measurements. The content of total clay minerals is about 25%, and the Samples of oil/brines and solid/brines were prepared according to the procedure proposed by Xie [6]. The method of ‘Drop Shape Analysis’ was applied to measure the contact angle, which is a technique to determine contact angles from the shape of axisymmetric menisci. The contact angle of the sample oil on quartz glass was tested using five different brines with TDS variation from 0.2 to 10% at the temperature of 65 degree Celsius. The experimental diagram and procedures of contact angle measurements were prepared referring to the procedure proposed by Xie [6]. All coreflood measurements were conducted under 65℃ and the core plugs used in the experiment were extracted from the reservoir, Table 1. The ITW was acquired by thermodynamic model calculation which is proposed by George Hirasaki[7]. The ingredients of formation brine and ITW are given by Table2. A Quizix-SP-5400 pump, with accurate control at constant low flow rate, was set up in the flooding system. The experimental procedures adopted in this paper refer to the procedures proposed by Wu [8].

Results and Discussions

The pHs value of the different brines/reservoir rock and brines/crude oil systems are tested in Table 3. The effect of brine salinity and composition on zeta potential at the surfaces of reservoir rock/brines and crude oil/brines are depicted in Table 3. ITW resulted in strong negative charges at reservoir rock and crude oil with the pHs of 8.2 and 8.5, respectively. Nevertheless, formation brine and 5.8% and 10% NaCl changed the surface charges weakly negative at both oil and rock with the lower magnitude of pHs compared to ITW. It was shown that the zeta potential is not only closely related to the types of the ions, but also the salinity of the brine which will alter the thickness of the double layer. Formation brine and 10% NaCl solution changed the surface charges to weak negative at both oil and rock with almost same magnitude shown as Table 3. But the 5.8% NaCl solution altered the surface charges stronger negative compared to formation brine and 10% NaCl solution. In conclusions, the influence of brine salinity and composition on the electric surface charge at the oil/brine and rock/brine interfaces is dominant to alter the surface charges, which was reported by Nasralla [2]. Contact angles for crude oil with the different brines were tested and the results given in Table 3, the error of the contact angle tests is about ±5%. It was apparent that Ions-tuning brine caused the mica surface to become more water-wet, while formation brine and NaCl solution with 10% and 5.8% mass concentration made the mica surface intermediate-wet. It proved that wettability alteration is extremely closely related to water salinity as reported by Nasralla and Nasr-El-Din [2].

Cores CQ1 and CQ2 were used to conduct coreflood experiments by flooding formation brine and Ions-tuning brine, respectively. Oil recovery of these two experiments was compared with what was obtained from formation brine injection to show the effect of water salinity on oil recovery during secondary mode, as shown in Fig.1 (A). Oil recovery was 30% OOIP with the injection of formation brine, and 45.6% by Ions-tuning flooding. This verifies the high potential of low-salinity water to enhance oil recovery during secondary injection mode, which was observed by most of the researchers. The incremental oil recovery by ITW compared to high salinity waterflood could be attributed to the expansion of the electric double layer, which is caused by low-salinity water as a result of increasing the magnitude of the negative electric charge at the interfaces of oil/brine and rock/brine, as depicted in Table 3. The rock wettability might be altered towards water-wetness, which was demonstrated by contact angle measurements in Table 3. Core CQ3, Fig.1 (B), was flooded by formation brine with 13PV, and then flooded by Ions-tuning water by 10PV to investigate the effect of ITW flooding in tertiary recovery mode. Formation brine injection produced 29.4% OOIP, ITW recovered additional oil 14.5% OOIP, respectively, which indicates that oil recovery can be improved by ITW in tertiary mode. Core CQ4 was used to conduct a coreflood experiment with formation brine in secondary mode, then 10% NaCl to be as tertiary mode, shown as Fig.2 (A). The NaCl brine with 10% mass concentration was flooded as tertiary mode to eliminate the influence of double layer expansion during the coreflood process since the zeta potential of NaCl 10% and formation brine with rock and oil is almost equivalent, as shown in Table 3. An interesting observation is that the additional oil recovery was 3.5% OOIP with the injection of 10% NaCl solution, which is about 10% OOIP less compared with ITW. Technically, there were no divalent ions in the 10% NaCl solution. If the multi-component mechanism is dominant to enhance oil recovery, 10% NaCl solution should recover more oil instead of 3% OOIP. Therefore, multi-component might be not one of the major mechanisms to recover more oil. Moreover, in order to unveil the importance of the double layer expansion in ITW, two concentrations of NaCl solution were used to conduct coreflood experiments. Fig.2 (B) shows that the displacement by 0.2% NaCl solution recovered approximately 10% additional OOIP after the 5.8% NaCl solution flooded for 18PV. Technically, there were no divalent ions in the 5.8% NaCl solution. But there is a big change of zeta potential at the interfaces of brine/rock and oil/brine with mass concentration of 0.2% and 5.8% which cause double layer expansion (Table 3). Consequently, multi-component exchange cannot explain why 0.2% NaCl solution can recover around 10% OOIP after 5.8% NaCl solution flooding from the experiment, as given in Fig.2 (B). On the contrary, it is significant to mention that the expansion of double layer is the major effect to improve oil recovery for ITW.

CONCLUSIONS

Based on the investigation presented in this study, the following conclusions can be drawn:

- Ions-tuning waterflooding showed a high potential to improve oil recovery in both secondary and tertiary injection mode.
- Zeta potential at the interfaces of oil/brine and brine/rock were strongly negative with Ions-tuning water.
- Multi-component ions exchange might be one of the mechanisms to recover more oil. However, electrical double layer expansion is a dominant effect to improve oil recovery in Chang Qing oil reservoir.

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Table 1 the core parameters of experiment

Sample	Flooding mode	Ka mD	Swi (%)	Original brine	Secondary flooding	Tertiary flooding	RF (HSW) (%)	RF (IAW) (%)
CQ1	Secondary	1.49	33.2	FB	FB		30.0	
CQ2		1.67	38.1	FB	ITW			45.6
CQ3	Tertiary	2.09	30.4	FB	FB	ITW	29.4	42.7
CQ4		1.67	40.1	FB	FB	NaCl/10%	30.5	33.7
CQ5		2.79	26.1	NaCl/5.8%	NaCl/5.8%	NaCl/0.2%	24.7	34.5

Table 2 the composition of the formation brine and synthetic brine

Sources	ingredients（mg/l）						Total salinity (mg/l)
	K^++Na^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	
Formation brine	19249	2460	317	308	34781	0	57115
Ions-tuning water	1900	200	30	30	3199	210	5569

Table 3 the magnitude of zeta potential at different surfaces and contact angle with brines

Samples	Oil/Brines Zeta potential(mV)	pH	Rock /Brines Zeta potential(mV)	pH	Contact Angle,°
Formation Brine	-7.7	6.8	-8.7	7.1	74
Ions-tuning water	-18.7	8.2	-21.7	8.5	39
Oil/NaCl (wt=0.2%)	-22.9	8.6	-25.3	8.8	37
Oil/NaCl (wt=5.8%)	-10.2	7.7	-12.0	7.5	54
Oil/NaCl (wt=10%)	-7.7	7.1	-8.8	7.2	75

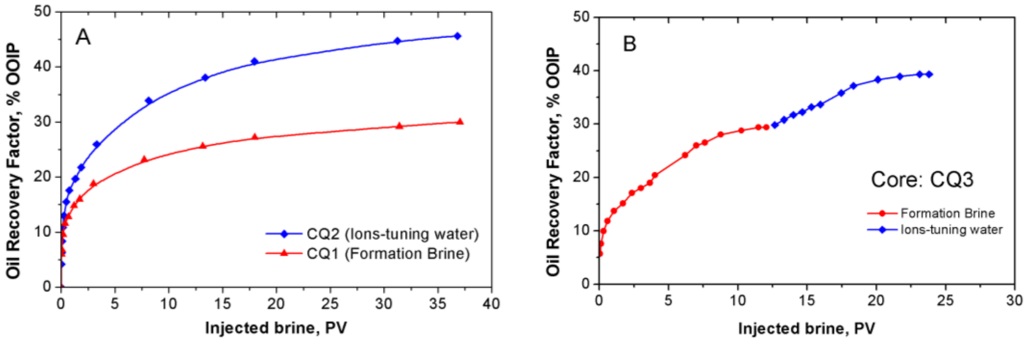

Fig.1 Oil recovery factor vs. injection PV at secondary (A: Core CQ1 and CQ2) and tertiary mode (B: Core CQ3).

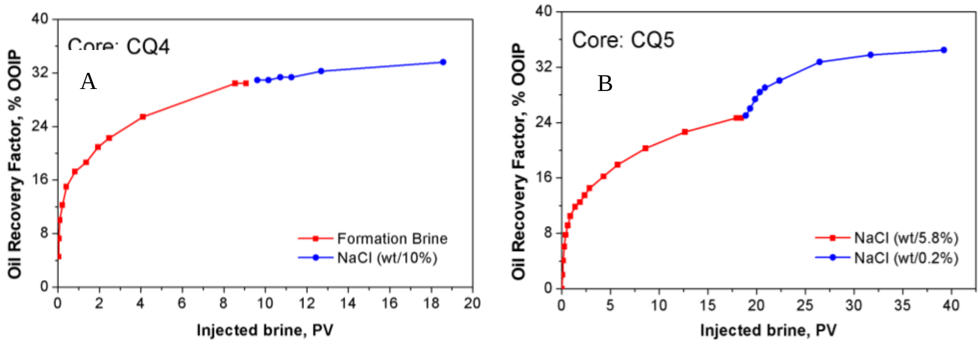

Fig.2 Oil recovery factor vs. injection PV at tertiary mode. A: formation brine displacement followed by NaCl 10% ; B: NaCl 5.8% displacement followed by NaCl 0.2%.

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