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Ions tuning water flooding experiments and interpretation by thermodynamics of wettability

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ABSTRACT

In recent years, ions tuning water flooding (ITWF) has become a promising technique to recover oil in sandstone reservoirs. In view of research results for the last decade, it is acknowledged that substantial oil recovery beyond conventional waterflooding from sandstone is due to the wettability alteration. However, the major contributor to wettability alteration is still uncertain. Therefore, this paper investigates this major mechanism and shows how it is involved in the process of IOR. Rock surface chemistry and wettability alteration studies were conducted to explain the mechanisms involved for improving oil recovery in low permeability sandstone reservoirs. Moreover, the thermodynamics of wettability during the ITWF was analyzed to characterize the surface forces between the surfaces of oil/water and water/rock. The major mechanism of ITWF to recover incremental oil was confirmed by coreflood experiments with five different brines. Zeta potential results showed that decreasing divalent cations and salinity makes the electrical charges become strongly negative at both oil/brine and brine/rock interfaces, which result in elevating the repulsive forces between the interface of oil/water and interface of water/rock, and as a result the rock turns more water-wet, which was confirmed by thermodynamics characterization. Different coreflood experiments showed that ITW (0.5569%) with 0.023% divalent cation as secondary (starting at Swi) and tertiary (starting at Sorw) modes recovered 15.6% and 15.1% OOIP, respectively. It demonstrates that the ITW can improve oil recovery in secondary and tertiary modes. Injecting brine (0.2% NaCl) as tertiary mode recovered 10.3% OOIP after 5.8% NaCl solution was flooded at the secondary mode. Furthermore, 10% NaCl as tertiary mode only recovered 3.3% OOIP after the formation brine flooded the secondary mode. It proved that the multi-component ions exchange is not dominant to recover additional recovery without double layer expansion. In conclusion, double layer expansion was caused by the highly negative zeta potential as a result of lower salinity and the divalent cation plays a major role in recovering additional oil. These findings can help in ions tuning waterflood to maintain higher potential to recover oil.

1. Introduction

Waterflooding technology has been the most successful approach to improve oil recovery. The key point to reach this success of waterflooding is that the differential pressure can be formed by the water injection which is necessary to displace oil out of formation. And also, waterflooding involves much lower cost investment and convenient operation. However, it was found that water chemistry and salinity level have a significant influence on oil recovery from the experiment in the laboratory and field trials (Mahani et al., 2011; Parracello et al., 2013; Xie et al., 2012b; Shaikh and Sharifi, 2013; Shalabi et al., 2014; Skrettingland et al., 2011). According to our recent research work and literatures published recently, the low salinity EOR-effect is not only dependent on the salinity but closely related to the ionic content and ionic types. Therefore, the principle of ions tuning waterflood (ITW) is not only to dilute the salinity of the injection brine but also to adjust the salinity and composition of the injection brine (Xie and Ma, 2012a; Xie et al., 2012b, 2013; Yousef et al., 2011).

In recent years, several mechanisms were proposed to account on how the ions tuning waterflood to recover additional oil. (1) Fines migration and clays swelling caused by ions tuning waterflood are the main mechanisms of improved oil recovery (Morrow and Buckley, 2011; Sohrabi and Emadi, 2013). (2) Multi-component ionic exchange between the rock minerals and the injected brine was proposed to be as the major mechanism to enhance oil recovery (Lager, 2006; Lager et al., 2008). (3) Expansion of the double layer to be as the dominant mechanism of oil recovery improvement (Nasralla and Nasr-El-Din, 2012). The general

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agreement among researchers is that ions tuning waterflood causes reservoirs to become more water-wet (Fjelde et al., 2012; Nasralla and Nasr-El-Din, 2012; Shalabi et al., 2014; Sohrabi and Emadi, 2013). Even though different mechanisms have been proposed to explain the wettability alternation, the primary mechanisms are still uncertain.

Tang and Morrow (1999) indicated that mobile fine particles play a key role in the sensitivity of oil recovery and refined oil was used with all other conditions held the same; but salinity had no effect on recovery. Hussain investigated the fines-free and fines-assisted waterflooding by laboratory experiment and developed a numerical one-dimensional model to interpret the mechanism of ions tuning waterflooding (Hussain et al., 2013). McGuire et al. (2005) investigated that the in-situ surfactant generation (saponification) as same as alkaline waterflooding by ions tuning waterflood is the main explanation to enhance oil recovery. Soraya et al. (2009) showed that the hypothesis of alkaline waterflooding and fines release/flow diversion is 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 being caused although they might play a positive role as they occur.

Lager et al. (2006) suggested that multi-component ionic exchange (MIE) between the mineral surface and the invading brine is the major mechanism enhancing oil recovery. Some researchers assume that oil polar compounds are bonded to clay surface with negative charges either through multivalent cations in case of carboxylate functions or adsorbed onto the mineral surface directly in case of cation exchange(Brady et al., 2012; Dang et al., 2013; Omekeh et al., 2012). Ligthelm et al. (2009) and Sandengen et al. (2011) 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 (Hirasaki, 1991). Repulsive electrostatic force will occur to keep the disjoining pressure high and maintain a thick water film which generates a water-wet rock surface if the solid/water and water/oil interfaces have similar charges (Dubey and Doe, 1993). Nasralla et al. (Nasralla and Nasr-El-Din, 2011a, 2011b; Nasralla et al., 2011) proposed that wettability alteration due to change of electrical charge at water/oil and water/rock interfaces is one of the dominant mechanisms of improving oil recovery by manipulating injected water chemistry.

Zeta potential is the electric potential in the electrical double layer (EDL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. The magnitude of the zeta potential is closely related to the surface charges at the oil/brine and rock/brine interfaces. The surface charges of interfaces of water/oil and water/rock are strongly affected by ionic strength of water (Alotaibi et al., 2010a). Therefore, the cation type and concentration impact on the surface charge of solids and oil/water interfaces. Moreover, it was found that NaCl solutions with low ionic strength resulted in stronger negative charges at interfaces of water/rock and water/oil compared to the high ionic strength solution (Buckley and Liu, 1998), and Ca^{2+} and Mg^{2+} reduced the zeta potential more effectively than Na^{+} (Alotaibi et al., 2010a; Nasralla and Nasr-El-Din, 2011a, 2011b; Nasralla et al., 2011).

Several mechanisms have been proposed to be the dominant reason to improve oil recovery by ions tuning water flooding. Moreover, the wettability change is claimed to be the dominant reason for incremental oil recovery. However, what the main causes (electrical double layer expansion, multi-component exchange and fines migration) to improve the wettability are still uncertain. Therefore, the main objective of this paper is to investigate the fundamental mechanisms to enhance oil recovery by ions tuning waterflood with the combination of DLVO theory, surface chemistry and coreflooding experiments.

2. Experimental

2.1. Zeta potential

Zeta potential of oil/brine and solid/brine interfaces was measured through Zetasizer Nano ZS manufactured by Malvern. The measurement principle of zeta potential was Electrophoretic Light Scattering. All the measurements were conducted at 65 °C. The core plugs extracted from the Chang 8 formation of Changqing Oilfield were crushed to very fine powders with the diameter of 100–100 μm which can satisfy the zeta potential measurement range. Samples of oil/brine and solid/brine mixed solution were prepared referring to the procedure proposed by Zhang (2006). The solutions of oil/brine were prepared at a volume ratio of 1:8 and the oil from the Changqing Oilfield. The samples of rock/brine mixed solution were prepared by adding 2 wt% of solids powder to the brine. The composition of the brines and the ingredients of oil sample are listed in Tables 1 and Fig. 2, respectively. The salinity of the formation brine is 58,430 mg/l with 2777 mg/l as the divalent cation. The ITW was formed by 10 times diluting the formation brine and adding sodium sulfate to adjust the zeta potential to become more negative. The solids powder was added to the solutions and stirred using a mixing rod to make sure that the solids power was well-distributed. Then the supernatant liquor was extracted by a syringe and injected into the measurement cell since the majority of solids particles deposited in the bottom of the test-tube contained particles with a larger diameter which would cause inaccurate results. Before the zeta potential tests, the measurement cell was flushed with ethanol to facilitate wetting. Full syringe was placed in one of the sample ports on the cell and the empty syringe into the other; the capillary was flushed with the experimental fluid into the empty syringe back and forth for more than 5 times to make sure that the capillary was full of the experimental fluid.

2.2. Contact angle

The method of 'Drop Shape Analysis' was applied to measure the contact angle. The contact angle of the sample oil on the quartz glass was tested using the solutions with different concentrations and ions type at temperature of 65 °C and the effect of high pressure on the contact angle was not considered from the experiment. The measurement device consisted of a test cell, a quartz glass holder, a capillary needle to introduce the oil droplet, an oil accumulator, a heating jacket and temperature controller, a

Table 1
Composition of the formation brine and ions tuning water (ITW).

Sources	Ingredients (mg/l)s							Total salinity (mg/l)
	$K^{+}+Na^{+}$	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	Ba^{2+}	
Formation brine	19,249	2460	317	308	35.220	0	876	58,430
Ions tuning water	1900	200	30	30	3199	210	0	5569