Low salinity injection into asphaltenic-carbonate oil reservoir, mechanistical study

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The impacts of salinity adjustment of displacing fluid have recently gained special attention to enhanced oil recovery (EOR). Different mechanisms have been studied widely in the literature while some of them are still subjugated to more scrutiny. The effects of diluted sea water on the interfacial properties of brine and asphaltenic-acidic crude oil and the wettability alteration of carbonate reservoir rock are investigated in this experimental observational work. The measurements of interfacial tension (IFT) and contact angle (CA) as two main parameters are studied. Besides, the effects of asphaltene and resin in the crude oil on the IFT values between the crude oil and aqueous solution are investigated.

The experimental results show that the lowest IFT values are obtained at high salinity conditions, while the surface rock wettability alterations are observed at low salinity conditions. Based on the obtained results, a combined mechanism is proposed to describe the wettability alteration towards more water wet at low salt conditions.

1. Introduction

Most of the original oil in place (OOIP) is trapped underground (up to 70% of the original oil in place) when the reservoir pressure decreases [1]. Water-flooding (known as the secondary oil recovery method) is the most popular and well-studied pressure maintenance technique to keep up oil production rate [2,3]. Despite this, the capillary forces in the pores and throats would entrap the oil ganglia to be remained unrecovered in the oil reservoir [4,5]. The magnitude of capillary force is directly proportional to the interfacial tension (IFT) and wettability condition of the rock surface. The enhanced oil recovery (EOR) methods are intended to change the effective parameters such as fluid/fluid interactions (i.e. IFT between the displacing and displaced phases) and fluid/solid interaction (i.e. wettability) in a way that is favorable for obtaining higher oil recovery efficiency [6]. Generally, the low salinity water injection as an EOR method refers to the ion compositions adjusting of the injected fluid. Besides the effect of IFT variation, the crude oil/brine/rock could be modified from oil wet condition towards the water wet condition which makes the oil movement easier [7].

Generally, the oil recovery from carbonates is well below 30% due to low water wetness, natural fractures, low permeability, and heterogeneous nature of rock properties [2,8]. Based on the fact that an optimal salinity of the dissolved salts in the injection water could yield the

highest oil recovery, the application of suitable brine salinity is important to improve oil recovery [9]. One of the leading investigation of the low salinity effects on oil recovery related to Martin in 1959 [10]. Afterwards, the studies on low salinity injection were gradually developed towards examination of this process using numerous laboratory core-flood experiments using low salinity on outcrop and reservoir core samples. The overall obtained results revealed the capability of this method for producing higher oil recovery [7,11–14], however, no significant low salinity water-flooding potential has been reported [15–16].

Although low salinity water flooding has received growing attention over the recent years, the effect of low salinity water flooding on carbonate rock has not been systematically investigated compared to that on sandstones [17]. Yousef et al. [18] reported improved oil recovery from tertiary-mode of low salinity water flooding, although the recovery from 100 times diluted seawater was negligible compared to that from 20 times diluted seawater. Moreover, Høgnesen et al. [19] investigated spontaneous imbibition into preferential oil-wet carbonates during a wettability alteration process. In their study, reservoir limestone, outcrop chalk cores, seawater and formation water were used at high temperature conditions. The results showed that sulfate present in the displacing brine could act as a wettability modifying agent and alter it from oil-wet to water-wet. Furthermore, Patil et al. [20] presented results from core-flooding experiments carried out to evaluate the potential of reservoir brine salinity of 22,000 total dissolved solids (TDS) to ultra-low salinity (i.e. 50–60 TDS). Their study revealed that a decrease in injection brine salinity at reservoir temperature caused a reduction in

residual oil saturation up to 20% and a slight increase in the Amott–Harvey wettability index and thus water-wetness of the core samples. Consequently, results revealed that oil recovery also increased from 40 to 68% as a result of changing the water salinity from 22,000 TDS to ultra low salinity. In addition, Winoto et al. [16] investigated the effect of low salinity water injection into sandstone and carbonate outcrops with gas permeabilities ranged from 1.49 to 7187 mD and porosity range from 10 to 39%. The average tertiary oil recovery was only 1.5% OOIP with the highest value of 5.8% OOIP and minimum zero.

Also, oil recovery using low salinity of connate and injected brine for six of the sandstones and three carbonates core plugs was investigated by Winoto et al. [16]. Six of the plugs showed an increase in recovery for the low salinity water floods, while three of them showed that the low salinity flooding hinders the oil recovery efficiency. It was reported that the effect of modifying injection brine compositions should always be tested with respect to specific reservoir conditions [15].

Moreover, effect of Mg^{2+} and SO_4^{2-} on wettability alteration of modified calcite surface to oil-wet by stearic acid (SA) is investigated using contact angle technique by Karoussi and Hamouda [21]. Their result showed that Mg^{2+} ions is capable to alter the modified calcite surface to more water-wet than that in the presence of SO_4^{2-} ions. Furthermore, Kumar et al. [22] reported that addition of divalent cations (Mg^{2+}, Ca^{2+}) to sodium-based petroleum sulfonate–lignosulfonate solutions exerted a strong influence on the coalescence behavior of oil droplets. In addition, Compton and Brown [23] demonstrated that the inhibition arises from competitive adsorption of Mg^{2+} and Ca^{2+} on the calcite surfaces.

Although several core flood tests are performed to find the effect of salinity and composition effects on the wettability and oil recovery, none of these investigations performed an experimental study to clarify the brine salinity and composition effects from real reservoir rock and fluid samples. The most common used method for measuring the wettability is Amott–Harvey method, although this method cannot accurately measure neutral wettability [24]. In contrast to Amott–Harvey method, wettability determination via contact angle (CA) measurement using real reservoir fluids is the best method to evaluate wettability [25].

On the other hand, bring into account all of these contradicting results and the importance of EOR from carbonate formations, indicates the necessity of further investigation of the effect of salinity on wettability. Generally, three factors are to be considered which are likely to influence the wettability of a solid surface in contact with water including: the penetration of water molecules into the solid, the change in orientation of polar groups in the solid surface, and the migration of polar groups of impurity molecules from the interior of the solid towards the surface [25].

In addition, inspecting the obtained results from the effect of salinity on the IFT of aqueous solutions/crude oil (with natural surfactant), some contradictory results can be addressed [26–33]. For example, IFT studies with formation brines and synthetic reservoir brines that have been performed by Isaacs and Smolek [29] and Xu [30] show that an increase in salinity of the aqueous phase decreases the IFT values although Yousef et al. [31] reported a contradicting trend. They studied the IFT variation using a crude oil of carbonate reservoir and different brines including synthetic field connate water, seawater and different diluted versions of seawater. They observed a general trend of IFT reduction as a result of the salinity reduction.

As discussed above, although several investigations have been performed during the last decades, no clear trend about the influence of salinity on the IFT variation has been proposed. It seems that the composition and type of crude oil have a profound effect on the IFT variation of different types of saline waters. Therefore, in this study the effects of aqueous solution salinity on the IFT of crude oil/aqueous solution were also specially considered by investigation of the impact of asphaltene and resin extracted from the used crude oil.

2. Experimental section

2.1. Drop shape analysis apparatus

In this study, a drop shape analysis (DSA 100, KRUSS, Germany) was used to measure both the IFT of oil sample/aqueous solution and equilibrium contact angle of crude oil/aqueous solution on the carbonate rock surface at the ambient pressure and temperature conditions. The DSA 100 instrument was in more details explained in our previous paper [33]. For IFT measurements, the crude oil droplet is positioned at the tip of the needle and then the image of the pendant crude oil drop in the aqueous solution (see Fig. 1(a)) was analyzed and the IFT was determined. In addition, contact angle was measured with sessile up experiment as shown in Fig. 1(b).

2.2. Extraction of asphaltene and resin

A petroleum fluid sample is commonly divided into three parts: oils (saturates and aromatics), asphaltenes and resins [34]. Resins and asphaltenes are similar to aromatics but are, larger, polar, contain more fused aromatic rings and more heteroatoms [35].

As the other active component of crude oil, resins and asphaltene could play a vital role in the IFT of aqueous phase/crude oil system, although their effects are not well understood. Asphaltenes and resins are two contiguous classes of components separated from a continuum of molecules raise this hypothesis that they may have a similar structure. However, the difference in size, aromaticity, polarity, and physical appearance dictate different properties for asphaltenes and resins [36]. Asphaltene and resin of crude oil considerably affect the IFT of aqueous solution and crude oil. It is normally expected that the IFT of hydrocarbon and water systems (without natural surfactant such as asphaltene and resin, which naturally exist in the crude oil) increases as the salt concentration increases [37]. Due to different content and type of resin and asphaltene in the crude oil, the IFT of crude oil/aqueous solution shows different and complex behavior as concentration of salt changes. Therefore, in this study, the effectiveness and contribution of asphaltene and resin on the equilibrium IFT of crude oil/aqueous solution are examined. Asphaltenes were extracted by dissolving the acidic crude oil (ACO) in n-heptane with the ratio of 40:1 followed by Soxhlet extraction for further purification [38].

In addition, resins were extracted from the same de-asphalted oil with the column chromatography method described elsewhere [39,40]. The maltene (de-asphalted oil + n-heptane) was adsorbed to a column of silica gel (Merck, 35–70 mesh ASTM); followed by rinsing of the saturates and aromatics by a solution of 70:30 n-heptane and toluene. Finally, the mixture of acetone, dichloromethane and toluene with the ratio of 40:30:30 was used to extract the resins from the column [38]. After that, a solution of 8 wt/wt.% of extracted asphaltene and resin from ACO in toluene was prepared and used to find the sole effect of the resin and asphaltene on the IFT.

2.3. Crude oil properties

Crude oils are complex mixtures of hydrocarbons and polar organic compounds of oxygen, sulfur, nitrogen, and metal-containing compounds (particularly vanadium, nickel, iron, and copper). Approximately 11,000 compositionally distinct components have been detected in one crude oil [41]. The analysis of used ACO such as gas chromatography (GC) and infrared (IR) spectroscopy was reported in the previous publications [33,42]. IR spectroscopic investigations indicated the presence of sulfoxide, sulfone, acid, and carbonyl functions in the used crude oil. In detail, the crude oil containing only small amounts of phenolic, amine and amide functionalities while the carboxyl signal has a high intensity [33,42].

In addition, one of the parameters, which well correlates with the concentration of surface active components present in the crude oil is