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Relation between brine-crude oil-quartz contact angle formed on flat quartz slides and in capillaries with brine composition: Implications for low-salinity waterflooding

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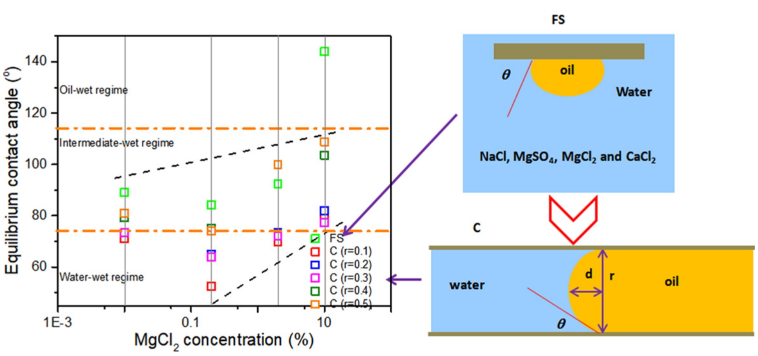
G R A P H I C A L   A B S T R A C T



A R T I C L E   I N F O

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A B S T R A C T

A good understanding of surface wetting is of significant important for Enhanced Oil Recovery (EOR) technologies especially low salinity waterflooding (LSWF), in which wettability alteration of rock surface was considered as the leading mechanism even though the reasons behind have not been conclusively revealed. To further investigate the effect of brine composition (salinity, ion types and valence) on surface wetting at pore level, the attention of this work was given to the brine-crude oil-quartz contact angles formed on flat quartz slides and in capillaries (r = 0.1–0.5 mm), and also to the relation between these two types of contact angles. The results showed that the dependence of the flat slide contact angles on brine composition was different from that in capillaries, and pore radius needs to be considered in wettability determination in porous media. In capillaries, the formed contact angles were found to decrease with the decrease in capillary radius. Moreover, the flat slide contact angles were slightly larger than the capillary contact angles for a given system but the relationship between these contact angles varied with salt type. In summary, it is believed that pore contact angles should be more appropriate to represent the wettability of a reservoir.

1. Introduction

Over the past decades, numerous works either using experimental methods or numerical simulation have been conducted to study low salinity waterflooding (LSWF), which generally confirmed the existence of low salinity effect (LSE) [1–6]. As reported, the oil recovery factor

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can be increased by 5–25% of the original oil in place (OOIP) through engineering water chemistry (ionic composition and/or salinity) for sandstone and carbonate lithologies. Thereafter, the worldwide research attention was continuously given to this emerging Enhanced Oil Recovery (EOR) technology due to its eco-friendly and economic features compared against other recognized methods such polymer flooding, surfactant flooding, alkaline flooding, *etc*. Hence, it is widely believed that LSWF will be one of the most promising EOR techniques in the near future, and knowledge of the physicochemistry changes of a reservoir induced by LSWF and the mechanisms behind are therefore of great significance for this process.

Despite the intensive studies of LSWF, its underlying mechanisms remain unclear largely due to the massive diversity in fluid chemistry, mineralization and reservoir conditions of each reservoir [7–9]. Therefore, to date, more than seventeen mechanisms have been proposed to explain the LSWF effect such as clay swelling and migration [10,11], multi-ion exchange (MIE) [12–14], local pH increase [15,16], double layer expansion (DLE) [17,18], wettability alterations [19,20], osmotic pressure [21], IFT reduction [4,22], *etc*. Of the possible mechanisms, wettability alteration of rock surface is thought to be the leading candidate for the LSWF effect.

Wettability represents the tendency of a fluid in a multiphase system to spread on solid surface or the affinity of solid surface toward a specific fluid [23,24]. To determine the wettability of a multiphase system, for example, brine-crude oil-rock surface system (oil reservoir), a number of qualitative and quantitative methods have been established such as traditional S_w-p_c curve [25,26], two-dimensional micromodels [27,28], microCT [29,30], nuclear magnetic resonance (NMR) measurement [31] and contact angle [32]. Due to the simplicity and being less time-consuming, contact angle is still the most extensively used method in EOR industry. The contact angle refers to the angle that a droplet forms on a solid surface. According to the Young' equation, the contact angle (θ) can be expressed as the balance of three interfacial forces (Eq. (1)) [33]:

$$cos\theta = \frac{\gamma_{ws} - \gamma_{os}}{\gamma_{ow}} \tag{1}$$

where γ_{ws} is the water-solid interface tension, γ_{os} is the oil-solid interface tension, and γ_{ow} is the oil-water interface tension.

Based on the contact angle, the wetting of a solid surface can be generally defined as water-wet (θ = 0–75°), intermediate-wet (75° < θ < 115°) and oil-wet (θ = 115–180°) states [34]. It has been shown that the wettability of a liquid on a solid surface is strongly dependent on the parameters of surface chemistry [35], pressure [36], temperature [37], surface roughness [38] and brine composition (salinity, ion types and valence). Brine composition affects the charge of the solid surface, which consequently determines the kind of substance adsorbed favorably. The dissolved ions in the brine move toward the charged surface forming an electrical double layer, and finally leading to a rapid decline in the electrical potential and overall hydrophilicity of the surface [39–41].

Since the brine composition is closely related to the interfacial behaviors of a multiphase system, a number of studies have been conducted in the last decades attempting to correlate brine composition with rock wettability, oil/water IFT, and oil displacement efficiency [42,43]. With regard to the effect of brine composition on the equilibrium contact angle, it was found that the hydrophilic surface exhibited a noticeably increase in the contact angle with the increasing NaCl concentration [44]. Leelamanie and Karube claimed that this change was likely attributed to the increase of the surface tension with electrolyte concentration (NaCl and $CaCl_2$) [45]. However, the relation between contact angel and salt concentration was not linear and was worth investigation for deeply understanding the LSWF especially when crude oil is present.

For contact angle measurement, flat glass surfaces and sliced rock slides are usually used as equivalent conditions to represent the wettability of a reservoir. Nevertheless, Li et al. realized that the contact angle in capillaries (porous media) for water and hydrocarbons were quite different from the contact angle measured on flat surfaces [46]. A more recent work reported by Al-Zaidi and Fan revealed that the contact angles of brine-air-glass on flat surfaces were higher than those in capillaries presumably due to line tension [47]. These unexpected observations also raised a question for LSWF, that is, the effects of brine composition and contact geometry on brine-crude oil-rock contact angle and surface wettability. In this case, herein we present an experimental study of brine-crude oil-quartz contact angle measurements on flat slides and in capillaries in different brines. The interests of this work can be summarized as 1. The response of surface wetting to brine composition; 2. The effect of capillary radius on contact angle and 3. The relation between the contact angles measured on quartz surface and in capillaries. These results are supposed to add more data to the existing data base of LSWF and also benefit the understanding of surface wetting in LSWF at pore level.

2. Experimental section

2.1. Materials

The inorganic salts used in this work including NaCl, $MgCl_2$, $CaCl_2$ and $MgSO_4$ were analytical reagent grade and supplied by Kelong Chemicals Co., Chengdu. The stock synthetic brines with salt concentration of 10.0 wt% were first prepared and then diluted with deionized water. The solubilities of the salts in water and solution pH values were tabulated in Table 1. The crude oil used in this work was kindly provided by Xinjiang Oilfield, China. Table 2 lists the basic properties of this oil. The quartz slides and capillaries with the predominant composition of SiO_2 were purchased from Kelong Chemicals Co., Chengdu. To minimize surface contamination, the slides and capillaries were cleaned with petroleum ether followed by deionized water. After that, the samples were placed in a furnace (350 ºC) to remove the contaminations if any. Each test was conducted using a new slide or a capillary.

2.2. Methodology

2.2.1. Contact angle measurement on flat quartz slides

Fig. 1 illustrates the experimental setup used to measure the contact angle on quartz slides. In a typical test, a cleaned quartz slide was first immersed in a brine solution as depicted in Fig. 1. An oil droplet with the volume of 0.5 µL was then positioned on the surface using a syringe.

Table 1
Solubilities of the salts, pH values and ionic strength of the brines.

Inorganic salts	Solubility @20 °C (g/100 mL)	Concentration (wt%)				Ionic strength (mol/L)			
		0.01	0.1	2	10	0.01	0.1	2	10
$MgSO_4$	25.5	6.61	6.02	5.29	5.19	0.0033	0.033	0.66	3.33
$CaCl_2$	74.5	6.45	6.46	6.72	7.01	0.0027	0.027	0.54	2.70
$MgCl_2$	54.6	6.63	6.42	5.58	5.29	0.0031	0.032	0.63	3.15
NaCl	35.9	7.01	6.24	5.82	6.06	0.0017	0.017	0.34	1.71