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Synergy effects of ions, resin, and asphaltene on interfacial tension of acidic crude oil and low–high salinity brines

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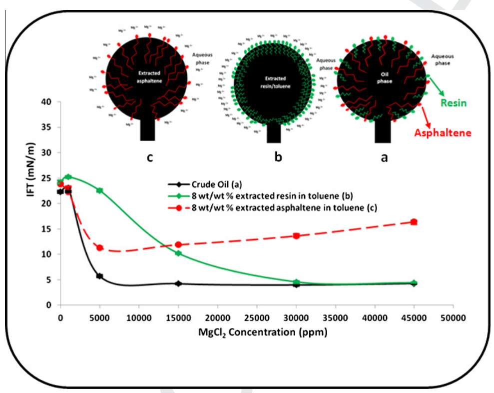
HIGHLIGHTS

- Asphaltene and resin of crude oil were extracted.
- IFT of combination of different salts/crude oil, resin and asphaltene were measured.
- Resin and asphaltene as natural surfactant in crude oil show synergistic effects.
- Salts unable to break the surface molecular arrangement of $MgCl_2$ and crude oil.

GRAPHICAL ABSTRACT



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ABSTRACT

It is well established that the heavy oil components including asphaltenes and resins play vital roles on the interfacial tension (IFT) of acidic crude oil (ACO) and aqueous solutions. Therefore, this experimental work is designed to investigate the possible synergism between salt ions, resin, and asphaltene on the IFT of ACO/low and high salinity brines containing $MgCl_2$/NaCl and $CaCl_2$. The results demonstrate that a complex ion of $MgCl_2$ – resin component created in the solution could occupy the sites at the interface at high $MgCl_2$ concentration. However, the results show that on the contrary, the molecular arrangement of $MgCl_2$ and asphaltene at low and high $MgCl_2$ concentration could be broken as the $CaCl_2$ is able to hackle the molecular management due to the high affinity of Ca^{2+} to asphaltene molecules compared to that of Mg^{2+}.

1. Introduction

Smart water (SW) or low salinity aqueous solutions can be made by adjusting/optimizing the ion composition of the injected fluid with especial concentration on the modification of surface properties of initial crude oil/brine/rock system. This modification should be in a way that the trapped oil becomes mobilized be extracted out of the porous media which increases oil recovery from the reservoirs [1].

The recognition of this technique raises from its several unique advantages including efficiency of displacing light to medium gravity crude oils, ease of injection into oil-bearing formation, water availability and affordability, environmentally friendly, no need for expensive chemicals, low damage problems and lower

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capital/operating costs especially for the fields were under waterflooding process [2,3]. Although low salinity water flooding has received growing attention over the recent years [4–12], the effect of low salinity water flooding on the interfacial tension (IFT) of the crude oil/low salinity system has not yet been systematically investigated.

On the other hand, the interfacial properties of crude oil/aqueous solutions can be complex and are not yet well understood since all of the effective parameters have their own complex nature. Having investigated the obtained results from the previously published literature, it is found that there is no unique proposed mechanism and trend on the effect of salinity on the IFT of aqueous solutions/crude oil (with natural surfactant including asphaltene and resin molecules) [11–15]. For instance, Xu [13] studied the effect of the brine composition on the IFT by changing the salinity and salt composition of the aqueous phase. Five systems were examined in his work using live crude oil, deionised water, NaCl, $CaCl_2$, formation brine, and 50% formation brine in deionised water. Among the examined systems, the live oil system in $CaCl_2$ solution had the highest equilibrium IFT values compared to the others.

Moreover, Yousef et al. [14] studied the IFT variation using a crude oil and different brines including synthetic field connate water, seawater and different diluted fluids of seawater. They reported a general trend of IFT reduction as a result of the salinity reduction. In addition, Moeini et al. [11] measured the IFT between heavy crude oil + NaCl and $CaCl_2$ aqueous solutions. Their results demonstrated that for both salts a significant reduction in the IFT at the beginning of the measurements was observed while this reduction trend was reversed to a gentle enhancement trend. In addition, in all the salt concentrations, higher IFT values were obtained using $CaCl_2$ compared to NaCl aqueous solution. More recently, Lashkarbolooki et al. [12], measured the IFT of an ACO in the presence of different aqueous solutions such as NaCl, KCl, Na_2SO_4, $MgSO_4$, $CaSO_4$, $CaCl_2$, and $MgCl_2$ in concentration range of 0–45,000 ppm. They showed that using ions especially divalent cations in the presence of chloride anion substantially decreases the IFT values. The results also show that the lowest IFT values are obtained at high salinity conditions (i.e. above 5000 ppm) especially if divalent ion of $MgCl_2$ is utilized. High values of IFT are obtained if monovalent salts such as NaCl and KCl are used.

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 introduce a profound effect on the IFT variation for different types of saline waters. In general, crude oil components such as asphaltene, resins, organic acids, and solids can significantly affect solubility of some polar organic compounds in oil and water and interact the oil–water interface. In this regards, several researchers investigated the interfacial rheological behavior of asphaltene at oil–water interface [16–19].

Having studies the effects of salt concentration on the IFT of a heavy crude oil and its polar components, Bai et al. [20] concluded that NaCl concentration had no significant effect on the IFT. The reason behind this conclusion is likely due to the phenomenon that most of the interfacial active substance might be oil-soluble and hence the effect of salt was observed to be minimal. Besides, Abdel-Wali [21] investigated the effect of polar compounds and salinity on the interfacial tension of oil/brine systems. The polar compounds present in the crude oil were varied by adding different amounts of oleic acid and octadecylamine to the crude oil. In that work, oleic acid was acting as an anionic surfactant resulting in a reduction of IFT values. However, the IFT increased as the brine salinity increased from 40,000 to 200,000 ppm NaCl that can likely be related to a reduction occurred on the solubility of oleic acid in water. Also, Sztukowsk and Yarranton [22] reported that the rheological properties of asphaltene–toluene/water interfaces are sensitive to asphaltene concentration and aging time. Recently, the effects of asphaltene, resin and salts, namely, NaCl, $CaCl_2$, and $MgCl_2$, on the IFT of ACO/aqueous solutions were investigated by Lashkarbolooki et al. [23]. They reported that there are three dominant parameters, which could affect the IFT. They include (a) the presence of natural surface-active agent such as asphaltene and resin in the crude oil, (b) the type of salts, and (c) salt concentration. Due to the presence of resins and asphaltenes, a dual effect can be observed for divalent salt concentrations. For the case of low divalent salt concentration, the asphaltene content leads to a greater reduction in the IFT compared with the resins. While at high concentration, the effect of the resin solution on IFT reduction is more pronounced.

Considering the shortcomings found in the previous works presented in the literature, a systematic experimental procedure was designed in the current investigation to study the synergism of ions, resin, and asphaltene on the IFT of ACO/low and high salinities of aqueous solutions. In the first step, the asphaltene and resins of the investigated ACO were extracted based on a standard method, which later is described in details. Afterward, two different solutions of 8 wt./wt.% of these components in toluene were prepared, and the IFT measurements were performed using aqueous solutions with different salinities. The mutual effects of different salts and their concentrations on the measured IFT were analyzed through this experimental work.

2. Experimental section

2.1. Drop shape analysis apparatus

In this study, a drop-shape analysis (DSA 100, KRUSS, Germany) apparatus was used for the measurement of the equilibrium IFT of the crude oil + brine system. In brief, for IFT measurements (see Fig. 1), a microsyringe was fitted with a U-shape needle and loaded with a fluid with lower density (i.e., crude oil). The syringe was placed in a motor driven piston and the tip of the U-shaped needle was positioned in an optically clear vessel and immersed in the aqueous phase. The crude oil droplet is positioned at the tip of the needle and then, the image of the drop was recorded using a CCD camera equipped with a macrolens.

Finally, the image of the equilibrium pendant drop is analyzed and the IFT is accordingly determined.

Two parameters of the pendant drop that should be experimentally determined are the equatorial diameter D and the diameter d at the distance D from the top of the drop (see Fig. 1) [24,25]. The IFT is then calculated from the following equation [24–26]:

$$\gamma = \frac{\Delta\rho g D^2}{H} \quad (1)$$

where g and $\Delta\rho$ are acceleration of gravity and the difference between the crude oil drop and the aqueous solution densities, respectively. The shape parameter (H) depends on value of the shape factor ($S = d/D$) [24–27].

2.2. Crude oil properties

2.2.1. Gas chromatography (GC) analysis

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined), although it can be used as a compound identifier. As it can be seen from Table 1,