Fluid Phase Equilibria 414 (2016) 149–155

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Effect of asphaltene and resin on interfacial tension of acidic crude oil/sulfate aqueous solution: Experimental study

Mostafa Lashkarbolooki [a,*], Shahab Ayatollahi [b]

[a] School of Chemical Engineering, Babol University of Technology, Babol, Iran
[b] School of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form
15 January 2016
Accepted 18 January 2016
Available online 20 January 2016

Keywords:
EOR
Sulfate anion
Asphaltene
Resin
Crude oil

ABSTRACT

Although the capability of using sulfate anion as a wettability modiffier is well established, no systematic investigation on the effect of sulfate ions and natural surfactants in the crude oil including asphaltene and resin on the interfacial tension (IFT) of acidic crude oil (ACO)/sulfate were performed. In this regards, the fluid/fluid interactions are tested through the IFT measurements for ACO, asphaltene and resin extracted from ACO in the presence of sulfate salts including Na_2SO_4, $MgSO_4$ and $CaSO_4$ while the concentration of each salt ranges between 0 and 45000 ppm. The obtained results demonstrate that the capability of asphaltene molecules is higher for IFT reduction compared with the resin molecules which can be related to the higher affinity of asphaltene to be arranged on the surface of ACO/sulfate aqueous solutions.

1. Introduction

Enhanced oil recovery (EOR) is the application of external forces in a manner that promotes favorable recovery conditions after primary and secondary oil recovery stages [1–3]. One of the well-established EOR methods is the injection of water, known as low salinity water-flooding or smart water (SW), into the depleted reservoir [4]. This technique could be enhanced by modifying the salt concentrations manipulating viscous forces, fluid/fluid interactions (IFT), and fluid/solids interactions (wettability) [5–7].

Because investigating the low salinity process is in its starting phase, vast numbers of efforts have been performed to find the main active mechanisms, although wettability alteration has been introduced as the main key mechanism [6–11]. Based on this fact, it is expected that the best results of oil recovery will be obtained if the low salinity water injection performs for the oil-wet toward intermediate-wet rock. According to a previously reported study, the composition of the injected water can affect the wetting properties; and the concentration of SO_4^{2-} (aq) appeared to be the key factor [6,7]. An increase in sulfate concentration and a decrease in the salinity able to activate the wettability alteration process [6,7]. Besides, IFT of the aqueous phase and crude oil is also known as the other effective parameter that could be manipulated by EOR methods [2,12,13]. A close look into the previously published literature on the IFT of crude oil/brine revealed contradicting results [14–20], and these results urge the necessity of performing more systematic investigations to find unique and reliable mechanisms of action for smart water injection. On the other hand, IFT of crude oil/brine are complex functions of temperature, pressure, salinity, TAN, and the amount of dissolved gases and asphaltenes [21] which makes it more difficult to deal with them compared to the pure systems [22,23].

In this regard, Lashkarbolooki et al. [5] investigated the effects of the concentration of different salts including NaCl, KCl, Na_2SO_4, $MgSO_4$, $CaSO_4$, $CaCl_2$ and $MgCl_2$ on the IFT of ACO/aqueous solutions. They found that the lower IFT is obtained if divalent anions solution utilizes compared with the solutions prepared by monovalent system especially if the divalent anions are bonded to chloride anions. On the other hands, asphaltene and resins can also play a vital rule in the IFT of aqueous phase/crude oil although its exact effects on the IFT are not well established [2,24]. In addition, to check the sole effects of the natural surface-active agents, Lashkarbolooki et al. [24] prepared solution of 8 wt/wt % of extracted asphaltene and resins/chloride aqueous solutions and then the IFT of these solutions in the presence of crude oil was measured. The results revealed that there are three dominant

* Corresponding author.
E-mail address: m.lashkarbolooki@nit.ac.ir (M. Lashkarbolooki).

http://dx.doi.org/10.1016/j.fluid.2016.01.032

parameters which affect the IFT, including (a) the presence of natural surface-active agents in the crude oil, (b) the type of salts, and (c) salt concentration [24]. Due to the presence of resins and asphaltenes, a dual effect observed for $MgCl_2$ and $CaCl_2$ aqueous solutions. In the case of low divalent salt concentration, the asphaltene content leads to a greater reduction in the IFT compared with the resins, although as the concentration was increased, the effect of resin solution for IFT reduction was dominant [24].

Although SW flooding has received growing attention over the recent years, the effect of natural surfactants such as asphaltene and resin on the IFT of ACO/sulfate aqueous solutions is not well organized. In the light of this shortcoming, in this study the effect and contribution of asphaltene and resin on the equilibrium IFT of ACO/sulfate aqueous solutions are examined. To check the sole effects of these natural surface-active agents, the asphaltene and resins of the used ACO were extracted. Afterward, two different solutions of 8 wt/wt % of these components in toluene were prepared followed by measurement of IFT values.

2. Experimental section

2.1. Drop shape analysis apparatus

A drop-shape analysis (DSA 100, KRUSS, Germany) apparatus (see Fig. 1) was used for the measurement of the equilibrium IFT of the crude oil + brine system. In brief, a microsyringe was fitted with a U-shape needle and loaded with the 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 determined [5,24]. In this way, 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) [25,26]. The IFT is then calculated from the following equation [25–27]:

$$\gamma = \frac{\Delta\rho g D^2}{H} \tag{1}$$

where g and $\Delta\rho$ are acceleration of gravity and the difference between crude oil drop and aqueous solution densities, respectively. The shape dependent parameter (H) depends on a value of the shape factor (S = d/D) [26–28].

2.2. Crude oil properties

Crude oils are complex mixtures of hydrocarbons and polar organic compounds of oxygen, sulphur, nitrogen, and metal-containing compounds (particularly vanadium, nickel, iron, and copper). Approximately 11000 compositionally distinct components have been detected in one crude oil [29]. To characterize the used crude oil, different analysis including total acid number measurement, gas chromatography (GC) and infrared (IR) spectroscopy were performed.

2.2.1. Total acid number (TAN)

One of the parameters, which well correlates with the concentration of surface active components present in the crude oil is the total acid number (TAN). In the petroleum industry, crude oil considered as an acidic crude oil if the TAN number of a crude oil is higher than 0.5 mg KOH/g [30]. The determined acid number is often considerably affected by carboxyl groups contained in asphaltenes and resins [31]. The TAN of the crude oils was measured using a potentiometric titration based on the ASTM D 664 method [32]. The TAN of a crude oil is the quantity of base expressed as milligrams of KOH required to neutralize the acidic components in 1 g of oil. The TAN is calculated as follows:

$$Acid\ number,\ mg\ KOH/g = (A - B) \times M \times 56.1/W \tag{2}$$

where, A is the volume of 0.1 mol/L in methanol used to titrate sample to end point. This occurs at the meter reading of the inflection point closest to the meter reading corresponding to the pH 11 aqueous buffer, or in case of ill-defined or no inflection point, to the meter reading corresponding to the pH 11 aqueous buffer, mL. A graph of potential or pH against volume added can be drawn and the end point of the reaction is half way between the jump in voltage or pH (see Fig. 2). B is the volume corresponding to A for blank titration (the mixture of toluene, isopropanol, water with the ratio of 50:49.5:0.5), mL, M is the concentration of the alcoholic KOH solution, mol/L and W is the sample mass, g [32]. The TANs of crude oil and 8 wt/wt % extracted asphaltene and resin in toluene based on ASTM D 664–1989 are shown in Table 1. In addition, the density of crude oil and 8 wt/wt % of extracted asphaltene and resin in toluene solutions were measured using a glass pycnometer (see Table 2).

2.2.2. Gas chromatography (GC) analysis

Gas chromatography (GC), is a common type of chromatography used in analytical chemistry for separating and analyzing compounds. 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. The obtained results from GC analysis are shown in Table 3. As it is listed in Table 3, ACO comprises of less naphthenes and aromatic components compared with normal and iso-parraffins. In addition, the GC

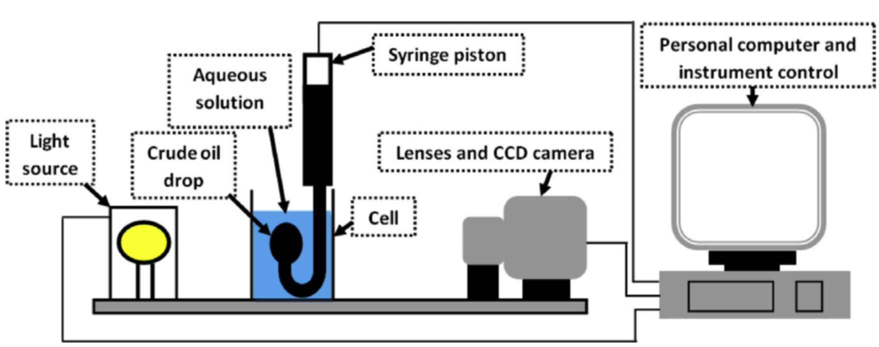

Fig. 1. Schematic diagram of the drop shape analyzer (DSA 100).