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Mechanistic study on the dynamic interfacial tension of crude oil + water systems: Experimental and modeling approaches

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ABSTRACT

This study investigates dynamic interfacial tension (DIFT) of acidic crude oil (ACO) and non acidic/basic crude oils (BCO) + deionized water (DW) as a function of pressure from 500 to 4000 psi, and temperature from 30 to 80 °C using an axisymmetric drop shape analysis (ADSA) technique. DIFTs are also modeled using dynamic adsorption model, mono-exponential decay model, and empirical equations. The results showed that if a reduction in the surface excess concentration due to increasing temperature overlooks the total entropy of the molecules in the system, an increase in IFT would be expected.

Introduction

The variation in capillary force within the pores and throats of porous media is one of the main sources of oil entrapment mechanisms in oil reservoir. Capillary forces acting in the interface region between oil and water are forces that act against the flow of oil during the displacement process [1–3]. It is well understood that the interfacial tension (IFT) is an important factor in enhanced oil recovery (EOR) processes [4,5]. In most of the previous studies the static IFT has been considered as the main controlling parameters, while it is evident the IFT changes by time, known as dynamic IFT (DIFT) that would directly influence capillary forces. In this regard, the DIFT of crude oil and water is an important factor for different processes of petroleum industries [6].

Although it is known that, IFT is a strong function of temperature and weak function of pressure of the system, no comprehensible trend has been yet reported [7]. For example, several authors have reported a decreasing trend of IFT with temperature, and an increasing trend with pressure for hydrocarbon/aqueous systems [8–17]. On the contrary, it has been reported that the IFT of hydrocarbon/aqueous systems reduces with pressure increase [18] or temperature reduction [8] that is in complete contrast to what is expected.

According to an extensive literature review and data mining carried out, it was generally found that IFT of crude oil/water systems decreases as temperature increases. However, manipulation of pressure introduces no significant effect on IFT. Despite the typical explained behavior, several contradicting trends were reported by several authors, who investigated different crude oil/brine systems [19–27]. For instance, Flock et al. [25] conducted several measurements by seven different samples of viscous crude oil using two different types of water (i.e. distilled water and heavy water). For two heavy oils it was found that the IFT initially decreases then increases if temperature increases while for another crude oil, only an increasing trend was observed. For all other systems, two different trends including no IFT change and decreasing IFT as a function of temperature were observed. Moreover, the influence of surfactants on the oil/water interfacial interactions was investigated by Xu et al. [27]. They revealed that asphaltene could play an important role on the interfacial interactions. Temperature affects IFT by manipulating (1) the kinetics of surfactant packing at the oil/water interface, (2) diffusion of the surfactant through the oil phase, and (3) solubilization differences between the polar and nonpolar ends of the surfactant molecule [28]. Recently, Moeini et al. [29] indicated that increasing the temperature reduces the IFT almost

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linearly due to the increased total entropy of the molecules at interface that consequently reduced free energy, which leads to lower IFTs. They associated the increasing trend of IFT with pressure to the strengthened intermolecular forces at each phase when the pressure increases, consequently solubility of oil in water at the interface reduces that leads to IFT enhancement.

Based on the literature survey and the best knowledge of the authors, no obvious trend and no exact mechanism behind these different trends have been already provided. It should be mentioned that since the most of researchers had investigated the equilibrium IFT as function of temperature and pressure, an ample space in the area of dynamic IFT measurement which is a vital parameter is still open for further investigation. Regarding these shortcomings, this work is dedicated to design a series of systematic experiments to find the effects of pressure and temperature on the DIFT of crude oil/water. At last, the measured DIFTs are also modeled with the dynamic adsorption model, the mono-exponential decay model, and the empirical equation. The main objective of this study is to further clarify and reveal the reasons of contradicting trends, which have been reported by numbers of authors with concurrent employment of dynamic IFT measurements and dynamic modeling. Based on the results of dynamic IFT and modeling, a novel mechanism is proposed.

Model of dynamic interfacial tension

Dynamic behavior of IFT of crude oil–water is mainly caused by the polar components or surfactants in the liquids [7,30]. The dynamic behavior of IFT is believed to be caused by the adsorption kinetics of interfacially active molecules at liquid interfaces. This adsorption kinetics of molecules to a liquid interface is controlled by transport processes in the bulk and the transfer of molecules from a solution state into an adsorbed state or vice versa [7,20]. Generally, there are many parameters to control the adsorption and desorption reactants at the interface area as well as the diffusive movement inside the two fluids [31–33]. Evans et al. [34] analyzed the combined dynamic effects of the adsorption kinetics using the mass transfer, micellisation equilibria and random sequential adsorption theory. On the other hand, Lankveld and Lyklema [35] proposed that the change of IFT could be fitted to a simple exponential decay, if the adsorption is limited by the activation energy barrier, as follows [36,37]:

$$\gamma_t = \gamma_e + (\gamma_0 - \gamma_e)e^{-t/\tau} \tag{1}$$

where γ_e is the IFT at equilibrium, γ_0 and γ_t are the IFT at the beginning and time t, respectively, t is time, τ is a parameter with the same unit as time that signifies the relaxation or adsorption time. Although this model is simple, several researchers have used Eq. (1) to model equilibrium IFT for asphaltenes [38] and crude oil systems [39,40].

In addition, a generalized dynamic surface tension model was proposed by Hua and Rosen [41]. They plotted the γ_t versus $\log((\gamma_0 - \gamma_t)/(\gamma_t - \gamma_e))$ and divided the total response into four regions: (I) induction region; (II) rapid fall region; (III) meso-equilibrium region where γ_t shows only a small change with time, and (IV) equilibrium region:

$$\frac{(\gamma_0 - \gamma_t)}{(\gamma_t - \gamma_e)} = \left(\frac{t}{t^*}\right)^n \tag{2}$$

where t^* and n are constants. t^* has the dimensions of time at the same unit as t, and n is a dimensionless parameter.

In general, two processes including (i) the transfer of molecules between the surface layer and the subsurface layer, which lies immediately below the surface at a thickness of a few molecular diameters; (ii) the exchange of molecules between the subsurface and the bulk solution, would control the dynamic adsorption phenomenon. The first step is an adsorption process and the second one is mainly diffusion, with occasional convection [7,31]. Normally, the kinetics part of the process is much smaller than the diffusive part; therefore the adsorption of common non-ionic surfactants is expected to be controlled by the diffusion coefficient [42–44].

Eqs. (3) and (4) were simplified by considering short time and long time diffusion-limited approximations[7]:

$$\gamma_t - \gamma_0 - 2RTC\sqrt{\frac{3Dt}{7\pi}} \tag{3}$$

$$\gamma_t = \gamma_e + \frac{RT\Gamma^2}{C}\sqrt{\frac{7\pi}{12Dt}} \tag{4}$$

where R is the universal gas constant (8.314 J/(mol K)), T is temperature (K), D is diffusivity (in the current work: diffusivity of natural surfactant in crude oil to the interface) (m^2/s), t is time (s), C is natural surfactant concentration (mol/m^3), Γ is surface excess concentration (mol/m^2) (in the current study: surface excess concentration of natural surfactants including asphaltene and resin), γ_t is the IFT of the system at surface age (time), γ_0 is the initial IFT and γ_e is the equilibrium IFT.

A short time approximation (i.e. Eq. (3)) provides adequate description of the beginning of the adsorption process for many surfactants while long time approximation of the general diffusion equation (i.e. Eq. (4)) is valid when the adsorption process is close to equilibrium conditions [45,46].

Eq. (3) shows that at the beginning of the adsorption process, there is linear relation between γ and $t^{1/2}$ which the diffusivity can be considered as the slope of this line [47]. Besides, a close examination of Eq. (4) shows that after a long time, linear relation is expected to be developed between γ and $t^{-1/2}$. It could be noted that if IFT is plotted versus $t^{-1/2}$, resulting straight line indicates that the process is diffusion controlled. The surface adsorption can be estimated from the slope of this line if the diffusivity is known or obtained from Eq. (3). In this study, diffusivity is estimated from Eq. (3) using fitting of the DIFT experimental data of the beginning of the adsorption process.

It should be noticed that all the mentioned models could be applied when IFT decreases as function of time to reach a minimum value at the equilibrium stage and then unaffected with interface aging time. These conditions are always generated for crude oil/aqueous solutions containing salts. In some cases, for instance crude oil/chemical surfactant, the IFT increased dramatically as the interface is aged [48]. Hence, such models could not be applied for these cases.

Experimental

To reliably investigate the effective mechanisms, it is essential to accurately measure the dynamic IFT at reservoir conditions. Regarding this necessity, throughout the years number of researchers has developed different kind of IFT measurement techniques for immiscible fluids. The most recent one is the pendant drop method [20,49,50]. In general, in the light of its accuracy and suitability in IFT measurements, the pendant drop method is one of the best suited methods especially for liquid–liquid systems.

A simple schematic of the used experimental setup is given in Fig. 1. In brief, the used apparatus is consisted of a high pressure/high temperature visual cell set, which is monitored using an on-line camera system that records the images for further processes using drop shape analysis software at desired pressure and temperature conditions [51]. In addition, the system is equipped with two manual high pressure pump to inject the bulk and drop