



Full Length Article

Effects of asphaltene, resin and crude oil type on the interfacial tension of crude oil/brine solution

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ABSTRACT

In recent years, the behavior of crude oil interfacial tension (IFT) as a function of salt concentration have been investigated. The results found in literature are highly controversial, thus the current experimental study aimed to clarify the reasons behind this by developing a methodology based on extracting asphaltene and resin from three different crude oils and performing elemental analysis on them. In addition, the effect of salinity on the IFT of three studied crude oil was compared with the synthetic crude oil consisted of different weight percent (wt%) of asphaltene and resin in toluene. The obtained results revealed that the IFT of crude oil as a function of salinity depended not only on the wt% of asphaltene and resin fractions but also on the aromaticity of asphaltene and resin. In fact, as the aromaticity of asphaltene increased, the performance of asphaltene decreased as a function of salinity while the aromaticity of resin led to a revers trend on IFT variation.

1. Introduction

Understanding the interfacial behavior between crude oil and underground fluids is considered as a critical issue in petroleum industry [1,2]. By and large, in hydrocarbon/aqueous systems, the IFT increases as salinity increases [3–6]. At the interface, water molecules are in contact with another phase and the hydrogen bonding is disrupted, creating a higher energy environment for the ions, causing the depletion of salts near the interface and leading to negative surface excess concentration of salts. Considering the results in the literature, four different trends can be observed while increasing the salt concentration: a) IFT increased [7], b) IFT decreased [8,9], c) no significant effect was observed [10] and d) IFT reduced initially and increased afterwards (under optimum concentration) [11–13].

Considering these inconsistent results, it can be deduced that the effect of salts on the IFT of crude oil depends on the type and amount of the existing surface active agents. One of the main reasons why the IFT of crude oil follows different patterns may be the different characteristics of asphaltene and resin fractions. Due to the importance of natural surfactants in the interfacial rheological behavior of crude oil and aqueous solution in the oil industry, they have attracted considerable attention [14–27]. For example, Acevedo et al. [14] reported that the high stability of the water-in-crude oil emulsions can be attributed to the establishment of mechanically strong films of natural surfactants around the water droplets. Also, Bauget et al. [19] performed an

experimental study to investigate the influence of asphaltenes and resins concentration on the static and dynamic properties of crude oil and air interfaces. They found that the adsorption process at the crude oil and air interface was not diffusion controlled but rather involved a re-organization of asphaltene molecules in a network structure. Moreover, it was reported that these films were formed by adsorption of asphaltenes and resins [20]. According to several studies, asphaltenes as micelles or colloids are dispersible in the crude oil medium by resins [21–23]. Furthermore, Andersen et al. [24] reported that asphaltene was not helpful to the start of micelle formation. However, it might exhibit a positive surface excess as a result of its polarity. On the other hand, resin molecules showed no active performance in the development of micelles and might be considered as being inert in terms of micellization [24]. Using molecular dynamics simulations Mikami et al. [25] demonstrated that in a model oil consisted of asphaltene and heptane, asphaltene molecules could accumulate at the interface of model oil and water. They also found that the aromatic plane was attracted toward the interfacial water molecules to form stable parallel structures. In cases that the number of asphaltene molecules in the interface system was enough to form a complete thin film, the IFT was sharply descended [25]. Yang et al. [26] reported that resins were capable of adsorbing more strongly than asphaltenes as supported by the lower IFT that they impart to crude oil-water interfaces. Moreover, it was reported that the properties of asphaltenic film were considerably affected by the concentration of asphaltenes and the oil phase

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aromaticity while properties of resin film are much less affected by these factors [26–28].

Possible synergistic effect between different salt ions and extracted resin, and asphaltene from acidic crude oil on the IFT was investigated by Lashkarbolooki et al. [29–32]. The results demonstrated that the ability of asphaltene fraction extracted from the heavy and acidic crude oil for IFT reduction was higher than the resin fraction. The higher affinity of asphaltene to the surface of acidic crude oil and aqueous solutions containing ions could be the main reason of such an observation. Since adsorption of asphaltenes and resins plays a main role at the crude oil and aqueous solution interface [23], the study of these effects are essential to understand the interfacial behavior of crude oil. The different behavior of IFT of crude oil as a function of salt concentration could be due to different rheological properties of resins and asphaltenes at the crude-brine interface. Literature search revealed a lack of fundamental understanding of the interfacial properties of asphaltenes and resins fractions of different crude oil type as a function of salt concentrations with their molecular infrastructures.

Herein, the influence of asphaltenes and resins structure on the equilibrium IFT of crude oils at different salt concentrations has been studied. To reach this goal, asphaltenes and resins of three types of crude oils (including light, medium and heavy crude oils provided from the south of Iranian reservoirs) have been extracted and elemental analysis has been conducted. Different weight percent (wt%) of dissolution of extracted compounds in toluene have been provided and their equilibrium IFT have been measured and compared with equilibrium IFT of crude oils in contact with different salt concentrations. In addition, the impacts of polar components of asphaltene and resin and their aromaticity on the IFT have been investigated.

2. Materials and experimental procedures

2.1. Materials

The characteristics of the used sea water (i.e. Persian Gulf water (PGW)) with total dissolved solids (TDS) of 43336 ppm are listed in Table 1. In addition, the API of three used crude oils with their asphaltene and resin contents are tabulated in Table 2.

The following procedure was utilized to isolate the asphaltenes and resins from three studied crude oils. Firstly, asphaltenes were extracted from crude oils via precipitation technique using *n*-heptane (purity > 99%, Merck, Germany) as extracting solvent, based on IP 143/90 [33] with volume ratio of 40:1. Then further purification was performed using soxhlet extractor [34]. Secondly, resins were removed from the same de-asphalted sample employing a column chromatography technique [35,36]. In this method, the mixture of de-asphalted oil and *n*-heptane known as maltene was adsorbed to a silica gel column (Merck, 35-70 mesh ASTM). Saturates and aromatics were washed subsequently by *n*-heptane and toluene (purity > 99%, Merck, Germany) with the ratio of 70:30. Finally, resins were extracted from the column using a mixture of toluene, dichloromethane (purity > 99%, Merck, Germany) and acetone (purity > 99%, Merck, Germany) with volume ratio of 30:30:40 [34].

With the exception of molecular weight and polarity, there is no principle chemical difference between resins and asphaltenes [37]. Asphaltenes contain different acidic and functional groups, such carbonyl functions, sulfur-oxygen functions, pyrrole (and indole) N–H

Table 1
Characteristics of intact and manipulated PGW.

Composition	Cl ⁻	Na ⁺ & K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	SO ₄ ²⁻
Concentration (ppm)	23,889	14,312	479	1626	0	3029
Diluted PGW (ppm)	0	1000	5000	15,000	30,000	43,336
Density (g/cm ³)	0.9979	0.9984	1.0011	1.0079	1.0191	1.0276

Table 2
Asphaltene and resin contents of the studied crude oils.

Crude oil type	API	Asphaltene (wt%)	Resin (wt %)	Resin/asphaltene ratio
Light crude oil	35.0	0.1	8.1	81.0
Medium crude oil	27.5	8.9	7.4	0.8
Heavy crude oil	20.5	11.0	13.0	1.2

functions, ester functions, and hydrogen-bonded hydroxyl groups [38–42].

Resins and asphaltenes as the polar fractions of crude oil are consisted of molecules comprising paraffinic, naphthenic, and aromatic hydrocarbons as well as functional groups comprising oxygen, nitrogen, and sulfur [43]. Because of this amphiphilic feature, these agents are capable of aggregating and being adsorbed to the interfaces. To gain further insight into the extracted asphaltenes and resins, the weights percent of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) of extracted asphaltenes and resins were provided by CHNSO elemental analyzer (Thermo Flash EA 1112 series). The results of CHNSO analysis of resins and asphaltenes fractions of the studied crude oils are listed in Table 3 (also see Fig. 1). The results of such calculation can be used to determine the aromatic and aliphatic parts of resin and asphaltene molecules [43]. Generally, H/C ratio was relatively higher in resins than asphaltenes, which depicted that resins were less aromatic than asphaltenes. In addition, it was revealed that the aromaticity of asphaltene and resin fractions of the used crude oils followed rather different patterns, e.g. in case of asphaltene: heavy < light < medium while in case of resin: light < heavy < medium. In more details, the medium crude oil consisted of 8.9 wt% of asphaltene molecules with high aromatic and aliphatic rings in their structures as well as 7.4 wt% of resins fractions with low aromatic and aliphatic rings.

The crude oil components could be also classified in terms of polarity. Chang and Fogler [44] reported that the polarity of the head as well as the length of the tails of the molecules could affect the amphiphilic nature efficiency. Although it is widely accepted that saturates contain nonpolar compounds [37], there is no such an agreement about the resins and asphaltenes fractions. Several researchers reported that the amount of polar compounds increases in order of aromatics < resins < asphaltenes [45–47].

In addition, Goual and Firoozabadi [48] claimed that the dipole moment increased sharply in order of crude oil < resins < asphaltenes. On the contrary, it has been shown that the amount of polar heteroatomic compartments related to the aromatic structure of resin is higher than that of asphaltene [49,50]. Due to the crucial influence of polar component in the IFT values, the wt% of polar components (i.e. S, O and N) of asphaltene and resin fractions of three crude oils were compared in Fig. 2. In the light crude oil, wt% of polar components of asphaltene was considerably higher than that of resin fraction while a reverse trend was observed for medium crude oil. However, the heavy crude oil consisted of almost the same amount of polar components.

Table 3
Result of CHNSO analysis of resin and asphaltene (based on wt%) extracted from the studied crude oil.

Atom	Light crude oil		Medium crude oil		Heavy crude oil	
	Asphaltene	Resin	Asphaltene	Resin	Asphaltene	Resin
C	68.35	79.46	81.82	77.04	80.96	80.03
H	6.14	8.90	6.93	9.36	7.84	9.52
N	0.00	1.95	1.82	1.78	0.00	0.00
S	7.73	3.34	3.88	3.35	7.36	3.81
O	17.78	6.35	5.55	8.48	3.84	6.64

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