

An Experimental Investigation of Water Effects on Asphaltene Surface Behavior through Interfacial Tension Measurements

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Abstract

As a physiochemical property, asphaltenes are known to be one of the most surface active compounds in crude oil. Due to such property, their behavior is most probably influenced by fluid-fluid interactions at the contact surface (interface). Potentially and naturally, in most cases, water is in contact with crude oil and is co-produced with it as well. Considering that asphaltene molecules are polar compounds similar to water molecules, asphaltenes are interfacially affected by water while they are absorbed to the interface. Such effects could be investigated by interfacial tension (IFT) changes when de-ionized water is used and dead-crude oil does not contain other surface active impurities like metallic compounds. In this study, extensive IFT experiments were conducted between three different oil samples and distilled water in a wide range of pressure from 2000 to 0 psia. The reversibility of asphaltene absorbance to the interface was also investigated by reversing the pressure path from 0 to 2000 psia. The results show that oil/water IFT changes with pressure, but upward/downward oscillations were detected. Such an oscillating behavior of IFT trends was related to asphaltene surface activity as the oil samples used did not contain other impurities. Oscillations were reduced as resin to asphaltene ratio was increased, suggesting the non-absorbable behavior of the asphaltenes stabilized by resins. A microscopic surface experiment on one of the samples showed that at a certain concentration and particle size, a rigid film of absorbed asphaltenes was created at the interface instantaneously. The high rigidity of such a film gives rise to a hypothesis, which states that water affects asphaltene surface behavior possibly through strong hydrogen bonding (H-bond). Reversing the pressure path revealed that asphaltene surface absorbance is partially irreversible. The experiments were conducted three times, and each data set was presented along with an average of three sets for each sample.

Keywords: Asphaltenes, Surface Activity, Surface Absorbance, Water Injection, EOR

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1. Introduction

The term asphaltene was first introduced by Boussingault (Boussingault, 1837) in 1837 to designate the material that precipitates out of petroleum upon the addition of petroleum ether. Today, asphaltenes are defined as follows: polydisperse heteroatoms with large molecular weight distributions, which are partially in colloidal state and partially are dissolved in oil. Their stability in crude oils is dependent on pressure, temperature, and the composition of the solution (Andersen and Stenby, 1996; Leontaritis, 1989; Leontaritis and Mansoori, 1988).

Asphaltenes are believed to be one of the most surface compounds in crude oil (Pillon, 2016; Sjöblom et al., 2015). Due to such an activity, they become absorbed to the contact surface. In most cases, water and oil are in contact, so it is most probable that asphaltene surface activity is affected by water molecules. As asphaltenes are being absorbed to the contact surface, it is expected that the interfacial characteristics of water/oil (W/O) contact are affected (Andersen et al., 2001; Cadena-Nava et al., 2007; Czarnecki and Moran, 2005; Fan et al., 2010; Ruiz-Morales and Mullins, 2015; Yang et al., 2007; Zhang et al., 2007). Fundamentally, the best indication of such changes would be the changes in interfacial tension value (IFT).

IFT is a very important parameter dealing with surface characteristics, so it has been investigated by many researchers. Some of these research works have used simple oils, and some have conducted experiments on crude oil-water IFT measurements. These works have mostly investigated the overall behavior of IFT between oil/water considering the effects of pressure, temperature, and water composition. Based on these works, no general trend against pressure, temperature, and composition could be identified for all types of oil samples. Some of major works are summarized in Table 1.

Table 1
Investigations on IFT between simple oils and water.

Researcher	Year	Oil	T (K)	p (MPa)	IFT method
Hassan et al. (Hassan et al., 1953)	1953	$C_3, C_4, C_5, C_6, C_8,$ and $i-C_8,$	299 to 355	1 to 204	Pendant drop
Jennings et al. (Jennings, 1967)	1967	Benzene and C_{10}	298 to 450	1 to 817	Pendant drop
Jasper et al. (Jasper and Duncan, 1967)	1967	$C_{13}, C_{14}, C_{15},$ and C_{16}	298 to 238	0.1	Drop weight
Jennings et al. (Jennings Jr and Newman, 1971)	1971	CH_4+C_{10}	296 to 450	0.1 to 81.6	Pendant drop
Motomura et al. (Motomura et al., 1983)	1983	$C_6, C_8, C_{10}, C_{12},$ and Benzene,	273 to 308	1 to 150	Pendant drop
Cai et al. (Cai et al., 1996)	1996	$C_6, C_8, C_{12}, C_{14},$ and C_{16}	298, 323	3.69 to 29.25	Pendant drop

Researcher	Year	Oil	T (K)	p (MPa)	IFT method
Rao et al. (Rao, 2001)	2001	C ₈	358, 398, 423	0 to 70	Pendant drop
Zeppieri et al. (Zeppieri et al., 2001)	2001	C ₆ , C ₇ , C ₈ , C ₉ , C ₁₀ , C ₁₁ , and C ₁₂	283, 333	0.1	Pendant drop
Al-Sahhaf et al. (Al-Sahhaf et al., 2005)	2005	C ₈ and C ₁₀	298, 338	0.69 to 31.05	Pendant drop
Aranda-Bravo et al. (Aranda-Bravo et al., 2008)	2008	i-C ₆ , i-C ₇ , and i-C ₈	303 to 343	P _{sat}	Pendant drop
Kashefi. (Kashefi, 2012)	2012	CH ₄	423	0.1 to 100	Pendant drop

Considering the effects of asphaltene absorbance, a general conclusion made by investigators is that asphaltenes could be absorbed to the W/O surface and could reduce IFT values (Jian et al., 2016; Moeini et al., 2014; Rane et al., 2013). For instance, Sjöblom et al. (1992) studied the IFT between octane and water and concluded that asphaltenes reduced the IFT. IFT reduction means higher solubility of water in crude oil. Andersen et al. (2001) also conducted another study on the effect of asphaltenes on water solubility in an organic solvent (toluene). Using Karl-Fischer titration method, they observed that water content was higher in the organic solvent when asphaltenes were dissolved. Khvostichenko and Andersen (2008) also found that the solubility of water in asphaltene-toluene solutions rises as the asphaltene concentration increases. Mikami et al. (2013) conducted a molecular dynamic simulation to investigate asphaltene effects on IFT between heptane and water. In their work, it was reported that increasing asphaltene concentration decreased IFT.

Other works have focused on the role of water in asphaltene surface activity. As a general conclusion, it is stated that water promotes asphaltene association due to intrinsic polarity of water molecules. This promotion could be through hydrogen bonding. Khvostichenko et al. (2004) investigated the role of water in an asphaltene-toluene solution and found out that water molecules existed as free molecules H-bound with asphaltenes. Jian et al. (2016) used pendant drop technique and molecular dynamics simulations and discussed the possibility of hydrogen bonding as the underlying mechanism for IFT reduction. Researches have also shown that IFT reduction is much more dependent on asphaltene surface concentration rather than bulk concentration.

Recently, some research works have tried to investigate asphaltene absorbance reversibility. Jeribi et al. (2002) observed visually a rigid skin at toluene-water interface only when asphaltene concentration was higher than 10 %. Although no skin was observed at lower concentrations, increasing pressure on the drop of asphaltene solution in toluene immersed in water caused distortion of the drop. They suggested that this was due to the irreversibility of the adsorption of asphaltene at the toluene-water interface. Freer and Radke (2004) showed that the adsorbed interfacial species at an oil-water interface form rigid skins during the retraction of an oil drop. They showed that most of asphaltenic surface active materials are irreversibly absorbed to the surface since, upon washout, the interfacial tension is increased only by 1.5 mN/m. Czarnecki and Moran (2005) presented a model explaining the

mechanism of water-in-oil (W/O) emulsion stabilization in petroleum systems (see Figure 1). According to their model, only a portion of asphaltenes is absorbed irreversibly.

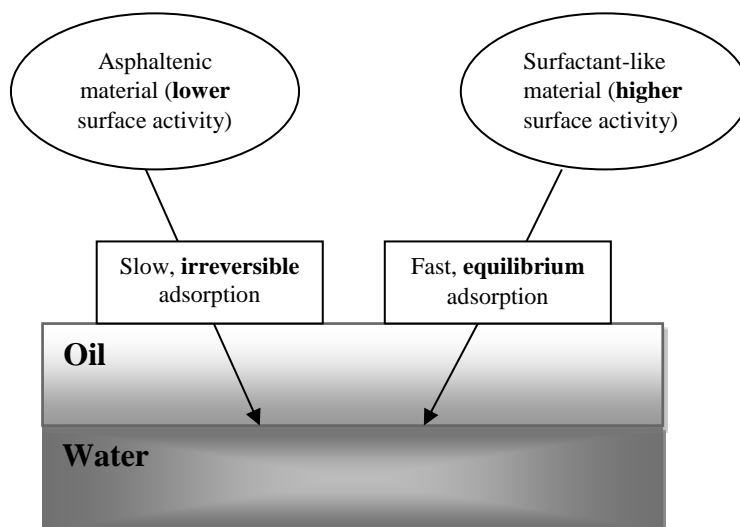


Figure 1

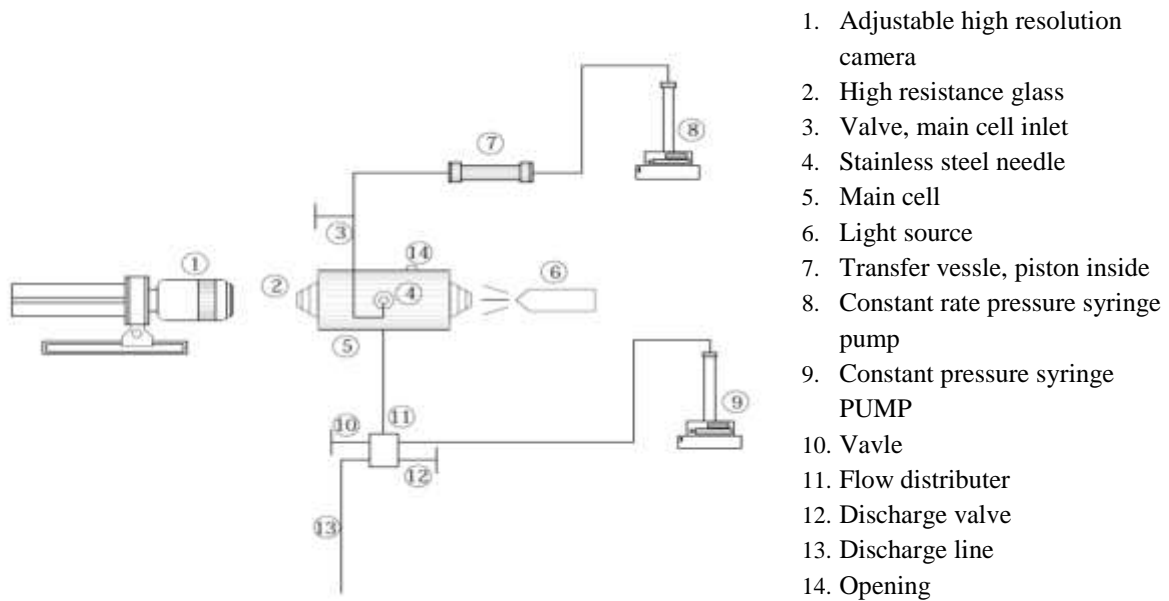
A model depicting the competition between asphaltenes and low-molecular-weight surfactants at the oil-water interface (Czarnecki and Moran, 2005).

Despite many research works on the evaluation of asphaltene surface activity, there are still debates on the kinetics of asphaltene absorbance, water effects, pressure effects, and the reversibility of these effects. In this paper, we aim to evaluate water effects on asphaltene surface activity. To this end, IFT's between 3 crude oil samples and distilled water were measured in a wide range of pressure from 2000 to 0 psia at 100-psia steps. By reversing the pressure path from 2000 to 0 psia, we studied the reversibility of asphaltene absorbance and IFT changes. Such tests were helpful to accurately determine pressure effects. The results showed a non-linear behavior of IFT against pressure with some oscillations. It was also revealed that these oscillations are less for the samples with a higher resin to asphaltene ratio. Unmatched trends of forward and backward pressure paths suggested that asphaltene absorbance should be partially irreversible. A microscopic image revealed an immediate creation of the rigid film of absorbed asphaltenes at W/O contact. These results could greatly help petroleum engineers to design an efficient water flooding process. They are also applicable to designing water-oil separation processes.

2. Method and materials

2.1. IFT measurements

The setup used in this study for IFT measurements is based on pendant drop theory, which states that a drop (fluid#1) will remain pendent on a needle surrounded by the other fluid, usually a visible one for image captivation purpose, until the buoyancy forces equals surface forces. Captive drop instrument, already available at Petroleum University Lab, was provided by Alberta Research Council. The needle size of 1/16 inch was used for calibration purposes. Figure 1 is a schematic representative of the IFT setup used in this study. iSpy software was used for image capturing and was set to save photos every 0.1 seconds. Therefore, it was possible to distinguish which image should be analyzed; the image before detachment was used for measurement. The method of Misak (Misak) was used for IFT calculations and Digimizer software was utilized for the image analysis.

**Figure 2**

A schematic of the IFT setup.

2.2. Density measurement

Herein, a high pressure-high temperature densitometer (DMA HPHT), provided by Anton Paar Company based in Austria, was used.

2.3. SARA test

There are several standard methods for SARA test, but the IP143 procedure was used herein. The results are shown in Table 2.

3. Results and discussion

3.1. Tests design

The experimental tests were designed in a way to enable the investigation of asphaltenes behavior at the oil/water interface. The IFT value between each oil sample and distilled water was measured in a pressure range from 2000 to 0 psi and again in a pressure range from 0 to 2000 psi at intervals of 100 psia. Each test was conducted 3 times for each sample to validate the results and assure reproducibility.

3.2. Discussion on results

In this section, IFT trends are presented as a function of pressure. The main focus of the discussions is on the trends and slopes. First of all, the IFT graphs related to data and their averages are presented. From these graphs, the main potential results are obtained. Figures 3 to 14 illustrate the blank test results. It should be mentioned that the main idea of discussion is based on a comparative study; therefore, discussions on each sample can be found in addition to comparisons with the other samples. It should be noted that asphaltenes behavior could be very different, so a true hypothesis for a sample could lead to meaningless results for another sample. Nonetheless, the aim of this project is to examine hypotheses previously stated by different researchers as well as presenting new inspiring

objective explanations based on the experimental data. It is worth noting that in all the cases, orange rectangle line shows the forward path, while blue triangle line represents the backward path.

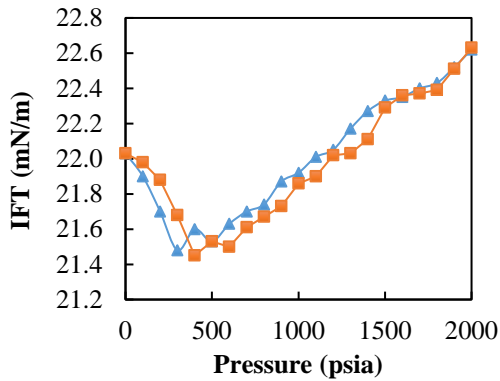


Figure 3
IFT vs. pressure for water/oil sample #1 at 25 °C Test #1.

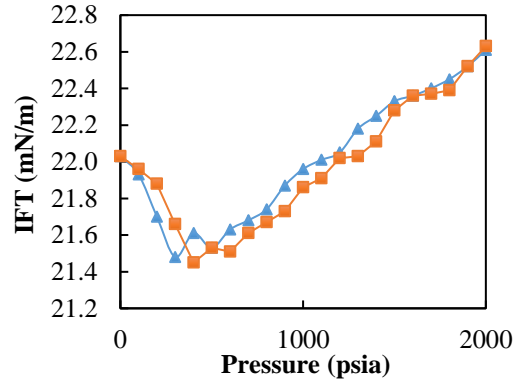


Figure 4
IFT vs. pressure for water/oil sample #1 at 25 °C Test #2.

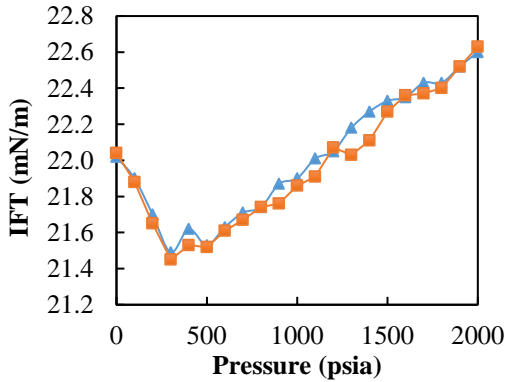


Figure 5
IFT vs. pressure for water/oil sample #1 at 25 °C Test #3.

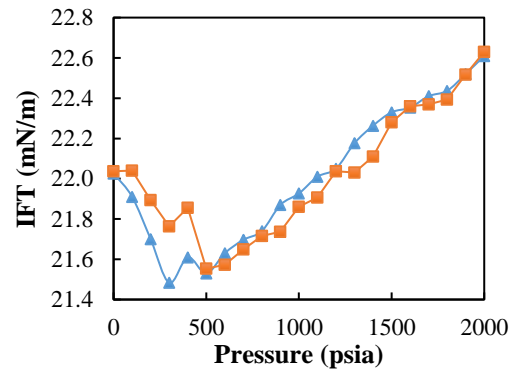


Figure 6
IFT vs. pressure for water/oil sample #1 at 25 °C average.

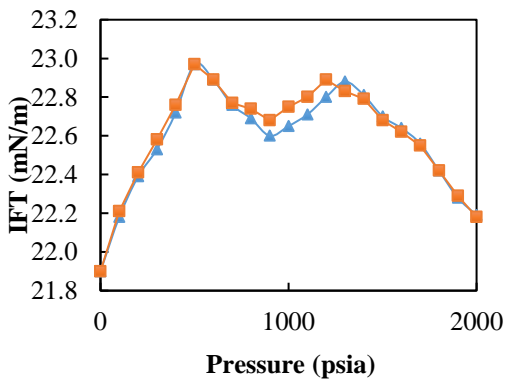


Figure 7
IFT vs. pressure for water/oil sample #2 at 25 °C Test #1.

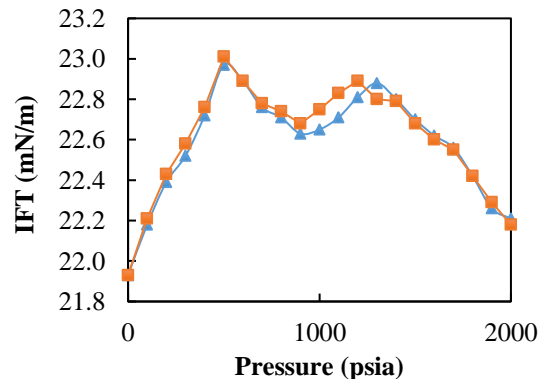


Figure 8
IFT vs. pressure for water/oil sample #2 at 25 °C Test #2.

3.3. Blank tests

Figures 3 to 6 show the results of the tests for sample 1. As given in Table 2, this sample has the lowest asphaltene content, while having the highest amount of resins (by weight). A focus on Figure 6, which is drawn based on the linear average of the data from Figures 3 to 5 at each specific pressure (forward and backward distinctly), confirms that IFT is changed slightly over pressure. A more deep focus reveals that there is hysteresis between the forward and backward data. Additionally, different slopes and sudden changes of IFT are obvious, and there are some oscillations in IFT values. Generally, the IFT value is decreased from 0 to 500 psi in both forward and backward paths, but it displays an increasing trend afterwards.

Table 2
SARA analysis.

Sample	Asphaltenes (%)	Saturates (%)	Aromatics (%)	Resins (%)
1	~2.80	56	12	28
2	~9.44	51	11	27
3	~4.35	48	39	8

Figures 7 to 10 delineate the results of sample 2. Considering Table 2, sample 2 has the highest amount of asphaltene content; however, it has roughly the same amount of resins as sample 1 has (by weight). As can be seen in Figure 10, the IFT value increases from 0 to 500 psi, but it then drops at pressures of 1300 to 2000 psi in both forward and backward paths. In the pressure range of 500-1300 psi, a huge oscillation can be seen in IFT. A hysteresis effect is also obvious in the pressure range of 700-1400 psi. Overall, the IFT value has slightly changed over pressure.

Finally, Figures 11 to 14 presents the data on sample 3. Referring to Table 2, this sample has the lowest amount of resin (by weight), yet it has the highest amount of aromatics (by weight). Similarly, for this sample, the changes in IFT value over pressure are small (see Figure 14). Generally, IFT decreases in the pressure range of 0-800 psi, and it then rises when pressure increases from 800 to 2000 psi. The hysteresis effect for this sample is not considerable, and forward and backward curves are almost similar.

In a comparative study, IFT trends for these samples do not show any similarities and are completely different. However, there is a general similarity as all the figures have shown a non-linear trend of IFT vs pressure. This observation provides a clue about the pressure dependence of asphaltene surface activity. As it can be seen in all the figures, there are some pressure ranges in which hysteresis effects are detectable. Hysteresis effects are mostly detectable for sample 1, in which forward IFT values are smaller at some data points, while backward IFT values are smaller at some other data points.

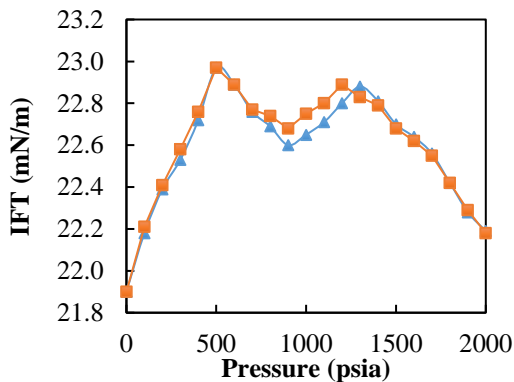


Figure 9
IFT vs. pressure for water/oil sample #2 at 25 °C Test #3.

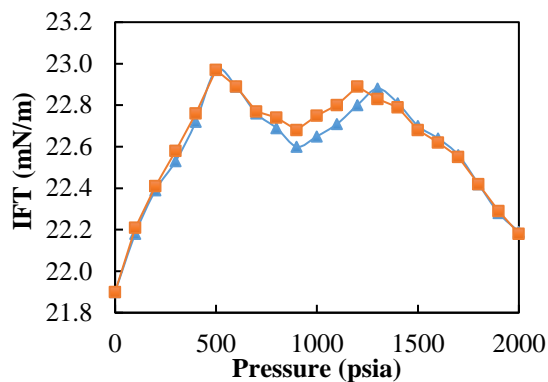


Figure 10
IFT vs. pressure for water/oil sample #2 at 25 °C average.

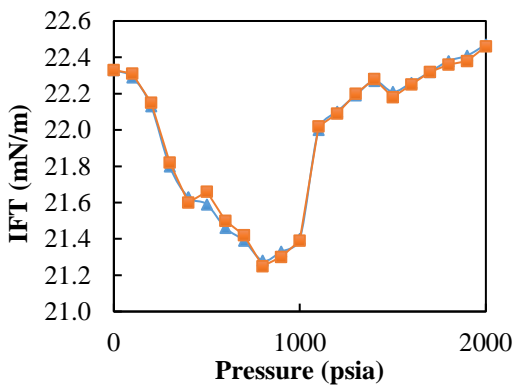


Figure 11
IFT vs. pressure for water/oil sample #3 at 25 °C Test #1.

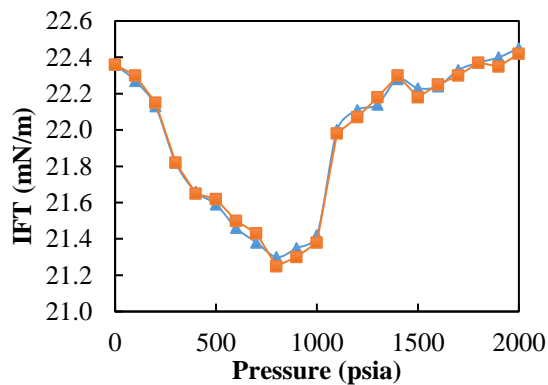


Figure 12
IFT vs. pressure for water/oil sample #3 at 25 °C Test #2.

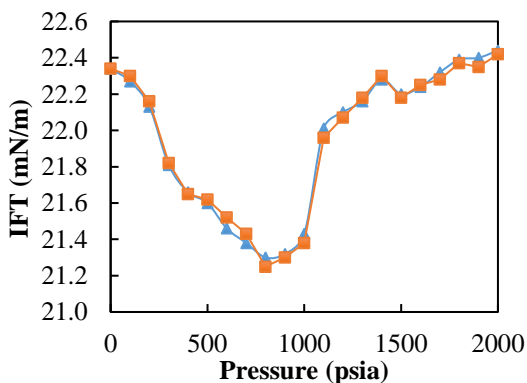


Figure 13
IFT vs. pressure for water/oil sample #3 at 25 °C Test #3.

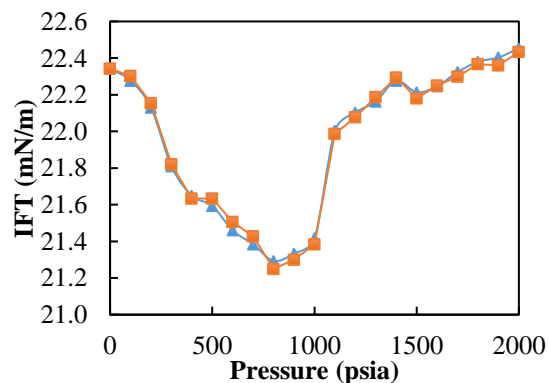


Figure 14
IFT vs. pressure for water/oil sample #3 at 25 °C average.

It is obvious that the hysteresis effects are not very noticeable, which can be explained as follows. First of all, we could rely on the hypothesis stating that hydrogen bonds are majorly responsible for asphaltene absorbance (Mikami et al., 2013). These bonds are proved to be reversible, so we can see that almost the same number of hydrogen bonds is created when the solution returns to its original

state. In addition to this, asphaltenes are categorized as slow and fast absorbing compounds (Mikami et al., 2013). As stated before, slow ones are absorbed irreversibly. Therefore, we could also expect that our measurement durations were not sufficiently enough for those of irreversible ones to become absorbed. Enough time for these asphaltenes to absorb has been reported to be within 600-1000 s (Jeribi et al., 2002; Pauchard et al., 2014). Although this hypothesis is somehow logical, a test on sample 1 diluted with n-C₇ confirmed that the proportion of slow absorbing asphaltenes on the interface was very low compared with that of fast absorbing ones. n-C₇ was added to activate asphaltene separation. We ran a test with duration of 1800 s, and the results showed that most of changes in IFT value occurred instantaneously (Figure 15). In other words, since fast absorbing asphaltenes become absorbed to the interface and make reversible hydrogen bonds, they leave no space for slow ones to be absorbed. However, we could also state that much more time is needed for the slow absorbing asphaltenes to be absorbed, for instance days to weeks. This time is very important to be accurately determined as we do not only deal with small time intervals of water-oil contact. Such a determination is beyond the scope of this study. Slight hysteresis effects suggest that fast reversible absorbing asphaltenes should have a high surface concentration.

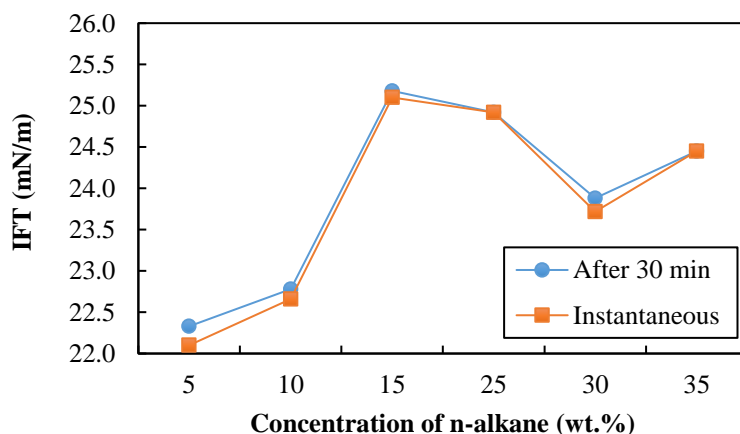


Figure 15

Effects of time on IFT changes and asphaltene absorbance kinetics.

The question that still exists is why hysteresis effects are mostly detectable for sample #1. This could be attributed to its very high value of resin to asphaltene ratio (R/A) compared to the two other ones, which have almost the same R/A ratios. R/A ratio for all the 3 samples are tabulated in Table 3. High resin content results in more stable asphaltenes which could not absorb anymore. The amount of these stable asphaltene has differed in the forward and backward paths. Due to such interactions between resins and asphaltenes, we have seen that hysteresis effects are much more detectable for sample #1 which has the highest R/A. In addition to stabilizing role of resin, it could also participate as an absorbing agent at W/O contact. This could also result in less space for asphaltenes on the contact surface. Such a competition has different kinetics in the forward and backward paths. Therefore, IFT values did not match exactly.

Table 3
Resin to asphaltene ratio of each sample.

Sample	Sample 1	Sample 2	Sample 3
Resin to asphaltene ratio	~9.3	~2.8	~1.8

The basis for explaining this behavior is the phenomenon that large self-associated asphaltene particles need to adsorb resin on their surfaces to be stable. If the needed amounts of resins are not provided, large self-associated particles are disintegrated and dispersed as separate asphaltene particles. These separate particles can be adsorbed on interface, make bonds with water molecules, and reduce the IFT. However, all of the disintegrated asphaltene particles could not be absorbed on the W/O contact. If this was the case, we would always expect the IFT to be reduced. Therefore, what happens is that some of the disintegrated asphaltene particles start again to be self-associated and become blocked from being absorbed. Another hypothesis that we state deals with asphaltene surface concentration and asphaltene particle size. It seems that asphaltenes make a rigid film on W/O contact, which allows asphaltenes to be absorbed up to a certain concentration and particle size. We named it as critical surface concentration and size (CSC-S). This rigidity could be due to very strong hydrogen bonding between asphaltenes and water molecules. In addition, some of resin could also be absorbed on contact surface as it is polar too. This gives rise to film rigidity and stability, which further prevents asphaltenes from being absorbed. A microscopic view of this rigid film is shown in Figure 16. Finding the exact concentration and size of the absorbed asphaltenes is beyond this study.

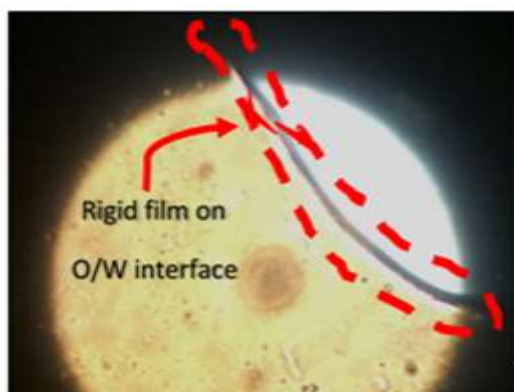


Figure 16

A microscopic view of oil/water interface.

The idea behind the hypothesis of CSC-S was examined through a series of microscopic surface studies; Figure 17 displays a series of these images. Moreover, as it can be seen in Figure 18, there is no significant change in film thickness in test duration. All such experiments were conducted at 0 psia and 28 °C. As it was very hard to perform such tests under a high-pressure condition due to stability issues, we were not able to afford further tests to strongly claim our hypothesis. Therefore, we suggest that further research works should be conducted to examine this hypothesis. In fact, one may need to conduct a full series of microscope tests within a wide range of pressure and dilution ratio to specifically study the CSC-S hypothesis. Our experiments were only performed for the crude sample #1.

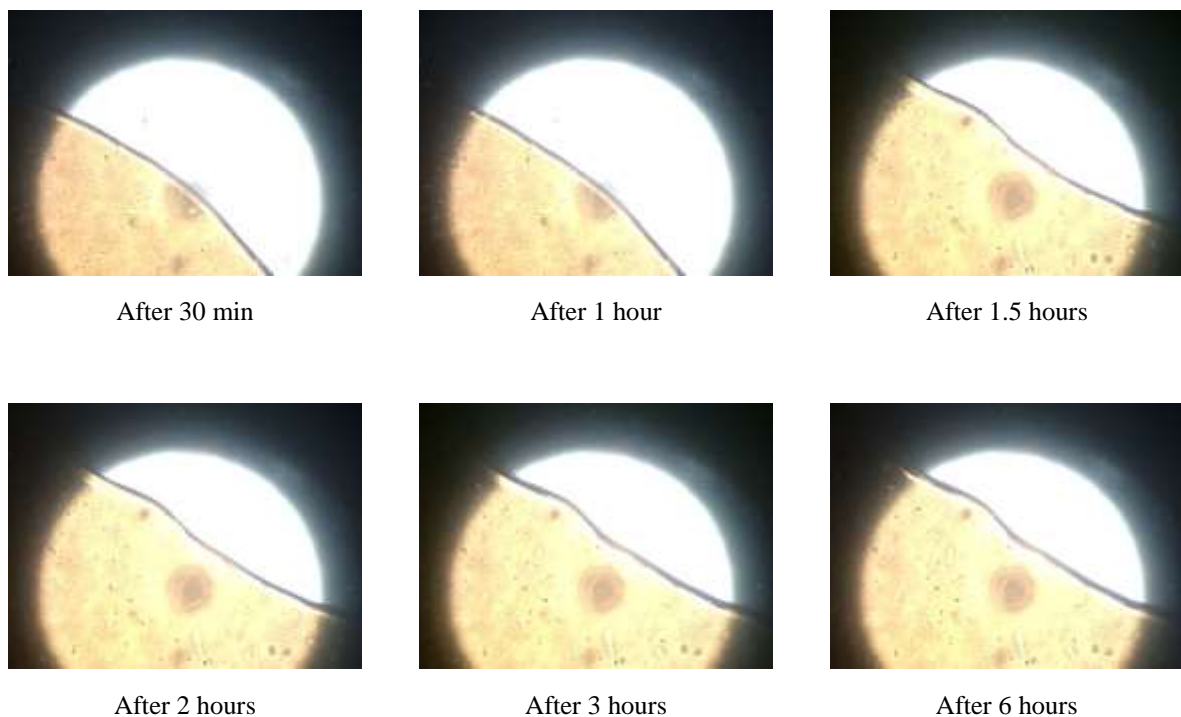


Figure 17
A microscopic view of the captured images of W/O contact surface.

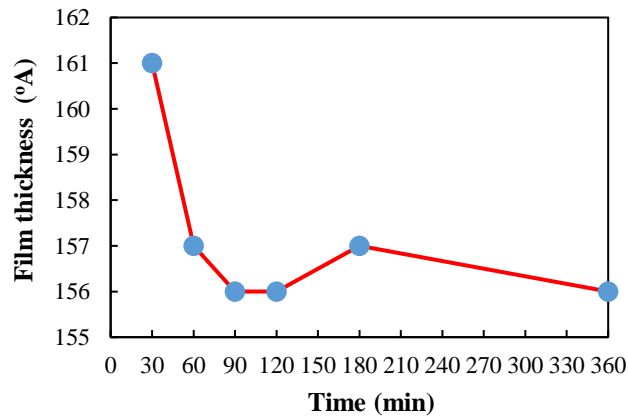


Figure 18
The variation of asphaltene film thickness against time.

4. Conclusions

In this paper, the goal was the investigation of water effects on asphaltene behavior in crude oil. To conduct such an investigation through an interfacial study, IFT versus pressure was measured in forward and backward trends for each oil sample against distilled water, and each test was repeated 3 times to validate the results. The conclusions can be summarized as follows:

- IFT between crude oil and water has a non-linear behavior against pressure with some oscillations. These oscillations are less for the samples with a higher resin to asphaltene ratio.
- Asphaltenes could absorb to the interface up to a certain concentration and particle size. A rigid film of the absorbed asphaltenes or asphaltenes + resins prevents further absorbance.

Still, the replacement of fast and slow absorbing asphaltenes could occur during a very long time.

- Asphaltene absorbance occurs instantaneously.
- Most of activated asphaltenes on the interface are fast moving, regarding their absorbance kinetics. These asphaltenes leave almost no space for the slow moving ones, which are indeed irreversible regarding their absorbance. Therefore, slight hysteresis effects are observed, and slight hysteresis proves the role of hydrogen bonding, which is reversible by nature.
- Hysteresis effects are more detectable for sample #1, which has a higher resin to asphaltenes ratio. A high resin to asphaltene ratio means more interactions, which could finally lead to considerable hysteresis.

As a future work, we recommend investigating the effects of dissolved salts, temperature changes, and asphaltene surface concentration on water-oil contact.

References

- Al-Sahhaf, T., A. Elkamel, A. Suttar Ahmed, and A. R. Khan, The Influence of Temperature, Pressure, Salinity, and Surfactant Concentration on the Interfacial Tension of the n-Octane-Water System, *Chemical Engineering Communications*, Vol. 192, No. 5, p. 667-684, 2005.
- Andersen, Simon Ivar, Jose Manuel Del Rio, Daria Khvostitchenko, Sarmad Shakir, and Carlos Lira-Galeana, Interaction and Solubilization of Water by Petroleum Asphaltene in Organic Solution, *Langmuir*, Vol. 17, No. 2, p. 307-313, 2001.
- Andersen, Simon Ivar, and Erling II Stenby, Thermodynamics of Asphaltene Precipitation and Dissolution Investigation of Temperature and Solvent Effects, *Fuel Science and Technology International*, Vol. 14, No. 1-2, p. 261-287, 1996.
- Aranda-Bravo, Carlos Gilberto, Ascención Romero-Martínez, Arturo Trejo, and Jacinto Águila-Hernández, Interfacial Tension and Density of Water+ Branched Hydrocarbon Binary Systems in the Range 303-343 K, *Industrial & Engineering Chemistry Research*, Vol. 48, No. 3, p. 1476-1483, 2008.
- Boussingault, M. Memoire Sur La Composition Des Bitumes, in *Annales De Chimie Et De Physique*, Vol. 64, No. 141, 837.
- Cadena-Nava, R. D., A. Cosultchi, and J. Ruiz-Garcia., Asphaltene Behavior at Interfaces, *Energy & Fuels*, Vol. 21, No. 4, p. 2129-2137, 2007.
- Cai, Bi-Yu, Ji-Tao Yang, and Tian-Min Guo., Interfacial Tension of Hydrocarbon+ Water/Brine Systems Under High Pressure, *Journal of Chemical & Engineering Data*, Vol. 41, No. 3, p. 493-496, 1996.
- Czarnecki, J. and Kevin M., On the Stabilization Mechanism of Water-in-oil Emulsions in Petroleum Systems, *Energy & Fuels*, Vol. 19, No. 5, p. 2074-2079, 2005.
- Fan, Yanru, Sébastien Simon, and Johan Sjöblom, Interfacial Shear Rheology of Asphaltene at Oil-water Interface and its Relation to Emulsion Stability: Influence of Concentration, Solvent Aromaticity and Nonionic Surfactant, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 366, No. 1-3, p. 120-128, 2010.
- Freer, E. M. and C. J. Radke, Relaxation of Asphaltene at the Toluene/Water Interface: Diffusion Exchange and Surface Rearrangement, *The Journal of Adhesion*, Vol. 80, No. 6, p. 481-496, 2004.

- Hassan, M. E., R. F. Nielsen, and J. C. Calhoun, Effect of Pressure and Temperature on Oil-water Interfacial Tensions for a Series of Hydrocarbons, *Journal of Petroleum Technology*, Vol. 5, No. 12, p. 299-306, 1953.
- Jasper, Joseph J. and Judith C. Duncan, Temperature-interfacial Tension Studies of Some 1-Alkenes Against Water, *Journal of Chemical and Engineering Data*, Vol. 12, No. 2, p. 257-259, 1967.
- Jennings Jr, Harley Y., The Effect of Temperature and Pressure on the Interfacial Tension of Benzene-water and Normal Decane-water, *Journal of Colloid and Interface Science*, Vol. 24, No. 3, p. 323-329, 1967.
- Jennings Jr, Harley Y., and George H. Newman, The Effect of Temperature and Pressure on the Interfacial Tension of Water Against Methane-normal Decane Mixtures, *Society of Petroleum Engineers Journal*, Vol. 11, No. 02, p. 171-175, 1971.
- Jeribi, M., B. Almir-Assad, D. Langevin, I. Henaut, and J. F. Argillier, Adsorption Kinetics of Asphaltenes at Liquid Interfaces, *Journal of Colloid and Interface Science*, Vol. 256, No. 2, p. 268-272, 2002.
- Cuiying, J., Poopari, M. R., Liu, Q., Zepa, N., Zeng, H., and Tang, T., Reduction of Water/oil Interfacial Tension by Model Asphaltenes: the Governing Role of Surface Concentration, *The Journal of Physical Chemistry B*, Vol. 120, No. 25, p. 5646-5654, 2016.
- Kashefi, Khalil, Measurement and Modelling of Interfacial Tension and Viscosity of Reservoir Fluids, Ph.D. Dissertation, Heriot-Watt University, 2012.
- Khvostichenko, D. S., S. I. Andersen, and A. I. Viktorov., Solubility and Binding of Water in Toluene Solutions of Asphaltenes, *Russian Journal of Applied Chemistry*, Vol. 77, No. 6, p. 1013-1018, 2004.
- Khvostichenko, Daria S., and Simon I. Andersen, Interactions between Asphaltenes and Water in Solutions in Toluene, *Energy & Fuels*, Vol. 22, No. 5, p. 3096-3103, 2008.
- Leontaritis, K. J., Asphaltene Deposition: A Comprehensive Description of Problem Manifestations and Modeling Approaches, in *SPE Production Operations Symposium*, Society of Petroleum Engineers, 1989.
- Leontaritis, Kosta J., and G. Ali Mansoori, Asphaltene Deposition: A Survey of Field Experiences and Research Approaches, *Journal of Petroleum Science and Engineering*, Vol. 1, No. 3, p. 229-239, 1988.
- Mikami, Yohei, Yunfeng Liang, Toshifumi Matsuoka, and Edo S. Boek, Molecular Dynamics Simulations of Asphaltenes at the Oil-water Interface: from Nanoaggregation to Thin-film Formation, *Energy & Fuels*, Vol. 27, No. 4, p. 1838-1845, 2013.
- Misak, Marvin D., Equations for Determining $1/H$ Versus S Values for Interfacial Tension Calculations by the Pendant Drop Method, 1968.
- Moeini, Farzaneh, Abdolhossein Hemmati-Sarapardeh, Mohammad-Hossein Ghazanfari, Mohsen Masihi, and Shahab Ayatollahi, Toward Mechanistic Understanding of Heavy Crude Oil/Brine Interfacial Tension: the Roles of Salinity, Temperature and Pressure, *Fluid Phase Equilibria*, Vol. 375, p. 191-200, 2014.

- Motomura, Kinsi, Hidemi Iyota, Makoto Aratono, Michio Yamanaka, and Ryohei Matuura, Thermodynamic Consideration of the Pressure Dependence of Interfacial Tension, *Journal of Colloid and Interface Science*, Vol. 93, No. 1, p. 264-269, 1983.
- Pauchard, Vincent, Jayant P. Rane, Sharli Zarkar, Alexander Couzis, and Sanjoy Banerjee, Long-Term Adsorption Kinetics of Asphaltenes at the Oil–water Interface: a Random Sequential Adsorption Perspective, *Langmuir*, Vol. 30, No. 28, p. 8381-8390, 2014.
- Pillon, Lilianna Z., *Surface Activity of Petroleum Derived Lubricants*, CRC Press, 2016.
- Rane, Jayant P., Vincent Pauchard, Alexander Couzis, and Sanjoy Banerjee, Interfacial Rheology of Asphaltenes at Oil–water Interfaces and Interpretation of the Equation of State, *Langmuir*, Vol. 29, No. 15, p. 4750-4759, 2013.
- Rao, Dandina N., *Fluid–fluid and Solid–fluid Interfacial Interactions in Petroleum Reservoirs*, *Petroleum Science and Technology*, Vol. 19, No. 1-2, p. 157-188, 2001.
- Ruiz-Morales, Yosadara, and Oliver C. Mullins, Coarse-grained Molecular Simulations to Investigate Asphaltenes at the Oil–water Interface, *Energy & Fuels*, Vol. 29, No. 3, p. 1597-1609, 2015.
- Sjöblom, Johan, Li Mingyuan, Alfred A. Christy, and Tiren Gu, Water-in-crude-oil Emulsions from the Norwegian Continental Shelf 7, Interfacial Pressure and Emulsion Stability, *Colloids and Surfaces*, Vol. 66, No. 1, p. 55-62, 1992.
- Sjöblom, Johan, Sebastien Simon, and Zhenghe Xu, Model Molecules Mimicking Asphaltenes, *Advances in Colloid and Interface Science*, Vol. 218, p. 1-16, 2015.
- Yang, Xiaoli, Vincent J. Verruto, and Peter K. Kilpatrick, Dynamic Asphaltene–resin Exchange at the Oil/Water Interface: Time-dependent W/O Emulsion Stability for Asphaltene/Resin Model Oils, *Energy & Fuels*, Vol. 21, No. 3, p. 1343-1349, 2007.
- Zeppieri, S., Rodríguez, J., and López De Ramos, A. L., Interfacial Tension of Alkane+ Water Systems, *Journal of Chemical & Engineering Data*, Vol. 46, No. 5, p. 1086-1088, 2001.
- Zhang, Li Yan, Patrick Breen, Zhenghe Xu, and Jacob H. Masliyah, Asphaltene Films at a Toluene/Water Interface, *Energy & Fuels*, Vol. 21, No. 1, p. 274-285, 2007.