Interfacial Properties Pertinent to W/O and O/W Emulsion Systems Prepared using Polyaromatic Compounds

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Abstract

Establishing interfacial science to understand molecular mechanisms of stabilizing water in heavy crude oil (W/O) emulsions is challenging due to non-transparent nature of crude oil even in diluted systems, as most of the interfacial measurements are based on visualization of the experimental systems. This study investigates whether interfacial properties measured using transparent O/W emulsion systems could be used to understand the stability of W/O emulsion systems. With the same chemistry of interfacially active polyaromatic compounds (C5Pe and C5PeC11) in xylenes as the model oil, the interfacial tension, crumpling ratio, dilatational rheology and coalescence time of W/O and O/W systems were measured. For less surface active C5PeC11, the interfacial tensions for W/O and O/W system were similar. For more surface active C5Pe, the interfacial tension of W/O system was lower than that of the O/W systems, while the film rigidity and viscoelasticity of the W/O system were higher than that of the O/W system. At low C5Pe concentration, the coalescence time for W/O systems was lower than that for O/W systems with the coalescence time for the W/O system being higher at higher C5Pe

concentrations. The results revealed that even though the reverse O/W system exhibits similar qualitative trends, care should be taken when quantitatively studying W/O emulsions using interfacial measurements of O/W systems due to the difference in most of the interfacial properties.

1 Introduction

Water-in-crude oil/diluted bitumen (W/O) emulsions encountered during crude oil production and bitumen processing are known to be very stable and the emulsified small water droplets are hard to remove. Such emulsions are undesirable for a number of reasons, such as additional volume (cost) for transportation, equipment corrosion and catalyst fouling at downstream refineries [1]. Therefore, these emulsions have to be treated to remove the dispersed water droplets and associated inorganic salts to meet the specifications for transportation, further refining, upgrading, storage, and export.

Unlike microemulsions, macroemulsions are generally anticipated to be thermodynamically unstable and hence to be phase separated with time [2, 3]. Persistent stability of W/O emulsions encountered in the oil industry is often attributed to a rigid, viscoelastic and mechanically strong interfacial film that surrounds water droplets and prevents their coalescence [2, 4-7]. Destabilization of the emulsions can be realized by the use of chemical, heating, mechanical and/or electrical treatments. Among these methods, chemical demulsification is considered to be the most efficient and cost-effective, which has been widely used in the oil industry [8-11]. However, the excess use of the chemicals is a serious concern that not only increases the cost of operations but is also sensitive to process conditions that may not always be effective.

The interfacial properties of emulsions and coalescence mechanisms of the water droplets have been investigated with the aim to improve the design of efficient and robust demulsifier chemicals [12-15]. Through the interfacial tension measurement, X-ray photoelectron spectroscopy characterization, micropipette experiments and shear rheology measurement, Pensini et al. [12] proved that the ethylene-oxide-propylene oxide (EO−PO)-based polymeric demulsifier is more interfacially active than asphaltenes (0.25 g/L) and can compete effectively with asphaltenes at the interface, penetrating and softening interfacial asphaltene films. The dilatational viscoelastic behavior of the W/O interface formed with 0.044 wt% surface-active fractions extracted from an Iranian heavy oil was studied by Sun et al. [13] Their results showed

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that the adsorption of demulsifier molecules at the oil-water interface leaves small voids at the interface of water droplets, which keeps the emulsifiers away from the interface. Ese et al. [14] investigated surface pressure-area isotherms and concluded that increased compressibility (reduced rigidity of the film) after demulsifier addition seems to be an important feature when breaking a stable emulsion.

In fact, interfacial tension has been widely studied in the oil industry [16-18] as a good indicator of the adsorption of surface-active molecules at the oil-water interface. While the crumpling ratio (CR) of the droplets reflects the degree of steric layer (skin) formation at the interface [7], dilatational rheology characterizes the viscoelasticity of the interfacial film [19, 20]. Studying interfacial dilatational rheology is a powerful tool to probe the adsorption and association of surface active molecules at oil-water interfaces, providing a better understanding of the microscopic properties of an interfacial film [21]. The stability of thin liquid films between two liquid droplets is reported to be critical for emulsion stability [22] while the coalescence time characterizes the stability of this thin liquid film [23, 24].

Investigations using optical methods were normally performed on an oil droplet in an aqueous phase as the measurements require the continuous phase to be transparent for good optical visibility of studied objects and non-transparent crude oil prohibits the measurement of water droplets in crude oil, which is more relevant to W/O petroleum emulsions. Asphaltenes of polyaromatic cores are recognized as the main components to stabilize W/O petroleum emulsions. However, the asphaltene solutions are nontransparent even at low asphaltene concentrations. Perylene family compounds such as C5Pe and C5PeC11 are of similar structural characteristics (containing a fused polyaromatic core) of asphaltene molecules and exhibit similar interfacial activities [25, 26]. Since the transparent solutions of C5Pe and C5PeC11 can be made to reasonable concentrations, they are used in this study as asphaltene model compounds [27-31]. It should be noted that there remains a gap between the two model systems and real crude oils comprising a mixture of different types of hydrocarbons, such as organic acids.

The current study aims to uncover the relationship between the measured interfacial properties using water-in-oil and oil-in-water systems. The objective of this study is to confirm whether the measurement of interfacial properties using the reverse (O/W) system could provide insights on

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stabilization mechanisms of W/O emulsions. To achieve this goal, interfacial tension, crumpling ratio, dilatational rheology, and coalescence time measurements were conducted using xylene containing surface active polyaromatic compounds C5Pe and C5PeC11 as the oil phase which is of good optical transparency.

2 Materials and Methods

2.1 Materials

C5Pe (N-(1-hexylheptyl)-N´-(5- carboxylicpentyl) perylene-3,4,9,10-tetracarboxylic bisimide) and C5PeC11 (N-(1-undecyldodecyl)-N´-(5-carboxylicpentyl) perylene-3,4,9,10-tetracarboxylic bisimide) were used as asphaltene model compounds. The only difference in molecular structure (Figure 1) between C5Pe and C5PeC11 is longer aliphatic chains of C5PeC11 that enhances its solubility in xylenes. The protocols utilized to synthesize C5Pe and C5PeC11 have been described in detail elsewhere [32].
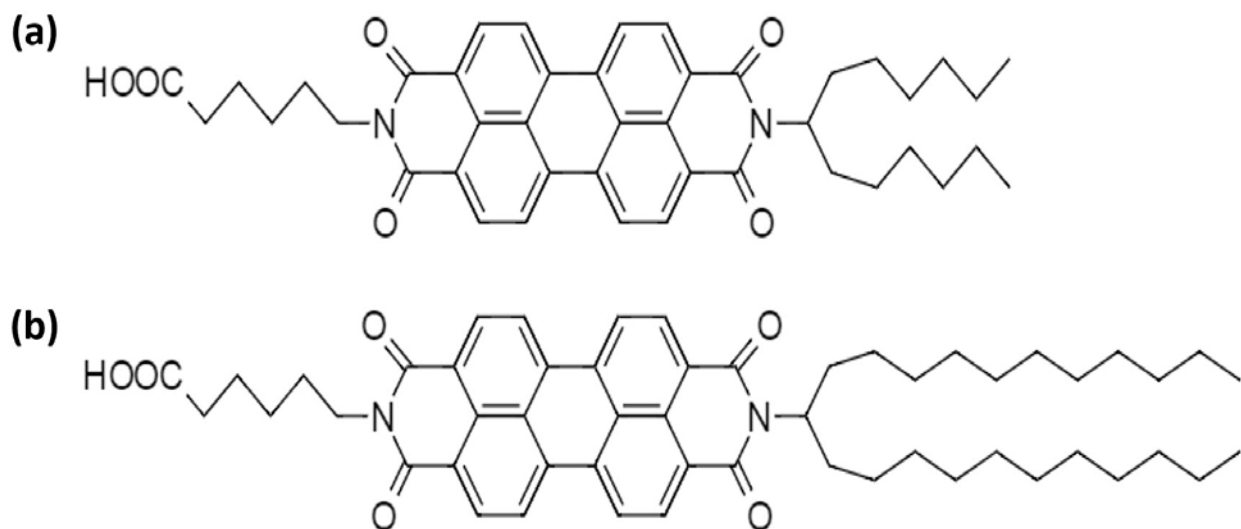

Figure 1. Molecular structure of the polyaromatic compounds used in this work: (a) C5Pe (MW = 689 g/mol) and (b) C5PeC11 (MW = 827 g/mol).

Solutions of C5Pe or C5PeC11 in xylenes (≥98.5%, ACS grade, Fisher Scientific, Canada) were used as model oil in this study. C5Pe (C5PeC11) in xylene solutions were prepared by sonicating (Crest 275DA Ultrasonic Cleaner, 50/60 Hz) a given amount of C5Pe (C5PeC11) in xylenes for 30 minutes. Deionized (DI) water of a resistivity > 18.5 MΩ·cm was purified with a Millipore

system and used throughout this study. Buffer solutions of pH 7 were provided by Fisher Scientific and used as received.

2.2 Methods

A Theta Optical Tensiometer T200 (Attention, Biolin Scientific, Finland) was used to study the interfacial properties of water and C5Pe/C5PeC11 in xylenes solutions (oil) by measuring the interfacial tension, crumpling ratio and interfacial dilatational rheology. An integrated thin film drainage apparatus (ITFDA) [33] was used to determine the coalescence time of water droplets in oil or oil droplets in water, which provides information on the rupture of the interfacial film.

Interfacial tension

Pendant drop technique was used to determine the dynamic interfacial tension of W/O (water droplets in diluted C5Pe/C5PeC11-in-xylenes solution) and O/W (droplets of diluted C5Pe/C5PeC11-in-xylenes solution in water) systems. For W/O systems, a water droplet of 10 μL in volume generated by a gastight syringe (Hamilton Co., USA) was immersed in 3 mL diluted C5Pe /C5PeC11-in-xylenes solution placed in a quartz cuvette. For O/W systems, an oil droplet of 10 μL in volume was immersed in 3 mL water. The interfacial tension was recorded after the droplets were in contact with the continuous phase for 10 minutes and 30 minutes, respectively.

For comparison, the interfacial tension of an oil-water interface was also measured using the Du Noüy Ring Method. In this case, 20 mL of water was loaded in the measurement cell first while the ring was immersed in water. The water phase was then covered by 15 mL of oil phase. After aging the interface for a desired period of time, the immersed ring is gradually pulled towards the interface while monitoring the force exerting on the ring. At the point when the liquid interface was vertical, the largest detachment force was detected by the electronic balance, which was converted to the interfacial tension.

Crumpling ratio

Similar to interfacial tension measurement, the size of the water (or oil) droplets was controlled to 10 μL in volume for crumpling ratio measurements. After aging of the droplets for a desired period of time, the water (or oil) droplet was retracted steadily into the syringe while the whole process was recorded. The crumpling ratio was quantified by dividing the projected area of the

droplet at the point when wrinkles (crumpling) were first observed on this droplet (A_f) by the projected area of the initial droplet (A_i). The point where the crumpling began was determined by analyzing the video frame by frame.

Dilatational Rheology

The pulsating droplet module (PD 200) was used to measure dilatational viscoelastic complex modulus (E) and hence the dilatational elastic modulus (E') of the oil−water interface. A water (oil) drop of 5 µL in volume was generated at the tip of the syringe needle and immersed in 3 mL oil (water) placed in a quartz cuvette. The drop was sinusoidally oscillated and the change in the interfacial tension and surface area was recorded. In this study, the maximum change in drop volume was set to be 10% and the oscillation frequency was set at 0.1 Hz, which is in the linear viscoelastic region as shown by the results in Figure S12 of the supporting information. This frequency was used to avoid the loss of accuracy at higher frequencies [34]. Each measurement was set to include 10 oscillations with a 10 s delay between consecutive measurements.

Coalescence time

A custom-built integrated thin film drainage apparatus (ITFDA) was used to measure the coalescence time of two water droplets in oil or two oil droplets in water. Details of the instrument setup can be found in Wang et al. [33]. Initially, a bottom water (or oil) droplet with semicircular shape was generated on a holder made of glass (for water droplet) or Teflon (for oil droplet). A top water (or oil) droplet was produced immediately by the capillary tube with the help of a gastight syringe. The droplets were held apart at a separation distance of 200±10 µm in oil (or water) as shown in Figure 2. During the aging period of 10 minutes, the two droplets were aligned. Right after the aging, the top droplet was driven downward at a constant velocity of 313 µm/s for a fixed distance of 313 µm so that the two droplets were brought in contact with an overlap of 119 µm. The drop−drop interaction process was recorded by a high speed video camera for a period of two minutes. During the holding period, the droplets could coalesce or remain as individual droplets. The coalescence time was determined as the time from the moment that contact between the drops was observed until their coalescence. In the case that coalescence did not occur, the droplets were considered stable. The coalescence time for the former case was determined by counting the time during the video playback. For repeating tests, fresh droplets were produced in a similar manner as described above. Although care was taken to

use droplets of the same size, it is not possible to get exactly the same size every time, especially the shape of these large drops could change considerably when the interfacial tension was low due to the addition of surface active molecules such as C5Pe or C5PeC11.
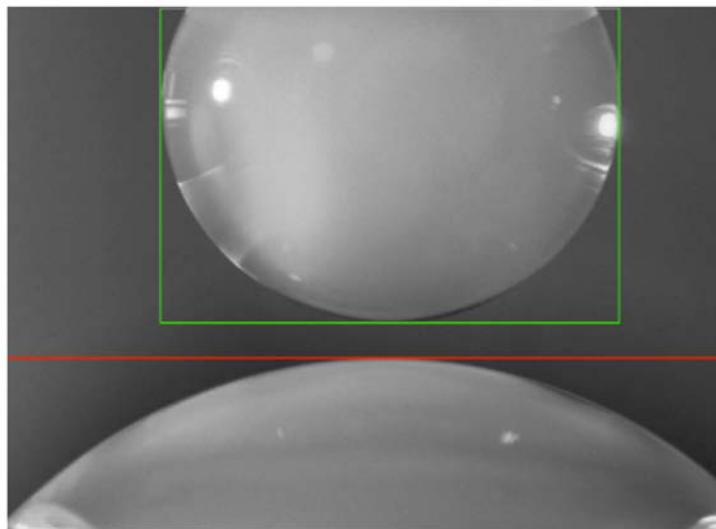

Figure 2. Two water (or oil) droplets are placed close to each other before the coalescence experiment. The square and horizontal lines are used to make sure the size of the droplets and initial distance are the same throughout different experiments. The radii of the droplets are $R_1 \sim 1.3$ mm (measured by the maximum horizontal dimension of the top droplet) and $R_2 \sim 2.8$ mm (calculated from the curvature of the semicircular bottom droplet). A typical video of coalescence measurement is shown in the supporting information.

3 Experimental Results

3.1 Interfacial tension measurement

The results of interfacial tension measurements using the pendant drop technique as a function of C5Pe/C5PeC11 concentration in xylenes are shown in Figures 3 and 4. The pH of the aqueous phase and droplet aging time were varied in this set of measurements. To improve the confidence of the results, each experiment was repeated for at least 3 times, and the interfacial tension difference between different measurements under the same condition was less than 0.2 mN/m.

In Figures 3 and 4, a decrease in interfacial tension with increasing the concentration of C5Pe (or C5PeC11) in xylenes is observed, which implies that more C5Pe (or C5PeC11) molecules can be

adsorbed at the oil-water interface at higher C5Pe (or C5PeC11) concentrations. The interfacial tension of water droplet in C5PeC11 solutions showed almost no changes upon aging from 10 minutes to 30 minutes, while the interfacial tension of the water droplet inC5Pe continues to decrease with aging from 10 mins to 30 mins, indicating further adsorption of C5Pe molecules at the interface with aging. The results of dynamic interfacial tension can be found in SI (Figure S11).
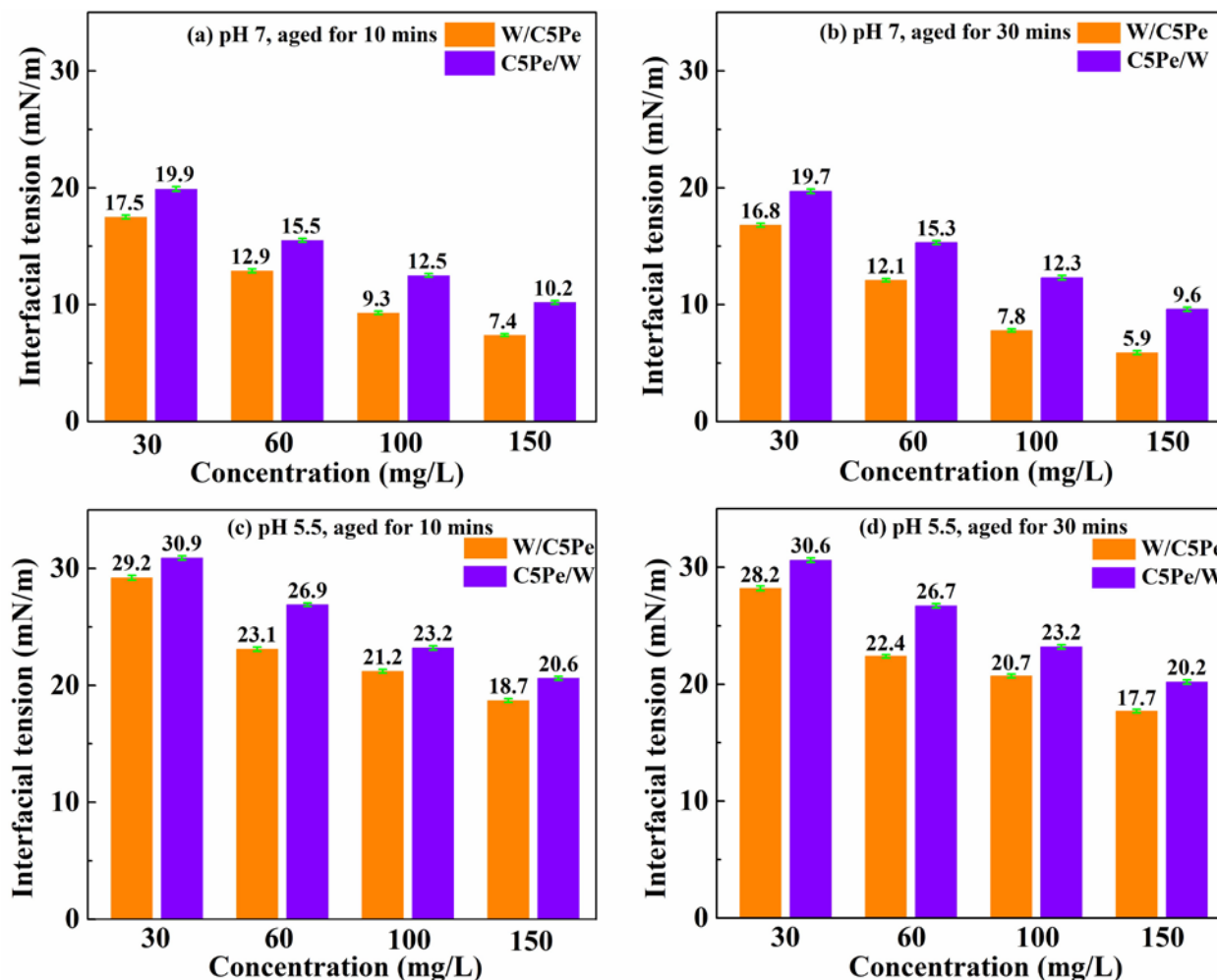

Figure 3. Interfacial tension of water−C5Pe in xylene solution as a function of C5Pe concentration: (a) aged for 10 mins and (b) aged for 30 mins with water at pH 7; and (c) aged for 10 mins and (d) aged for 30 mins with water at pH 5.5.

Figures 3 (a) and 3 (b) show that over the C5Pe concentration range in xylenes from 30 mg/L to 150 mg/L, the interfacial tension of W/O system is always lower by 1~4 mN/m than that of O/W

systems (at water pH of 7), indicating that the oil-water interface in W/O system can accommodate more C5Pe molecules and/or lead to a tighter packing of C5Pe molecules as the surface area is the same for W/O and O/W systems. Despite small, such difference between the two systems may have a significant impact on film rigidity of the two systems as will be seen from the crumpling ratio and dilatational modulus discussed in the following sections. The same trend of the interfacial tension was obtained in Figures 3 (c) and 3 (d) for the same systems but at pH 5.5 of the aqueous phase, although the interfacial tension values are much higher than that for the systems at pH 7. With the pKa of C5Pe at approximately pH 6 (Figure S1 in supporting information) [35], C5Pe is fully protonated at pH 5.5 while it is probably partially or even fully ionized at pH 7. The ionized C5Pe molecules are clearly much more interfacially active as anticipated, leading to the observed lower interfacial tension at higher pH.
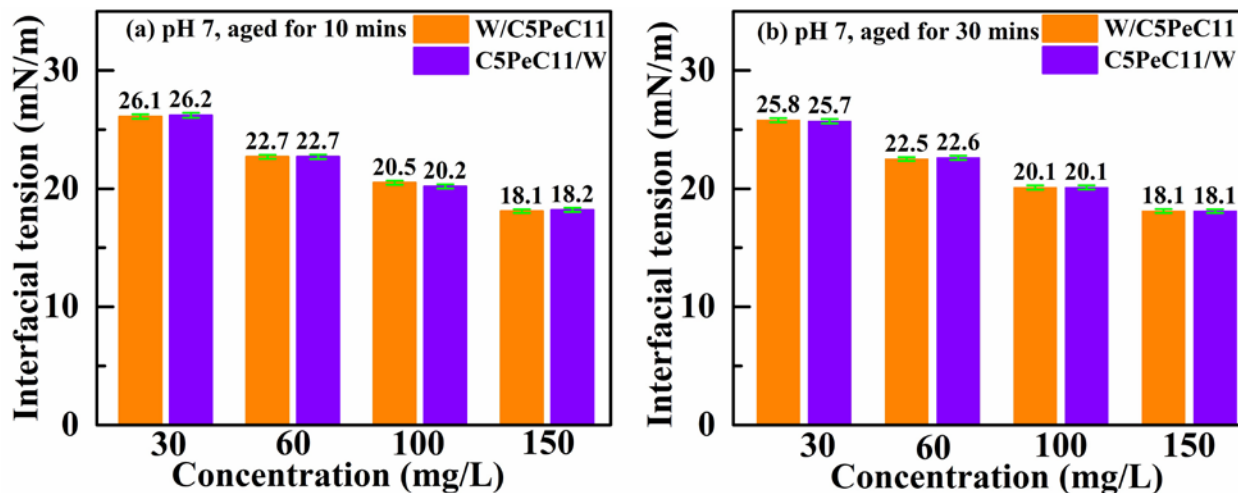

Figure 4. Interfacial tension of water−C5PeC11 in xylene solution as a function of C5PeC11 concentration: (a) aged for 10 mins and (b) aged for 30 mins with water at pH 7.

As shown in Figure 4 for C5PeC11, the interfacial tension became constant after 10 minutes of aging for both W/O and O/W systems for all the C5PeC11 concentrations examined. This result suggests that the interface in the C5PeC11 system reached equilibrium after 10 minutes, which is much faster than that in the corresponding C5Pe system. However, the xylene−water interfacial tension in the C5PeC11 system is much higher than that in the C5Pe system, indicating less surface active nature of C5PeC11 than C5Pe. More interestingly, the interfacial tensions for a given C5PeC11 concentration are the same for W/O and O/W system, which is different from the

C5Pe case. The same interfacial tension for O/W and W/O in C5PeC11 system appears to be the result of less C5PeC11 molecules at the xylene−water interface due to its better solubility in xylenes. In this case, the amount of surface active C5PeC11 molecules at the oil−water interface is essentially the same for the two systems.

The observed difference in interfacial tensions of C5Pe systems in Figure 3 obtained using the pendant drop method might be attributed to the reservoir effect, i.e., more C5Pe molecules were available for adsorption in the W/O system than in the O/W system. To check this hypothesis, interfacial tension measurements were also performed using the Du Noüy ring method for planer oil-water interface. The measured interfacial tension matched well with that measured using the W/O case (Figure 5 (a)), showing that the larger amount of C5Pe in the continuous phase indeed provides more material to attach to the interface. For C5PeC11, the interfacial tensions measured using Du Noüy ring method for planer oil-water interface matched well with that measured using O/W and W/O systems (Figure 5 (b)), as anticipated. In fact, by studying 12 different ionic and non-ionic surfactants, Miller et al. [36] reported that in solutions of highly surface active surfactants (especially at low concentration), the concentration within the drop becomes essentially lower as compared to the initial concentration due to the adsorption of the surfactant molecules at the drop surface, while surfactant depletion due to adsorption does not occur with the bubble profile (or du Nouy ring, or Wilhelmy plate method), where the volume of the studied solution is large. In addition, for surfactant of low surface activity, no difference was found as in the case of C5PeC11 in this research. Overall, the reservoir effect leads to the difference in the interfacial tensions of W/O and O/W systems.

3.2 Crumpling ratio

The contraction behavior of asphaltene films at the oil-water interface has been shown to shed the light on the role of asphaltene films in stabilizing water droplets from coalescence in emulsions [37-39]. Similarly, the adsorption of C5Pe or C5PeC11 molecules at the xylene-water interface was investigated by crumpling experiments. The arrangement of surface active species, such as asphaltenes, resins, and inorganic solids, at the liquid-liquid interface, can create a "skin-like" interfacial layer around the droplet. Upon removal of the liquid inside the droplet, the area of the skin becomes larger than the area of a Laplacian droplet of the reduced volume and the interface crumples as a result of irreversible adsorption and/or assembling of adsorbed species at

the interface. The projected area of the droplet surface when crumpling becomes visually evident divided by the projected area of the initial droplet is defined as the crumpling ratio.
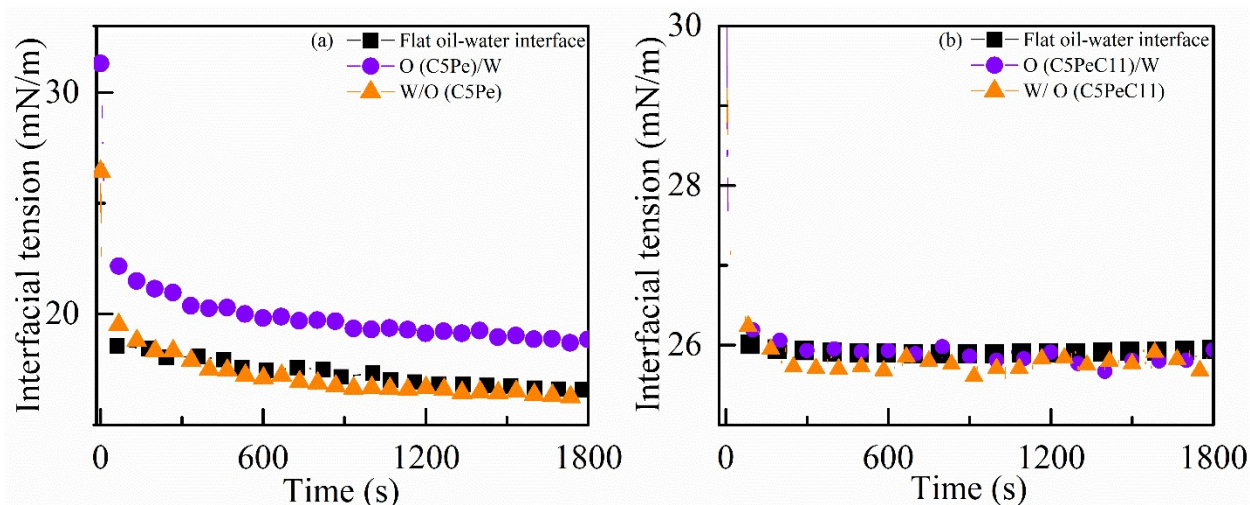

Figure 5. Comparison of interfacial tensions measured using pendant drop method and Du Noüy ring method: (a) for water−C5Pe in xylene solution and (b) for water−C5PeC11 in xylenes solution, both aged for up to 30 mins. Note: V_{water}:V_{oil} = 4:3 for Du Noüy ring method; V_{water}:V_{oil} =1:300 in W/O case and 300:1 in O/W case for pendant drop method.

The results of volume contraction experiments are summarized in Figure 6. Each data point in Figure 6 is an average of at least three independent measurements and the error bars represent the standard deviation of all the measurements. Only crumpling ratio of C5Pe−water system is shown here as no crumpling was detected for C5PeC11−water system up to 150 mg/L C5PeC11 concentration for both W/O and O/W systems. The absence of the crumpling of water−C5PeC11 in xylene solution interface indicates the absence of C5PeC11 skins at xylene−water interface, most likely as a result of more reversible nature of C5PeC11 adsorption and/or minimal molecular association between C5PeC11 molecules at the interface due to steric hindrance of longer aliphatic tails [40] and its high solubility in xylenes. Compared with C5PeC11, less bulky hydrophobic tails of C5Pe molecules which has weaker steric repulsion in xylene allows stronger association with each other by attractive forces such as π-π stacking, forming an inter-linked crumpling C5Pe interfacial film [35].
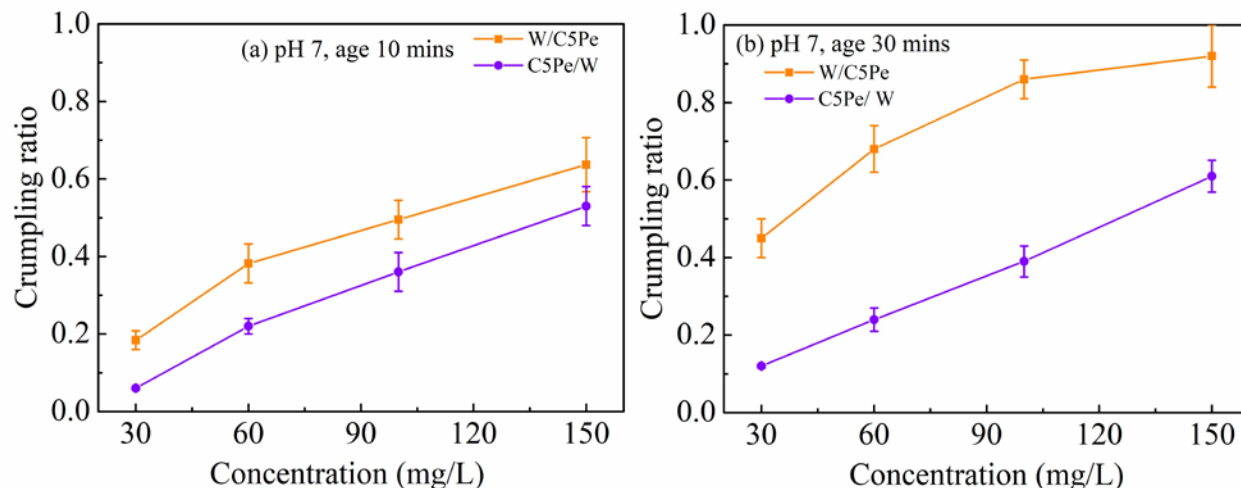
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Figure 6. Crumpling ratio of water−C5Pe in xylene systems as a function of C5Pe concentration with the droplets of pH=7 being aged for 10 mins (a) and 30 mins (b).

It is interesting to note a much higher crumpling ratio for the W/O system than that for the O/W system (Figure 6), despite the same chemistry of both systems. Such a significant difference in the crumpling ratio of the two systems is most likely linked to the amount and irreversible nature of the adsorption that lead to different packing patterns of C5Pe molecules at the oil-water interfaces. According to interfacial tension results, more C5Pe molecules are adsorbed at the oil-water interface for W/O systems than for O/W systems due to the reservoir effect, leading to tighter packing of the C5Pe molecules at the interface. The tighter packing resulted in a stronger association of C5Pe molecules of the W/O systems. As the film is contracted during the retraction of the water droplets as in the W/O system, the bulky hydrophobic tails of C5Pe molecules are more easily jammed up (squeezed), leading to crumpling at relatively small volume reduction of the droplet (i.e., large crumpling ratio) due to the irreversible nature of the interfacial film formation. For the O/W system, the relatively loose packing allows more contraction of the droplets before the steric repulsion among the hydrophobic tails in xylene comes into play, leading to a smaller crumpling ratio. Such differences in crumpling ratio also confirm the formation of interfacial layers of elastic nature as illustrated by the results of interfacial rheology shown in Figure 7. It is not surprising to see higher crumpling ratio at higher C5Pe concentrations in xylene as more C5Pe molecules are expected to adsorb at the xylene-water interface as shown in Figure 3. When much less reversibly adsorbed molecules were at the O/W interface, which is the case for C5PeC11, crumpling would not occur. Overall, the

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difference in the C5Pe adsorption amount at the oil−water interface plays a big role in the crumpling of the interface.

In addition, an obvious increase in the crumpling ratio was observed with increasing aging from 10 mins to 30 mins for the W/O system, while the crumpling ratio increased slightly for the O/W system. This trend corresponds well with the change in interfacial tension as shown in Figure 3: the interfacial tension of O/W system almost reach equilibrium after 10 minutes aging whereas the interfacial tension of W/O systems continues to decrease. Therefore, the more adsorbed C5Pe molecules at the interface for longer aging leads to the higher crumpling ratio.

3.3 Dilatational rheology

Dilatational rheology is an important physicochemical property of oil-water interfaces, in particular for curve systems as encountered in the current study. By inducing a change in the interfacial area while measuring the interfacial tension, dilatational measurement provides important information on the dilatational viscoelasticity (viscoelastic modulus) of the interface, which arises in response to surface expansions and compressions [19].

Similar to crumpling ratio, only dilatational rheology of C5Pe system was measurable and no viscoelasticity was detected for C5PeC11 system up to a C5PeC11 concentration of 150 mg/L. The measured viscoelasticity of the W/O and O/W systems of C5Pe is shown in Figure 7. Each experiment was repeated for 3 times which showed the same trend. It is interesting to note a rapid increase in viscoelasticity of the interfacial films for W/O system, followed by a gradual increase. In contrast, only a much slower and gradual increase in the viscoelasticity of the interfacial films for O/W system was observed, indicating a significant difference of interfacial rheological properties in O/W and W/O emulsion systems. The observed rapid increase in interfacial rheology would correspond to the increased adsorption of C5Pe molecules at the xylene-water interface to build stronger interfacial layers, while the gradual increase comes most likely from the molecular rearrangement with the further addition of a small amount of C5Pe molecules to the interface. For the W/O systems, the viscoelasticity was observed at relatively small C5Pe concentrations (100 mg/L) and increased with increasing C5Pe concentration to 150 mg/L. For O/W system, no viscoelasticity is measured for C5Pe concentrations less than 300 mg/L. Even for 300 mg/L C5Pe in xylene, the measured viscoelasticity of the interfacial film is

still lower than that of 100 mg/L C5Pe in xylene for the W/O system. It can be concluded that W/O system has higher viscoelasticity of the interfacial film compared with O/W system, which is consistent with the crumpling ratio result. The dilatational result further confirmed tighter packing and stronger association of C5Pe molecules at the interface for W/O system than for O/W systems, most likely as a result of the increased amount of C5Pe molecules at the corresponding oil−water interface.
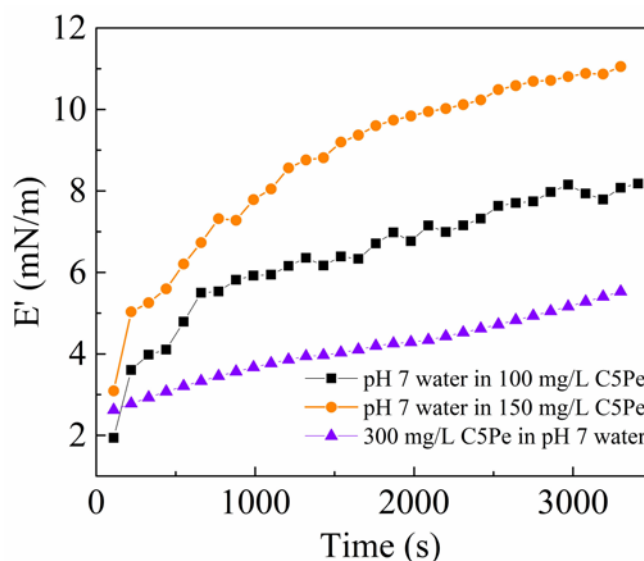

Figure 7. Dilatational modulus of water−C5Pe in xylene solution system as a function of measurement time.

3.4 Coalescence time

The coalescence times between the droplets were measured at different concentrations of C5Pe or C5PeC11 and the results are shown in Figure 8. Each data point in this figure is an average of 5 measurements with the error bars representing the standard deviation of the measurements. In general, the coalescence time increases with increasing the concentration for both polyaromatic compounds. However, the droplets in C5PeC11−water system can coalesce much easier than in C5Pe−water system as shown by a shorter coalescence time for both W/O and O/W emulsion systems. The finding correlates well with the observed absence of drop crumpling and low viscoelasticity of C5PeC11−water system.

Interestingly, the coalescence of water droplets in the W/O emulsion system is always faster than that of oil droplets in the O/W emulsion system for C5PeC11−water system. The absence of

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electrostatic repulsion of water droplets in oil along with favorable migration of C5PeC11 molecules on water droplets into the oil phase than oil droplets into water seems responsible for such difference.
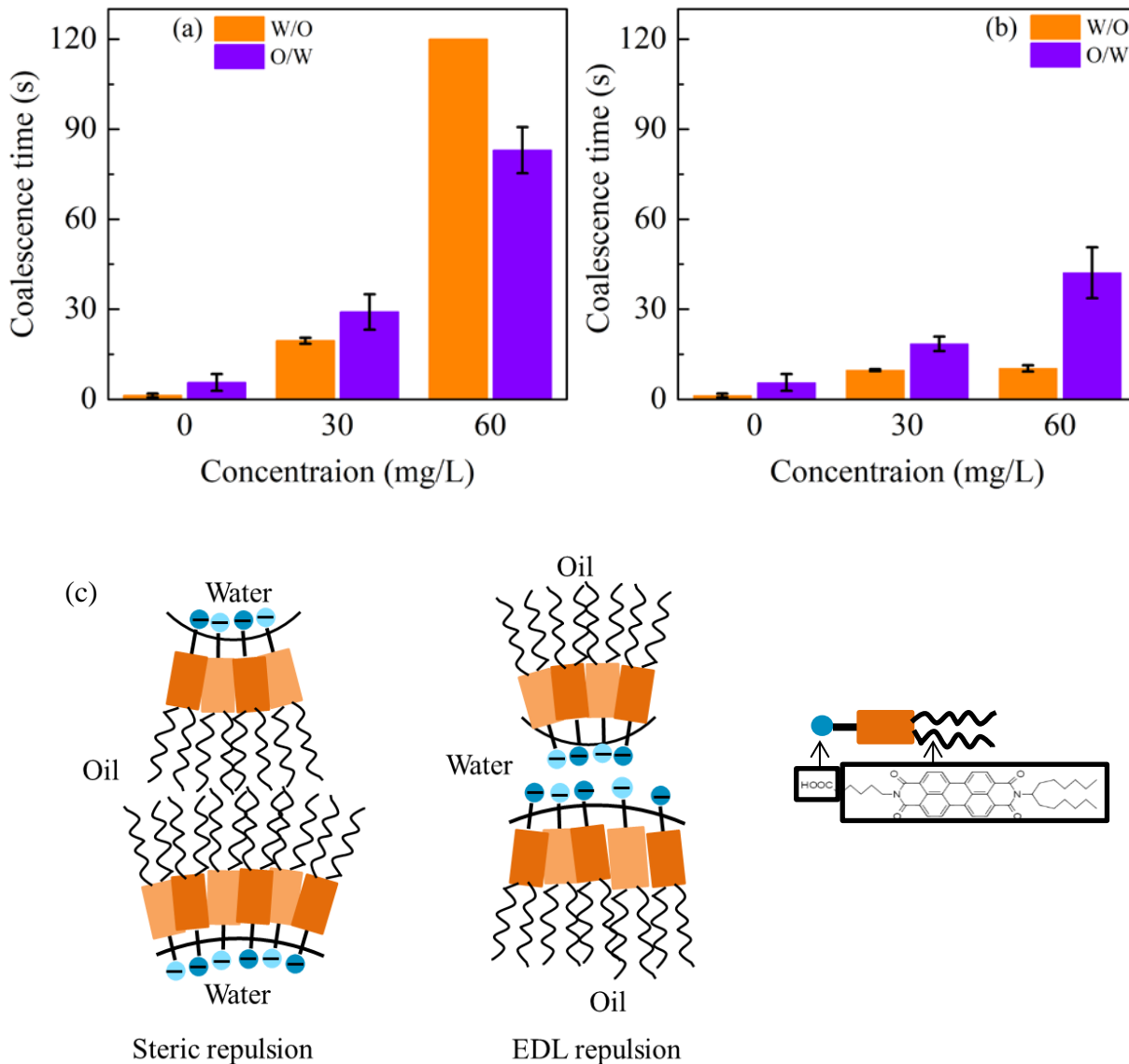

Figure 8. Experimental observations of coalescence times for (a) C5Pe, (b) C5PeC11 of various concentrations in the W/O and O/W systems. The viscosity of oil and water was 0.8 and 1 mPa.s, respectively, and (c) schematic figures showing steric repulsion for the W/O system and EDL repulsion for the O/W system respectively (slightly colored molecules are used to demonstrate the stacking of poly-aromatic cores).

For C5Pe−water system, the advantage of W/O system was diminished with the increasing concentration of C5Pe (i.e. 60 mg/L), as shown by the longer coalescence time of water drops (W/O system) than the oil drops (O/W system), when the steric repulsion (see supporting information) as well as film rigidity and viscoelasticity became so significant (as indicated by the crumpling ratio (Figure 6) and dilatational rheology results (Figure 7) to hinder the coalescence. Specifically, coalescence time for O/W system at 60 mg/L C5Pe concentration was around 80 s, while for W/O case coalescence did not occur during the experimental time of 120 s. As the measurement limit for ITFDA is 120s, systems with coalescence time higher than 120 s are considered stable. It should be noted that at higher concentration (i.e. 100 mg/L and 150 mg/L), the coalescence times for both W/O and O/W systems are all over 120 s. Theoretically, the coalescence times are related to the time it takes for the thin liquid film between the drops to drain to a critical thickness where surface forces become relevant for the film to thin and rupture. The disjoining pressure (Π), which generally arises from electric double layer (EDL) interaction, van der Waals (vdW) interaction, steric interaction, hydrophobic (HB) interaction, and so on [41-43], is system dependent and is responsible for the liquid film rupture when the film is sufficiently thin to make an attractive disjoining pressure. It should be noted that the forces contributing to the disjoining pressure are not exactly the same in the two systems. In the O/W system, the electrostatic double layer forces (Figure 8 (c)) and steric repulsion that stabilize the oil droplets are overcome by the attractive vdW forces to realize the rupture of the thin liquid film. The hydrophobic attraction between oil droplets in the current systems is negligible due to the orientation of polar groups facing the aqueous phase to impart hydrophilic nature of the oil droplet surface. Therefore, vdW force is considered to be the driving force to induce the film rupture between the oil droplets. On the other hand, steric interaction is the main repulsive force in the W/O system, attributed to the adsorption of C5Pe molecules (Figure 8 (c)). This steric force originated from the adsorbed C5Pe or C5PeC11 molecules at the xylene-water interfaces should be much weaker in the O/W system due to the orientation and compaction of polyaromatic molecules at the interface [44]. Similar to the O/W system, the attractive vdW forces in W/O systems are responsible for the film rupture at low concentrations. At high concentrations, the larger steric repulsive force due to the formation of a steric layer from stacking of molecules at the interface would override the attractive surface forces and prevent the droplets from coalescence. The drainage phenomena are modeled by the Stokes-Reynolds-

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Young-Laplace (SRYL) theory that has been proven to be accurate for systems involving bubbles, drops and deformable surfaces in general [45, 46]. The theoretically modeling results for the thin film rupture (see Theoretical Modelling in supporting information) showed a similar trend as the coalescence time experimental results, which further confirmed the difference in coalescence time for W/O and O/W systems.

By investigating O/W and W/O configurations of the same chemistry, it became evident that the different adsorption amount due to the reservoir effect that affects the arrangement of molecules at the interface is important and has effects on measurements such as crumpling ratio, dilatational rheology and coalescence time that could have not been observed using flat oil-water interfaces. In general, though similar trends are observed in most situations, the O/W configuration does not quantitatively represent the W/O systems in terms of crumpling ratio, dilatational rheology and coalescence time. In particular, due to different film drainage process as well as the different interfacial film rigidity and viscoelasticity, coalescence time of the W/O system cannot be represented by the reversed system.

4 Conclusions

A systematic study of O/W and W/O systems was performed to understand their difference using asphaltene model compounds. Interfacial tension measurements indicated that the used asphaltene model compounds are very interfacially active and the adsorption amounts of C5Pe molecules at the oil-water interface for W/O and O/W systems are different due to the reservoir effect when oil is used as the continuous phase. The measurements of the crumpling ratio of the W/O system showed the presence of skin like structures around the drop, which became more pronounced with increased concentration. On the other hand, the reversed O/W system showed less pronounced crumpling, which was attributed to less adsorption amount and therefore loose packing of the C5Pe molecules at the interface. A similar trend was found for interfacial dilatational rheology measurement, further confirming tighter and stronger molecular packing at the oil-water interface of W/O system.

Regarding the coalescence time, a longer coalescence time of oil drops in water than that of water drops in water for both C5PeC11−water and C5Pe−water systems at low C5Pe concentration is observed. The role of film rigidity, film viscoelasticity, and steric repulsion on

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the coalescence time is especially significant for the high concentration of C5Pe model compound (i.e. 60 mg/L), leading to longer coalescence time of water drops in oil for C5Pe/water system.

In summary, our results are consistent with previous literature about the accepted understanding that asphaltenes cause stabilization of the emulsion by creating a 'skin' around the water drops, which prevents coalescence. We have shown that many characteristics change for the reversed W/O system. Results obtained in this work indicate that the investigation of the stability of water in oil emulsions by using oil in water emulsions that have much better visualization features can only give qualitative trends.

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Competing Interests Statement

The authors declare no competing interest.

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