

# Adsorption of Asphaltenes at Model Oil/Brine Interface: Influence of Solvent Polarity

Wei Wang, Fujun Sheng, Guifang Ou, Yansong Zhao, and Guangyu Sun\*

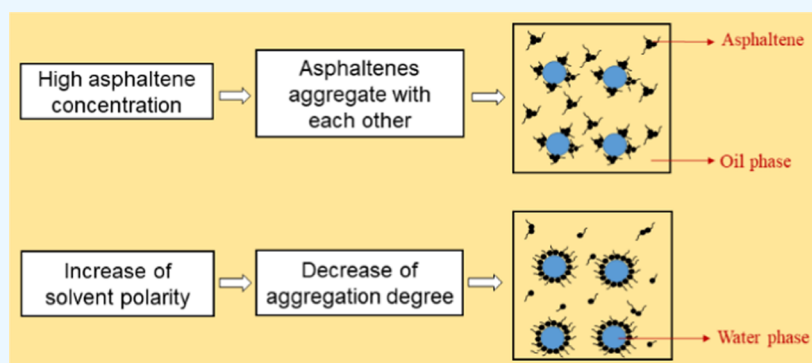
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**ABSTRACT:** With the exploitation of heavy oil worldwide, the influence of asphaltene aggregation in the oil phase on the stability of crude oil emulsion has been paid more and more attention. Under this background, the effects of solvent polarity on model oil/brine water interfacial properties and emulsion stability are investigated in this study. It is demonstrated that there is a critical asphaltene concentration for the formation of a stable emulsion. This critical concentration is then found to increase from 80 to 500 ppm with the mixing ratio of methylnaphthalene to *n*-decane changed from 2:3 to 7:3. The dynamic light scattering experiment shows that the average aggregate size increases abruptly from 132.8 to 261.1 nm at 2:3 mixing ratio of methylnaphthalene to *n*-decane once the asphaltenes are added to above the critical concentration. Accordingly, the diffusion coefficient of the asphaltenes decreases sharply from  $4.36 \times 10^{-12}$  to  $5.68 \times 10^{-13}$  m<sup>2</sup>/s. Similar conclusions are also found for the other mixing ratios of 1:1, 3:2, and 7:3. Besides, the aggregation degree of asphaltenes weakens, and the diffusion coefficient enlarges at the same asphaltene concentration with the enhancement of the solvent polarity. Further, the interfacial experiments manifest that the equilibrium interfacial dilation modulus decreases from 38.42 to 23.65 mN/m with the mixing ratio of methylnaphthalene to *n*-decane increased from 2:3 to 7:3. It can thus be inferred that the structural strength of the interfacial film decreases with the enhancement of the solvent polarity.

## 1. INTRODUCTION

In the process of crude oil production, water-in-oil emulsion is inevitably formed due to the shearing caused by valves and pumps.<sup>1</sup> The formation of emulsion, on the one hand, increases the frictional resistance during pipeline transportation, thus resulting in the increase of transportation costs.<sup>2,3</sup> On the other hand, it will bring a great number of safety hazards inevitably, such as the corrosion of pipeline and process equipment.<sup>4–8</sup> Therefore, the factors influencing emulsion stability and the technologies facilitating demulsification are receiving more attention. Asphaltene is one of the main polar components in crude oil, which is soluble in toluene but insoluble in small molecules of normal alkanes.<sup>9,10</sup> Due to its amphiphilic attribute, asphaltene can adsorb at the oil/water interface spontaneously, stabilizing the emulsion with its unique molecular structure.<sup>11–14</sup> In view of this, the effects of asphaltene on oil–

water interfacial properties and further on emulsion stability have been concerned widely all over the world.

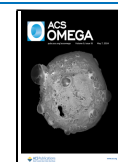
Existing literature shows that a viscoelastic interfacial film will be formed to hinder droplet coalescence when asphaltenes are adsorbed at water–oil interfaces.<sup>15–17</sup> The detailed configuration of asphaltenes adsorbed at the oil–water interface has been intensively explored with different molecular simulation methods such as all-atom molecular dynamics, coarse grain dissipative particle dynamics, and coarse grain molecular

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dynamics. However, no consensus has been reached so far about the structure and orientation of asphaltenes at the interface. Some simulation results show that the asphaltene molecules adsorb at the interface as monomers,<sup>18</sup> while others manifest that they migrate to the interface in the form of nanoaggregates.<sup>19,20</sup> As for the orientations at the interface, there are studies indicating a parallel adsorption structure due to the interattraction between the polycyclic aromatic plane and the water molecules,<sup>21</sup> but the perpendicular configuration is also acquired by many researchers.<sup>22,23</sup> de Oliveira et al. find that the asphaltene molecules preferentially parallel to the interface at low concentrations, but they become tilted to the interface at higher concentrations.<sup>19</sup> Ruiz-Morales and Mullins find that the orientation is related to the peripheral moieties of the asphaltene molecule.<sup>18</sup> Lv et al.<sup>9</sup> prove that asphaltene molecules tend to orientate diversely at the interface so as to reduce the interactions that prevent aggregation. Moreover, the polar group of the asphaltene molecules is surrounded by hydrogen bond networks that act as anchors to maintain the asphaltenes at the interface. It makes the asphaltenes aggregate stably at the interface, playing an emulsion stabilizing role. Singh et al.<sup>24</sup> probed how molecular structure and heteroatom type affect the way asphaltenes behave structurally in the oil–water system. The results show that both the orientation of asphaltene molecules at the interface and the relative position and angle of asphaltenes with the interfacial film vary with different molecular structures.

It is now common knowledge that the size of asphaltene aggregates increases with the asphaltene concentration in the oil phase. However, as Alvarado et al. put forward in their latest work, there is still no consensus regarding the role of asphaltenes at the oil–water interface.<sup>25</sup> Scholars are divided over the particle size of asphaltene aggregates at the interface and the effect of the solvent aromaticity. According to Rane et al.<sup>26</sup> and Mohammadi et al.,<sup>27</sup> cross-linking does not occur at the interface and only asphaltene monomers are adsorbed, so the bulk nanoaggregates do not contribute to the adsorption process. This is not in line with the opinions of Alvarado et al.<sup>25</sup> As for the effect of solvent aromaticity, Mohammadi et al. hold that a higher concentration of *n*-heptane in solvent results in faster and more asphaltene adsorption at the oil–water interface and thus promotes emulsification.<sup>27</sup> By contrast, the experimental results of Al-Sahhaf et al. indicate that a very tight model oil emulsion can be formed at a threshold value of 30% toluene, and less stable emulsions are formed at lower toluene content (below 20%) or higher toluene content (above 40%).<sup>28</sup> Similarly, McLean and Kilpatrick prove that the emulsions are the most stable when the crude medium is 30–40% toluene.<sup>29</sup> More differently, Liu et al. demonstrate that asphaltenes tend to form larger clusters at higher content of toluene.<sup>30</sup> There are different results, even with regard to the size distribution of asphaltene aggregates. According to Duran et al., the volume mean diameters of asphaltenes are tens to hundreds of micrometers, depending upon the *n*-heptane content.<sup>31</sup> However, the average size of the asphaltene aggregates is only about 0.5  $\mu\text{m}$  based on the work of Ghorbani et al.<sup>32</sup>

Rane et al.<sup>33</sup> further explored the adsorption mechanism of asphaltenes and deemed that the adsorption at the interface is controlled by diffusion. The asphaltenes are adsorbed at the interface as monomers in a low concentration range. Once the concentration becomes higher than the critical aggregation concentration, asphaltenes are adsorbed as aggregates. Fan et al.<sup>34</sup> found that the variation trend of the overall stability of the

emulsion is completely consistent with that of the interfacial shear elastic modulus. That is, the higher the interfacial shear elastic modulus, the stronger the stability of the emulsion. Nguyen et al.<sup>35</sup> further discovered that interfacial compressibility is also an important parameter to characterize the stability of emulsion. When the interfacial film is compressed, the asphaltene aggregates adsorbed on it are squeezed closer to each other. The aggregates filled the entire interface to form a harder coalescence-resisting film, thus showing the ability to stabilize the emulsion.

Given the above, there are still many unclear conclusions to be clarified about the aggregation behavior of asphaltenes, their adsorption at the oil–water interface, and their influence factors. This work aims to explore these unanswered questions. In this study, the interfacial adsorption kinetics of the asphaltenes different in aggregation states is systematically investigated. Further, the mechanism for the initial stage of adsorption is characterized by the Gibbs–Duhem equation.<sup>27</sup> Besides, the aggregation state of the asphaltenes in the model oils with different polarities is validated by the dynamic light scattering (DLS) method. Finally, the influence of the asphaltene aggregation state on the macroscopic stability of the water-in-model crude oil emulsion is investigated with interface experiment and bottle test.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** The asphaltenes utilized in this study were extracted from heavy oil recovered from the Tahe oilfield of China. The basic physical properties of the oil sample are listed in Table 1. 1-methylnaphthalene, *n*-heptane, and *n*-decane were

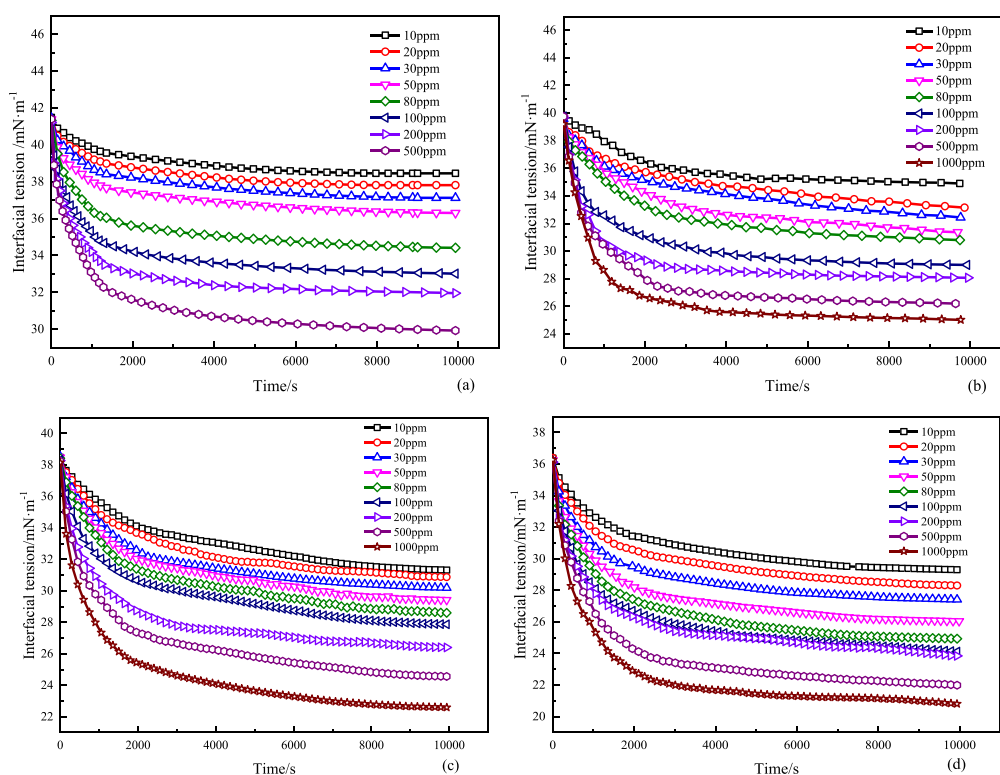
**Table 1. Compositions and Basic Physical Properties of the Tahe Heavy Oil**

property	value
saturates	29.6%
aromatics	34.5%
resins	10.8%
asphaltenes	25.1%
wax content	<0.1%
density at 20 °C	0.972 g·cm <sup>-3</sup>
viscosity at 50 °C	5484 mPa·s
API density	14.1

purchased from Macklin Chemical Reagent Co., Ltd. in China, whose purities are 96, 98, and 98%, respectively. Sodium chloride was purchased from Sinopharm Group Chemical Reagents Co., Ltd. in China.

**2.2. Asphaltene Extraction.** First, *n*-heptane was mixed with Tahe heavy oil at a ratio of 1:40 at room temperature. After a homogeneous mixture was formed by magnetic stirring, the mixture was centrifuged for 20 min with a rotational speed of 8000 rpm. Then, the precipitate obtained by centrifugation was placed in a vacuum drying oven to dry for 24 h. Finally, the granular asphaltenes were obtained. According to the weighing result, the yield of extracted asphaltenes accounts for about 23.9 wt % of the total crude oil.

**2.3. Preparation of Model Oil and Brine.** First, the asphaltenes were dissolved in 1-methylnaphthalene homogeneously with ultrasonic treatment so as to prepare a stock solution with 5000 ppm of asphaltene concentration. Then, a certain amount of stock solution was taken out to be diluted by 1-methylnaphthalene and *n*-decane, respectively, until the



**Figure 1.** Dynamic interfacial tension at different asphaltene concentrations (10 to 1000 ppm) in solvents with different polarities at 30 °C: (a) methylnaphthalene: *n*-decane = 2:3, (b) methylnaphthalene: *n*-decane = 1:1, (c) methylnaphthalene: *n*-decane = 3:2, and (d) methylnaphthalene: *n*-decane = 7:3.

asphaltene concentrations were 10, 20, 30, 50, 80, 100, 200, 500, and 1000 ppm and the mix ratios of 1-methylnaphthalene to *n*-decane were 2:3, 1:1, 3:2, and 7:3, respectively. Finally, the prepared asphaltene model oils were treated ultrasonically for an additional 1 min. Meantime, the sodium chloride solution (0.05 mol/L) was prepared as a representative of brine water in the produced fluid.

**2.4. Determination of Particle Size Distribution of Asphaltene Aggregates.** A particle size analyzer (Zetasizer Nano ZS-90, Malvern Panalytical Ltd., U.K.) was used to measure the asphaltene particle size. The average value of three groups of parallel experiments under each condition was taken.

**2.5. Measurement of Interfacial Tension and Dilational Viscoelasticity.** An interfacial tensiometer (Tracker H, Teclis, France) that adopts the pendant drop method was used for the measurement of interfacial tension and dilational viscoelasticity. The droplet contour is continuously extracted for real-time analysis. The interfacial tension is calculated according to the Young–Laplace equation with the droplet shape identified. The interfacial dilational viscoelasticity is calculated according to eq 1. A spherical axisymmetric drop with a volume of 5  $\mu\text{L}$  was formed in a thermostated cell filled with brine. The droplet contour can then be captured in real time, and the interfacial tension could be obtained accordingly.

The acquisition of the interfacial dilational viscoelasticity was conducted as follows. After the drop was formed, the model oil–brine interface was disturbed sinusoidally by controlling the motor. The oscillation frequency is 0.1 Hz, and the amplitude is 8% of the total drop area.

$$\varepsilon = \frac{d\gamma}{d \ln A} \quad (1)$$

where  $\varepsilon$  is the interfacial dilational modulus,  $\gamma$  is the interfacial tension, and  $A$  is the interfacial area.

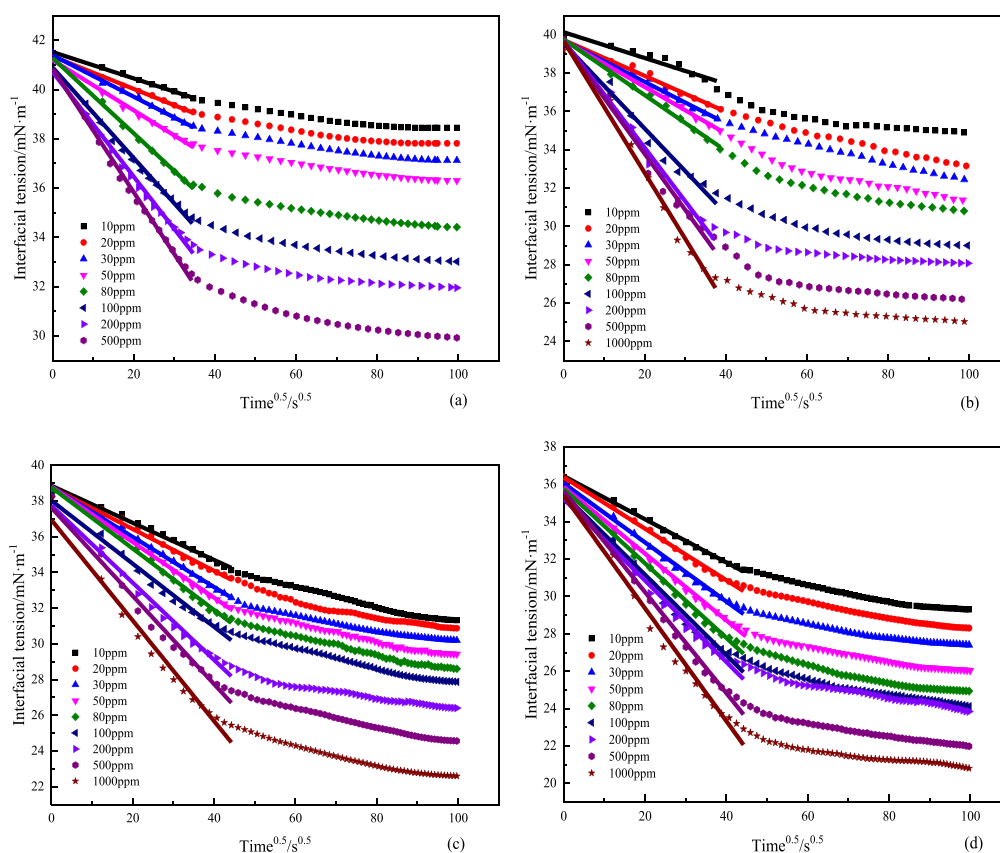
**2.6. Preparation and Stability Measurement of Model Oil Emulsion.** The asphaltene model oil and model brine water with the volume ratio of 7:3 were heated in advance for 20 min at 50 and 70 °C, respectively. Then, a high-speed homogenizer made in China (AD500S–H 12G) was used to stir the oil–water mixture (40 mL) for 20 min at the stirring rate of 18,000 rpm. Finally, the model emulsion was transferred to a 50 mL colorimetric tube and placed in a water bath preset at the designated temperature. According to microscopic observation, the model oil emulsion is of the water-in-oil (W/O) type. The evolution of the oil separation rate of the W/O emulsion with time is used to evaluate the emulsion stability. The lower the oil separation rate at the same placing time, the higher the stability of the emulsion. The calculation of the oil separation rate at a different time is shown in eq 2.

$$f_t = \frac{V_t}{V_0} \times 100\% \quad (2)$$

where  $f_t$  is the oil separation rate at a different time,  $V_0$  is the total original oil content in the emulsion, and  $V_t$  is the volume of the oil separated from the colorimetric tube at any time  $t$ .

### 3. RESULTS AND DISCUSSION

**3.1. Interfacial Adsorption Kinetics of Asphaltenes in Solvents with Different Polarities.** The solvents with different polarities were obtained by changing the mixing ratio of methylnaphthalene and *n*-decane in the model oil. In this study, the asphaltene concentrations of 10, 20, 30, 50, 80, 100, 200, 500, and 1000 ppm were prepared, and meanwhile the mixing ratios of methylnaphthalene to *n*-decane were set to be



**Figure 2.** Relationship between dynamic interfacial tension and  $t^{0.5}$  at different asphaltene concentrations (10 to 1000 ppm) in solvents with different polarities at 30 °C: (a) methylnaphthalene: *n*-decane = 2:3, (b) methylnaphthalene: *n*-decane = 1:1, (c) methylnaphthalene: *n*-decane = 3:2, and (d) methylnaphthalene: *n*-decane = 7:3.

**Table 2.** Slope of the Fitted Curves in the Rapid Diffusion Stage

asphaltene concentration/ppm	slope value ( $\text{mN}\cdot\text{m}^{-1}\cdot\text{s}^{-1/2}$ )			
	in solvent with methylnaphthalene: <i>n</i> -decane = 2:3	in solvent with methylnaphthalene: <i>n</i> -decane = 1:1	in solvent with methylnaphthalene: <i>n</i> -decane = 3:2	in solvent with methylnaphthalene: <i>n</i> -decane = 7:3
10	-0.05360	-0.06749	-0.10393	-0.11551
20	-0.06606	-0.09373	-0.11710	-0.13768
30	-0.08428	-0.10793	-0.14040	-0.15812
50	-0.10199	-0.12184	-0.15558	-0.17838
80	-0.15289	-0.14541	-0.17173	-0.19956
100	-0.18397	-0.22257	-0.17677	-0.21511
200	-0.21258	-0.27953	-0.28613	-0.24808
500	-0.25089	-0.29252	-0.30694	-0.31022
1000		-0.34445	-0.34767	-0.35173

2:3, 1:1, 3:2, and 7:3, respectively. Then, the dynamic interfacial tension between the model oil and brine was measured at the above different mixing ratios and asphaltene concentrations. The experimental results are shown in Figure 1. It is demonstrated that the dynamic interfacial tension decreases with the increase of asphaltene concentration in all four solvents, which demonstrates that asphaltene is an interfacial active substance no matter how the polarity of the solvent changes. Moreover, the interfacial tension decreases at a higher rate at the initial moment, and then, the rate of decline gradually decreases, approaching the equilibrium state. This indicates a rapid diffusion-controlled adsorption of asphaltenes from the bulk to the interface in the initial stage of adsorption.

Based on the existing theoretical research, the adsorption kinetics controlled by diffusion mechanism can be described by the Gibbs–Duhem equation,<sup>36</sup> as shown in eq 3. It demonstrates that the interfacial tension is linearly related to  $t^{0.5}$  at the initial stage of adsorption.

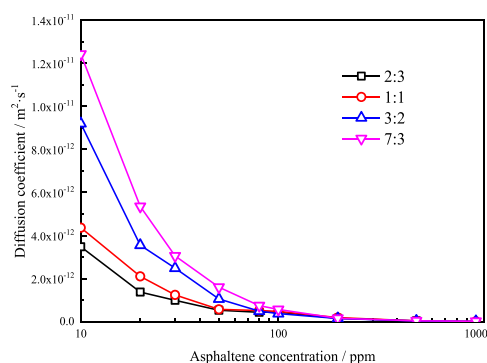
$$\gamma(t) = \gamma_0 - 2RTC\sqrt{\frac{Dt}{\pi}} \quad (3)$$

where  $\gamma$  is the dynamic interfacial tension at any time  $t$ ,  $\gamma_0$  is the interfacial tension at the initial time, i.e., the interfacial tension without asphaltene adsorption,  $R$  is the universal gas constant,  $T$  is the test temperature,  $C$  is the volume concentration of the adsorbed material, and  $D$  is the diffusion coefficient.



Therefore, the relationship between the dynamic interfacial tension and  $t^{0.5}$  at different asphaltene concentrations is established in different solvents at 30 °C, as shown in Figure 2. The results show that the interfacial tension at the initial stage of adsorption is linearly related to  $t^{0.5}$  indeed. As the proportion of methyl-naphthalene in the solvent increases, the polarity of the solvent is strengthened, thus prolonging the linear relationship between the interfacial tension and  $t^{0.5}$ . That is, the time of the rapid diffusion-controlled stage is prolonged with an increase of solvent polarity. After linear fitting of the curves in the rapid diffusion stage, it is found that the absolute value of the slopes increases with the increase of the asphaltene concentration. Meanwhile, it can be observed from Table 2 that the absolute slope value of the IFT with time is increased with the increasing proportion of methyl-naphthalene in the solvent. That is to say, the IFT decreases faster with an increase in the solvent aromaticity. This may be related to the polarity of the adsorbed asphaltenes at the interface. In the study of Yarranton et al.,<sup>37</sup> it was found that the interfacial activity of asphaltene molecules is inversely related to solubility. Hence, the polarity of the adsorbed asphaltenes at the interface is stronger when the oil phase is more aromatic. Moreover, Fossen et al. also discovered that the interfacial activity of asphaltenes is related to their solubility in the bulk phase.<sup>38</sup> This is probably the reason the IFT decreases when the polarity of the solvent increases. The calculated slope values are listed in Table 2.

Finally, the diffusion coefficients of asphaltenes in the model oils are calculated according to eq 3 in which the dynamic interfacial tension at any time can be obtained in Figure 1. The calculation results are shown in Figure 3. The diffusion



**Figure 3.** Diffusion coefficients of asphaltenes with different concentrations in the bulk phase to the interface in the four solvents with different polarities at 30 °C.

coefficient values are in line with the previous studies.<sup>11,39</sup> The reported equilibrium diffusion coefficient of asphaltenes ranges from  $1 \times 10^{-13}$  to  $5 \times 10^{-13}$  m<sup>2</sup>/s. It can be seen that the diffusion coefficient of asphaltenes in the model oil enlarges with the increasing proportion of methyl-naphthalene in the solvent, demonstrating that the aggregation degree of the asphaltenes weakens with an increase of solvent polarity. It is worth noting that the diffusion coefficient undergoes an abrupt change between the asphaltene concentration of 50–80, 80–100, 100–200, and 200–500 ppm, respectively, when the mixing ratio of methyl-naphthalene to *n*-decane is 2:3, 1:1, 3:2, and 7:3. This is probably caused by the formation of larger asphaltene aggregates once the asphaltene concentration exceeds the critical value. Moreover, the aggregation degree of asphaltenes in the solvent weakens with an increasing proportion of methyl-naphthalene.

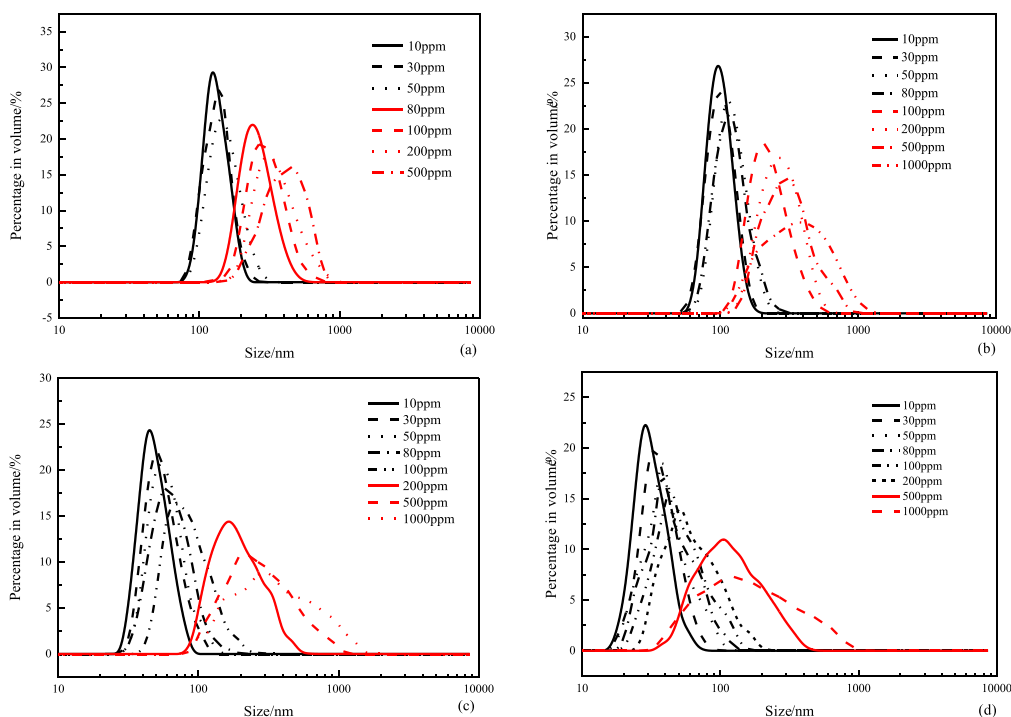
On the other hand, the higher the asphaltene concentration, the greater the aggregation degree. According to eq 3,  $D^{0.5}$  is positively correlated with the absolute slope value and inversely proportional to the asphaltene concentration when the asphaltene concentration is lower than the critical value. The relative variation of the asphaltene concentration is greater than that of the slope value; therefore, the diffusion coefficient decreases with the increase of asphaltene concentration. Once the asphaltene concentration increases above the critical value, more and more asphaltenes will aggregate with each other, forming larger asphaltene aggregates that are harder to adsorb at the interface. Therefore, the adsorption kinetics of asphaltenes at the interface are no longer solely controlled by the diffusion mechanism, resulting in the slow reduction of the diffusion coefficient.

### 3.2. Validation of the Aggregation State of Asphaltenes in Model Oils with Different Polarities.

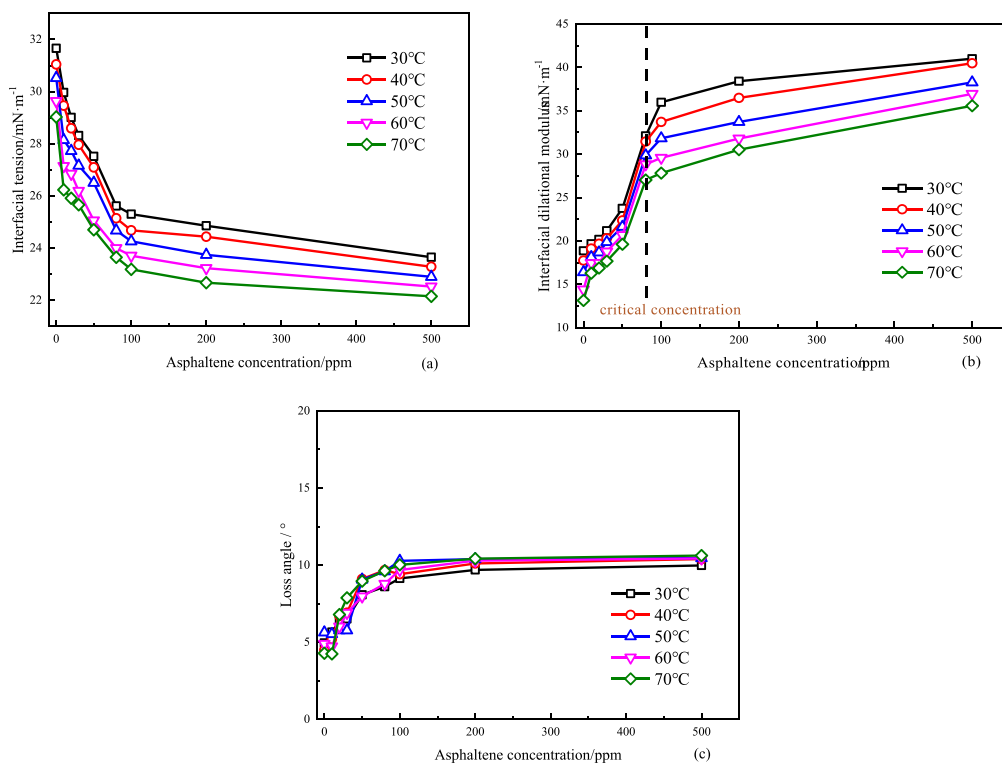
Four model oils with different solvents were prepared to investigate the aggregation states of asphaltenes in different polarity environments. The dynamic light scattering (DLS) method was utilized to measure the asphaltene size distribution in the four model oils. The results are displayed in Figure 4. The aggregate size measured in this experiment matches with the results of Ghorbani et al.<sup>32</sup> It can be observed that the particle size distribution is more concentrated below the asphaltene concentration of 50 ppm (black lines in Figure 4a) in the model oil, with the mixing ratio of methyl-naphthalene to *n*-decane being 2:3. When the asphaltene concentration is higher than 50 ppm (red lines in Figure 4a), the particle size distribution becomes more scattered. The concentration at which the pattern of the particle size distribution is transformed (i.e., the transition concentration) increases to 80, 100, and 200 ppm, respectively, with the mixing ratio ranging from 1:1 to 3:2 and further to 7:3. This concentration range accords with the reported aggregation concentrations of the asphaltene nano-aggregates and clusters based on the Yen–Mullins model.<sup>40–42</sup> In addition, the aggregate size increases slightly with the increase in asphaltene concentration below the transition concentration. By contrast, the average particle size increases abruptly once the asphaltene concentration exceeds the transition concentration. For example, the average size increases obviously by 128.3 nm (from 132.8 to 261.1 nm) at the mixing ratio of 2:3 when the asphaltene concentration increases from 10 to 80 ppm. At a mixing ratio of 1:1, the size increases by 133.1 nm (from 100.3 to 233.4 nm) when the asphaltene concentration increases from 10 to 100 ppm. The same phenomenon also applies to the mixing ratios of 3:2 and 7:3. It can be inferred that small spherical aggregates are formed at lower concentrations in all of the model oils with different polarities. The stronger the polarity of the solvent, the smaller the size of the asphaltene aggregates at this low concentration. When asphaltenes reach a higher concentration, they cluster into larger particles. The stronger the polarity of the solvent, the higher the transition concentration at which the abrupt increase of the particle size occurs.

### 3.3. Effect of Solvent Polarity on the Model Oil–Brine Interfacial Properties.

The interfacial experiments were conducted at 30, 40, 50, 60, and 70 °C, respectively. The interfacial tension, interfacial dilational modulus, and loss angle were measured at these different temperatures and asphaltene concentrations. The results are detailedly shown in Figures 5, 6, 7, and 8, with the interfacial tension values in good agreement with the calculation results.<sup>43</sup>



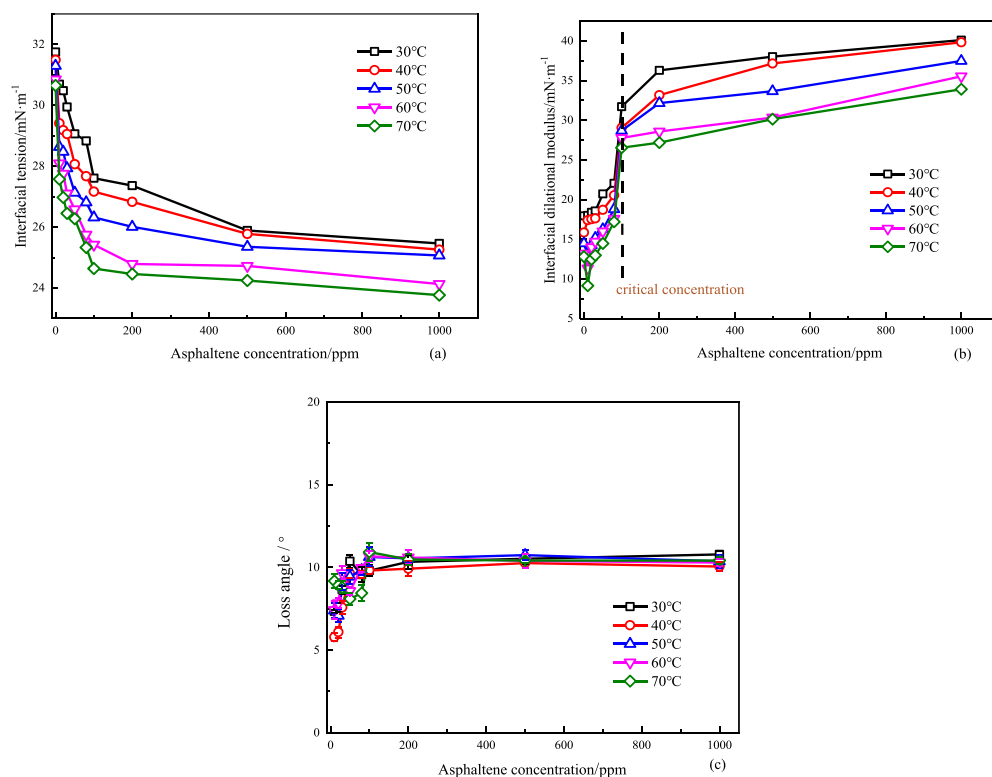
**Figure 4.** Size distribution of asphaltene aggregates in the model oils with different polarities at 30 °C: (a) methyl-naphthalene: *n*-decane = 2:3, (b) methyl-naphthalene: *n*-decane = 1:1, (c) methyl-naphthalene: *n*-decane = 3:2, and (d) methyl-naphthalene: *n*-decane = 7:3.



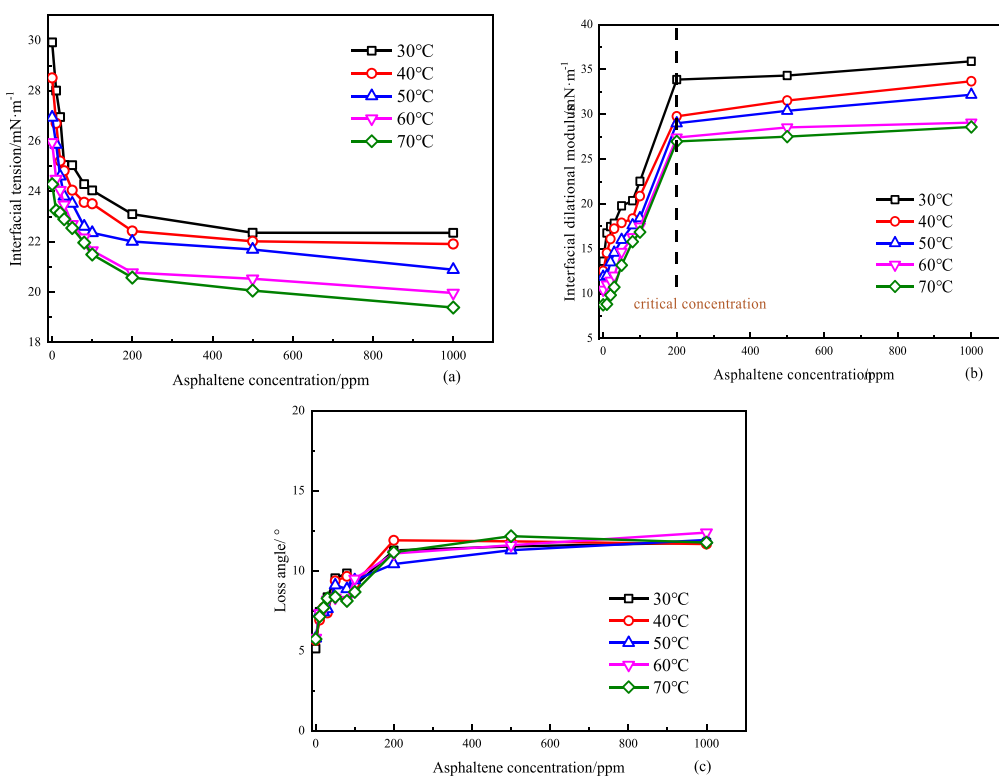
**Figure 5.** Relationship between interfacial rheological properties and asphaltene concentration at the 2:3 ratio of methyl-naphthalene to *n*-decane: (a) interfacial tension, (b) interfacial dilatation modulus, and (c) interfacial loss angle.

From the perspective of equilibrium interfacial tension, it is found that the interfacial tension decreases with the increasing proportion of methyl-naphthalene in the solvent at the same asphaltene concentration owing to the different adsorption states of asphaltenes at the interface. The aggregation degree of asphaltene weakens as the solvent polarity strengthens, resulting

in the formation of tiny-size aggregates. The amount of tiny asphaltene aggregates adsorbed at the interface is greater than that of the larger ones due to the small adsorption sites occupied at the interface. Therefore, the equilibrium interfacial tension decreases with the enhancement of the solvent polarity. When the asphaltene concentration is lower than 80, 100, 200, and 500



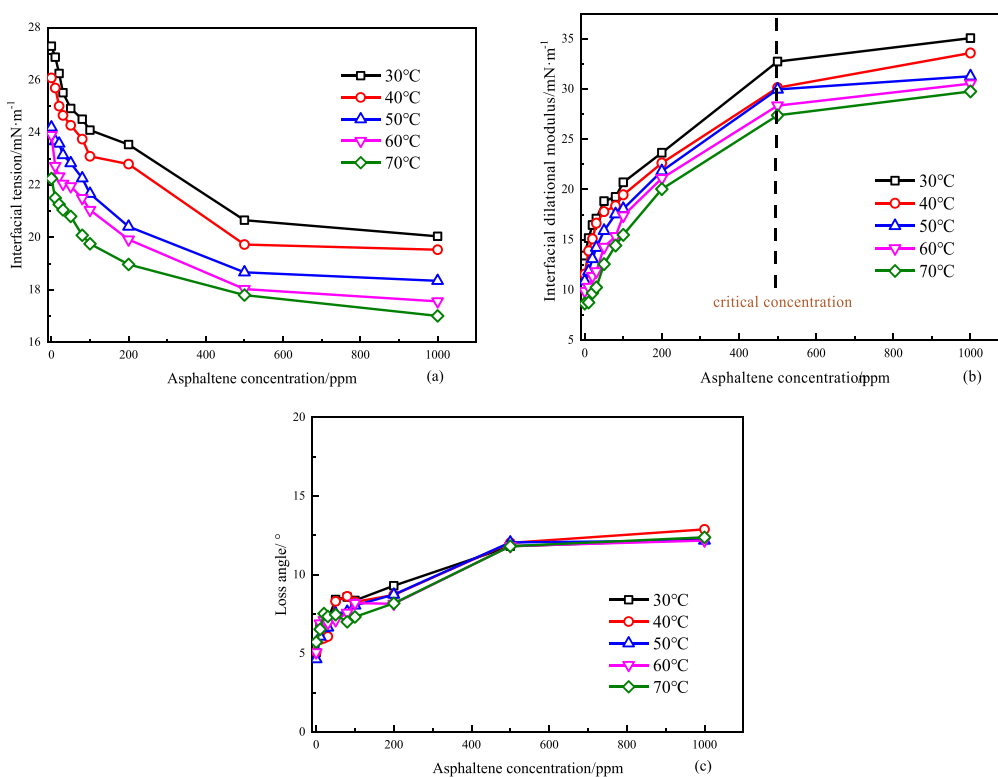
**Figure 6.** Relationship between interfacial rheological properties and asphaltene concentration at the 1:1 ratio of methyl-naphthalene to *n*-decane: (a) interfacial tension, (b) interfacial dilatation modulus, and (c) interfacial loss angle.



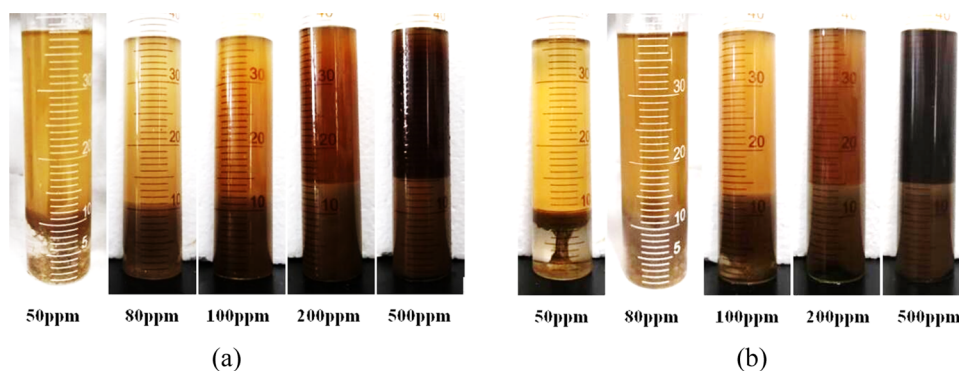
**Figure 7.** Relationship between interfacial rheological properties and asphaltene concentration at the 3:2 ratio of methyl-naphthalene to *n*-decane: (a) interfacial tension, (b) interfacial dilatation modulus, and (c) interfacial loss angle.

ppm in the four solvents in sequence, the equilibrium interfacial tension decreases rapidly with the increase of the concentration. However, once the concentration exceeds 80, 100, 200, and 500

ppm, the declining trend of the interfacial tension slows down. Therefore, it is inferred that the adsorption amount of asphaltene at the interface is large enough, and their adsorption



**Figure 8.** Relationship between interfacial rheological properties and asphaltene concentration at the 7:3 ratio of methylnaphthalene to *n*-decane: (a) interfacial tension, (b) interfacial dilatation modulus, and (c) interfacial loss angle.



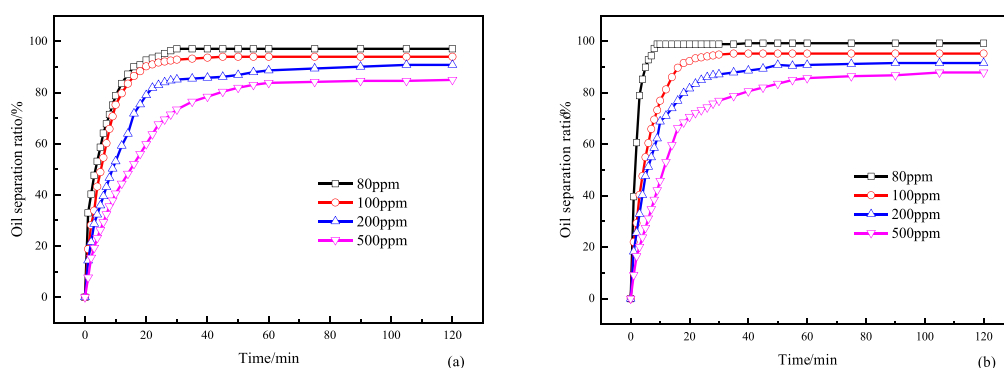
**Figure 9.** Bottle test result of the model oil emulsions with the 2:3 ratio of methylnaphthalene to *n*-decane at (a) 50 and (b) 70 °C.

tends to reach a saturation state when the concentration in the four solvents reaches 80, 100, 200, and 500 ppm.

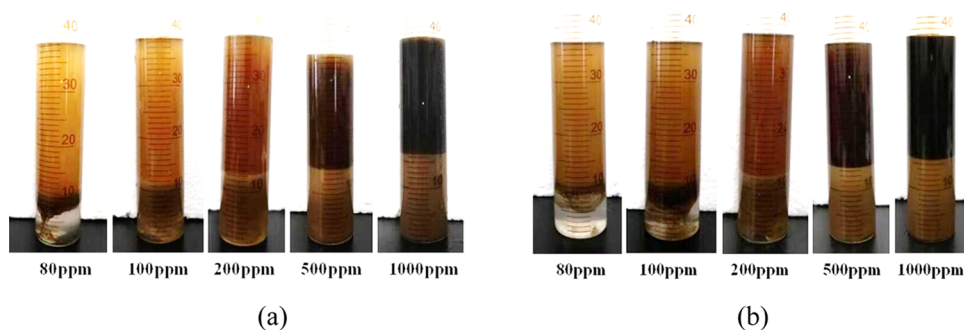
In terms of interfacial viscoelasticity, the interfacial dilatational modulus increases with the increase of asphaltene concentration in all four solvents. More precisely, the rising of the interfacial dilatational modulus becomes faster when the asphaltene concentration is lower than 80, 100, 200, and 500 ppm, respectively, in the solvent with 2:3, 1:1, 3:2, and 7:3 ratio of methylnaphthalene to *n*-decane. As the asphaltene concentration increases above this value, the rising trend tends to become smoother and an obvious inflection point can be observed. The inflection point is marked in Figures 5b–8b and determined as the asphaltene “critical concentration”. In this work, the term “critical concentration” refers to the concentration at which the size of asphaltene aggregates changes abruptly, demonstrating an inflection in the diffusion coefficient, the interfacial rheological properties, and the emulsion stability simultaneously. It is not exactly consistent with the acknowl-

edged critical nanoaggregation concentration (CNAC). The result manifests that the addition of more asphaltenes can improve the structural strength of the interfacial film in all four solvents. However, when the concentration increases to the critical value, the adsorption of asphaltenes at the interface will gradually reach a saturation state. In addition, it is found that the stronger the polarity of the solvent, the lower the interfacial dilatational modulus at the same asphaltene concentration. This result is supported by the study of Fan et al.<sup>34</sup> According to their conclusion, the solubility of asphaltenes in the oil phase is increased with the enhancement of the solvent polarity and more asphaltenes tend to stay in the oil phase rather than adsorb at the interface. Moreover, the formation of the network structure at the interface is also directly related to the aggregation state of asphaltenes, and their ability to stabilize the emulsion is enhanced when the aggregates become larger. Therefore, the adsorption of asphaltenes at the interface in the form of larger aggregates is essential for emulsion stability.

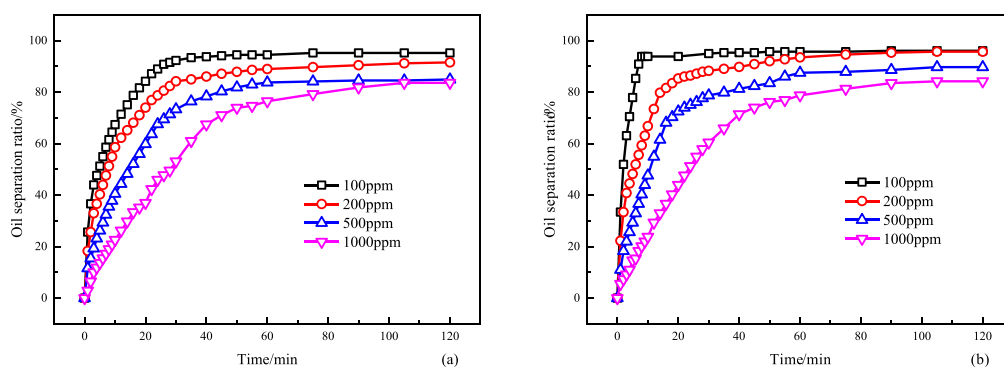




**Figure 10.** Evolution of oil separation ratio with quiescence time in the emulsions prepared with the 2:3 ratio of methylnaphthalene to *n*-decane at different asphaltene concentrations and at the temperature of (a) 50 and (b) 70 °C.



**Figure 11.** Bottle test result of the model oil emulsions with the 1:1 ratio of methylnaphthalene to *n*-decane at (a) 50 and (b) 70 °C.



**Figure 12.** Evolution of oil separation ratio with quiescence time in the emulsions prepared with the 1:1 ratio of methylnaphthalene to *n*-decane at different asphaltene concentrations and at the temperature of (a) 50 and (b) 70 °C.

As for the effect of temperature, it is clear that the kinetic energy of molecules increases with the increase of temperature, so the interaction between molecules weakens, resulting in a decrease in the interfacial film strength correspondingly. In a macroscopic view, it is observed that the interfacial dilatational modulus reduces with the increase of temperature. In contrast, the influence of temperature on the loss angle is not obvious in all four solvents. As can be seen from Figures 5–8, the loss angle curves at different temperatures overlap with each other, indicating that the ratio of the interfacial viscous modulus to the elastic modulus is almost unaffected by temperature.

**3.4. Effect of Solvent Polarity on the Stability of Water-in-Oil Emulsion.** The stability of asphaltene-containing emulsions prepared with different ratios of methylnaphthalene to *n*-decane (2:3, 1:1, 3:2, and 7:3) was tested at 50 and 70 °C, respectively. First, the asphaltene-containing model oil with a specific volume ratio of methylnaphthalene to *n*-decane was preheated with brine water at 50 or 70 °C for 20 min. Then, the

oil–water mixture with a total volume of 40 mL was stirred for 20 min at a stirring rate of 18,000 rpm. Finally, the prepared model emulsion was transferred into a 50 mL colorimetric tube. The emulsion stability was tested with the bottle test method at 50 and 70 °C, and the oil–water separation rate was recorded within 2 h immediately after the preparation of the emulsion. The results are shown in sequence from Figures 9, 10, 11, 12, 13, 14, 15, and 16. As can be seen from Figures 9, 11, 13, and 15, there is almost no free water sedimented in 2 h (except for the low asphaltene concentration cases). The mixtures are divided into an upper oil layer and a lower emulsion layer. Based on this, the change of the emulsion stability over time is characterized by how much the upper model oil layer separated from the emulsion. The results show that the separation amount of the oil phase in the emulsions at 70 °C is larger than that at 50 °C in all four solvents, indicating that the emulsions are more unstable at higher temperatures. Another conclusion can be drawn from Figures 10, 12, 14, and 16 that the oil separation rate decreases

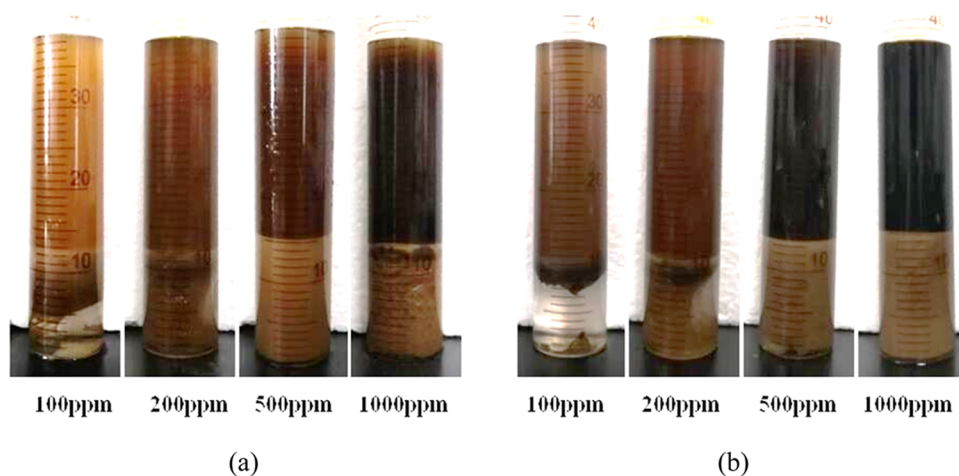


Figure 13. Bottle test result of the model oil emulsions with the 3:2 ratio of methyl-naphthalene to *n*-decane at (a) 50 and (b) 70 °C.

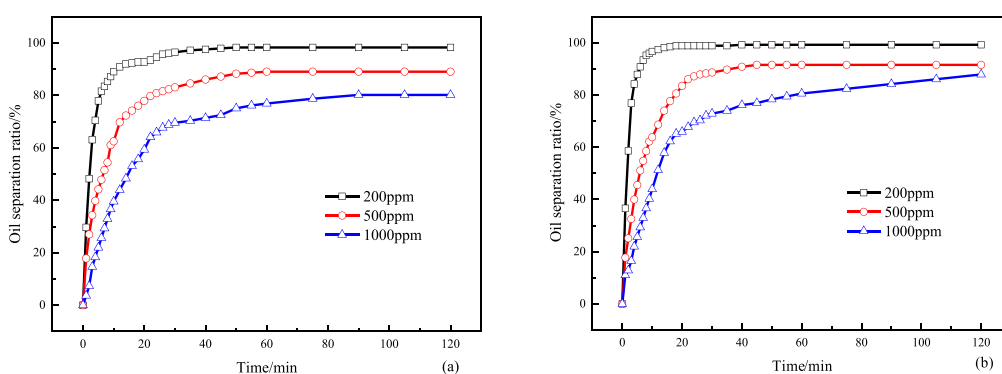


Figure 14. Evolution of oil separation ratio with quiescence time in the emulsions prepared with the 3:2 ratio of methyl-naphthalene to *n*-decane at different asphaltene concentrations and at the temperature of (a) 50 and (b) 70 °C.

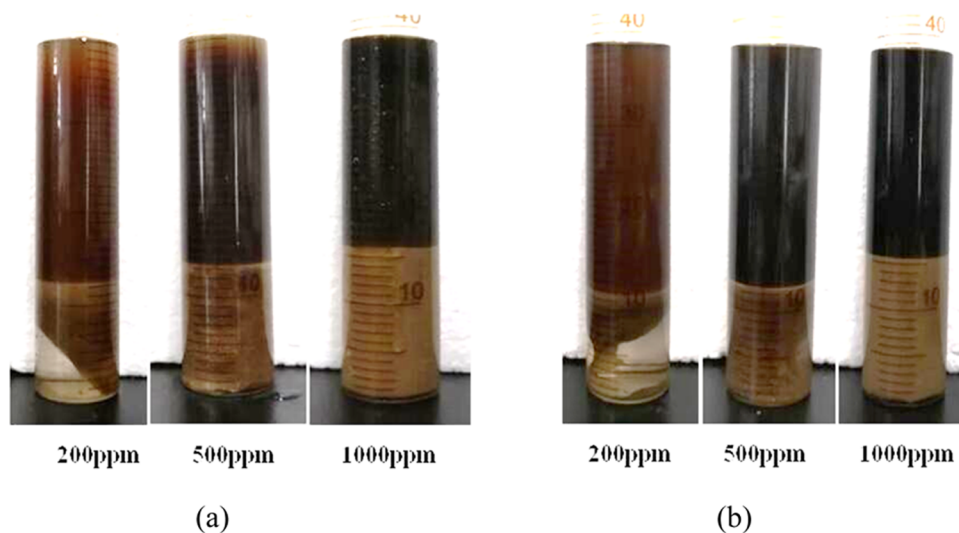
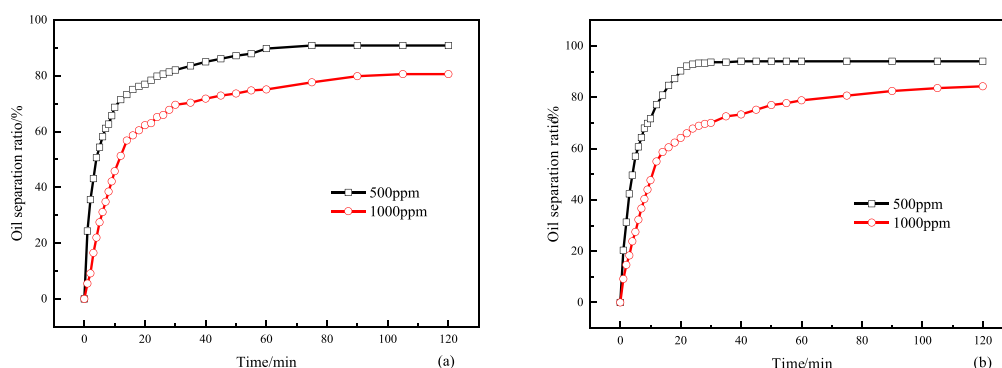


Figure 15. Bottle test result of the model oil emulsions with the 7:3 ratio of methyl-naphthalene to *n*-decane at (a) 50 and (b) 70 °C.

with the increase of asphaltene concentration in the model oil, that is, the oil–water separation slows down at a higher asphaltene concentration.

Figure 9 shows the bottle test result of the emulsion stability with a 2:3 ratio of methyl-naphthalene to *n*-decane after quiescence for 2 h. During the experiment, obvious oil–water separation could be observed immediately after the emulsion was transferred to the colorimetric tube for the model oil

containing not more than 50 ppm asphaltenes. That is to say, if the asphaltene concentration is not higher than 50 ppm, then a stable emulsion cannot be formed. When the concentration is increased to 80 ppm and above, there is no water layer sedimented in the oil/water mixture within 2 h. The similar phenomenon is also observed for the 1:1 ratio at 80 ppm, for the 3:2 ratio at 100 ppm, and for the 7:3 ratio at 200 ppm.



**Figure 16.** Evolution of oil separation ratio with quiescence time in the emulsions prepared with the 7:3 ratio of methylnaphthalene to *n*-decane at different asphaltene concentrations and at the temperature of (a) 50 and (b) 70 °C.

By combining Figures 5 and 10, it can be inferred that the interfacial dilational modulus is lower than 21.63 and 19.62 mN/m at 50 and 70 °C, respectively, when the asphaltene concentration is below 80 ppm. Under such conditions, a stable emulsion cannot be formed. When the asphaltene concentration is 80 ppm and above, the interfacial dilational modulus increases sharply to higher than 29.87 and 27.02 mN/m, respectively, supporting the stability of the emulsions. Likewise, when the ratio of methylnaphthalene to *n*-decane is 1:1, 3:2, and 7:3, the stability change of the emulsions and their interfacial strength change occur synchronously at 100, 200, and 500 ppm, respectively. It is then concluded that there is a critical concentration for asphaltenes to form a stable emulsion, and this critical value increases as the mixing ratio of methylnaphthalene to *n*-decane enlarged.

Based on the experimental results of emulsion stability, the oil separation ratio with time at the initial stage (0–20 min) is further linearly fitted, and the slope is listed in Table 3. The

**Table 3.** Change Slope of the Oil Separation Ratio with Time at 500 ppm Asphaltene Concentration

ratio of methylnaphthalene to <i>n</i> -decane	slope/min <sup>-1</sup>	
	at 50 °C	at 70 °C
2:3	3.76	4.24
1:1	4.09	4.70
3:2	5.55	5.94
7:3	5.76	6.55

values in Table 3 reflect the separation rate of the oil phase. The larger value in Table 3 indicates a quicker water–oil separation. It can be seen that the slope increases with the increase of methylnaphthalene content in the solvent, and the higher the temperature, the steeper the slope at the same ratio. Then, the oil separation ratio of the emulsions prepared with the four solvents was compared at the same asphaltene concentration after quiescence for 2 h, as shown in Table 4. The larger value in Table 4 manifests that more oil is separated from the emulsions after 2 h. It is concluded that a higher content of methylnaphthalene in the solvent leads to a higher oil separation ratio at the same temperature. At the same methylnaphthalene/*n*-decane proportion, the oil separation ratio enlarges with the increase of the temperature. In other words, the stronger the polarity of the solvent, the more unstable the emulsion formed.

**Table 4.** Oil Separation Ratio in the Different Emulsions Containing 500 ppm Asphaltene Concentration

ratio of methylnaphthalene to <i>n</i> -decane	oil separation ratio/%	
	at 50 °C	at 70 °C
2:3	84.94	87.91
1:1	86.08	89.74
3:2	89.05	91.58
7:3	90.84	93.98

#### 4. CONCLUSIONS

Solvent polarity affects the adsorption behavior of asphaltenes at the model oil/brine interface and further the macroscopic stability of the emulsion. The variation of the emulsion stability with the solvent aromaticity and its mechanism behind are verified through the experimental results in this work. In addition, the size distribution of asphaltene aggregates in different solvents is determined, settling the controversy in a previous work. Moreover, the adsorption behavior of asphaltenes in different solvents is probed from the perspective of interfacial rheology. The following conclusions can be drawn in this study.

- (1) The asphaltenes are interfacially active no matter how the polarity of the solvent changes.
- (2) The time of the rapid diffusion-controlled stage is prolonged with the enhancement of solvent polarity. Meanwhile, the diffusion coefficient of asphaltenes in the model oil enlarges with the increasing proportion of methylnaphthalene in the solvent, demonstrating that the aggregation degree of the asphaltenes weakens with the enhancement of solvent polarity.
- (3) The particle size increases abruptly once the asphaltene concentration exceeds the transition concentration. The stronger the polarity of the solvent, the higher the transition concentration at which the abrupt increase of particle size occurs.
- (4) The dynamic interfacial tension decreases faster and the ultimate equilibrium interfacial tension becomes lower with the enhancement of solvent polarity.
- (5) The adsorption of asphaltenes at the interface in the form of larger aggregates is essential for the emulsion stability. Therefore, the stronger the polarity of the solvent, the more unstable the emulsion formed.

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### Notes

The authors declare no competing financial interest.

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