Effects of Asphaltene Concentration and Test Temperature on the Stability of Water-in-Model Waxy Crude Oil Emulsions

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ABSTRACT: In oil fields, the formation of water-in-waxy crude oil emulsion is inevitable. The dissolved/crystallized state wax can interact with asphaltenes and then greatly affect the emulsion stability. However, studies on this aspect are still insufficient. In this work, the effects of the test temperature (30 °C well above the wax appearance temperature (WAT) and 15 °C well below the WAT) and asphaltene concentration (0∼1.5 wt %) on the stability of the water-in-model waxy crude oil emulsions containing 10 wt % wax were systematically investigated. When the model crude oils contain no wax, the flowability of the oils is good and the asphaltene concentration has little influence on the oil rheology. Increasing the asphaltene concentration facilitates the adsorption of asphaltenes to the oil−water interface, thus reducing the interfacial tension and water droplet size while enhancing the interfacial dilatational modulus. The stability of the emulsions improves with the increase in the asphaltene concentration, but the emulsions are still unstable. When the model crude oils contain 10 wt % wax, the WAT slightly decreases from the initial 25 to 24 °C after the addition of asphaltenes. The oil rheology is greatly improved by the addition of 0.05 wt % asphaltenes. With the further increase of the asphaltene concentration, the improved rheological ability of the asphaltenes deteriorates rapidly. At the asphaltene concentration of 1.5 wt %, the oil rheology is dramatically aggravated. The stability of the emulsion containing 10 wt % wax is mainly controlled by two aspects: on the one hand, the dissolved-state wax (30 °C) could facilitate the adsorption of asphaltenes to the interface, further reduce the interfacial tension and the water droplet size, and enhance the interfacial dilatational modulus; on the other hand, the wax crystals precipitated in the oil phase (15 °C) can form a stronger network structure at relatively high asphaltene concentrations (0.5∼1.5 wt %) and then immobilize the water droplets. The above two aspects greatly improve the sedimentation and coalescence stabilities of the emulsions at 15 °C. In addition, we did not find persuasive evidence showing that the wax could crystallize around the water droplets and strengthen the oil−water interfacial films.
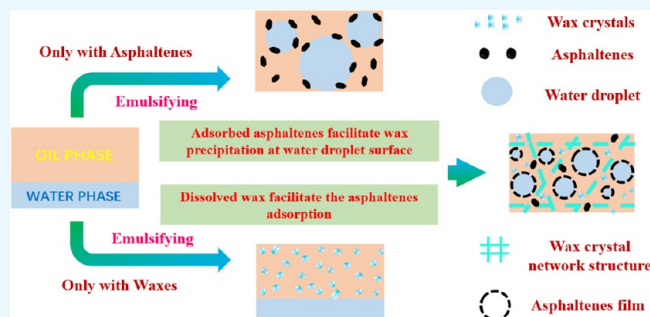
1. INTRODUCTION

In oil fields, the crude oil is extracted together with a large amount of brine. During the oil recovery process, the two liquid phases often form water-in-crude oil (W/O) emulsion with the native materials such as resins, asphaltenes, and naphthenic acid, as the emulsifiers.[1] The formation of relatively stable W/O emulsions is often unwanted: the formed emulsions not only make it difficult to dehydrate the crude oil[2] but also increase the crude oil pipelining cost and reduce the pipelining security because of the increased viscosity and volume of the emulsions.[3,4] In locations where gas hydrate blockage becomes a serious problem, however, the W/O emulsions facilitate the formation of flowable hydrate sludges thus eliminating the need for gas hydrate inhibitors.[5,6] Obviously, the W/O emulsion's stability greatly affects the oil recovery efficiency, and a full understanding of the factors affecting the stability of the W/O emulsion is necessary to tackle the above problems more efficiently.

The W/O emulsion's stability is influenced by many factors,[1−6] including the viscosity of the oil phase, the water phase volume fraction, the oil/water density differential, the salt in water phase, the type of emulsifier, and more importantly, the interfacial properties of the oil−water interface. The interfacial tension and interfacial rheology have a great impact on the W/O emulsion's stability.[7] With the decrease in the oil−water interfacial tension, the water phase is easier to be dispersed into the oil phase and then the formed water droplets become smaller, which is helpful to the emulsion stability. However, the interfacial tension is not always in direct relation to the emulsion stability: the surface active materials with high interfacial tension reducing ability may not be suitable emulsifiers.[1,2] It is widely accepted that the

rheology of the oil−water interfacial film formed by surface active materials plays a crucial role in the stability of emulsions,[1,2,7] i.e., the interfacial film stabilization mechanism. During the past few decades, interfacial shear/dilatational rheometers have been developed to measure the rheology (such as the interfacial viscosity and interfacial modulus) of the oil−water interfacial films from which the macroscopic stability of the emulsion could be evaluated.[7]

Compared with resins, asphaltenes have more complicated fused aromatic rings, higher average molecular weight, and stronger polarity. The asphaltene molecules have poor solvency in crude oil, but self-associate into colloidal aggregates with the assistance of resins through a solvation effect.[8] It has been verified that the native naphthenic acids, resins, and asphaltenes could stabilize the W/O emulsion among which the asphaltenes play a key role.[1−6] The aggregated asphaltene particles could adsorb on the water droplet surface and then form the interfacial films with stronger structural strength,[9] which greatly inhibit the coalescence of water droplets. Similar to the colloidal particle emulsifiers (Pickering emulsions[10]), the adsorption of asphaltenes on the water droplet surface is normally irreversible, but some researchers found the asphaltenes adsorbed at the interface could desorb into the oil phase.[11] This controversy is probably caused by the different association state of the asphaltenes. The influences of asphaltene subfractions,[12−14] oil solvent composition,[15] organic acids,[16,17] resins,[18] oil-soluble polymers[19,20] and temperature[21] on the structural strength of the oil−water interfacial films formed by asphaltenes have been studied in detail. The results showed:[12−21] the aggregating state of asphaltenes in the oil phase is obviously changed by the above factors, thus influencing the structural strength of asphaltenes interfacial films and the emulsion stability; the more aggregated asphaltenes facilitate the formation of stronger asphaltene interfacial films, and then further improve the emulsion stability.

Waxy crude oil is determined as the oil containing wax ≥5 wt %. The wax is mainly composed of the C_{18}~C_{40} normal alkanes.[22] When the waxy crude oil's temperature is less than its wax appearance temperature (WAT), the wax will crystallize into wax crystals because of oversaturation. The precipitated wax crystals often lead to the deterioration of waxy crude oil rheology and wax deposition, which create serious difficulties for oil recovery.[23] The precipitated wax crystals cannot stabilize the W/O emulsion by themselves.[24] With the aid of oil-soluble emulsifiers such as glycerol monooleate,[25] span 80,[26] and polyethylene-co-polyethylene glycol,[27] however, the wax molecules could crystallize surrounding the water droplets and form wax crystal films, which could further inhibit the coalescence of water droplets through the interfacial film stabilization mechanism. In addition, the wax crystal precipitated in the oil phase is liable to construct a continuous three-dimensional network, which can also improve the emulsion stability through the network stabilization mechanism.[25−27]

It has been widely agreed that colloidal asphaltenes could participate in the wax crystallizing process by the co-crystallization/nucleation effects and modify the precipitated wax crystal's morphology, thus greatly affecting the low temperature rheology and wax deposition behavior of waxy crude oils.[28−30] The interactions between asphaltenes and wax will also influence the stability of the W/O emulsion stabilized by asphaltenes. Early in 1998, Mouraille et al.[31] investigated

the stability of W/O emulsions stabilized by asphaltene rich crude (B1) and wax rich crude (B2) at room temperature (23 °C) and 10 °C. The emulsion stability at room temperature is increased by enhancing the proportion of B1 in the oil phase. They considered that the improved emulsion stability is due to the increased asphaltene concentration and the composition of the oil solvent, which may affect the asphaltenes' ability to stabilize emulsions. At 10 °C, the emulsion stability is dramatically improved by a small addition of B1 in B2. They deduced that the interaction between the waxes from B2 and the asphaltenes from B1 greatly affects the emulsion stability. Yanes et al[32] investigated the effects of n-hexadecane and a commercial paraffin wax pool on the stability of water-in-heavy oil emulsions. The addition of paraffin wax decreases the oil−water interfacial tension and makes the emulsions easier to be formed and more stable, which are attributed to the asphaltene solubility variation induced by the paraffin wax addition. Meanwhile, the authors considered that the precipitated wax crystals could adsorb at the oil−water interface, which also facilitates the emulsion stability. Based on the conductivity tests of the model oils containing asphaltenes and the oil−water interfacial measurement, Sun et al.[33] discovered that adding the dissolved-state waxes could flocculate asphaltenes into larger aggregates and increase the interfacial dilatational modulus, which improved the emulsion stability. Zhang et al.[6] found the wax crystals could precipitate surrounding the water droplets with the aid of adsorbed asphaltenes, and the wax crystals crystallized in the oil phase could form network structures, both of which improve the W/O emulsion stability and then influence the gas hydrate slurry formation. Chen et al.[34] discovered that when the emulsifiers could not interact with the wax molecules through the co-crystallization or nucleation effect, the wax will not crystallize on the water droplet surface and form the wax crystal film. The adsorbed asphaltenes trigger the wax crystallization of paraffin on the water droplet surface, and then strengthen the water droplet interfacial film thus further preventing the water droplet coalescence.

In this paper, the effects of test temperatures (30 °C above the WAT, and 15 °C below the WAT) and asphaltene concentration (0~1.5 wt %) on the stability of water-in model waxy crude oil emulsions containing 10 wt % wax were systematically investigated. First, the effect of asphaltene concentration on the crystallizing characteristics, rheological properties, and asphaltene dispersing state of the model waxy crude oils was investigated. Then the model waxy crude oil−water interfacial properties were tested, and the effects of the asphaltene concentration, wax, and test temperature on the interfacial properties were analyzed. Finally, the sedimentation and coalescence stabilities of the emulsions were determined and the emulsion stabilizing mechanisms were well discussed based on the interfacial properties of the emulsions and the macroscopic rheology of the model waxy crude oils.

2. EXPERIMENTAL SECTION

2.1. Materials. The water used here is double distilled water. NaCl and xylene are analytical grade with the purity ≥99 wt %. A small amount of NaCl is dissolved in double distilled water to prepare the brine with 0.05 mol/L NaCl, which is used to simulate the produced water. The wax contains mainly normal alkanes (> 95 wt %) and was purchased from Mclean Chemical Reagent Co. of China. As shown in Figure S1 of the supporting information file, the

carbon number distribution of wax is $C_{20}\sim C_{42}$ with the peak carbon number at C_{29}. The asphaltenes were obtained from Tahe heavy oil of China using the *n*-heptane extraction method. The detailed extraction method and the elemental composition of the extracted asphaltenes are shown in Section 2 in the Supporting Information.

The model waxy crude oils were prepared by dissolving/dispersing some wax and asphaltenes in xylene. After the addition of the wax and asphaltenes in xylene, the oil samples were sealed in glass bottles, heated to 80 °C, and magnetically stirred for 12 h to make sure the asphaltenes are well dispersed in the oil phase. The asphaltene concentration is fixed at zero, 0.05, 0.15, 0.5, and 1.5 wt %, while the wax content is unchanged at 10 wt %.

The water-in model waxy crude oil emulsions were prepared by dispersing a certain amount of brine water into the model oils with the aid of a AD500S-H 12G homogenizer at 18,000 rpm. In each emulsion system, the total volume was controlled at 50 mL and the model waxy crude oil/brine volume ratio was fixed at 7:3. The model waxy crude oil/brine mixture was first maintained at 60 °C for 20 min and then slowly cooled to 30 °C (well above the WAT). After that, the mixture was emulsified at 30 °C for 10 min to obtain the water-in-model waxy crude oil emulsion samples.

2.2. Methods. *2.2.1. Wax Precipitation Measurement of the Model Waxy Crude Oils.* The exothermic curves of the model waxy crude oils were measured using a Mettler-Toledo DSC 821e calorimeter. The temperature scanning range was 60 to −20 °C and the cooling rate was controlled at 10 °C/min. Based on the exothermic curves, the WAT and the cumulative precipitated wax crystal amount of the model waxy crude oils were obtained according to the methods mentioned in the former papers.[22,35]

The microstructure of precipitated wax crystals in the model waxy crude oils was observed by an Olympus BX53M microscope fitted with a Linkam LTS350 automatic thermal stage under polarized light. A drop of the model waxy crude oil was first placed in the thermal stage and maintained at 60 °C for 20 min. Then, the loaded oil sample was cooled from 60 to 15 °C at 0.5 °C/min cooling rate. After that, the wax crystals precipitated at 15 °C in the model waxy crude oil were photographed and recorded.

2.2.2. Dispersion State Test of Asphaltenes in the Model Waxy Crude Oils. The microstructure of asphaltenes in the model waxy crude oils was observed using the Olympus BX53M microscope under normal light at 30 °C. The particle size distribution of asphaltenes in the model waxy crude oils was also measured at 30 °C using a Mastersize3000 particle size analyzer (Malvern Co., England).

2.2.3. Rheological Measurement of the Model Waxy Crude Oils. The rheological properties of the model waxy crude oils were tested through the TA DHR-1 controlled-stress rheometer. The testing system is a standard coaxial cylinder. The model waxy crude oil was first maintained at 60 °C for 20 min. Then, the oil sample was poured into the rheometer and cooled from 60 to 10 °C at 0.5 °C/min. The rheology of the model waxy crude oil was tested under two modes during the cooling process. Under the shearing mode, a 10 s^{-1} shear rate was exerted to the oil sample, and then the viscosity−temperature curve of the model waxy crude oil could be obtained. Under the oscillation mode, a small amplitude oscillation was exerted to the oil sample, and then the viscoelastic parameters of the oil sample such as the G' (elastic

modulus), G'' (viscous modulus), δ (loss angle) and gelation point, could be obtained. The oscillation frequency was controlled at 1 Hz, while the shear strain amplitude was controlled at 0.0005. Because the rheological tests are a temperature dropping process, the wall-slipping phenomenon could be identified at the temperatures (the gel structure of the oil is very strong) at which the viscosity and the viscoelastic parameters of the oils change dramatically. In the temperature test range of 60∼10 °C, we do not find the wall-slipping phenomenon.

2.2.4. Interfacial Tension and Dilatational Modulus Measurements. The developments of the model waxy crude oil/brine interfacial tension and dilatational modulus with time were measured through a Tracker-H pendant drop tensiometer. Before tests, the model crude oil was diluted 10 times with xylene to decrease the asphaltene concentration and wax content to measurable values. Then, a small oil drop was dropped in the brine to initiate the test. Two steps were included in a complete interfacial experiment. In the first step, the oil drop/brine system was maintained at 30 °C for 20 min to study the isothermal adsorption behavior of asphaltenes; in the second step, the oil drop/brine system was cooled to 0 °C at a cooling rate of 1 °C/min to evaluate the effect of test temperature and wax precipitation on the interfacial properties. Based on the interfacial pressure difference and the pendant drop contour, the dynamic interfacial tension could be directly calculated through the Young−Laplace equation.[18−20]

The interfacial dilatational modulus (E) was tested by the small amplitude dilatation/contraction oscillation method, the oscillating frequency was constant at 0.1 Hz and the oscillating amplitude was 10% of the oil drop's interfacial area.

2.2.5. Stability Test and Microscopic Observation of the Emulsions. After emulsification, the prepared emulsion was immediately transferred to two colorimetric tubes (20 mL volume each tube). One tube was laid in a 30 °C water bath and the other was put in a 15 °C water bath. Then, the macroscopic variation of the emulsion in the subsequent 24 h was observed and recorded. The water droplets will sediment with the increase in time because of the density differential, and the emulsion system changes into two separated parts: the upper part is the pure oil phase while the lower part is a concentrated emulsion phase. The sedimentation stability of the emulsion at different times could be expressed as follows:

$$f_o = \frac{V_{so}}{V_{to}} \times 100\% \tag{1}$$

where V_{so} is the volume of the separated oil phase, V_{to} is the volume of the total oil in emulsion, and f_o is the oil separation rate.

Right after emulsification, a drop of the prepared emulsion was placed into the thermal stage of a microscope to observe the microscopic structure of the emulsion. The water droplet size distribution could be calculated based on the microscopic image of the emulsion. Next, the emulsion was cooled to 15 °C to observe the microstructure of the precipitated wax crystals in the emulsion by using polarized light. In addition, the microscopic structure of the emulsion at 24 h was also observed and recorded.

No continuous water phase was observed in the emulsion after 24 h, but this did not mean that the emulsion coalescence stability is good. The coalescence stability of the emulsion was

qualitatively evaluated according to the microscopic images of the emulsion at 0 and 24 h.

3. RESULT AND DISCUSSION

3.1. Wax Precipitating Properties of the Model Waxy Crude Oils. The effect of asphaltene concentration on the WAT and cumulative amount of wax crystals in the model waxy crude oils with 10 wt % wax is shown in Figure 1. As seen
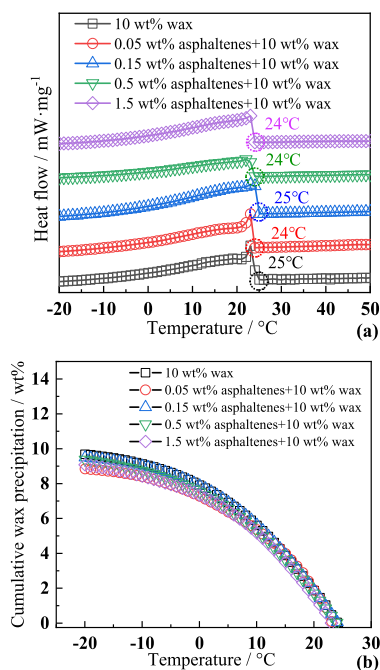
Figure 1. Effect of asphaltene concentration on the WAT (a) and cumulative wax crystal amount (b) of the model waxy crude oils with 10 wt % wax.

in Figure 1a, the WAT of the model crude oil without asphaltenes is 25 °C. After the addition of 0.05 wt % asphaltenes, the WAT of the oil slightly decreases to 24 °C, indicating that the asphaltenes could solubilize some wax. The further increase of asphaltene concentration could not decrease the WAT of the oils further. It has been widely accepted that the asphaltenes could interact with wax molecules through both the nucleation effect and co-crystallization effect.[36,37] The nucleation effect would increase the WAT of the oils but the co-crystallization would decrease the WAT. The final WAT of the oils is the result of the competition of the two effects. The asphaltenes used here show a stronger co-crystallization effect with wax, and then the value of WAT slightly decreases by 1 °C. The addition of asphaltenes could not obviously decrease the cumulative wax crystal amount of the oils (see Figure 1b). At −20 °C, the cumulative wax crystal amount of the model waxy crude oils is around 9 wt %, meaning that most of the wax precipitate into crystals at this temperature.

It is clear from Figure 2 that the addition of asphaltenes changes the precipitated wax crystal's morphology outstandingly. As shown in Figure 2a, the wax crystals in the model waxy crude oil without asphaltenes are relatively big and have a needle-like shape. The addition of 0.05 wt % asphaltenes makes the needle-like wax crystals aggregate into bigger wax aggregates with a small amount, which are difficult to form a three-dimensional network and will be helpful to the improvement of the oil rheology. With the increase in the

asphaltene concentration to 0.15 wt %, the asphaltenes could provide more nucleation sites for wax and then the precipitated wax crystal changes into small needle-like particles with a relatively large number (see Figure 2c, compared with Figure 2a). With further increasing the asphaltene concentration, the nucleation effect becomes more obvious, and the wax crystal size decreases while the wax crystal number increases outstandingly. For example, at the asphaltene concentration 1.5 wt %, the precipitated wax crystal size is only several microns but the wax crystal number is much more higher (see Figure 2e).
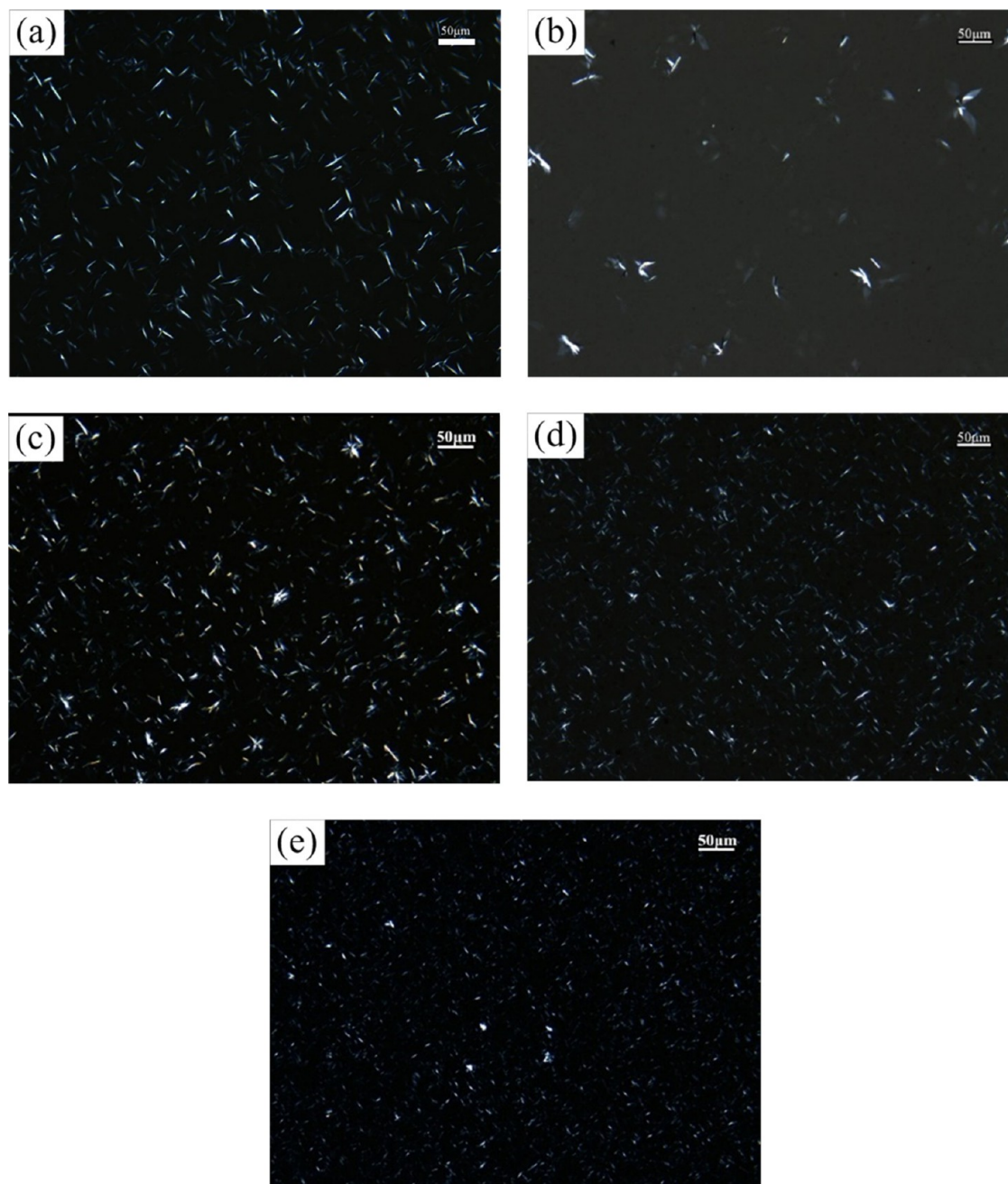
3.2. Dispersion State of Asphaltenes in the Model Waxy Crude Oils. The effect of asphaltene concentration on the microstructure of the asphaltenes in the model crude oils without wax is shown in Figure S3 of the support information file, and the particle size distribution of asphaltenes is described in Figure 3a. The asphaltenes become more aggregated and the asphaltene particle size increases with increasing asphaltene concentration. The average asphaltenes particle size is 231 nm at the asphaltene concentration of 0.05 wt %, then increases from 364 nm at 0.15 wt % asphaltenes to 592 nm at 0.5 wt % asphaltenes, and then to 843 nm at 1.5 wt % asphaltenes.

The effect of asphaltene concentration on the microstructure of the asphaltenes in the model waxy crude oils with 10 wt % wax is shown in Figure S4 of the support information file, and the particle size distribution of asphaltenes is shown in Figure 3b. Compared with xylene, dissolved wax is a poor solvent of asphaltenes, therefore, the addition of 10 wt % wax leads to the further aggregation of asphaltenes into bigger aggregates. The average asphaltene aggregate size is 422 nm at the asphaltene concentration 0.05 wt %, which then increases from 596 nm at 0.15 wt % asphaltenes to 1131 nm at 0.5 wt % asphaltenes, and then to 1244 nm at 1.5 wt % asphaltenes.

3.3. Rheology of the Model Waxy Crude Oils. As shown in Figure 4a, when the model crude oils contain no wax, although the viscosity of the oils increases as the temperature drops, the oil viscosity at the temperature range 10∼40 °C is very small (0.8∼1.2 mPa·s), meaning that the asphaltenes in the oil phase cannot increase the oil viscosity significantly. The oil viscosity increases very slowly with increasing asphaltene concentration. For example, the oil viscosity at 15 °C increases from 1.03 mPa·s with 0.05 wt % asphaltenes to 1.09 mPa·s with 1.5 wt % asphaltenes. It could be concluded that the asphaltene concentration (≤1.5 wt %) has a slight influence on the viscosity of the model crude oils without wax.

When the model crude oils contain 10 wt % wax, however, the viscosity and viscoelastic parameters of the oils are greatly influenced by both the temperature and the asphaltene concentration. As shown in Figures 4b and 5, the oil viscosity, G' and G'' are very small while the δ approaches to 90° at the temperatures around or above the WAT, and the effect of asphaltene concentration on the oil viscosity and viscoelastic parameters could be neglected. As shown in Table 1, the oil viscosity, G', and G'' are very small at 30 °C (above the WAT) even when the asphaltene concentration increases to 1.5 wt %. Meanwhile, the value of G'' is about 10 times that of G', which means that the rheological behavior of the model waxy crude oils is viscous dominant.

At the temperatures below the WAT, the continuous crystallization of wax crystals leads to the rapid increase of the oil viscosity, G', and G'' but the quick decrease of the δ with the temperature drop. For the model waxy crude oil only
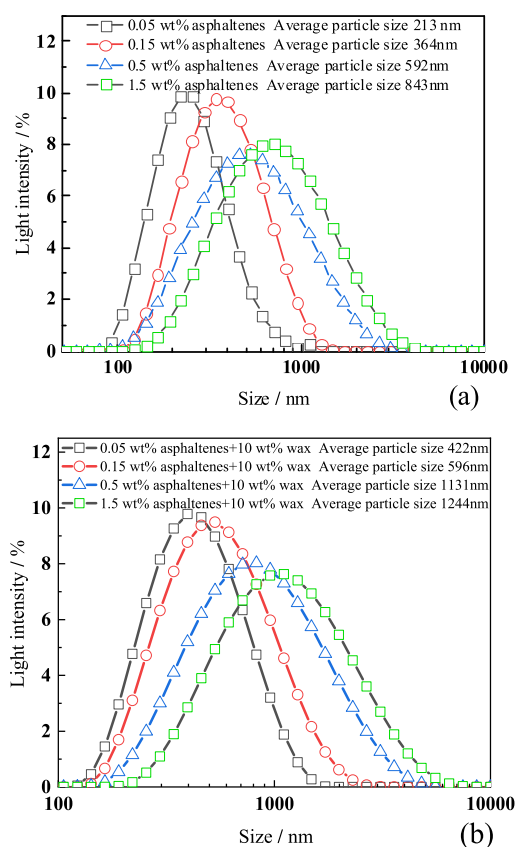
Figure 2. Effect of asphaltene concentration on the morphology of precipitated wax crystals in the model waxy crude oils with 10 wt % wax at 15 °C: (a) none; (b) 0.05 wt %; (c) 0.15 wt %; (d) 0.5 wt %; (e) 1.5 wt %.

with 10 wt % wax, the gelation point is 22 °C (see Figure 5); the viscosity, G' and G'' at 15 °C (below the WAT) are 91.5 mPa·s, 20,926.8, and 8328.8 Pa, respectively (see Table 1). After the addition of asphaltenes in the oil phase, the gelation point of the oils slightly decreases by 0.6~1.2 °C (see Figure 5) but the viscosity, G' and G'', of the oils change outstandingly (see Table 1). At 0.05 wt % asphaltene concentration, the asphaltenes facilitate the formation of big wax aggregates with small amount (see Figure 2) and then improve the oil rheology. For example, the viscosity, G' and G'' of the oil with 0.05 wt % asphaltenes at 15 °C decrease obviously to 17.5 mPa·s, 1279.2 and 803.5 Pa, respectively. The rheological improving ability of asphaltenes decreases with further increasing the asphaltene concentration because of the increased number and decreased size of the wax crystals (see

Figure 2). When the asphaltene concentration increases to 1.5 wt %, the asphaltenes even seriously aggravate the oil rheology. For example, the viscosity, G' and G'' of the oil with 1.5 wt % asphaltenes at 15 °C increase outstandingly to 299.6 mPa·s, 63870, and 12835.6 Pa, respectively. Obviously, the model waxy crude oil with 1.5 wt % asphaltenes forms a relatively strong gel structure at 15 °C. We believe that with the increase in the asphaltene concentration, the nucleation sites of wax crystals increase, leading to the formation of smaller wax crystals with a larger number. This kind of wax crystals has a larger specific surface area and the interaction among the wax crystals should be stronger, which results in poor rheology of the oil sample.

3.4. Model Waxy Crude Oil−Water Interfacial Properties. The effect of asphaltene concentration on the interfacial

Figure 3. Effect of asphaltene concentration on the particle size distribution of asphaltenes in the model crude oils without wax (a) and in the model waxy crude oils containing 10 wt % wax (b).
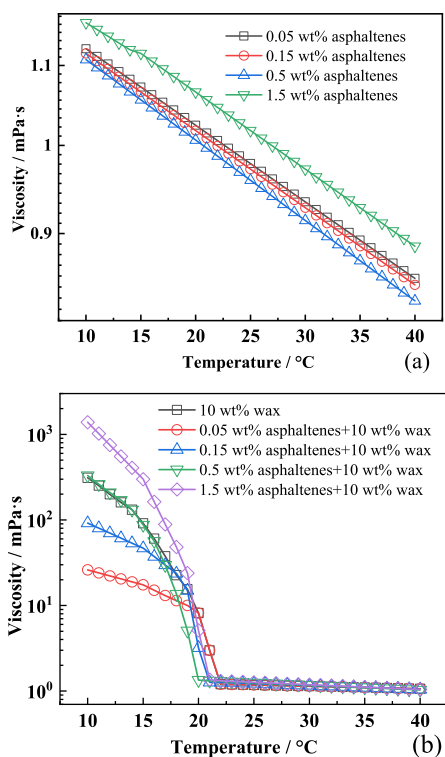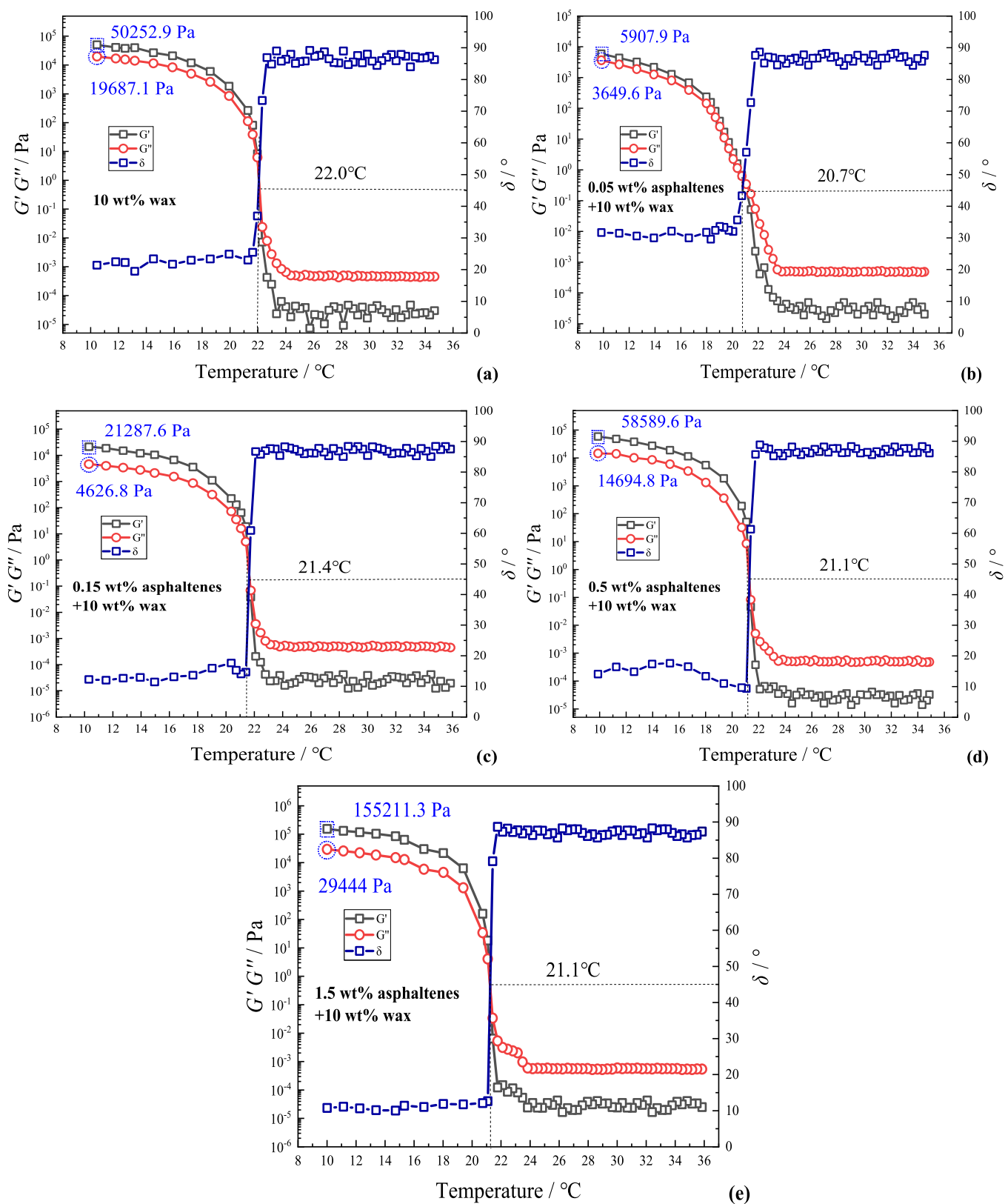

Figure 4. Effect of asphaltene concentration on the viscosity–temperature curves of the model crude oils without wax (a) and the model waxy crude oils with 10 wt % wax (b).

tension and interfacial dilatational modulus of the diluted model crude oil (without wax)-water interface during the isothermal (30 °C) and cooling process (30 to 0 °C) is shown in Figure 6a,b. During the isothermal process, the interfacial tension decreases while the interfacial modulus increases with time because of the continuous adsorption of asphaltenes to the interface. During the cooling process, both the interfacial tension and the interfacial modulus increase gradually with time. For example, at the fixed asphaltene concentration of 0.005 wt % (see Table 2), the values of γ at 30, 15, and 0 °C are 21.81 ± 0.38 mN·m^{-1}, 22.12 ± 0.32 mN·m^{-1}, and 22.55 ± 0.2 mN·m^{-1}, respectively; the values of E at 30, 15, and 0 °C are 6.95 ± 0.25 mN·m^{-1}, 8.43 ± 0.23 mN·m^{-1}, and 10.19 ± 0.2 mN·m^{-1}, respectively. It is well accepted that the oil−water interfacial tension decreases by increasing the temperature.[38] Consequently, the oil−water interfacial tension will increase during the cooling process. Meanwhile, the temperature drop makes the asphaltenes unstable and then strengthen the interactions of the adsorbed asphaltenes at the interface, which will enhance the interfacial modulus of the asphaltenes film. With the increase in the asphaltene concentration, more asphaltenes can be adsorbed at the oil−water interface. Therefore, the interfacial tension decreases while the interfacial modulus increases with increasing the asphaltene concentration. For example, at the fixed temperature of 15 °C (see Table 2), the value of γ gradually decreases to 19.82 ± 0.15 mN·m^{-1} with 0.015 wt % asphaltenes, 19.24 ± 0.12 mN·m^{-1} with 0.05 wt % asphaltenes, and 18.33 ± 0.14 mN·m^{-1} with 0.15 wt % asphaltenes; the value of E gradually increases to 9.69 ± 0.19 mN·m^{-1} with 0.015 wt % asphaltenes, 12.57 ± 0.29 mN·m^{-1} with 0.05 wt % asphaltenes, and 14.30 ± 0.28 mN·m^{-1} with 0.15 wt % asphaltenes.

As shown in Figure 6c,d, the addition of 1 wt % wax obviously decreases the interfacial tension but increases the interfacial modulus. For example, at the asphaltene concentration of 0.15 wt % and temperature of 15 °C (see Table 2), the γ decreases to 18.01 ± 0.10 mN·m^{-1} while the E increases to 18.19 ± 0.27 mN·m^{-1}. In the Pickering emulsion system, it has been found that destabilizing the dispersed nanoparticles favors the particle adsorption at the interface and the formation of Pickering emulsions.[10,39] Similar to the Pickering emulsions, the dissolved wax makes the asphaltenes unstable in the oil phase and then facilitates their adsorption to the oil−water interface. Therefore, the diluted model crude oil−water interfacial tension decreases but the interfacial modulus increases after adding 1 wt % wax. In addition, the WATs of the diluted model crude oils with 1 wt % wax are marked in Figure 6c,d. We could not find the obvious changes of the interfacial properties at temperatures less than the WAT. Therefore, the data in Figure 6 could not be used to verify that the wax molecules could crystallize at the oil−water interface and change the interfacial properties.

Figure S4 of the support information file shows the morphology of the precipitated wax crystals in the emulsions with 10 wt % wax at 15 °C. If a substantial amount of wax precipitates around the water droplet surface, then there will be spherical or circular wax crystal films in the images of Figure S4. Unfortunately, we cannot see the spherical or circular wax crystal film in Figure S5. Therefore, the wax crystal images in Figure S5 could not be used to verify the formation of a wax crystal film surrounding the water droplet. In our view, in addition to the water droplets, a large amount of asphaltene aggregates are dispersed in the oil phase. Both the small water
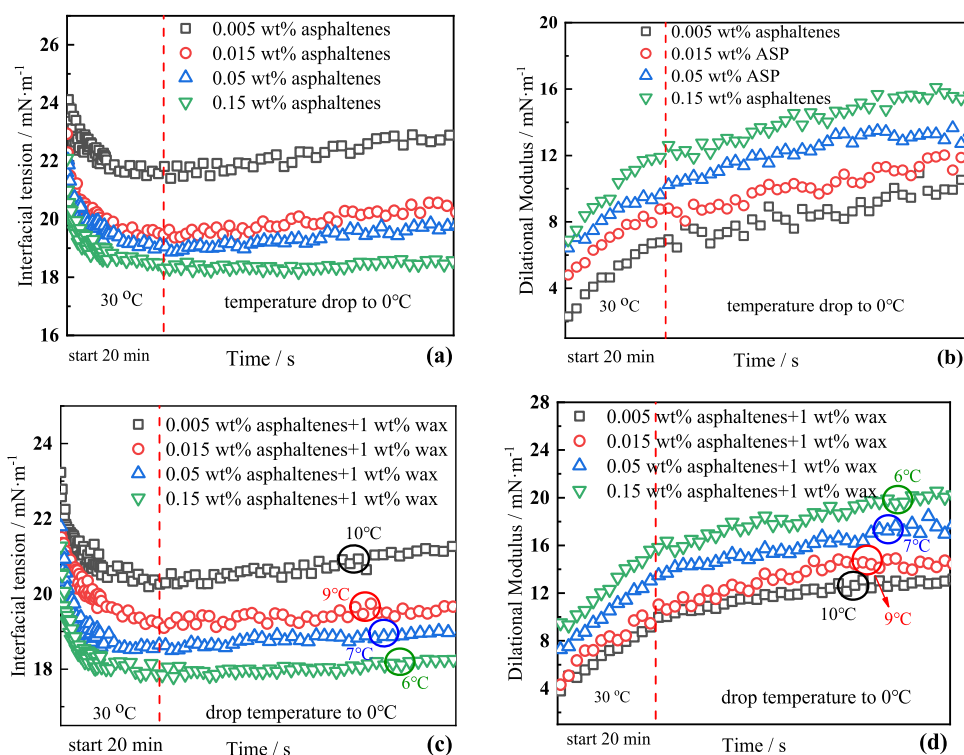
Figure 5. Effect of asphaltene concentration on the viscoelastic properties of the model waxy crude oils with 10 wt % wax: (a) none; (b) 0.05 wt %; (c) 0.15 wt %; (d) 0.5 wt %; (e) 1.5 wt %.

droplets and asphaltene aggregates could be used as the nucleation sites for wax crystal precipitation. Compared with the water droplets, asphaltene aggregates are smaller in size, more numerous, and have a stronger nucleation effect.

Therefore, the wax molecules preferentially precipitate with the asphaltene aggregates as the heterogeneous nucleation sites, thus the waxes could not form a wax crystal layer around the water droplets.

Table 1. Effect of Asphaltene Concentration on the Rheological Parameters of the Model Waxy Crude Oils

model crude oil	pour point/°C	viscosity at 30 °C/mPa s	viscosity at 15 °C/mPa s	G' at 30 °C/Pa	G'' at 30 °C/Pa	G' at 15 °C/Pa	G'' at 15 °C/°
10 wt % wax		1.14	91.5	3.56×10^{-5}	4.8×10^{-4}	20,926.8	8328.8
0.05 wt % asphaltenes +10 wt % wax		1.14	17.5	2.85×10^{-5}	4.96×10^{-4}	1279.2	803.5
0.15 wt % asphaltenes +10 wt % wax		1.16	46.8	3.88×10^{-5}	4.83×10^{-4}	10,461.1	2112.5
0.5 wt % asphaltenes +10 wt % wax		1.17	87.5	3.25×10^{-5}	4.99×10^{-4}	18,964.4	6021.7
1.5 wt % asphaltenes +10 wt % wax		1.19	299.6	2.48×10^{-5}	5.40×10^{-4}	63,870.0	12,835.6

Figure 6. Effect of asphaltene concentration on the interfacial tension (a,c) and interfacial modulus (b,d) of the diluted model waxy crude oil−water interface during the isothermal (30 °C) and cooling processes (30 to 0 °C).

3.5. Emulsion Stability at Different Temperatures.

For the emulsions without wax, the effect of temperature on the emulsion stability could be neglected due to the low viscosity of the model crude oils at 30 and 15 °C. The macroscopic stability of the emulsions after 24 h is shown in Figure 7a. The emulsion cannot be successfully prepared when there are no asphaltenes in the oil phase. A small amount of asphaltenes (0.05 wt %) could stabilize the water-in-model crude oil emulsions. Although no water phase was separated from the emulsions after 24 h, much oil was separated from the emulsion (the upper black layer) indicating the poor sedimentation stability of the emulsions. With the increase in the asphaltene concentration, the sedimentation stability of emulsions improves gradually. As shown in Figure 7e, the oil separation rate of the emulsions decreases from to 88 vol % with 0.05 wt % asphaltenes to 78 vol % with 1.5 wt % asphaltenes.

To better explain the sedimentation stability of the emulsions, the microstructure of the emulsions immediately after emulsification was photographed and is shown in Figure 8. Meanwhile, the water droplet size distribution is obtained

and shown in Figure 10a by analyzing the images in Figure 8. It should be noticed that the water droplets less than 1 μm cannot be counted because of the resolution of the images. It is clear that the water droplet size decreases with increasing asphaltene concentration. As shown in Figure 8, the peak emulsion droplet size decreases from 28 μm with 0.05 wt % asphaltenes to 10 μm with 1.5 wt % asphaltenes. The larger the water droplet size, the easier the water droplet is to sediment. Therefore, the sedimentation stability of the emulsions improves with the increase in the asphaltene concentration.

For the emulsions with 10 wt % wax, the effect of temperature on the emulsion stability is outstanding due to the huge rheological changes of the model crude oils at 30 and 15 °C. As shown in Figure 7b, the dissolved wax cannot stabilize the emulsions by itself. The dissolved paraffin improves the sedimentation stability of the emulsions at 30 °C to some extent. The oil separation rates of the emulsions at 30 °C are 81 vol % with 0.05 wt % asphaltenes and 62 vol % with 1.5 wt % asphaltenes (see Figure 7e). Obviously, the emulsion sedimentation stability is still poor. The microstructure of the emulsions with 10 wt % wax immediately after

Table 2. Effect of Asphaltene Concentration on the Model Waxy Crude Oil–Water Interfacial Tension and Dilatational Modulus at 30, 15, and 0 °C

| model crude oil	equilibrated γ at 30 °C/mN·m⁻¹	γ at 15 °C/mN·m⁻¹	γ at 0 °C/mN·m⁻¹	equilibrated E at 30 °C/mN·m⁻¹	E at 15 °C/mN·m⁻¹	E at 0 °C/mN·m⁻¹
0.005 wt % asphaltenes	21.81 ± 0.38	22.12 ± 0.32	22.55 ± 0.20	6.95 ± 0.25	8.43 ± 0.23	10.19 ± 0.20
0.015 wt % asphaltenes	19.47 ± 0.22	19.82 ± 0.15	20.23 ± 0.14	8.82 ± 0.12	9.69 ± 0.19	11.64 ± 0.10
0.05 wt % asphaltenes	19.05 ± 0.18	19.24 ± 0.12	19.81 ± 0.10	10.24 ± 0.33	12.57 ± 0.29	13.39 ± 0.25
0.15 wt % asphaltenes	18.30 ± 0.17	18.33 ± 0.14	18.56 ± 0.10	12.61 ± 0.31	14.30 ± 0.28	15.61 ± 0.13
0.005 wt % asphaltenes +1 wt % wax	20.26 ± 0.19	20.77 ± 0.12	21.26 ± 0.12	9.97 ± 0.25	12.27 ± 0.19	13.17 ± 0.15
0.015 wt % asphaltenes +1 wt % wax	19.24 ± 0.31	19.34 ± 0.29	19.66 ± 0.20	10.62 ± 0.30	13.85 ± 0.21	14.44 ± 0.11
0.05 wt % asphaltenes +1 wt % wax	18.65 ± 0.28	18.73 ± 0.17	19.06 ± 0.16	13.48 ± 0.25	15.84 ± 0.22	17.74 ± 0.21
0.15 wt % asphaltenes +1 wt % wax	17.84 ± 0.19	18.01 ± 0.10	18.25 ± 0.10	15.91 ± 0.29	18.19 ± 0.27	20.22 ± 0.21

emulsification was photographed and is shown in Figure 9. Based on the images of Figure 9, the water droplet size distribution is obtained and shown in Figure 10b. Clearly, the dissolved wax facilitates the asphaltene adsorption at the oil–water interface and then further decreases the water droplet size. As shown in Figure 10b, the peak water droplet size decreases from 22 μm with 0.05 wt % asphaltenes to 2 μm with 1.5 wt % asphaltenes. Therefore, compared with the sedimentation stability of the emulsions without wax, the sedimentation stability of the emulsions with 10 wt % wax at 30 °C improves to some extent.

As shown in Figure 7c, the precipitated wax crystals cannot stabilize the emulsions by themselves, meaning that the asphaltenes are the key emulsifier of the emulsions. The precipitated wax crystals can form network structures at 15 °C, then the sedimentation stability of the emulsions at 15 °C is greatly improved. With the increase in the asphaltene concentration, the strength of the network structure enhances quickly (see Figure 5 and Table 1). Therefore, the sedimentation stability of the emulsions improves rapidly with increasing asphaltene concentration. As shown in Figure 7e, the oil separation rates of the emulsions at 15 °C are 75 vol % with 0.05 wt % asphaltenes and 61 vol % with 0.15 wt % asphaltenes. At the asphaltene concentration ≤ 0.15 wt %, the network structure at 15 °C is weak, and then the emulsion sedimentation stability is poor. With the further increase of the asphaltene concentration (≥0.5 wt %), the network structure at 15 °C is strengthened greatly. As shown in Figure 7e, the oil separation rates of the emulsions at 15 °C are 17 vol % with 0.5 wt % asphaltenes and zero with 1.5 wt % asphaltenes, meaning that the wax crystal network could immobilize the emulsion droplets thus inhibiting sedimentation (see the lower image in Figure 7d, the emulsions cannot flow when the tubes containing the emulsions are placed horizontally).

In Figure 7a~c, we could not find the separated water phase in the emulsion system, but it does not mean that the coalescence stability of the emulsions is good. As shown in the upper image of Figure 7d, after the removal of the upper separated oil phase, it is found that the concentrated emulsion phase at 30 °C loses the flowability and looks like a gel. We consider that the interactions among the emulsion droplets lead to the gelation of the concentrated emulsions, and the gel-like structure immobilizes the emulsion droplets thus inhibiting the separation of water phase from the emulsions. Therefore, we cannot use the traditional ways to evaluate the coalescence stability of the water-in-model crude oil emulsions. Here, the coalescence stability of the emulsions is qualitatively studied by comparing the microscopic images of the emulsions at the initial time (0 h) and 24 h later.

Figure 11 shows the effect of the asphaltene concentration on the coalescence stability of the emulsions without wax. The water droplet size at 24 h is much bigger than that at the initial time even if the asphaltene concentration is high (1.5 wt %). This phenomenon indicates that the coalescence of the water droplets does take place during the sedimentation process, and the emulsions without wax have poor coalescence stability.

The effects of temperature and asphaltene concentration on the coalescence stability of the emulsions with 10 wt % wax are described in Figure 12. The coalescence stability of the emulsions at 30 °C is still poor, but the coalescence stability of the emulsions at 15 °C improves outstandingly. The formed wax crystal network structure at 15 °C plays a key role in the coalescence stability of the emulsions: when the asphaltene
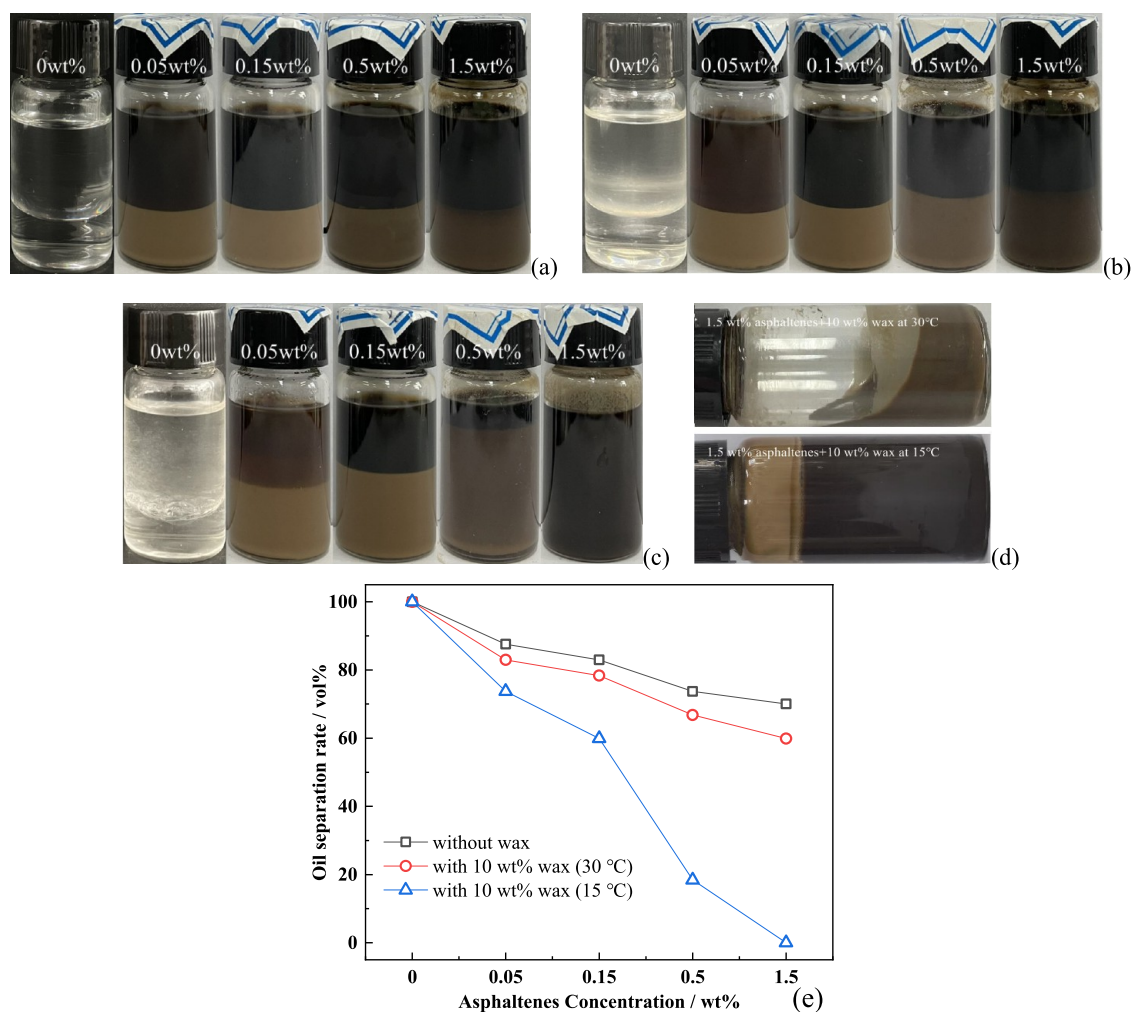
Figure 7. Effects of test temperature and asphaltene concentration on the sedimentation stability of emulsions after 24 h: (a) without wax; (b) with 10 wt % wax at 30 °C; (c) with 10 wt % wax at 15 °C; (d) gel structure of the concentrated emulsion phase; (e) oil separation rate curves.
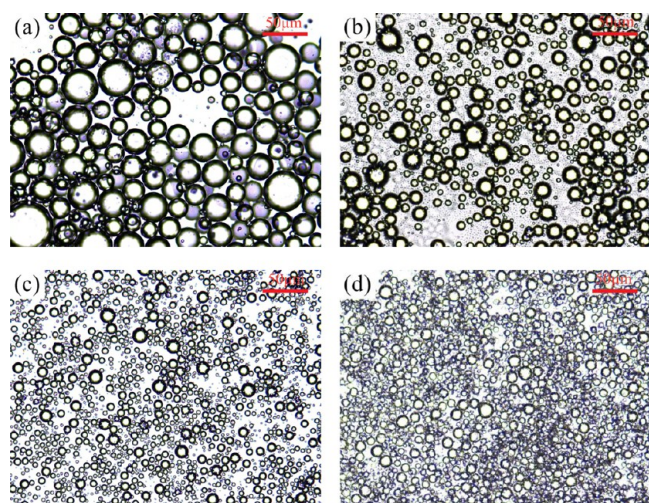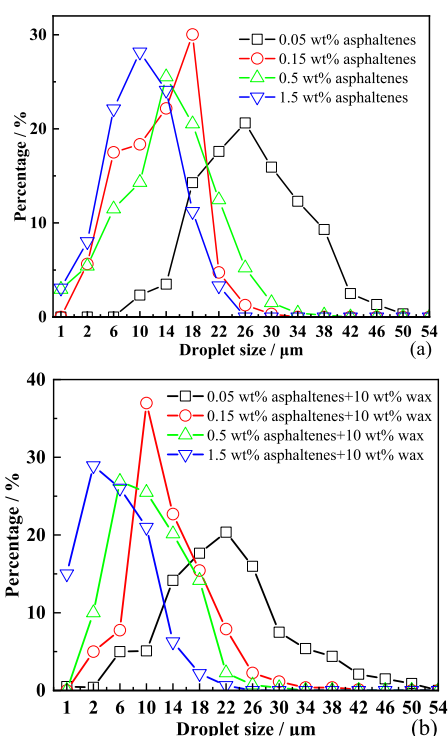

Figure 8. Effect of asphaltene concentration on the microstructure of the emulsions without wax: (a) 0.05 wt %; (b) 0.15 wt %; (c) 0.5 wt %; (d) 1.5 wt %.
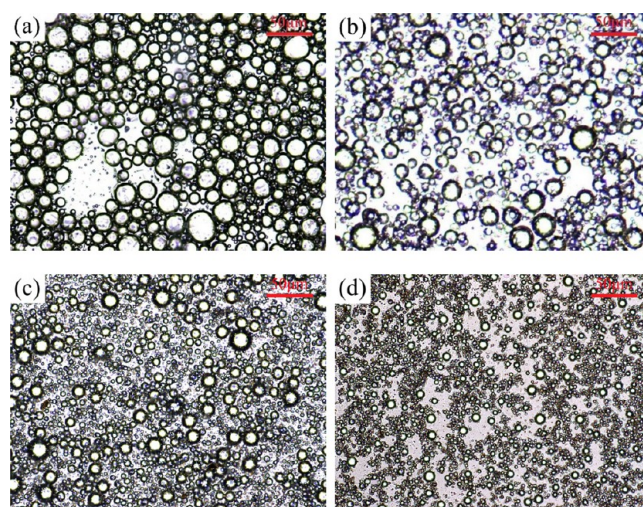
Figure 9. Effect of asphaltene concentration on the microstructure of emulsions containing 10 wt % wax: (a) 0.05 wt %; (b) 0.15 wt %; (c) 0.5 wt %; (d) 1.5 wt %.

concentration is 0.05 wt %, the formed network structure is relatively weak and then the improvement of the coalescence stability is modest; at the asphaltene concentration 1.5 wt %, the formed network structure is the strongest and then the

emulsion coalescence stability is the best (the water droplet size is nearly unchanged after 24 h).

Figure 10. Effect of asphaltene concentration on the water droplet size distribution of the emulsions: (a) without wax; (b) containing 10 wt % wax.
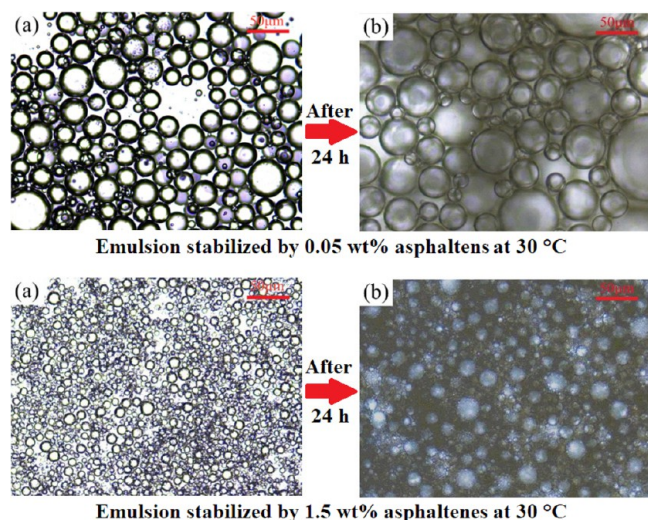
Figure 11. Effect of asphaltene concentration on the coalescence stability of the emulsions without wax: (a) at 0 h; (b) after 24 h.

4. CONCLUSIONS

In this paper, the effects of test temperature (30 and 15 °C) and asphaltene concentration (0~1.5 wt %) on the stability of water-in model waxy crude oil emulsions containing 10 wt % wax were systematically investigated through the wax precipitation and rheological tests of the model crude oils, dispersion state test of the asphaltenes in the oil phase, diluted model crude oil–water interfacial property measurement, emulsion stability measurement, and microscopic observation of the emulsion droplets. The conclusions are put forward as follows:
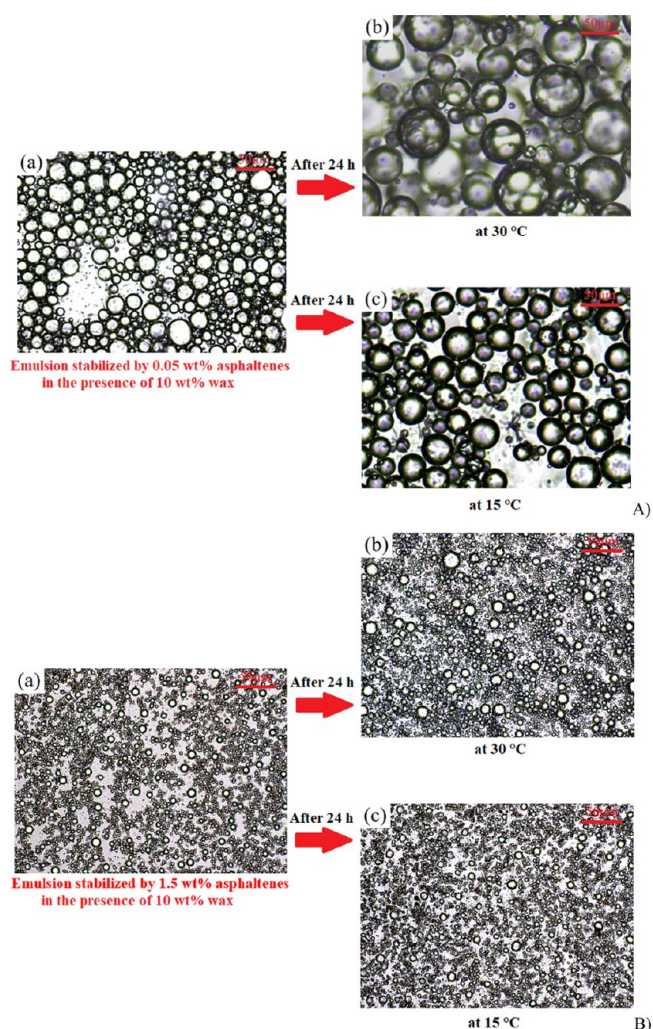
Figure 12. Effects of test temperature and asphaltene concentration on the coalescence stability of the emulsions containing 10 wt % wax. (A) With 0.05 wt % asphaltenes; (B) with 1.5 wt % asphaltenes: (a) at 0 h; (b) after 24 h at 30 °C; (c) after 24 h at 15 °C.

a) For the model crude oils without wax, the flowability of the oils is good and the asphaltene concentration has little influence on the oil rheology. Increasing the asphaltene concentration facilitates the asphaltene adsorption at the oil–water interface, thus reducing the interfacial tension and the water droplet size while enhancing the interfacial dilatational modulus. The stability of the emulsions improves with the increase in the asphaltene concentration, but the emulsions are still unstable mainly due to the weak structure of the continuous oil phase.

b) For the model waxy crude oil with 10 wt % wax, the WAT slightly decreases from the initial 25 to 24 °C after adding 0.05 wt % asphaltenes. The further increase of the asphaltene concentration has little influence on the WAT of the oils. The oil rheology is greatly improved after adding 0.05 wt % asphaltenes. With the further increase of asphaltene concentration, the rheological improving ability of the asphaltenes deteriorates rapidly. At the asphaltene concentration 1.5 wt %, the oil rheology is dramatically aggravated.

c) The stability of the emulsion containing 10 wt % wax is mainly controlled by two aspects. On the one hand, the

dissolved-state wax (30 °C) could facilitate the asphaltene adsorption at the oil−water interface, further reduce the interfacial tension and the water droplet size while enhancing the interfacial dilatational modulus; on the other, the wax crystals precipitated in the oil phase (15 °C) can form a strong network structure at relatively high asphaltene concentrations (0.5∼1.5 wt %) and then immobilize the water droplets. The above two aspects greatly improve the sedimentation and coalescence stabilities of the emulsions at 15 °C. In addition, we did not find persuasive evidence showing that the wax could crystallize at the water droplet surface and strengthen the oil−water interfacial films.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07174.

Carbon number distribution of the paraffin wax, the microstructure of the asphaltenes in model crude oil, and the precipitated wax crystals in the water-in-model crude oil emulsions (PDF)

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Notes

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