Study on the Kinetic Process of Asphaltene Precipitation during Crude Oil Mixing and Its Effect on the Wax Behavior of Crude Oil

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ABSTRACT: As an important component of crude oil, asphaltene precipitation and deposition are harmful to petroleum production and processing. In previous research, the impacts of asphaltene precipitation on crude oil characteristics were preliminarily explored. In this paper, by mixing different types of crude oil, the dynamic process of asphaltene precipitation and its effect on the crystallization and gelation behaviors of mixed crude oil were in-depth analyzed and discussed using the high-speed centrifugation technique, microscopic observation, differential scanning calorimetry (DSC) thermal analysis, and rheological test. The results showed that the asphaltene precipitation mainly occurred in the early stage of crude oil mixing and was influenced by crude oil composition. As the precipitation time increased, the driving force for asphaltene precipitation was gradually weakened until a dynamic equilibrium between asphaltene precipitation and dissolution was reached. Meanwhile, once the asphaltene precipitation occurred, the crystallization and gelation processes of crude oil were significantly affected. It was discovered that the change in the existing state of asphaltenes due to their precipitation is an important factor affecting the interaction of asphaltenes and waxes, which is critical for the technological development of oil and gas flow assurance.

1. INTRODUCTION
Crude oil is a complex mixture mainly composed of normal alkanes, aromatic hydrocarbons, napthenes, asphaltenes, resins, etc.\textsuperscript{1} Precipitation and deposition of normal paraffins (waxes) with high molecular weight and asphaltenes have brought many problems to crude oil mining, transportation, etc., which have aroused widespread concern in the petroleum industry.\textsuperscript{2,3}

As an important component of crude oil, asphaltenes are defined that are insoluble in \textit{n}-heptane but soluble in toluene, and these are dispersed in crude oil as a single phase in the form of colloidal particles.\textsuperscript{4,5} Under the influence of temperature, pressure, and composition, asphaltenes can aggregate, grow, and then precipitate from crude oil. According to related reports, many experimental procedures and modeling methods described the dynamic behavior and thermodynamic state of asphaltenes under different conditions.\textsuperscript{12−17} Anisimov et al.\textsuperscript{18} found that the size of basic aggregates was about 1 \textmu m and eventually reached 4–5 \textmu m in alkane solutions. In addition, Joshi et al.\textsuperscript{19} found that the size of precipitated asphaltenes was about 1–3 \textmu m using light scattering. Simultaneously, many techniques have detected the onset of asphaltene precipitation, such as extraction and gravimetric methods, viscosity analysis, optical microscopy, and refractometry.\textsuperscript{20–29} It was found that asphaltene precipitation was closely related to the type of precipitant, pressure, temperature, contact time, and precipitant concentration.\textsuperscript{30−37} Mullins\textsuperscript{38} found that when the asphaltene concentration in crude oil was greater than 0.01 wt %, it existed in the form of nanoparticles. However, clusterlike aggregates with larger sizes will be formed at higher concentrations.

Recently, regarding the interaction between asphaltenes and waxes, many studies have found that asphaltenes can change the characteristics of crude oils or simulated oils. Kriz et al.\textsuperscript{39} found that when the asphaltene concentration added to the system was 0.01 wt %, the wax appearance temperature (WAT) and yield stress of the system could be significantly increased; however, when the concentration was increased to 0.02 wt %, the WAT and yield stress decreased rapidly. Chanda et al.\textsuperscript{40} found that asphaltene can improve the flow characteristics of waxy oil when used alone or with a pour point depressant. Moreover, the accumulation degree of asphaltenes in crude oil is an important factor influencing
the flow characteristics. Venkatesan et al.\textsuperscript{41} believed that due to the addition of asphaltenes, the yield stress and gelation temperature reduced. Oliveira et al.\textsuperscript{42} showed that asphaltene can play a role as a pour point depressant, but it had little effect on the WAT of crude oil. Oh\textsuperscript{43} found that asphaltene can reduce the pour point and yield stress of the simulated oil.

In summary, most of the current research studies on the interaction between asphaltenes and waxes are focused on adding asphaltenes to a system and then analyzing the effect of asphaltenes on system properties. A few studies have paid attention to the changes in asphaltenes during crude oil mixing. However, it often involved the mixing process of different crude oils in oil industries. For example, heavy oil is often mixed with light oil to reduce viscosity for pipeline transportation; before petroleum refining, crude oils with different compositions will also be blended. In the above cases, it will destroy the stable balance of asphaltenes and cause its precipitation. To this end, this study analyzed the kinetics of asphaltene precipitation and further obtain the rate of asphaltene precipitation. The obtained asphaltenes were named as "precipitated asphaltenes", and the residual asphaltenes in crude oil were named as "unprecipitated asphaltenes". The specific steps are as follows: weighing a certain amount of BO-1 crude oil at each stirring time and loading it into four centrifugal tubes. Afterward, high-speed centrifugation was carried out at 40 °C (centrifugation speed, 11 000 rpm; centrifugation time, 30 min). Then, we poured the upper liquid of centrifugal tubes, added 20 mL of n-heptane to each centrifugal tube, and oscillated ultrasonically for another 10 min to remove the liquid oil remaining in the centrifuged cake. After that, the centrifugation operation was performed again under the same conditions. We repeated the above centrifugation and cleaning operations until the upper layer liquid was colorless. Finally, we placed the centrifugal tubes in an oven at a temperature of 120 °C and a pressure of $-5.00 \times 10^3$ Pa to dry them until there was no quality change within 2 days. Then, we cooled the asphaltenes in centrifugal tubes to room temperature, and the amount of precipitated asphaltenes could be obtained.

### 2.2.2. Determination of the Amount of Precipitated Asphaltenes. In this paper, the asphaltene quality obtained by centrifugal separation was used to reflect the kinetics of asphaltene precipitation and further obtain the rate of asphaltene precipitation. The obtained asphaltenes were named as "precipitated asphaltenes", and the residual asphaltenes in crude oil were named as "unprecipitated asphaltenes". The specific steps are as follows: weighing a certain amount of BO-1 crude oil at each stirring time and loading it into four centrifugal tubes. Afterward, high-speed centrifugation was carried out at 40 °C (centrifugation speed, 11 000 rpm; centrifugation time, 30 min). Then, we poured the upper liquid of centrifugal tubes, added 20 mL of n-heptane to each centrifugal tube, and oscillated ultrasonically for another 10 min to remove the liquid oil remaining in the centrifuged cake. After that, the centrifugation operation was performed again under the same conditions. We repeated the above centrifugation and cleaning operations until the upper layer liquid was colorless. Finally, we placed the centrifugal tubes in an oven at a temperature of 120 °C and a pressure of $-5.00 \times 10^3$ Pa to dry them until there was no quality change within 2 days. Then, we cooled the asphaltenes in centrifugal tubes to room temperature, and the amount of precipitated asphaltenes could be obtained.

### 2.2.3. Average Size and Fractal Dimension of Wax Crystals. The microscopic image of wax crystals was taken with a Nikon’s OPTIPHOT2-POL transmitted light polarizing microscope equipped with a Linkam PE60 hot/cold stage (temperature control in the range of $-20$ to 90 °C, with a precision of ±0.1 °C). Wax crystal images were captured by a matching Cool SNAP 3.3M microscope special CCD digital camera, and the average size and fractal dimension of wax crystals were obtained using ImageJ software. The specific process is as follows: The test slide and oil sample were preheated to 40 °C, respectively, and maintained at this temperature for 5 min. Then, the oil sample was evenly spread on the test slide using a cell scraper and covered with a cover glass. After that, the test slide was cooled to 15 °C statically at a rate of 0.5–4 °C/min on the hot/cold stage. When the temperature of the test slide decreased to 15 °C, a snapshot of the oil sample was taken to obtain the microscopic images of wax crystals.

### 2.2.4. Differential Scanning Calorimetry (DSC) Thermal Analysis. A TADSCQ20+RCS (40/90) was used to analyze the thermal characteristics of the crude oil mixture. During the process, dry N$_2$ was used for purging, and liquid nitrogen cooling equipment was used for cooling down. The specific test methods are as follows: 4–8 mg of test oil was taken into a specific aluminum crucible and the crucible was sealed. After that, it was placed in a DSC test tank and heated to 80 °C to melt all of the wax in the sample. After 1 min, under a N$_2$ atmosphere (flow rate was 50 mL/min), the sample was cooled from 80 to $-20$ °C at a cooling rate of 5 °C/min. In the study, to eliminate the influence of thermal history and shear history of the oil sample on the test results, two heating/cooling processes were used, and the crystallization and melting characteristics of oil sample were obtained from the second heating/cooling process.

### 2.2.5. Gelation Characteristics. The gel temperature and storage modulus of the oil sample were obtained by a HAAKE RS-150H-controlled stress rheometer using a temperature scanning method. The rheometer test system was a Z41Ti coaxial cylinder system with a rotor diameter of 41.42 mm and
an outer cylinder diameter of 43.40 mm. The temperature control system adopted an F8/C35 programmable water bath (control accuracy was ±0.1 °C). During the cooling process, the rheometer performed a small-amplitude oscillating shear scan with an oscillating frequency $f$ of 0.5 Hz and an oscillating shearing amplitude of 0.0005 ± 0.0001. The specific process is as follows: (1) the rheometer test system and oil sample were preheated to 40 °C, respectively, and maintained for 5 min; (2) 12 mL of oil sample was loaded into the rheometer and kept at 40 °C for another 15 min; and (3) the oil sample was cooled at a cooling rate of 0.5 °C/min and simultaneously sheared to the set temperature.

3. RESULTS AND DISCUSSION

3.1. Kinetic Process of Asphaltene Precipitation during Crude Oil Mixing. To reflect the kinetics process of asphaltene precipitation in the mixed crude oil by the amount of asphaltene precipitation, obviously, it must ensure that there was no asphaltene precipitation in crude oils A and B. To this end, we conducted asphaltene microscopic observations for crude oils A and B, respectively, as shown in Figure 1. It can be seen that almost no precipitated asphaltenes can be seen in the scope of microscopic vision, i.e., the asphaltenes in crude oils A and B were stably dissolved in their original systems. In other words, we can also think that no asphaltene precipitation occurred in the crude oil mixture at the moment when A and B were mixed ($t = 0$ h).

As shown in Figure 2, at each mixing ratio, as the precipitation time went on, the amount of precipitated asphaltenes gradually increased until a stable value was reached after 24 h, which was a similar conclusion to our previous research. Simultaneously, in terms of the rate of asphaltene precipitation in Table 2, at a mixing ratio of 4:1, the values at 0–1, 1–12, 12–24, and 24–48 h were, respectively, 1.62, 0.025, 0.015, and 0 g/h. Obviously, at 0–1 h, it was much higher than those at 1–12, 12–24, and 24–48 h. In other words, it can be inferred that in the mixed early stage, due to changes in the environment of the crude oil system, the unstable asphaltenes had appeared, resulting in a large amount of asphaltenes rapidly precipitated in a short time. As the mixing process continued, the driving force of asphaltene precipitation gradually weakened, and the asphaltene precipitation and dissolution will gradually reach a dynamic equilibrium.

To further analyze the conclusion of asphaltene precipitation, we tracked the dynamic process of asphaltene precipitation at a mixing ratio of 4:1, as shown in Figure 3. It can be found that at $t = 1$ h, compared with before mixing, a large amount of precipitated asphaltenes suddenly appeared in the field of view. As the experiment time continued to 48 h, the amount of precipitated asphaltenes increased, and their size also increased. However, relative to the change within 1 h, the driving force for asphaltene precipitation obviously weakened, which also showed that for crude oil mixing, the initial stage will be a critical period for asphaltene precipitation.

In addition, in terms of the rate of asphaltene precipitation in Table 2, it can be seen that at $t = 1$ h, as the mixing ratio of crude oil A and B decreased gradually, that is, the proportion of crude oil B increased gradually, the kinetic rate of asphaltenes precipitation also increased gradually. As we all know, the composition of crude oil was the decisive factor for its characteristics. Before and after crude oil mixing, the contents of saturated and aromatic components in crude oil were changed. It can be seen in Table 1 that the content of saturated components in crude oil A was less than that of crude oil B, but the content of aromatic components was higher. In the period of 0–1 h, when crude oil A was added to B, the content of saturated component in BO-1 crude oil increased suddenly compared with that in crude oil A at this time, while the aromatic component decreased relatively. This change obviously directly destroyed the stable asphaltene equilibrium in an original system. In a short time, a large amount of asphaltenes was precipitated. In the periods of 1–12 and 12–24 h, the role of saturated and aromatic components in BO-1 crude oil continued, leading to continued asphaltene precipitation. However, due to the limited impact of composition changes, the precipitation rate gradually decreased. In the period of 24–48 h, the destroyed asphaltene balance was re-established, and the amount of precipitated asphaltene was basically unchanged, which was also similar to the conclusion of Maqbool’s research.

Additionally, as shown in Figure 4, at a mixing ratio of 4:1, the mass of the unprecipitated asphaltenes can be obtained by subtracting the mass of precipitated asphaltenes. It can be seen that the mass of the unprecipitated asphaltenes in BO-1 crude oil still accounted for a large proportion. This also showed that during crude oil mixing, if purely depending on the influence of the crude oil component changes, the driving force for

### Table 2. Kinetic Rate of Asphaltene Precipitation

| mixing ratio (crude oil A/B) | 0–1 h | 1–12 h | 12–24 h | 24–48 h |
|-----------------------------|-------|--------|---------|--------|
| 4:1                         | 1.62  | 0.025  | 0.015   | 0      |
| 3:1                         | 1.80  | 0.041  | 0.023   | 0      |
| 2:1                         | 2.07  | 0.041  | 0.015   | 0.004  |
| 1:1                         | 2.79  | 0.025  | 0.041   | 0.008  |

Figure 1. Asphaltene micrographs for crude oil A (left) and crude oil B (right) at 40 °C.

Figure 2. Amount of precipitated asphaltenes as a function of time for BO-1 crude oil at 40 °C.
asphaltene precipitation was relatively weak, resulting in less asphaltene precipitation.

3.2. Effect of Asphaltene Precipitation on the Crystallization and Gelation of Crude Oil. It should be noted that, for the convenience of analysis, subsequent studies were carried out on the system with a mixture ratio of 4:1, studying the characteristics of wax crystals, crystallization heat, and gelation structure.

3.2.1. Analysis of Average Size and Fractal Dimension of Wax Crystal. As shown in Figure 5, as the amount of precipitated asphaltenes increased, the average size and fractal dimension of wax crystals in BO-1 crude oil gradually increased.

Combined with the case of asphaltene precipitation, when t = 1 h, most of the asphaltenes in BO-1 crude oil were the unprecipitated asphaltenes, and they were evenly dispersed. Over time, the unprecipitated asphaltenes gradually aggregate to become precipitated asphaltenes. Obviously, this change directly caused the size distribution of asphaltene particles to increase. In addition, combined with the presence of its surface functional groups, the precipitated asphaltenes had a large spatial structure. As the oil temperature decreased below WAT, due to the presence of external nucleation centers, wax molecules will be easier to directly precipitate and grow on the surface of precipitated asphaltenes. In this case, it was easier to promote the formation of large-sized wax crystals so that the fractal dimension of wax crystals increased with time.

After the precipitated asphaltenes were separated, as shown in Figure 6, the average size and fractal dimension of wax crystals in BO-2 crude oil were significantly reduced. This also showed that the precipitated asphaltenes indeed affected the crystallization of wax molecules, provided the crystalline core for wax molecules, and changed the growth of wax crystals.

3.2.2. Analysis of Crystallization Heat and Cumulative Amount of Wax Precipitation. To further study the effect of asphaltene precipitation on wax crystallization, Figures 7 and 8 show the DSC thermograms of the oil samples during cooling and heating. To ensure the reliability of test results, WATs of BO-1 crude oil with stirring times of 1 and 48 h were repeatedly verified, and the standard deviations were 0.43 and 0.53 °C, respectively.

As can be seen from Figures 7 and 8, asphaltene precipitation had almost no effect on the WAT and melting wax point of BO-1 crude oil, but the crystallization heat and cumulative amount of wax precipitation (from WAT to −20 °C) were increased.

When oil temperature was higher than WAT, wax molecules contained higher energy, and wax crystallization behavior did not occur. As oil temperature decreased below WAT, the effect of asphaltenes on wax molecules was gradually reflected. As time went on, the precipitation effect between asphaltenes became stronger. In this case, the nucleation of the precipitated asphaltenes increased, which directly lead to an increase in the cumulative amount of wax precipitation. As for the heat
released during wax crystallization, as the cumulative wax precipitation increased from 1 to 48 h, it caused an increase in the total latent heat of phase change. Simultaneously, some specific wax molecules in the liquid phase can be in contact with the surface-specific structure of precipitated asphaltene through their alkyl carbon chains, and a phenomenon similar to “quasi-crystallization” occurred, resulting in the exotherm of the liquid phase.

3.2.3. Analysis of Gelation Temperature and Storage Modulus. To further study the effect of asphaltene precipitation on the gelation characteristics of BO-1 crude oil, the gelation temperature and storage modulus were measured, as shown in Figures 9 and 10. In addition, to ensure the reliability of experimental results, the gelation temperature of BO-1 crude oil at 1 h was measured three times, and the standard deviation was 0.2 °C. In other cases, it showed similar results.

As shown in Figure 9, the gelation temperature of BO-1 crude oil decreased as the amount of precipitated asphaltenes increased. In other words, as asphaltenes precipitated, the establishment of the wax crystal network structure was delayed to a certain extent. After separating the precipitated asphaltenes, the gelation temperature of the BO-2 crude oil was higher than that before the precipitated asphaltenes separated. Obviously, the precipitated asphaltenes played an important role in the whole gelation process of crude oil. As mentioned before, the precipitated asphaltenes themselves had a larger structure and aggregation degree than unprecipitated asphaltenes. In addition, because the precipitated asphaltenes can play a role similar to that of polymer additives, wax molecules can naturally precipitate and grow on their surfaces as crystallization sites. During the cooling process, the
precipitated asphaltenes can easily induce the formation of large-sized wax crystals. From the point of the substance surface characteristics, the large-sized wax crystals had smaller specific surface areas and surface energy, and they are more stable and can exist alone in an oil system. Obviously, losing the mutual bonding of wax crystals, the establishment of the gel network structure for crude oil was delayed. However, after the precipitated asphaltenes separated, wax molecules lose their external crystalline core. In this case, it can only rely on the wax molecule itself aggregation into cores. As the small-sized wax crystals had large specific surface areas and surface energy, they easily combined with each other to reduce the surface energy. In other words, the small-sized wax crystals will be the first choice for crystallization, and they can quickly form a gel network structure. Meanwhile, the gelation temperature after the precipitated asphaltenes separated was higher than that of asphaltenes before precipitation, which exactly illustrated that the presence of precipitated asphaltenes inhibited the establishment of the gel network structure.

In addition, this article also analyzed the storage modulus of the gel structure formed. As shown in Figure 10, after the precipitated asphaltenes were removed, compared with before separation, the storage modulus of BO-2 crude oil increased at the same temperature, i.e., the strength of the formed gel network structure became stronger and stronger.

Previous studies on colloidal systems have found that when small-sized particles were added to the system, they increased the connection points between large-sized particles, resulting in increased structural strength. ten Brinke et al.\textsuperscript{45} found that the storage modulus increased by more than 10 times and the yield stress reached more than 3 times. In crude oils studied in this paper, as asphaltene gradually precipitated, the presence of precipitated asphaltenes or asphaltene clusters with larger sizes and structures reduced the connection points between solid particles. In this case, the size distribution of wax crystals increased considering the effect of precipitated asphaltenes. On the one hand, the space structure of precipitated asphaltenes was large and cannot be closely connected with the gelatinous network structure. Once a shearing action was applied, the formed gelled structure will break from the connection positions between these asphaltenes and wax crystals. On the other hand, the gelatinous network structure formed by small-sized wax crystals had good integrity, which also increased the strength of the gel structure to a certain extent.

4. CONCLUSIONS

This paper examined the process of asphaltene precipitation in the mixing process of crude oils. On this basis, the effect of asphaltene precipitation on crystallization and gelation of mixed crude oil was studied. The results show that the dynamics of asphaltene precipitation during crude oil mixing was complex and moderate and related to the combined action of aromatic components and alkanes in crude oils. Meanwhile, the presence of precipitated asphaltenes can significantly affect the crystallization process of wax molecules and gelation characteristics. As the quality of precipitated asphaltenes increased, the WAT and melting wax point of mixed crude oil were unchanged, but the crystallization enthalpy, amount of wax precipitation, and cumulative wax precipitation gradually increased. This indicated that the asphaltene precipitation changed the crystallization behavior of wax molecules, and the existing state of asphaltenes was an important factor affecting...
the interaction between asphaltenes and waxes. As the asphaltene precipitation intensified, the gelation temperature and storage modulus of crude oil decreased, i.e., the strength of the formed gelatinous network structure was getting weaker.

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Notes
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