Investigating the Rheology and Stability of Heavy Crude Oil-in-Water Emulsions Using APG08 Emulsifiers

Bo Dong, Zongyu Qin, Yiwei Wang, Jiahui Zhang, Zhen Xu, Aixian Liu,* and Xuqiang Guo

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: This work investigates the performance of isooctyl glucoside (APG08) as an emulsifier for the preparation of a Karamay heavy crude oil-in-water emulsion to facilitate its pipeline transportation. First, various factors affecting the rheology and stability of prepared emulsions were studied. The results revealed that the viscosity and stability of emulsions increased with increasing oil content, surfactant concentration, mixing speed, mixing time, and pH of the aqueous phase. Emulsion viscosity was initially unchanged with the increase in homogenization temperature and then increased while emulsion stability decreased. Meanwhile, the optimal values of key parameters were 75 wt % oil content, 0.5 wt % surfactant concentration, temperature of 30 °C, mixing speed of 750 rpm, mixing time of 10 min, and aqueous phase pH of 11.14, resulting in a viscosity reduction of 88.82% and emulsion stability up to 48 h at 96.27%. In addition, a qualitative relationship between the stability and rheology of emulsions was elaborated by analyzing the experimental results. The findings showed that an increase in emulsion stability was accompanied by an increase in emulsion viscosity. Therefore, emulsion viscosity cannot become very high while improving emulsion stability to ensure proper transportation.
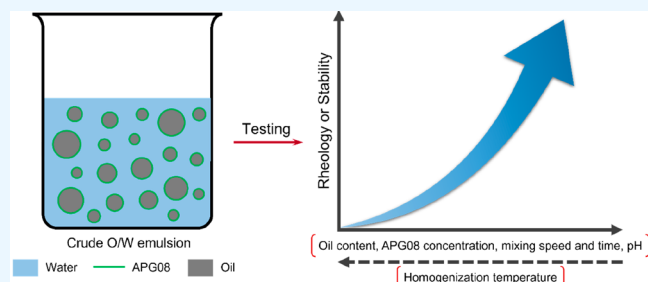
1. INTRODUCTION

Fossil fuels, such as oil, natural gas, and coal, play a leading role in satisfying the world's energy demands. In addition, crude oil is considered to remain the most important energy resource for the next five decades.[1] With the continuous growth of world energy consumption, the reserves of conventional crude oil are gradually declining each year. Therefore, a need for heavy unconventional crude oil represented as an alternative resource is being developed.[2] The fundamental features of heavy crude oils are high viscosity, high density, and heavy components, distinguishing them from conventional light oils.[3] However, due to the high viscosity and complex composition of heavy crude oil,[4] it is subject to many technical difficulties during production, transportation, and refining processes.[5,6] Thus, the key to solving these difficulties is to reduce the high viscosity of heavy crude oil.[7]

In order to transport heavy crude oil from the reservoir to the refinery through pipelines, commonly used viscosity reduction approaches mainly include heating, dilution with light hydrocarbon liquids or solvents, pour point reduction, developing a core annular flow, drag reducing additives, and in situ partial upgrading.[8,9] However, these approaches have some limitations and drawbacks to varying degrees, including high energy consumption, high cost, difficult operation, undesirable viscosity reduction effects, and other problems.[10] Another favorable approach for pipeline transportation of heavy crude oil is the formation of oil-in-water (O/W)

emulsions.[11] In this approach, droplets of the oil phase become dispersed into the aqueous phase, through the use of suitable surfactant agents, to form a stable (O/W) emulsion.[12,13] The formation of an emulsion significantly reduces the viscosity and pour point of the crude oil. Meanwhile, surfactant molecules can be adsorbed on the inner wall of the pipe to form a water layer, which dramatically reduces the friction resistance between the crude oil and pipe wall during transportation.[14] Transportation costs and problems are reduced because of the significant reduction in viscosity and flow resistance. This approach is also considered to be a very effective technique for transporting highly viscous crude oils in cold regions. Also, as water is the continuous phase, the risks of sediment deposition in pipes as well as clogging and corrosion of pipelines are greatly reduced.[12,13]

The formation of emulsions is highly dependent on many operating factors such as surfactant type and concentration, oil content, temperature, mixing speed, mixing time, water salinity, and pH.[8,15] The rheology and stability of the emulsion, which
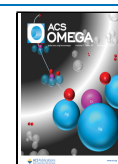
are important criteria for improving efficient pipeline transport of heavy crude oil, need to be investigated.[11] Azodi and Nazar[11,16,17] have studied the effects of various operating parameters on the viscosity and stability of two heavy crude oil types in water emulsions using three commercial emulsifiers and the Taguchi experimental design method. They found that the viscosity and stability of emulsions increase with increasing oil content and emulsifier concentration. Ashrafizadeh and Kamran[18] have presented an experimental study to investigate the diverse factors affecting the viscosity and stability of O/W emulsions for two Iranian oil samples by the addition of Triton X-100 surfactant. They observed that the viscosity of emulsions increases by increasing oil content, surfactant concentration, mixing speed, mixing time, salt concentration, and pH of the aqueous phase, except for the homogenization temperature. The stability of emulsions decreases with increasing oil content while increasing the surfactant and salt concentration, mixing time, mixing speed, aqueous phase pH, and homogenization temperature improved emulsion stability. Abdurahman et al.[19] have also investigated the influence of various factors on the stability and viscosity of stable crude O/W emulsions for two Malaysian oil samples using Triton X-100 surfactant. The experimental results showed a similar regularity to the results of research conducted by Ashrafizadeh and Kamran. Ashrafizadeh et al.[20,21] have investigated the influence of sodium carbonate (Na_2CO_3) concentration, as a natural surfactant, as well as water salinity, mixing time, and homogenization speed on the stability and viscosity of Iranian Paydar heavy crude oil in water emulsions. Their study revealed that emulsion stability increases with increasing surfactant concentration in the aqueous phase, homogenization speed, and homogenization duration. They also found an initial slow increase in emulsion viscosity when Na_2CO_3 concentration increased from 2000 to 6000 ppm and then observed a rapid increase in emulsion viscosity when Na_2CO_3 concentration increased from 6000 to 15000 ppm. Kumar and Mahto[13,22,23] have studied the effects of optimal parameters on the rheology, stability, and droplet size distribution of O/W emulsions for India heavy crude oil through the use of synthesized surfactants. They observed that the apparent viscosity of the emulsion decreases as the oil content and water salinity decrease as well as the water phase pH increases. Furthermore, the apparent viscosity of the emulsion first decreases and then increases with increasing surfactant concentration. The stability of the emulsion increases with an increase in oil content, surfactant concentration, and water phase pH. Sun et al.[1,24] have studied the influence of various factors on the rheology and stability of heavy oil-in-water emulsions prepared by compounded amphoteric/nonionic surfactants and inorganic/organic alkalis. They found that the apparent viscosity increases with increasing formulated surfactant content and oil−water ratio, whereas an increase in temperature leads to a decrease in apparent viscosity. Moreover, the apparent viscosity initially increases as the mixing speed increases, and then it decreases. They also discovered that the emulsion stability increases with increasing surfactant and alkali concentrations, but an increase in temperature is unfavorable for emulsion stability. Moreover, emulsion stability initially decreases and then increases as the oil−water ratio increases. Pang et al.[25] investigated the effect of pH and salinity on emulsion stability, droplet size, and distribution as well as rheological behavior. They found that stability of emulsions decreased with increasing salinity.

Moreover, the increase or decrease in pH both improved emulsion stability and reduced droplet size. Equally, rheological behavior of emulsion was also greatly affected by salinity and pH. Shear thinning behavior was more pronounced in lower salinity and pH environments. Chen et al.[26] combined the advantages of surfactant addition and dilution, using a toluene in water emulsion prepared with AES-DOA mixed surfactants to emulsify extra heavy oil. They found that addition of toluene reduced the viscosity of extra heavy oil, thus promoting the emulsification. Furthermore, the emulsion droplet size decreased with increasing toluene content, which contributed to improve the stability of extra heavy O/W emulsion.

Stable O/W emulsions for transporting heavy crude oils can be prepared using a variety of surfactants, mainly including cationic, anionic, and nonionic surfactants.[27] Nonionic surfactants are relatively inexpensive and not only have high surface activity, good wettability, and high salinity resistance but also have good compatibility with other chemicals.[14,28] Also, their emulsions are easily separable, and these surfactants do not form unwanted organic residues affecting the oil's properties,[23] such that they have been widely applied in oil fields. Isooctyl glucoside (APG08) is a nonionic surfactant, which is environmentally friendly, biodegradable, nontoxic, and low foaming.[29,30] Alkyl glycosides have been used in many fields, such as daily chemicals, pharmaceuticals, petrochemicals, and agriculture. However, not many studies have been reported regarding the use of APG08 as an emulsifier for reducing the viscosity of heavy crude oil.

In current research, an attempt has been made to use APG08 to facilitate the transport of heavy crude oil by forming a stable O/W emulsion. First, this study investigated the effects of oil content, surfactant concentration, homogenization temperature, mixing speed, mixing duration, and pH of the aqueous phase on the rheology and stability of the produced emulsions. These emulsion parameters were then optimized one by one with rheology and stability as evaluation indicators. Second, the relationship between the stability and rheology of emulsions was proposed based on the experimental results, which provides a theoretical reference for efficient transportation of heavy crudes as O/W emulsions.

2. EXPERIMENTAL SECTION

2.1. Materials and Instruments. The heavy crude oil samples used were collected from the Karamay oil field (Xinjiang, China). The physical and chemical properties of Karamay crude oil are shown in Table 1. The rheological properties of heavy crude oil were measured using the Anton

Table 1. Physical and Chemical Properties of Crude Oil Samples

property	quantity
water content (% w/w)	0.03
density at 20 °C (g·cm^{-3})	0.9171
wax content (% w/w)	1.15
sulfur content (% w/w)	0.176
pour point (°C)	4
initial boiling point (°C)	197
component content (% w/w)	
resins	4.94
asphaltenes	2.42

Paar viscometer model RheolabQC. The apparent viscosity of heavy crude oil versus shear rate at 50 °C is shown in Figure 1. A heavy crude oil sample exhibited non-Newtonian shear thinning flow behavior within a shear rate range of 10−300 s^{-1} at 50 °C.
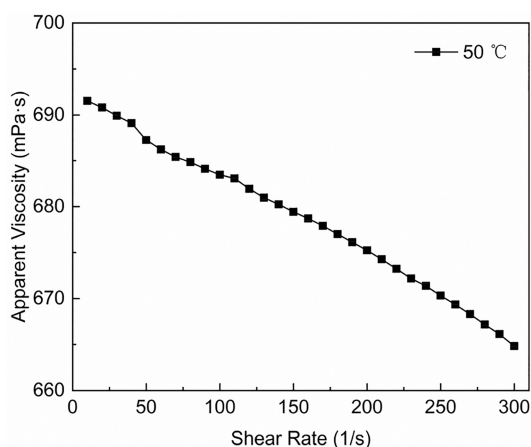

Figure 1. Apparent viscosity of heavy crude oil versus shear rate at 50 °C.

The nonionic surfactant APG08 (CAS: 125590-73-0, chemical formulation $C_{14}H_{28}O_6$) was used to prepare O/W emulsions. This surfactant was purchased from Shandong Usolf Chemical Technology Co., Ltd. (Linyi, China) with 60% purity. Deionized water was used for preparing the aqueous phase of the emulsion. Na_2CO_3 was used to adjust the pH of the water phase, with Na_2CO_3 (≥99.8% purity) purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The main experimental instruments used during the preparation of emulsions and their key parameters are given in Table 2.

2.2. Preparation of Emulsions. The experimental procedures are shown in Figure 2. First, the aqueous phase was prepared by adding surfactant into deionized water and heating in a water bath at 50 °C for 30 min. The heavy crude oil sample was preheated at 50 °C for 30 min to remove gas bubbles. Next, the aqueous phase was added to the heavy crude oil sample to form a mixture, which was then held in a water bath at a constant experimental temperature for 30 min. Finally, mixtures were stirred with a digital motor blender (100 W, 0−3000 rpm) to prepare O/W emulsions. The produced emulsions were then used for rheology and stability measurements. In this study, emulsions were prepared in six series by successively varying one parameter, including oil content (70−80 wt %), surfactant concentration (0.3−0.9 wt %),

homogenization temperature (30−70 °C), mixing speed (500−1500 rpm), mixing duration (3−20 min), and pH of the aqueous phase (6.70−11.15). The surfactant concentration (wt %) in the aqueous phase was based on the total weight of the emulsion, whereas Na_2CO_3 concentration (ppm) was based only on the weight of water in the emulsion.

2.3. Viscosity Measurement of Emulsions. Rheological measurements were performed using an Anton Paar ViscoQC 300 rotational viscometer with a standard spindle of CC26. The apparent viscosity of prepared emulsions was determined over a shear rate range of 10−300 s^{-1} at a constant temperature of 50 °C. All viscosity measurements were repeated several times until similar data were obtained for each sample. The measurement limits of viscosity at different shear rates are presented in Table 3.

The percentage of viscosity reduction was calculated using eq 1, expressed as

$$\% \text{ viscosity reduction} = \left(\frac{\mu_O - \mu_{O/W}}{\mu_O} \right) \times 100 \tag{1}$$

where μ_O is the viscosity of the heavy crude oil, and $\mu_{O/W}$ is the emulsion viscosity measured under the same conditions of temperature and shear rate.

2.4. Stability Measurement of Emulsions. Emulsion stability was measured using the bottle-test method.[23] After the stirring process, each emulsion sample was immediately transferred into a separate graduated 50 mL stoppered glass tube. Then the tube was placed into a water bath at the corresponding homogenization temperature. The volume of separated water from emulsion samples was recorded after 24 and 48 h.

The emulsion stability was calculated using eq 2, expressed as

$$\% \text{ emulsion stability}$$
$$= \left(1 - \frac{\text{volume of separated water (mL)}}{\text{total volume of water (mL)}} \right) \times 100 \tag{2}$$

3. RESULTS AND DISCUSSION

3.1. Effects of Oil Content. The effects of oil content of the emulsion on its apparent viscosity and stability were investigated. For this, the APG08 concentration in the emulsion was held constant at 0.5 wt % while at a temperature of 50 °C and pH of 6.70. The speed and time of mixing were 500 rpm and 10 min, respectively. Furthermore, the oil content of the emulsion was varied from 70 to 80 wt %.

Table 2. Experimental Instruments

| experimental instruments	types	producers	minimum indexing value	accuracy	purpose
electronic balance	YP10002	Shanghai Hengji Scientific Instrument Co., Ltd.	0.01 g	±0.02 g	weighing oil and water
electronic analytical balance	FA2004	Hunan Lichen Instrument Technology Co., Ltd.	0.0001 g	±0.0002 g	weighing surfactant
digital thermostatic water bath	HH-601	Changzhou Jintan Liangyou Instrument Co., Ltd.	0.1 °C	±0.5 °C	controlling temperature
digital motor blender	JJ-1A-100W	Shanghai Yushen Instrument Co., Ltd.	1 rpm	±5 rpm	mixing emulsions
digital pH meter	FE22	Mettler-Toledo Instruments (Shanghai) Co., Ltd.	0.01 pH	±0.01 pH	measuring the pH of the aqueous phase
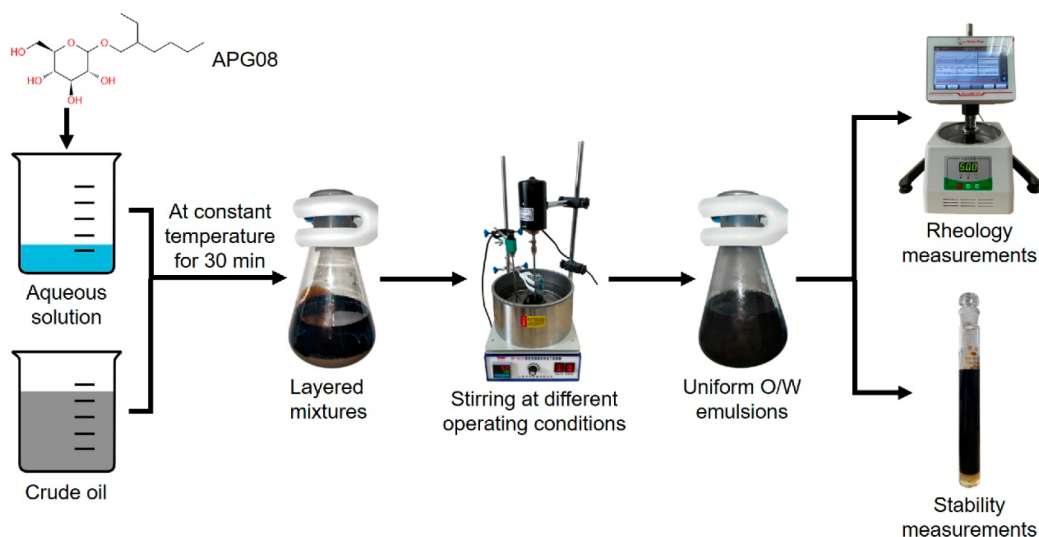
Figure 2. Brief schematic diagram of crude oil-in-water emulsion preparation and testing.

Table 3. Measurement Limits of Viscosity

shear rate (1/s)	viscosity limit (mPa·s)
50	315
100	157
150	105
200	78.7
250	63
300	52.5

The effects of oil content on the apparent viscosity of the emulsion versus shear rate are shown in Figure 3a. All five emulsions exhibited non-Newtonian shear thinning behavior, but they tended toward Newtonian fluid behavior at lower oil content and higher shear rate.[13] Moreover, the viscosity of emulsions increased slightly with increasing oil content from 70 to 75 wt %. This might be attributed to the fact that more interfacial area between the oil and aqueous phases might have been produced with the increase in oil content. This would have reduced the size of oil droplets and thinned the liquid film between oil droplets,[24,31] making it easy for oil droplets to collide with each other under shearing and resulting in an increase in the viscosity of emulsions. However, the viscosity of emulsions increased significantly as the oil content increased from 75 to 80 wt %. Also, for 80% oil content in the emulsion, the apparent viscosity exceeded the measurement limit of the viscometer above 130 s^{-1} shear rate because of higher oil content. At 130 s^{-1} shear rate, the apparent viscosity of the emulsion with 80 wt % oil content was 112 mPa·s, whereas it was merely 37.82 mPa·s with 70 wt % oil content. This phenomenon was attributed to the mass fraction of dispersed phase (heavy oil) gradually increasing as the oil content continued to increase, with O/W and W/O type emulsion droplets beginning to occur simultaneously. At this time, the viscosity of the emulsion depended not only on the viscosity of the aqueous phase but also on the viscosity of the oil phase, and since the viscosity of heavy oil was extremely high, the emulsion viscosity increased significantly. Therefore, an increase in oil content resulted in an increase in emulsion viscosity.

Figure 3b,c shows the influence of oil content on the stability of the emulsion. First, the stability of the emulsion

after 48 h was lower than that after 24 h. Furthermore, the stability of the emulsion gradually increased as the oil content in the emulsion increased. The reason for this effect was that, when oil content increased, the number of emulsified oil droplets increased and their size became smaller. The production of smaller-sized oil droplets led to increased interfacial area, allowing more interactions between one particle and another,[13] which resulted in increased emulsion stability. However, the emulsion began to demonstrate a phase inversion when the oil content was above 75 wt %, making it difficult for water to separate from the oil phase, thus resulting in a low water separation rate and high emulsion stability.[32] Consequently, when viscosity and stability were taken into account, the oil content of 75 wt % was considered an optimal value for performing the rest of the experiments.

3.2. Effects of Surfactant Concentration. The influence of APG08 surfactant on the apparent viscosity and stability of these emulsions was investigated. The oil content in the emulsion was held constant at an optimum value of 75 wt %, and other conditions included a temperature of 50 °C, pH of 6.70, mixing speed of 500 rpm, and mixing duration of 10 min. The APG08 surfactant concentration in emulsions was varied from 0.3 to 0.9 wt % with respect to the total weight of the emulsion.

Figure 4a shows the effects of surfactant concentration on the apparent viscosity of the emulsion versus shear rate. Increasing the surfactant concentration from 0.3 to 0.5 wt % led to a significant increase in the apparent viscosity. On one hand, increasing the surfactant concentration resulted in an increased number of surfactant molecules adsorbed at the oil–water interface, which resulted in a strong interfacial film and decreased coalescence of dispersed oil droplets.[24] On the other hand, increasing the surfactant concentration lowered the interfacial tension between oil and water, which facilitated breakage of droplets into smaller ones.[18,19] These effects mentioned above provided a better distribution of oil droplets in the continuous phase, resulting in an increased emulsion viscosity. However, the apparent viscosity of the emulsion slightly increased above 0.5 wt % concentration. This might have been because excess surfactant molecules began to aggregate to form micelles with the further increase in surfactant concentration,[33] which were unfavorable for
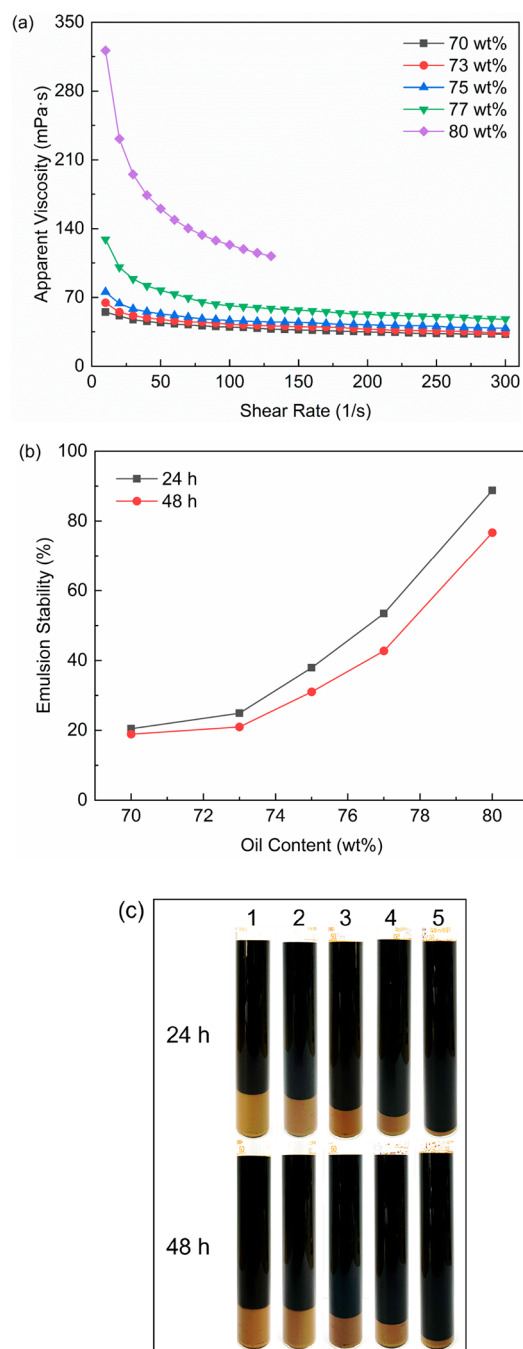
Figure 3. Influence of oil content on the rheology and stability of emulsion (a) rheology, (b) stability, and (c) stability measurement (1−5: 70, 73, 75, 77, 80 wt %).

Figure 4. Influence of surfactant concentration on the rheology and stability of the emulsion (a) rheology, (b) stability, and (c) stability measurement (1−4: 0.3, 0.5, 0.7, 0.9 wt %).

surfactant adsorption onto oil−water interfaces. Also, these surfactant micelles would slightly increase the viscosity of the aqueous phase, such that emulsion viscosity also slightly increased.[24]

Figure 4b,c illustrates the influence of the surfactant concentration on the stability of the emulsion. The stability of the emulsion increased significantly as the surfactant concentration increased from 0.3 to 0.5 wt %, but the stability of the emulsion only slightly increased above 0.5 wt % concentration. This was probably because the increase in surfactant concentration caused an increase in the number of barriers at the oil−water interface, which provided a better
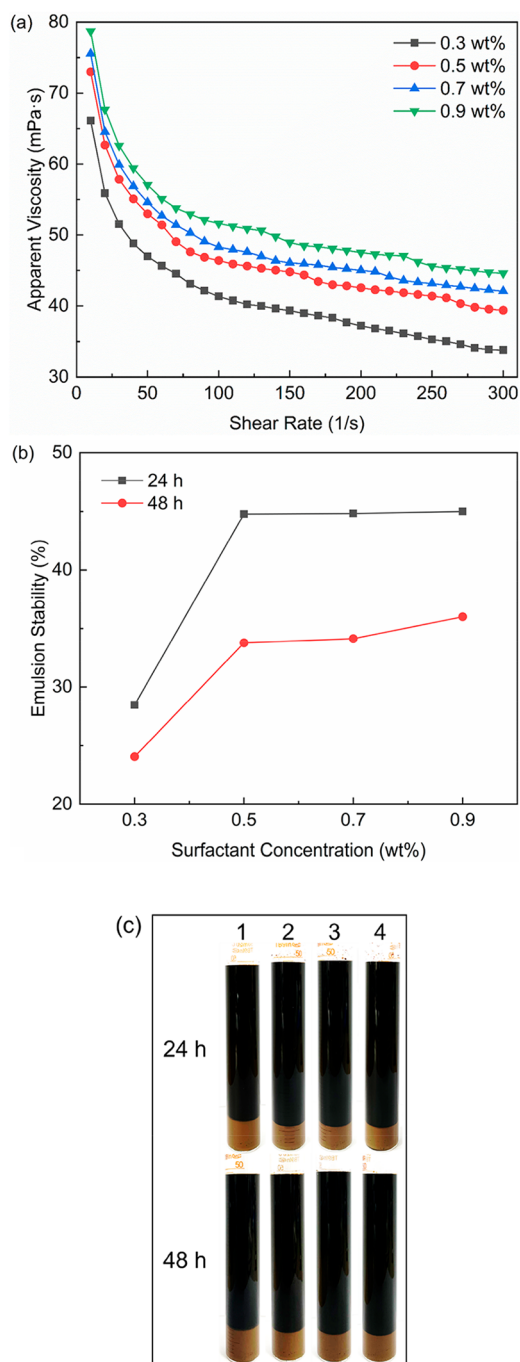
distribution of dispersed droplets in the aqueous phase and thus resulted in better stability of the emulsion.[18,19] However, as the surfactant concentration continued to increase, more surfactant molecules were adsorbed to interfaces, gradually reaching saturation, and emulsion stability thus showed little increase. Consequently, considering viscosity along with stability, a surfactant concentration of 0.5 wt % was considered optimal for performing further experiments.

3.3. Effects of Homogenization Temperature. The influence of homogenization temperature on the apparent viscosity and stability of emulsions was investigated. The

emulsions were prepared using a constant oil content of 75 wt %, surfactant concentration of 0.5 wt %, mixing speed of 500 rpm, mixing duration of 10 min, and pH of 6.70. The homogenization temperature was varied from 30 to 70 °C.

Figure 5a presents the influence of homogenization temperature on the apparent viscosity of the emulsion versus shear rate. The viscosity of the emulsion remained basically unchanged from 30 to 50 °C. However, the viscosity of the emulsion appeared to increase above 50 °C, with a significant increase in emulsion viscosity especially at 70 °C. These results might be explained by the fact that, when the temperature was
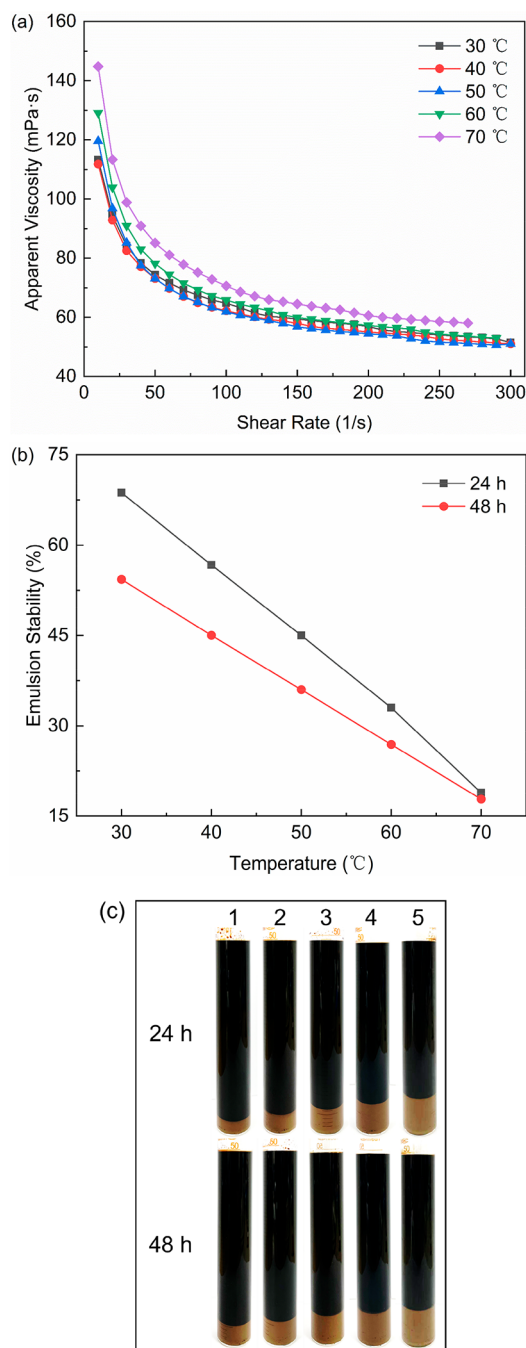

Figure 5. Influence of temperature on the rheology and stability of the emulsion (a) rheology, (b) stability, and (c) stability measurement (1−5: 30, 40, 50, 60, 70 °C).

higher, the emulsification performance of the surfactant became worse. Therefore, a uniform and stable O/W emulsion could not be formed, or even a phase inversion occurred, which led to a significant increase in apparent viscosity.

The effects of homogenization temperature on the stability of the emulsion are shown in Figure 5b,c. Increasing homogenization temperature led to a significant decrease in emulsion stability. This result might be explained by the following: (1) Brownian motion of oil droplets was accelerated as the temperature increased, which facilitated flocculation and coalescence between oil droplets. (2) The oil phase density decreased as the temperature increased, and the density difference between the oil and water phases increased, which accelerated the separation rate of the two phases. (3) A higher temperature made it easier for surfactant molecules to detach from oil−water interfaces, which caused the interfacial film structure to become looser. These effects made the flocculation and agglomeration of oil droplets easier and faster, leading to a decrease in emulsion viscosity. Consequently, considering viscosity along with stability, the temperature of 30 °C was considered the optimum value for performing the rest of the experiments.

3.4. Effects of Mixing Speed. The effects of mixing speed on the apparent viscosity and stability of emulsions were investigated at different mixing speeds of 500, 750, 1000, 1250, and 1500 rpm. The other operating conditions for preparing emulsions were oil content of 75 wt %, surfactant concentration of 0.5 wt %, temperature of 30 °C, mixing duration of 10 min, and pH of 6.70.

Figure 6a presents the influence of mixing speed on the apparent viscosity of the emulsion versus shear rate. Increasing the mixing speed resulted in increased apparent viscosity. This was attributed to the fact that many droplets with smaller sizes were produced as the mixing speed increased, which made the mutual friction between droplets larger, thereby increasing the viscosity of the emulsion.

Figure 6b,c shows the influence of mixing speed on the stability of the emulsion. Increasing the mixing speed from 500 to 750 rpm significantly increased the emulsion stability. When the mixing speed was further increased from 750 to 1500 rpm, the stability of the emulsion increased rather slowly. This was explained by the fact that emulsions were not sufficiently stirred at 500 rpm mixing speed, resulting in poor emulsion stability. However, when the mixing speed increased to a range of 750 to 1500 rpm, oil droplets were more uniformly dispersed in the aqueous phase, which led to increased interfacial area and increased particle-to-particle interactions,[18] causing a significant improvement in emulsion stability. Consequently, considering viscosity as well as stability, the mixing speed of 750 rpm was considered optimal for further experiments.

3.5. Effects of Mixing Duration. The effects of mixing duration on the apparent viscosity and stability of emulsions were investigated at different mixing durations of 3, 5, 10, 15, and 20 min. The other operating conditions for preparing emulsions were oil content of 75 wt %, surfactant concentration of 0.5 wt %, temperature of 30 °C, mixing speed of 750 rpm, and pH of 6.70.

Figure 7a displays the effects of mixing duration on the apparent viscosity of the emulsion versus shear rate. This result showed an effect similar to that of mixing speed, with the increased mixing duration leading to the increased emulsion viscosity. This was attributed to the fact that the size of oil
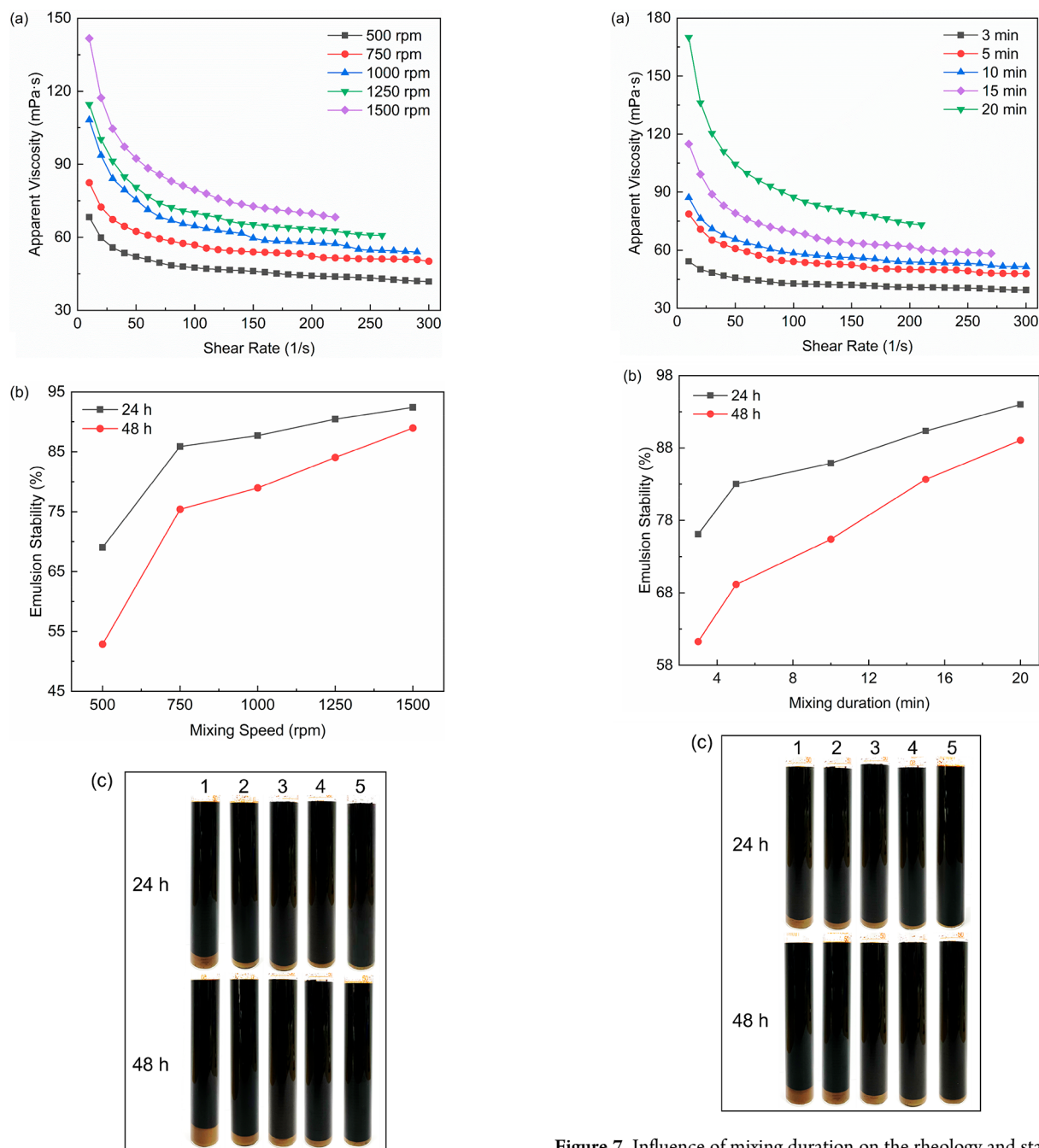
Figure 6. Influence of mixing speed on the rheology and stability of the emulsion (a) rheology, (b) stability, and (c) stability measurement (1−5: 500, 750, 1000, 1250, 1500 rpm).

droplets decreased as the stirring time increased, which increased the number of oil droplets and thinned the liquid films, thus resulting in increased apparent viscosity. The effects of mixing duration on the stability of the emulsion are shown in Figure 7b,c. The increase in mixing duration also caused an increase in emulsion stability due to the production of more and smaller droplets. Therefore, the results showed that the increase in speed or duration of mixing led to increased viscosity and stability of emulsions. These obtained results were in agreement with the findings of Ashrafizadeh et al.[18] as well as those of Abdurahman et al.[19] Consequently, when
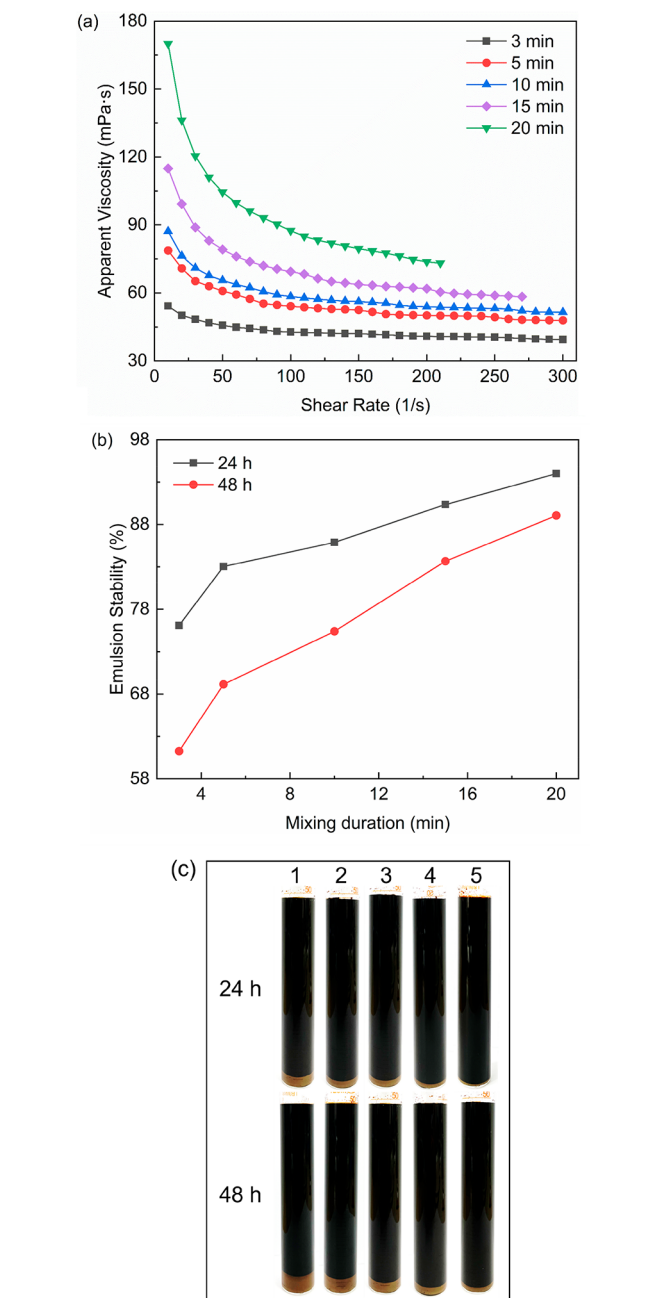

Figure 7. Influence of mixing duration on the rheology and stability of the emulsion (a) rheology, (b) stability, and (c) stability measurement (1−5: 3, 5, 10, 15, 20 min).
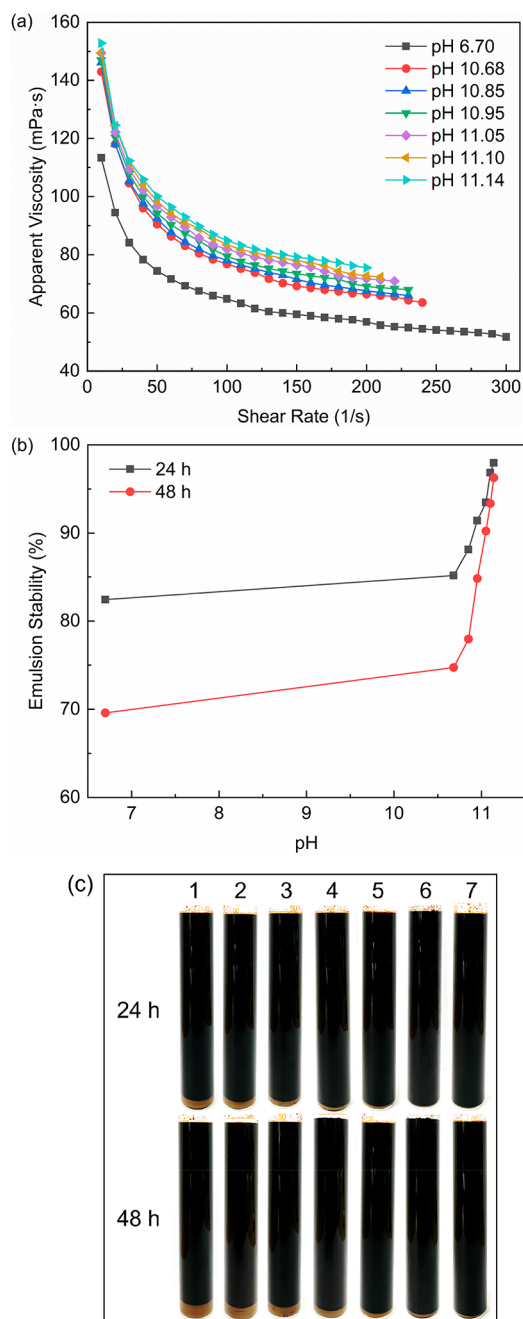
viscosity as well as stability was considered, a mixing duration of 10 min was found to be optimal for further experiments.

3.6. Effects of pH. The effects of pH of the aqueous phase on the apparent viscosity and stability of the emulsion were investigated. Emulsions were prepared with an oil content of 75 wt %, surfactant concentration of 0.5 wt %, temperature of 30 °C, mixing speed of 750 rpm, and mixing duration of 10 min. The pH of the aqueous phase was adjusted using a certain amount of Na_2CO_3. As Na_2CO_3 solution was a buffer solution, it was capable of maintaining the pH of the aqueous phase practically within 10.65−11.15 in a range of 500−1000 ppm of Na_2CO_3 concentrations,[20] as shown in Table 4.
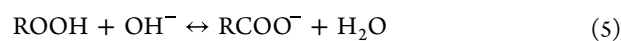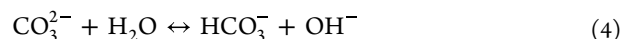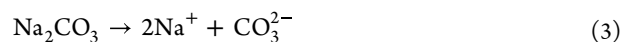
Figure 8a presents the influence of aqueous phase pH on the apparent viscosity of the emulsion versus shear rate. The

Table 4. pH of Aqueous Solutions as a Function of Na$_2$CO$_3$ Concentration at 30 °C

concentration of Na$_2$CO$_3$ (ppm)	pH of the aqueous phase
0	6.70
500	10.68
1000	10.85
2000	10.95
3000	11.05
4000	11.10
5000	11.14

Figure 8. Influence of pH on the rheology and stability of the emulsion (a) rheology, (b) stability, and (c) stability measurement (1−7: pH of 6.70, 10.68, 10.85, 10.95, 11.05, 11.10, 11.14).

viscosity of the emulsion increased significantly as the pH of the aqueous phase increased up to 10.68. This was mainly attributed to the fact that heavy crude oil usually contains a certain amount of surface-active components such as asphaltenes, resins, naphthenic acids, and fatty acids.[3] As the pH of the solution increases, these components can form natural surfactants when interacting with hydroxide ions produced by the hydrolysis of Na$_2$CO$_3$,[23] as shown in eqs 3−5.

$$Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-} \tag{3}$$

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^- \tag{4}$$

$$ROOH + OH^- \leftrightarrow RCOO^- + H_2O \tag{5}$$

These produced surfactants contributed to the formation of more and smaller oil droplets, which increased the emulsion viscosity. Then, as the pH of the aqueous phase continued to increase, the viscosity of the emulsion marginally increased. The reason for this result was that the adsorption of APG08 and produced surfactants was basically saturated at the oil−water interface, which caused a slight enhancement in emulsion viscosity.

Figure 8b,c displays the influence of pH on the stability of the emulsion. An increase in the pH of the aqueous phase caused a significant increase in emulsion stability. The reasons for this phenomenon were as follows: organic acids in heavy crude oil could interact with hydroxide ions to produce surfactants as the solution pH increased, which facilitated the breakage of oil droplets into lots of smaller ones, resulting in a decrease in droplet size of the oil phase.[23] In addition, these produced surfactants were negatively charged, which increased the charge density on the oil droplet surfaces in emulsions, which caused an increase in the absolute value of the zeta-potential of the droplets.[18,23] These effects above made the oil droplet approach and coalescence with each other more difficult, resulting in the formation of more stable emulsions. Consequently, considering viscosity along with stability, a pH of 11.14 in the aqueous phase was considered optimal for preparing emulsions.

After a series of parameter experiments and optimizations for these emulsification processes, the emulsion viscosity at 200 s^{-1} shear rate and 50 °C was 75.47 mPa·s, and the percentage of viscosity reduction was 88.82%. The emulsion stabilities at 24 and 48 h were 97.97 and 96.27%, respectively. The maximum value of viscosity to allow heavy crude oil transportation ranges from 250 to 400 mPa·s at 37.8 °C,[34] and actual flow takes place at shear rates around 500 s^{-1} in most crude oil transportation pipelines.[22] Meanwhile, the emulsion stability should not be too high to prevent difficulties in subsequent demulsification. Therefore, prepared emulsions could meet the requirements of pipeline transportation due to shear thinning properties. Furthermore, it is important to maximize oil throughput while keeping the surfactant requirement minimum for preparing the most efficient emulsion for transportation. Several selected research results on the viscosity and stability of heavy crude oil in water emulsion for pipeline transportation are shown in Table 5. The results showed that the prepared O/W emulsion with APG08 as emulsifier provided higher oil delivery and lower surfactant amount while ensuring viscosity and stability. Thus, the produced emulsion has a good prospect in crude oil transportation.

3.7. Relationship between Rheology and Stability of Emulsions. Stability and rheology are the main evaluation

Table 5. Previous Experiments on the Viscosity and Stability of Heavy Crude Oil in Water Emulsion

authors	year	oil content	surfactants	surfactant concentration	pH	viscosity reduction	stability
Ashrafizadeh and Kamran[18]	2010	60 vol %	Triton X-100	2 wt %	8	83% (25 °C)	100% (24 h, 25 °C)
Ashrafizadeh et al.[20]	2012	60 vol %	Na_2CO_3	2000 ppm	11.3	96% (25 °C)	40% (4 days, 25 °C)
Kumar and Mahto[13]	2016	60 vol %	4-(1,1,3,3-tetramethylbutyl)phenyl polyethylene glycol	2 wt %		83% (25 °C)	100% (56 days, 20 °C)
Kumar and Mahto[22]	2017	60 vol %	tritriethanolamine monosunflower ester	2 wt %		96% (25 °C)	100% (6 days, 15 °C)
Kumar and Mahto[23]	2017	55 vol %	polyethylene glycol monolinoleate	1 wt %	11	97% (10 °C)	87% (6 days, 20 °C)
Sharma et al.[35]	2019	50 vol %	SDS	0.262 wt %		97% (30 °C)	100% (50 days, 15−45 °C)
this work	2022	75 wt %	APG08	0.5 wt %	11.1	88% (50 °C)	96% (48 h, 30 °C)

Table 6. Correlation between Stability and Rheology of Emulsions

factors	levels	rheological equations	correlation coefficients R^2	consistency indexes K(Pa·s)	24 h stability (%)	48 h stability (%)
oil content	70 wt %	$\mu = 0.0833\gamma^{-0.163}$	0.9925	0.0833	20.47	18.90
	73 wt %	$\mu = 0.0957\gamma^{-0.176}$	0.9873	0.0957	24.92	20.98
	75 wt %	$\mu = 0.1096\gamma^{-0.182}$	0.9915	0.1096	37.93	31.03
	77 wt %	$\mu = 0.2291\gamma^{-0.277}$	0.9919	0.2291	53.44	42.75
	80 wt %	$\mu = 0.7823\gamma^{-0.403}$	0.9973	0.7823	88.75	76.67
surfactant concentration	0.3 wt %	$\mu = 0.0977\gamma^{-0.184}$	0.9934	0.0977	28.47	24.07
	0.5 wt %	$\mu = 0.1026\gamma^{-0.167}$	0.9874	0.1026	44.78	33.78
	0.7 wt %	$\mu = 0.1031\gamma^{-0.159}$	0.9847	0.1031	44.83	34.14
	0.9 wt %	$\mu = 0.1058\gamma^{-0.153}$	0.9842	0.1058	45.00	36.00
mixing speed	500 rpm	$\mu = 0.0877\gamma^{-0.130}$	0.9849	0.0877	69.02	52.86
	750 rpm	$\mu = 0.1076\gamma^{-0.136}$	0.9831	0.1076	85.90	75.41
	1000 rpm	$\mu = 0.1673\gamma^{-0.203}$	0.9905	0.1673	87.72	78.95
	1250 rpm	$\mu = 0.1731\gamma^{-0.193}$	0.9856	0.1731	90.43	84.04
	1500 rpm	$\mu = 0.2307\gamma^{-0.23}$	0.9926	0.2307	92.41	88.97
mixing time	3 min	$\mu = 0.0647\gamma^{-0.087}$	0.9868	0.0647	76.09	61.28
	5 min	$\mu = 0.1060\gamma^{-0.141}$	0.9872	0.1060	83.05	69.15
	10 min	$\mu = 0.1169\gamma^{-0.146}$	0.9874	0.1169	85.90	75.41
	15 min	$\mu = 0.1767\gamma^{-0.201}$	0.9924	0.1767	90.33	83.67
	20 min	$\mu = 0.3037\gamma^{-0.269}$	0.9963	0.3037	93.99	89.05
pH of aqueous phase	6.70	$\mu = 0.1770\gamma^{-0.216}$	0.9920	0.1770	82.43	69.59
	10.68	$\mu = 0.2436\gamma^{-0.248}$	0.9927	0.2436	85.16	74.74
	10.85	$\mu = 0.2445\gamma^{-0.245}$	0.9928	0.2445	88.14	77.97
	10.95	$\mu = 0.2450\gamma^{-0.240}$	0.9938	0.2450	91.42	84.82
	11.05	$\mu = 0.2456\gamma^{-0.235}$	0.9927	0.2456	93.49	90.23
	11.10	$\mu = 0.2466\gamma^{-0.232}$	0.9960	0.2466	96.85	93.36
	11.14	$\mu = 0.2477\gamma^{-0.228}$	0.9916	0.2477	97.97	96.28

indicators for the transport technology of heavy crude oil as an O/W emulsion. From the experimental results regarding the effects of various factors on emulsion properties in the previous section, a qualitative relationship was observed that might exist between stability and rheology of emulsions. It is generally the case that the higher the stability is, the higher the apparent viscosity. Thus, further research and analysis of experimental results were needed to verify the possible relationship between emulsion stability and rheology.

Some prior experimental results[16,36] have suggested that the rheological behavior of heavy crude oil-in-water emulsions within a range of shear rates can be expressed by the following power-law equation:

$$\tau = K\gamma^n \tag{6}$$

$$\frac{\tau}{-\gamma} = \mu = K\gamma^{n-1} \tag{7}$$

where τ is the shear stress, μ is the apparent viscosity, γ is the shear rate, K is the consistency index, and n is the flow

behavior index.[37−39] Meanwhile, the K value is the metric of fluid viscosity, with a higher viscosity meaning a larger K value. For a Newtonian fluid $\mu = K$ and $n = 1$. For pseudoplastic fluids, n varies from 0 to 1, such that the exponent $n−1$ in eq 7 is negative. Experimental data of the apparent viscosity versus shear rate were analyzed using a nonlinear curve fitting method to estimate the parameter K in eq 7. Moreover, statistical analyses were also performed to evaluate the accuracy of the fit. The correlation coefficient R^2 employed in this evaluation used eq 8, expressed as

$$R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \overline{y}_i)^2} \tag{8}$$

where y_i is the experimental result, $\hat{y}_i$ is the predicted result by the fitting equation, and $\overline{y}_i$ is the average of the experimental result. A high value of R^2 indicates a high degree of correlation. The maximum value of R^2 is unity.

Therefore, the correlation between stability and rheology of heavy crude oil-in-water emulsions, the rheological equations,

consistency indexes K, correlation coefficients R^2, 24 and 48 h emulsion stability were investigated and summarized in Table 6.

As seen from the data in Table 6, the viscometric results of the emulsions studied here conformed to the power-law equations. The values of correlation coefficient R^2 were all around 0.99, indicating a high degree of correlation and that eq 7 correlated well with the experimental results. The shear rate exponents were negative values, which indicated that emulsions displayed non-Newtonian, shear thinning (pseudo-plastic) behaviors. In addition, an extremely important finding was that the values of consistency index K followed the same trend as 24 and 48 h stability, with the increased K value generally accompanied by an increased emulsion stability. Meanwhile, as the K value was a characterization of viscosity, increased emulsion viscosity was also consistent with increased emulsion stability. This phenomenon could be analyzed using Stokes' law as follows:[40]

$$v = -\frac{2gr^2\Delta\rho}{9\eta} \qquad (9)$$

where v is the phase separation velocity of emulsion, η is the viscosity of the aqueous phase, r is the radius of the oil droplet, $\Delta\rho$ is the density difference between the oil phase and the aqueous phase, and g is the acceleration due to gravity. According to Stokes' law, the phase separation velocity of emulsion decreases with decreased oil droplet size and increased aqueous phase viscosity, and emulsion stability increases with a decreased phase separation velocity of emulsion. Furthermore, emulsion viscosity also increases with decreased oil droplet size and increased aqueous phase viscosity. Therefore, emulsion stability and emulsion viscosity have a tendency to increase or decrease simultaneously. Moreover, the increasing trends of the K value and stability were also discovered to be a little more similar in terms of oil content, surfactant concentration, mixing speed, and mixing time. However, in the case of aqueous phase pH, the K value first increased significantly as pH increased and then increased very slightly, whereas emulsion stability increased smoothly throughout. The reason for this phenomenon was mainly related to the droplet size distribution of the emulsions, the structure of the interfacial films, electrostatic repulsion between oil droplets, and aqueous phase viscosity. By optimizing the operating conditions concerning oil content, surfactant concentration, mixing speed, and mixing time, the dispersed oil droplets were better distributed in the aqueous phase. More droplets with smaller sizes were produced, which led to an increase in emulsion viscosity. Moreover, more surfactant molecules were uniformly adsorbed onto oil–water interfaces, resulting in a tighter interfacial film structure. Excess surfactant molecules resulted in an increase in aqueous phase viscosity. At the same time, the electrostatic repulsion between oil droplets was increased. All of these effects could reduce the chances of droplet coalescence/flocculation, leading to better emulsion stability.[23] In addition, Na_2CO_3 was used to increase the pH of the aqueous phase, which increased the surface charge density of emulsions and electrostatic repulsion between oil droplets. Hence, the emulsion stability increased with increased pH. Nevertheless, the emulsion viscosity finally reached an equilibrium due to the saturated adsorption of surfactant molecules at oil–water interfaces. It should be noted that the rheology and stability of emulsions regarding temperature are

not shown in Table 6. This was because emulsion viscosity was measured at a constant temperature of 50 °C here, whereas the emulsion stability was measured at different temperatures (30–70 °C), with the emulsion stability decreasing with increased homogenization temperature. Also, it was found that increasing the homogenization temperature typically resulted in lower emulsion viscosity.[15,36] Consequently, for homogenization temperature, the decrease in emulsion stability was accompanied by a decrease in emulsion viscosity. From all of these observations, a qualitative relationship between stability and rheology of heavy crude oil-in-water emulsions was deduced. An increase or decrease in emulsion stability was accompanied by an increase or decrease in emulsion viscosity. In summary, the stability and rheology of emulsions should be considered simultaneously in the transportation of heavy crudes as O/W emulsions. Therefore, emulsion viscosity cannot become very high in the goal to fulfill the requirements of pipeline transportation while also improving emulsion stability.

4. CONCLUSIONS

In the present study, oil-in-water emulsions were successfully prepared using Karamay crude oil samples and water in the presence of nonionic surfactant APG08. The influences of various operating factors on the rheology and stability of the prepared emulsions were investigated. Based on the experimental results, the following main conclusions were drawn:

(1) Emulsion viscosity was found to increase as the oil content, surfactant concentration, mixing speed, mixing time, and pH of the aqueous phase increased. The emulsion viscosity was first basically unchanged with an increase in homogenization temperature and then increased.

(2) Emulsion stability was found to increase with increasing oil content, surfactant concentration, homogenization temperature, mixing speed and time, and pH of the aqueous phase.

(3) The optimal operating conditions were oil content of 75 wt %, surfactant concentration of 0.5 wt %, homogenization temperature of 30 °C, mixing speed of 750 rpm, mixing time of 10 min, and pH of 11.14 in the aqueous phase. The percentage of viscosity reduction at 200 s^{-1} shear rate was 88.82%, and the emulsion stability up to 48 h was 96.27% under these conditions.

(4) The power-law equation fitted better with the rheology data of the prepared emulsions. Also, there was a qualitative relationship between stability and rheology of the emulsion. The increase in emulsion stability was accompanied by an increase in emulsion viscosity, such that both indicators should be considered simultaneously.

■ AUTHOR INFORMATION

Corresponding Author

Aixian Liu − *Faulty of Engineering, China University of Petroleum Beijing at Karamay, Karamay 834000, China;* ⊙ orcid.org/0000-0002-7713-8222; Email: 1854@cupk.edu.cn

Authors

Bo Dong − *State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Beijing), Beijing 102249, China*

Zongyu Qin − *State Key Laboratory of Heavy Oil Processing, China University of Petroleum (Beijing), Beijing 102249, China*

Yiwei Wang − Faulty of Engineering, China University of
Petroleum Beijing at Karamay, Karamay 834000, China

Jiahui Zhang − State Key Laboratory of Heavy Oil Processing,
China University of Petroleum (Beijing), Beijing 102249,
China; ● orcid.org/0000-0003-1844-7241

Zhen Xu − Faulty of Engineering, China University of
Petroleum Beijing at Karamay, Karamay 834000, China

Xuqiang Guo − Faulty of Engineering, China University of
Petroleum Beijing at Karamay, Karamay 834000, China;
● orcid.org/0000-0002-0781-1477

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c04684

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Sun, N.; Jing, J.; Jiang, H.; An, Y.; Wu, C.; Zheng, S.; Qi, H. Effects of surfactants and alkalis on the stability of heavy-oil-in-water emulsions. SPE J. 2017, 22 (01), 120−129.

(2) MacDonald, B. A.; Miadonye, A. Improvement on the Viscosity Models for the Effects of Temperature and Pressure on the Viscosity of Heavy Crude Oils. J. Chem. Eng. Data 2017, 62 (3), 924−930.

(3) Lee, J.; Babadagli, T. Comprehensive review on heavy-oil emulsions: Colloid science and practical applications. Chem. Eng. Sci. 2020, 228, 115962.

(4) Stebeleva, O. P.; Minakov, A. V. Application of Cavitation in Oil Processing: An Overview of Mechanisms and Results of Treatment. ACS Omega 2021, 6 (47), 31411−31420.

(5) Meriem-Benziane, M.; Abdul-Wahab, S. A.; Benaicha, M.; Belhadri, M. Investigating the rheological properties of light crude oil and the characteristics of its emulsions in order to improve pipeline flow. Fuel 2012, 95, 97−107.

(6) Shi, H.; Ruban, A.; Timoshchenko, S.; Nikrityuk, P. Numerical Investigation of the Behavior of an Oil-Water Mixture in a Venturi Tube. Energy Fuels 2020, 34 (11), 15061−15067.

(7) Liu, J.; Yang, F.; Xia, J.; Wu, F.; Pu, C. Mechanism of Ultrasonic Physical-Chemical Viscosity Reduction for Different Heavy Oils. ACS Omega 2021, 6 (3), 2276−2283.

(8) Hart, A. A review of technologies for transporting heavy crude oil and bitumen via pipelines. J. Pet. Explor. Prod. Technol. 2014, 4 (3), 327−336.

(9) Martínez-Palou, R.; Mosqueira, M. D. L.; Zapata-Rendón, B.; Mar-Juárez, E.; Bernal-Huicochea, C.; de la Cruz Clavel-López, J.; Aburto, J. Transportation of heavy and extra-heavy crude oil by pipeline: A review. J. Pet. Sci. Eng. 2011, 75 (3−4), 274−282.

(10) Huang, X.; Zhou, C.; Suo, Q.; Zhang, L.; Wang, S. Experimental study on viscosity reduction for residual oil by ultrasonic. Ultrason. Sonochem. 2018, 41, 661−669.

(11) Bu-Ali, Q.; Mohammed Redha, Z.; Jung, M.; Abdulla, H.; Ahmed, O. An experimental design approach investigating the effects of operating variables on the viscosity of heavy crude oil-in-water emulsions using lecithin as a natural surfactant. Pet. Sci. Technol. 2021, 39 (23−24), 1098−1115.

(12) Souas, F.; Safri, A.; Benmounah, A. A review on the rheology of heavy crude oil for pipeline transportation. Petrol. Res. 2021, 6 (2), 116−136.

(13) Kumar, S.; Mahto, V. Emulsification of Indian heavy crude oil in water for its efficient transportation through offshore pipelines. Chem. Eng. Res. Des. 2016, 115, 34−43.

(14) Chen, X.; Wang, N.; Xia, S. Research progress and development trend of heavy oil emulsifying viscosity reducer: a review. Pet. Sci. Technol. 2021, 39 (15−16), 550−563.

(15) Hasan, S. W.; Ghannam, M. T.; Esmail, N. Heavy crude oil viscosity reduction and rheology for pipeline transportation. Fuel 2010, 89 (5), 1095−1100.

(16) Azodi, M.; Solaimany Nazar, A. R. An experimental study on factors affecting the heavy crude oil in water emulsions viscosity. J. Pet. Sci. Eng. 2013, 106, 1−8.

(17) Azodi, M.; Nazar, A. R. S. Experimental Design Approach to Investigate the Effects of Operating Factors on the Surface Tension, Viscosity, and Stability of Heavy Crude Oil-in-Water Emulsions. J. Dispersion Sci. Technol. 2013, 34 (2), 273−282.

(18) Ashrafizadeh, S. N.; Kamran, M. Emulsification of heavy crude oil in water for pipeline transportation. J. Pet. Sci. Eng. 2010, 71 (3−4), 205−211.

(19) Abdurahman, N. H.; Rosli, Y. M.; Azhari, N. H.; Hayder, B. A. Pipeline transportation of viscous crudes as concentrated oil-in-water emulsions. J. Pet. Sci. Eng. 2012, 90−91, 139−144.

(20) Ashrafizadeh, S. N.; Motaee, E.; Hoshyargar, V. Emulsification of heavy crude oil in water by natural surfactants. J. Pet. Sci. Eng. 2012, 86−87, 137−143.

(21) Hoshyargar, V.; Ashrafizadeh, S. N. Optimization of Flow Parameters of Heavy Crude Oil-in-Water Emulsions through Pipelines. Ind. Eng. Chem. Res. 2013, 52 (4), 1600−1611.

(22) Kumar, S.; Mahto, V. Emulsification of Indian heavy crude oil using a novel surfactant for pipeline transportation. Pet. Sci. 2017, 14 (2), 372−382.

(23) Kumar, S.; Mahto, V. Use of a Novel Surfactant To Prepare Oil-in-Water Emulsion of an Indian Heavy Crude Oil for Pipeline Transportation. Energy Fuels 2017, 31 (11), 12010−12020.

(24) Sun, N.; Jiang, H.; Wang, X.; Jin, K. Research on factors affecting heavy oil-in-water emulsion rheology and pressure drop. J. Dispersion Sci. Technol. 2018, 39 (3), 411−422.

(25) Pang, S.; Pu, W.; Xie, J.; Chu, Y.; Wang, C.; Shen, C. Investigation into the properties of water-in-heavy oil emulsion and its role in enhanced oil recovery during water flooding. J. Pet. Sci. Eng. 2019, 177, 798−807.

(26) Chen, Q.; Zhu, Y.; Wang, M.; Ren, G.; Liu, Q.; Xu, Z.; Sun, D. Viscosity reduction of extra-heavy oil using toluene in water emulsions. Colloids Surf., A 2019, 560, 252−259.

(27) Esmaeili, H.; Esmaeilzadeh, F.; Mowla, D. Effect of Surfactant on Stability and Size Distribution of Gas Condensate Droplets in Water. J. Chem. Eng. Data 2014, 59 (5), 1461−1467.

(28) Vegad, G. D.; Jana, A. K. Viscosity Reduction of Indian Heavy Crude Oil by Emulsification to O/W Emulsion Using Polysorbate-81. J. Surfactants Deterg. 2021, 24 (2), 301−311.

(29) Wang, Y.; Wang, S.; Liu, Z.; Ma, R.; Sun, Q.; Liu, A.; Yang, L.; Gong, J.; Guo, X. The formation of structure I hydrate in presence of n-octyl-β-D-glucopyranoside. Fluid Phase Equilib. 2022, 556, 113373.

(30) Sun, Q.; Chen, B.; Li, X.; Guo, X.; Yang, L. The investigation of phase equilibria and kinetics of CH 4 hydrate in the presence of bio-additives. Fluid Phase Equilib. 2017, 452, 143−147.

(31) Domian, E.; Brynda-Kopytowska, A.; Oleksza, K. Rheological properties and physical stability of O/W emulsions stabilized by OSA starch with trehalose. Food Hydrocolloids 2015, 44, 49−58.

(32) Gorbacheva, S. N.; Ilyin, S. O. Morphology and Rheology of Heavy Crude Oil/Water Emulsions Stabilized by Microfibrillated Cellulose. Energy Fuels 2021, 35 (8), 6527−6540.

(33) Qiao, W.; Cui, Y.; Zhu, Y.; Cai, H. Dynamic interfacial tension behaviors between Guerbet betaine surfactants solution and Daqing crude oil. Fuel 2012, 102, 746−750.

(34) Muñoz, J. A. D.; Ancheyta, J.; Castañeda, L. C. Required Viscosity Values to Ensure Proper Transportation of Crude Oil by Pipeline. *Energy Fuels* **2016**, *30* (11), 8850−8854.

(35) Sharma, R.; Deka, B.; Mandal, A.; Mahto, V. Study the influence of sodium dodecyl sulfate on emulsification of heavy and waxy crude oils to improve their flow ability in low temperature conditions. *Asia-Pac. J. Chem. Eng.* **2019**, *14* (1), No. e2279.

(36) Al-Roomi, Y.; George, R.; Elgibaly, A.; Elkamel, A. Use of a novel surfactant for improving the transportability/transportation of heavy/viscous crude oils. *J. Pet. Sci. Eng.* **2004**, *42* (2−4), 235−243.

(37) Rahimi, M. A.; Ramazani S.A, A.; Alijani Alijanvand, H.; Ghazanfari, M. H.; Ghanavati, M. Effect of ultrasonic irradiation treatment on rheological behaviour of extra heavy crude oil: A solution method for transportation improvement. *Can. J. Chem. Eng.* **2017**, *95* (1), 83−91.

(38) Al-Dawery, S. K.; Al-Shereiqi, S. K. Waste bio materials based viscosity reduction and rheological properties of crude oil. *J. Pet. Explor. Prod. Technol.* **2019**, *9* (3), 2109−2121.

(39) Gudala, M.; Banerjee, S.; Naiya, T. K.; Kumar, G. S. Experimental and Correlation Development of Heavy Oil Viscosity Using Bio-Additives. *Energy Fuels* **2019**, *33* (7), 6313−6326.

(40) Yang, Q.; Ke, D.; Yang, M.; Hong, J.; Ran, Q.; Wang, X. Effect of salt concentration on the phase separation of bitumen emulsions. *Colloids Surf., A* **2013**, *425*, 1−5.