Impact of temperature, homogenization condition, and oil property on the formation and stability of crude oil emulsion

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Abstract

Water-in-oil (W/O) emulsions have garnered significant attention in the petroleum industry due to their adverse effects, such as reduced oil recovery, increased pressure drop, and equipment corrosion. This study investigated the influences of temperature, homogenization conditions, and crude oil properties on emulsion formation and stability. We focused on nine crude oils with varying viscosities, observing the emulsion formation process and analyzing functional groups, the percentage of resolved water, and emulsion particle sizes. Under all conditions, W/O emulsions for most oils underwent a

transformation from multiple emulsions, including water-in-oil-in-water (W/O/W) and water-in-oil-in-water-in-oil-in-water (W/O/W/O/W) emulsions. As the temperature increased, the variation in W/O emulsion amount at the end of the transformation differed based on oil viscosity, while emulsion stability showed no significant differences. However, W/O emulsion stability increased after 24-hour aging at high temperatures. Additionally, four hypotheses regarding the final changes in W/O emulsion amount with temperature were consistent with the emulsion formation process. Regarding the effect of homogenization conditions, increasing shear intensity resulted in a larger amount of W/O emulsion with high stability. This was attributed to changes in the activity of different natural surfactants with increasing shear intensity. Furthermore, the final amount of W/O emulsion was primarily influenced by hydrogen-bonded O-H, followed by hydrogen-bonded N-H. The mechanisms underlying the influence of different factors on emulsion formation and stability are described.

Keywords: Temperature; Homogenization speed & duration; crude oil emulsion; W/O emulsion; Formation & stability

1. Introduction

Undesirable emulsification has become a critical issue in the petroleum industry [1-4]. Crude oil emulsions are encountered during the initial stages of the oil recovery process [5]. Even in low salinity water flooding (LSWF), a popular method for enhanced oil recovery (EOR) in recent years, emulsion formation can pose challenges due to aqueous-phase injection [6-7]. Emulsification occurs during oil transportation, processing, and storage as well [8-9]. Emulsions, with their larger particle sizes compared to oil or water, can obstruct porous media in reservoirs, leading to inefficient displacement and reduced oil recovery [10-11]. The increase in viscosity induced by added water in emulsions can result in elevated pressure drops [12]. The consequences of emulsification in the petroleum industry are far-reaching, including a decrease in oil quality, higher transportation costs, catalyst poisoning in refineries downstream, and corrosion of facilities, pipelines, and tanks [3, 13, 14]. This not only

escalates production costs but also reduces the yield of valuable crude oil [4]. Therefore, it is imperative to gain a comprehensive understanding of crude oil emulsion formation and stability to address the challenges posed by emulsification in the petroleum industry [5].

Various types of crude oil emulsions, including water-in-oil (W/O), oil-in-water (O/W), water-in-oil-in-water (W/O/W), and oil-in-water-in-oil (O/W/O) emulsions, can be found in oilfields [4]. Among them, the W/O emulsion, often referred to as 'chocolate mousse,' poses the most common and challenging issue in the petroleum industry [15-20]. The primary reason for the formation of crude oil emulsions is typically attributed to increased energy resulting from turbulence, mixing, or agitation [4, 10, 18, 21]. Studies by Chen and Tao investigated the effects of stirring intensity and mixing time on emulsion stability, using commercial diesel as the oil phase and sorbitan monooleate as the emulsifier [22]. They found that more stable emulsions were obtained with increasing stirring speed or extended mixing time. However, speeds exceeding 2500 rpm had minimal contributions to emulsion stability, and mixing times longer than 15 minutes even reduced stability due to emulsifier release from the oil-water interface [22]. Ashrafizadeh and Kamran, using West Paydar crude oil, a model oil, and surfactant Triton X-100, explored how speed (ranging from 1000 to 15000 rpm) and mixing duration (5 to 40 minutes) influenced emulsion stability [23]. Their study concluded that both speed and mixing time increases benefited emulsion stability but had an insignificant effect on emulsion viscosity, as determined by measurements of separated water and viscosity tests [23]. A similar trend was observed by Ghannam, who found that high speed improved emulsion stability due to the significant reduction in droplet size, resulting in smaller emulsion particles with a higher interfacial area, enhancing interactions between droplets and, consequently, stability [24, 25]. Uetani et al. measured the water content of emulsions formed by crude oil during agitation at speeds ranging from 3500 to 15000 rev/min [26]. Their findings indicated that high shear rates increased emulsion stability, attributed to the smaller droplets dispersed in the oil phase, which was supported by micrographs of emulsions formed by two model oils at different shear rates [27]. While the effects of

shear rate and mixing duration on emulsion stability have been widely investigated, it has mostly been limited to specific crude oils. Consequently, there remains a gap in understanding their influences on emulsion formation for crude oils with different properties.

Heat energy, influenced by temperature changes, plays a significant role in emulsion stability. It can impact the properties of both phases, surfactant effectiveness, asphaltene precipitation, and the behaviour of interfacial films [3, 4, 28, 29, 30]. Nour and Yunus conducted an evaluation of temperature's effect on the stability of emulsions formed by three crude oils with varying viscosities (23.35, 11.52, and 6.22 cP) and found that the percentage of separated water increased from 30ºC to 50ºC, indicating reduced emulsion stability at higher temperatures [16]. Similarly, a decrease in the relative volume of emulsions formed by diesel as the temperature increased (30~70 ºC) suggested a negative impact of temperature on emulsion stability. High temperatures can cause surfactants to become loosely adsorbed on the interfacial film, leading to increased coalescence and emulsion destabilization [22]. Ghannam argued that high temperatures reduce phase viscosities, providing water droplets with more kinetic energy, leading to enhanced collisions between droplets and decreased emulsion stability [24]. Electrorheological studies also support this, as the critical electric field (CEF) of emulsions decreases at higher temperatures, indicating lower stability [31-32]. Kang et al. studied the stability of heavy oil emulsions from the Jilin Oil Field at different temperatures (25 ºC, 45 ºC, and 55 ºC) and found that high temperatures reduce oil phase and emulsion viscosities, strengthening Brownian movement and demulsifying the emulsions [33]. Uetani et al. maintained emulsions at various temperatures (20~70 ºC) and suggested that high temperatures reduce emulsion stability due to increased water content with rising temperatures, a conclusion similar to that of Kang et al. [26]. Ismail et al. prepared emulsions at various temperatures, ranging from 25 ºC to 110 ºC, and observed a decrease in the frequency of droplets smaller than 3 μm and an increase in the interfacial tension of emulsions at higher temperatures, attributed to lower asphaltene solubility as temperature increases [34]. However, they also found that emulsions formed at higher temperatures

had greater stability based on separated water percentages. This discrepancy was explained by the softening of bituminous particles at higher temperatures [23]. The impact of temperature on emulsion formation and stability remains unclear, and the investigation of the emulsion formation process, which significantly influences emulsion stability, has often been overlooked. Some studies have attributed shifts in emulsion stability to changes in viscosity or interfacial tension [12, 23, 24, 31, 34]. However, changes in interfacial tension with temperature have been inconsistent across different publications, likely due to variations in crude oil properties [35-39]. Asphaltenes and resins, with their functional group content, are considered the natural surface-active agents in crude oils [30, 40, 41, 42, 43]. Liu et al. reported that emulsion stability increased initially due to the synergistic effect between asphaltenes and resins with increasing resin concentration and then decreased [44], which aligns with previous studies [1, 45]. In contrast, Pu et al. demonstrated the effect of Resin/Asphaltene on the stability of emulsions formed by simulated oils, showing variations with ageing time [46]. A deeper understanding of the impact of crude oil properties on emulsion stability is still needed.

In this study, we observed the emulsion formation processes of various crude oils under different temperatures and homogenization conditions. We also analyzed the influence of emulsion formation on the final stable W/O emulsion. Furthermore, evaluated the effects of temperature, shear intensity, and crude oil properties on emulsion stability. Finally, we explored and described the mechanisms through which these factors impact crude oil emulsions. The outcomes of this study address the current lack of observational data on W/O emulsion formation in the existing research. The insights into methods and their corresponding mechanisms for reducing W/O emulsion formation by manipulating the investigated factors may contribute to preventing the damages caused by emulsification in the petroleum industry.

2. Materials and Methods

2.1 Crude oil and de-ionized water

The Japan Organization for Metals and Energy Security (JOGMEC) supplied a diverse set of nine stock-tank crude oils; their characteristics can be found in **Table 1**. The viscosity of the crude oils exhibited a wide range, spanning from 1.43 cP to 20.88 cP, while both the Total Acid Number (TAN) and Total Base Number (TBN) values ranged from <0.05mg KOH/g to 0.36 mg KOH/g. Furthermore, the compositions of the crude oils in terms of Saturates, Aromatics, Resins, and Asphaltenes (SARA) exhibited significant variations.

Table 1. Properties of 9 crude oils applied in the present study

Items	Crude oils								
	1#	**2#**	**3#**	**4#**	**5#**	**6#**	**7#**	**8#**	**9#**
Density (15ºC, g/cm^3)	0.810	0.830	0.851	0.856	0.857	0.862	0.880	0.881	0.884
API gravity	43.1	38.9	34.6	33.8	33.5	32.5	29.2	28.9	28.4
Viscosity (25ºC, cP)	1.43	3.62	5.87	6.90	7.89	8.81	17.47	18.03	20.88
TAN (mgKOH/g)	0.17	<0.05	<0.05	<0.05	0.06	0.10	0.19	0.17	0.24
TBN (mgKOH/g)	0.05	0.08	0.17	0.18	0.21	0.19	0.36	0.28	0.29
Saturates (wt.%)	57.8	51.0	37.6	36.5	34.7	35.9	27.7	26.5	26.2
Aromatics (wt.%)	32.8	44.5	54.3	53.7	55.9	52.3	54.8	56.1	54.3
Resins (wt.%)	8.0	3.8	5.0	6.4	5.1	8.3	9.4	9.5	10.2
Asphaltene (wt.%)	1.4	0.7	3.1	3.4	4.3	3.5	8.1	8.0	9.3

where the total acid number was marked in TAN, and the total base number is TBN.

Figure 1 shows the mass percentage of molecules with different carbon numbers in crude oils. The significant differences in carbon number of molecules fall between 5 and 15 and beyond 30. When examining the changes in mass percentages of carbon numbers alongside crude oil density or viscosity, a strong correlation emerges, indicating that its composition largely influences the physical properties of crude oil. To avoid the influence of brine ions, de-ionized (DI) water, purchased from Kansai Distilled Water Co., Ltd. (Japan), was selected for preparing all emulsions.

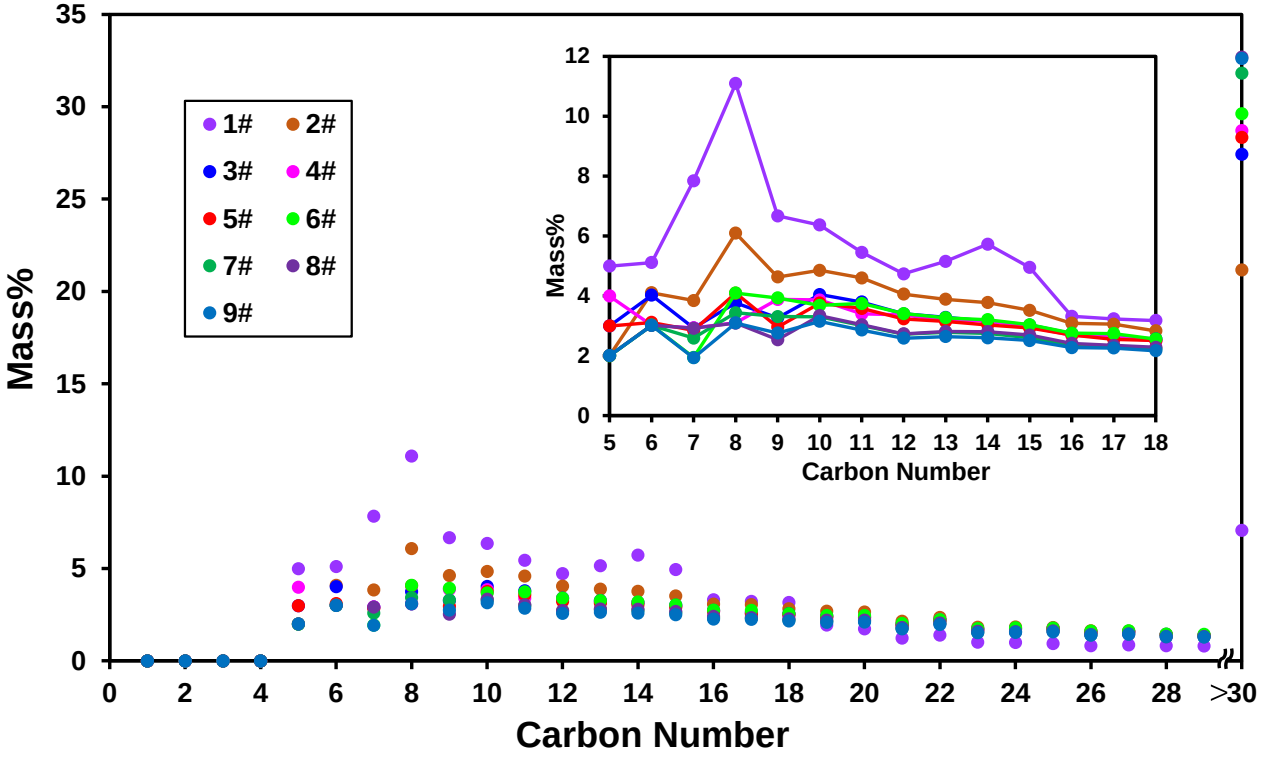


Figure 1. Mass% of molecules with different carbon numbers in crude oils

2.2 Experimental design

Figure 2 illustrates the experimental procedures in this study. The emulsion preparations for measurements of ζ-potential and emulsion transformation processes are shown in **Figure 2 (a) and (b),** respectively. The emulsion was prepared by homogenizing 1 mL crude oil with 9 mL DI water in a 15 mL test tube made of polypropylene, where a homogenizer (T 10 basic UL TRA-TURRAX S004) and a sterile plastic rotor (S10D-7G-KS-110) were used. For the ζ-potential, the prepared emulsion was immediately collected with a 3 mL sterile syringe and injected into a test cell with two Pt electrodes. Then, the ζ-potential measurement was carried out at 25 ºC by a Zeta-potential & Particle size analyzer (ELSZ-1000, Otsuka Electronics Co., Ltd, Japan). For emulsion transformation analysis, the emulsion was prepared by homogenizing crude oil with DI water for 5 seconds under different temperatures and homogenizing speeds. After that, 1.5 mL suspension was quickly extracted and put on a glass plate to observe the transformation process of crude oil emulsion with time by microscope (UM6-CAM). **Figure 2 (c)** describes the W/O emulsion preparation and resolved water

measurement. Crude oil was homogenized with DI water in a volume ratio of 1 to 9 under different conditions for 15 minutes. Then, the sample was rested for 24 hours at the corresponding temperature. After that, the sample in the test tube was centrifugated by Micro Refrigerated Centrifuge (Model 3700) at 10,000 rpm for 5 minutes. The sample was separated into three layers: top oil, the second layer, and resolved water. Moreover, the observation of the second layer by microscope was conducted. Meanwhile, the resolved water volume and its pH were also measured, where three samples under the same condition were used to obtain the reported average value. The percentage of resolved water was determined as follows [9]:

$$\%Resolved\ water = \frac{V_{resolved\ water}}{V_{initial\ water}} \times 100\% \quad (1)$$

For a better understanding of the crude oil property effect, the second layer obtained at 20ºC (**Figure 2 (c)** homogenization condition: 30000 rpm, 15 min) was measured by attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) where the FT/IR-6200 served as the data analyzer.

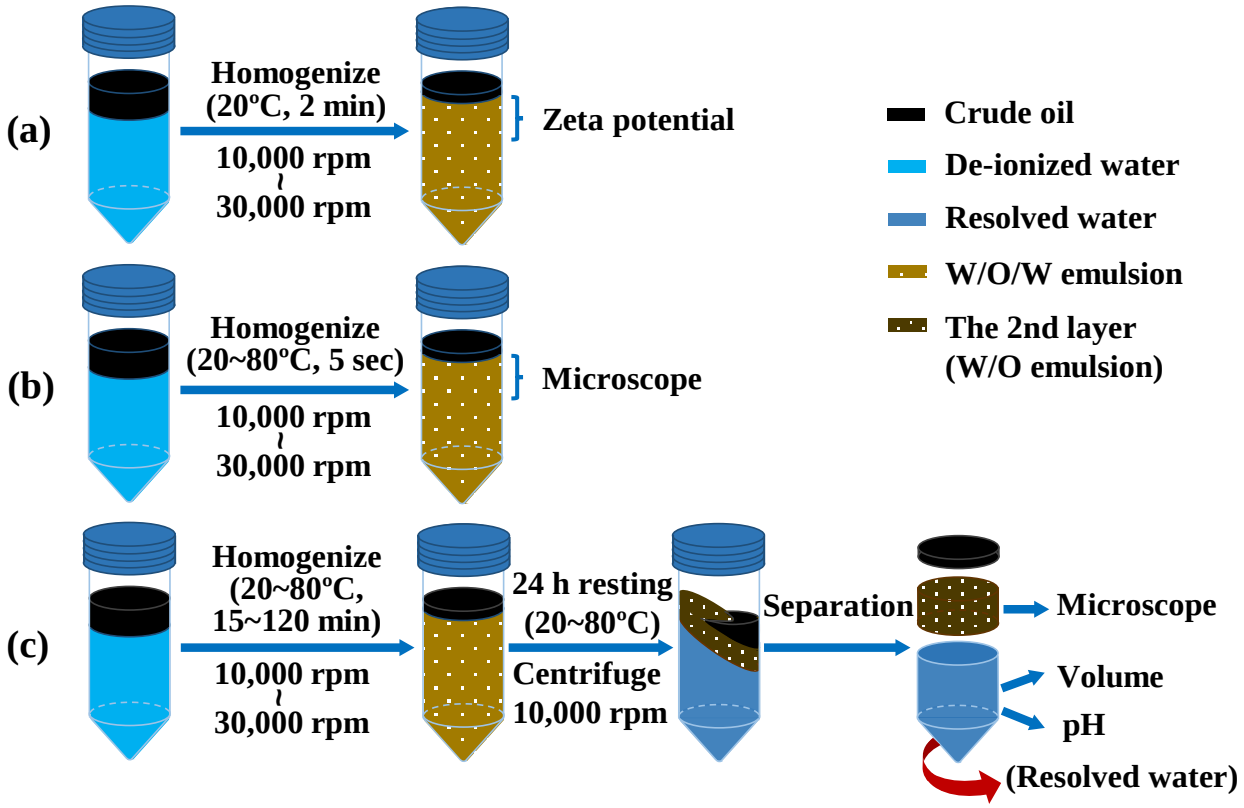


Figure 2. Experiment process: (a) and (b) emulsion preparation for zeta potential and microscope measurements, respectively; (c) emulsion generation under various conditions and phase separation

3. Results and discussion

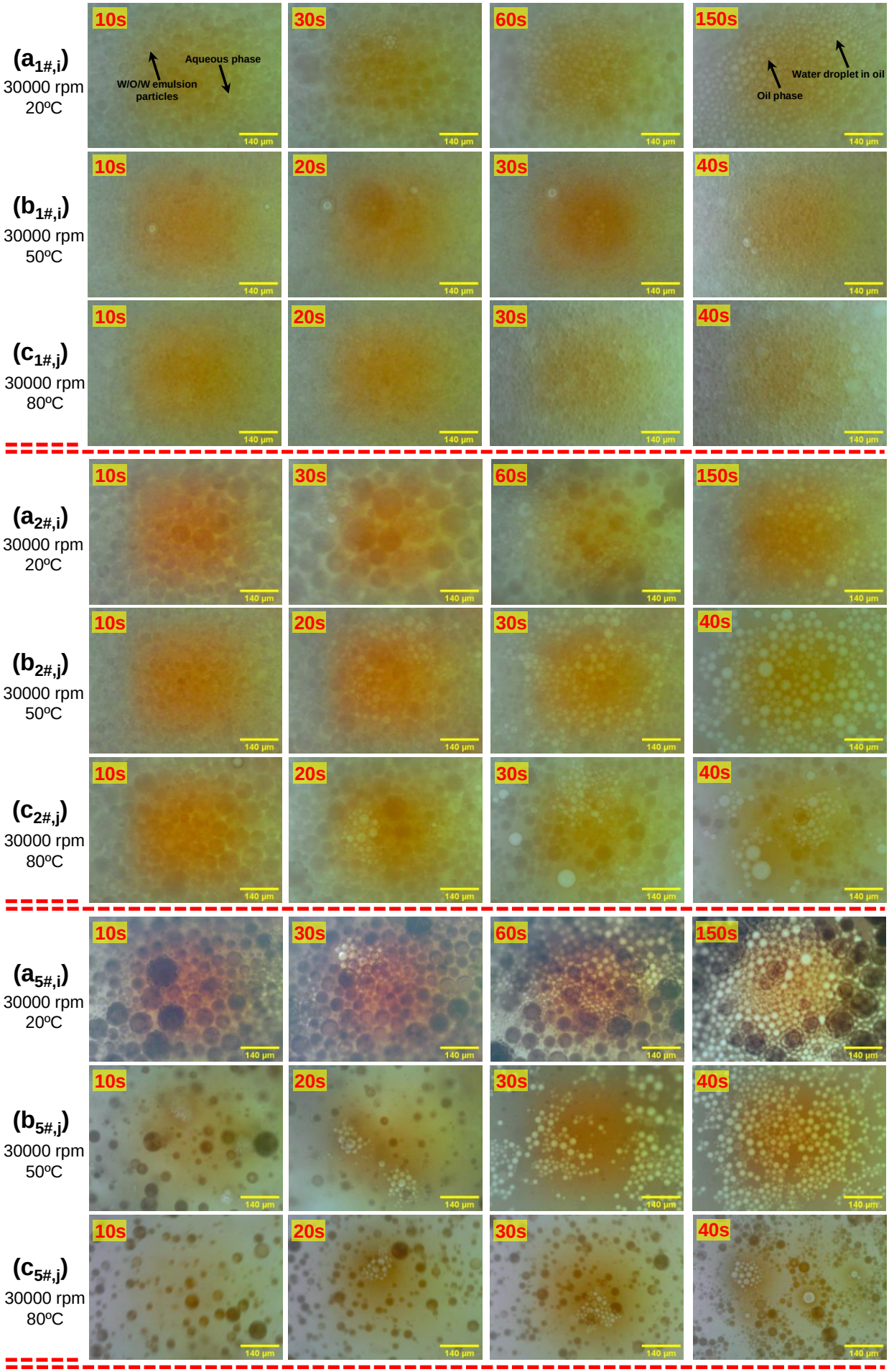
3.1 Temperature effect on emulsion formation and stability of crude oils

In our previous study [9], the emulsion formation was confirmed to be a significant step for analyzing crude oil emulsion stability. Four crude oils (1#, 2#, 5#, and 8#) with different density and viscosity were selected to observe emulsion transformation. **Figure 3** shows the emulsion type changes at 20 ºC, 50 ºC, and 80 ºC after 5-second homogenization at a speed of 30000 rpm. W/O/W emulsions for four crude oils were formed under various temperatures (**Figure 3 (*i* = 10 s and *j* = 10 s)**). Meanwhile, the particle sizes of W/O/W emulsions formed by the crude oils (except for crude oil 2#) became smaller with increasing temperature. Elevated temperatures can lower the viscosity of crude oil and reduce the interfacial tension between crude oil and water. This, in turn, facilitates the dispersion of crude oil on the surface of W/O/W emulsion particles, ultimately leading to the creation

of smaller W/O/W particles characterized by a thicker oil film. For the same crude oil, the colour shade of the W/O/W emulsion particle indicates the thickness of its oil film, with darker colours indicating thicker oil films. The colour difference in W/O/W emulsions formed by different crude oils at the same temperature was due to the solubility of asphaltene in crude oil and the viscosity of crude oil. Besides, there seems to be a good correlation between crude oil composition and the oil film colour of W/O/W emulsion, in which the oil films of crude oil 1# and 2# with higher mass% of light molecule weights than crude oil 5# and 8# were light-coloured (**Figure 1**). On the other hand, increasing temperature accelerated the rate of emulsion transformation (ex. **Figure 3 ($a_{5\#,30s}$)** and **($b_{5\#,30s}$)**).

The transformation of W/O/W to W/O emulsion for crude oil 1#, 2#, 5#, and 8# occurred for all conditions (**Figure 3**). However, the detailed transformation process varied depending on the crude oils. For crude oil 1#, the lowest viscosity resulted in more W/O/W emulsion particles formed. W/O/W emulsions at high temperatures were relatively stable due to the high negative surface potentials caused by the highest TAN/TBN ratio and the temperature-induced deprotonation of carboxyl groups. The amount of W/O emulsion transformed from W/O/W emulsion reduced sharply with increasing temperature (**Figure 3 ($a_{1\#,30s}$), ($b_{1\#,30s}$),** and **($c_{1\#,30s}$)**). The key factor behind this phenomenon is the reduction in the thickness of the oil film and the extrusion deformation that occurs at high temperatures (ex. **Figure 3 ($c_{1\#,40s}$)**). This leads to a tendency for the W/O/W emulsion particles to fracture into separate water and oil phases rather than transforming into a W/O emulsion. For crude oil 2#, the merging happened between some W/O/W emulsion particles (ex. **Figure 3 ($c_{2\#,10\,s}$)** and **($c_{2\#,30\,s}$)**). More W/O emulsion particles were transformed at 50 ºC but broken at 80 ºC because of the viscoelasticity varying of oil film (**Figure 3 ($b_{2\#}$)** and **($c_{2\#}$)**). When the viscosity and heavy molecule component increased (as in the case of crude oil 5#), more W/O emulsions formed without significant breaking of W/O/W emulsion particles at 20 ºC, in comparison to the other three oils (**Figure 3 ($a_{1\#,150s}$), ($a_{2\#,150s}$), ($a_{5\#,150s}$),** and **($a_{8\#,150s}$)**). When increasing the

temperature to 50 ºC, the ratio of resin to asphaltene and the heat resistance of both natural surfactants (resin and asphaltene) may dominate the emulsion transformation of crude oil 5#. The decrease in W/O emulsion formation as temperature decreases and the enhanced stability of W/O/W emulsion are believed to be attributed to the temperature-dependent effectiveness of natural surfactants with varying molecular weights (**Figure 3 ($a_{5\#}$)**). Compared with crude oil 5#, more W/O/W emulsion of crude oil 8# was broken into free water and oil, and less W/O emulsion was transformed at 20 ºC (**Figure 3 ($a_{5\#}$)** and **($a_{8\#}$)**). Because of the stable solubility of surface-active substances from 20 ºC to 80 ºC, there were no significant changes in the amount of W/O emulsion transformed (**Figure 3 ($a_{8\#,150s}$), ($b_{8\#,40s}$),** and **($c_{8\#,40s}$)**).


(a1#,i)
30000 rpm
20ºC
10s
30s
60s
150s
Aqueous phase
W/O/W emulsion particles
Water droplet in oil
Oil phase
140 μm
(b1#,i)
30000 rpm
50ºC
10s
20s
30s
40s
(c1#,j)
30000 rpm
80ºC
(a2#,i)
30000 rpm
20ºC
(b2#,j)
30000 rpm
50ºC
(c2#,j)
30000 rpm
80ºC
(a5#,i)
30000 rpm
20ºC
(b5#,j)
30000 rpm
50ºC
(c5#,j)
30000 rpm
80ºC

233

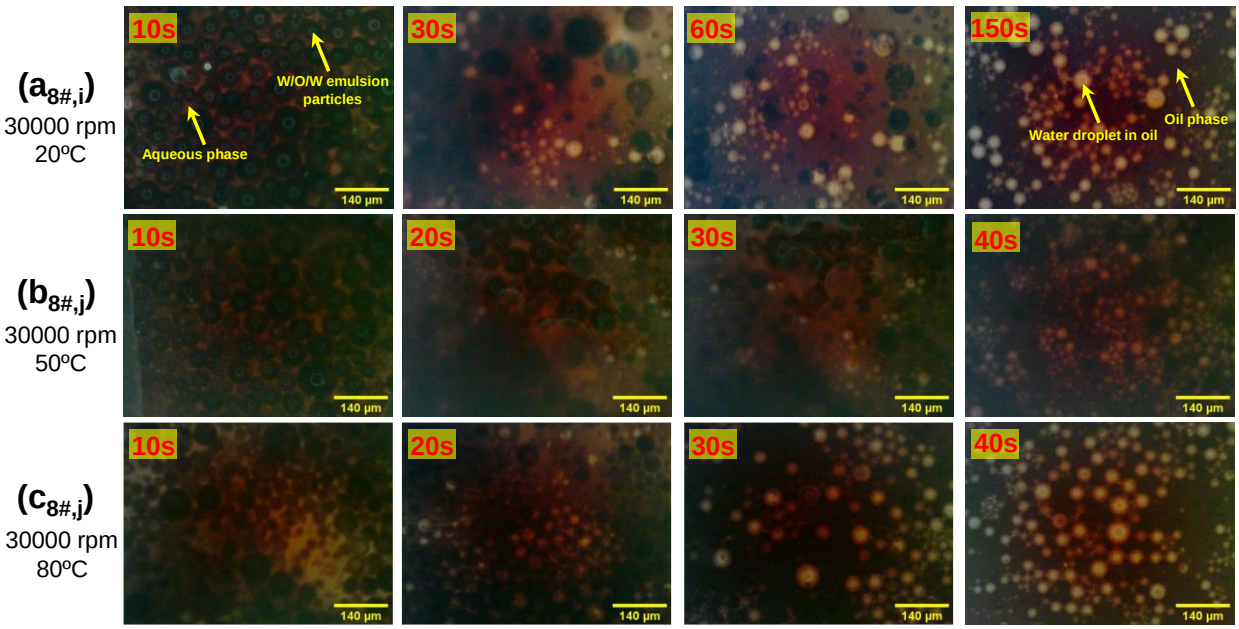


Figure 3. Micrographs of emulsion formation of crude oils at different temperatures ($a_{x,i}$: microscope experimental images of emulsion formation process (x = crude oil 1#, 2#, 5#, and 8#; i = 10 s, 30 s, 60 s, and 150 s; j = 10 s, 20 s, 30 s, and 40 s) after 5-second homogenization)

To quantify the temperature effect on the amount of W/O emulsion transformed, the resolved water was measured according to **Figure 2 (c)** (30000 rpm, 15 min), and the results are shown in **Figure 4**. It is important to highlight that as the percentage of resolved water decreases, a greater quantity of W/O emulsion transformed. Four hypotheses regarding the changes in %Resolved water due to temperature effects are observed in the following scenarios: (a) within crude oil 1#; (b) across crude oils 2#, 3#, and 4#; (c) in the case of crude oils 5# and 6#; and (d) among crude oils 7#, 8#, and 9#. The change in the quantity of resolved water influenced by temperature aligns with the patterns observed in various emulsion formation processes (**Figure 3**). This correlation is primarily attributed to factors such as viscosity (related to oil composition) and the difference between TAN and TBN. At elevated temperatures, such as 80 ºC, there is a notable reduction in W/O emulsion formation, especially when the oil viscosity is not substantially higher than 10 cp.

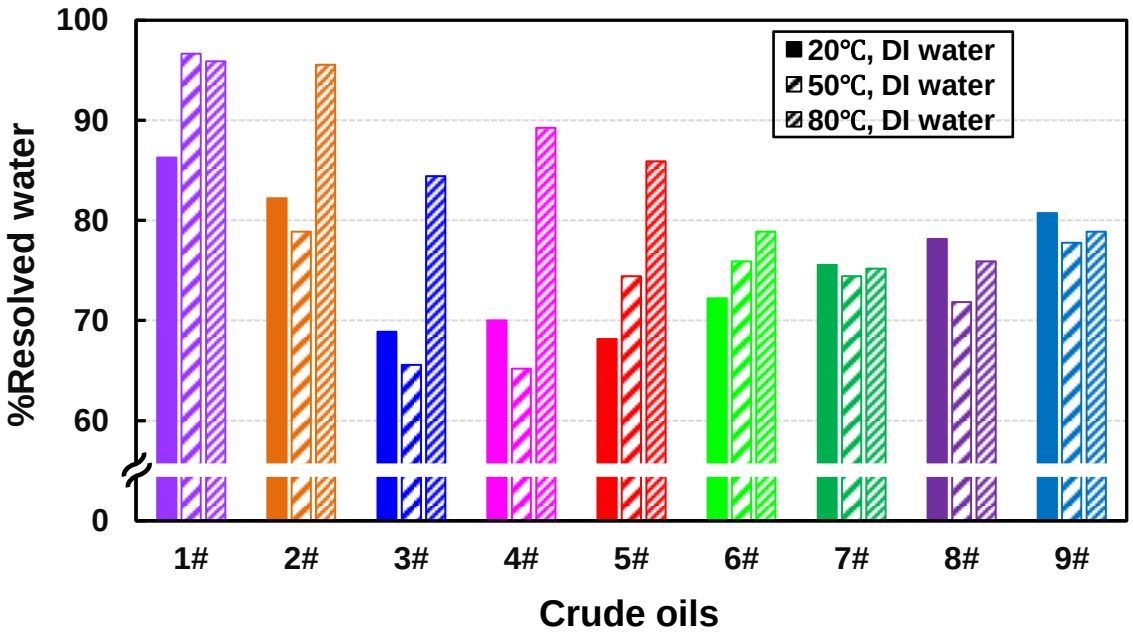


Figure 4. Resolved water percentage of various crude oils at different temperatures

In order to assess the impact of temperature on the stability of W/O emulsions in crude oils, the second layers formed at three different temperatures were examined, and the results are presented in **Figure 5**. As emulsion particles increase in size, their kinetic stability decreases, as noted in ref. [9, 47]. Furthermore, as the temperature rises, the stability of W/O emulsions formed individually by the nine crude oils diminishes, particularly in the case of oils with lower viscosity. The distinct impacts of temperature on %Resolved water and the stability of W/O emulsions in different oils imply that the percentage of resolved water is a suitable metric solely for analyzing the quantity of W/O emulsion formed under different temperature conditions (**Figure 4** and **Figure 5**). When comparing the W/O emulsion observed during the emulsion formation process with that obtained after centrifugation at 20 ºC, there appears to be no significant change in particle size, except for crude oil 1# (**Figure 3 ($a_{2\#,150s}$), ($a_{5\#,150s}$), ($a_{8\#,150s}$)** and **Figure 5 (20ºC; 2#, 5#, 8#)**). There were minimal differences in particle size observed for the emulsions of crude oil 8# at 50 ºC and 80 ºC. This phenomenon is attributed to the equilibrium achieved by various natural surfactants in crude oil as they respond to increasing temperatures. However, the opposite trend was observed for the other three oils (crude oil 1#, 2#, and 5#) at 50ºC and 80ºC. In these cases, W/O emulsions with larger particle sizes were

obtained. This is because higher temperatures promote the coalescence of water droplets in W/O emulsions after homogenization, leading to the formation of larger W/O emulsion particles.

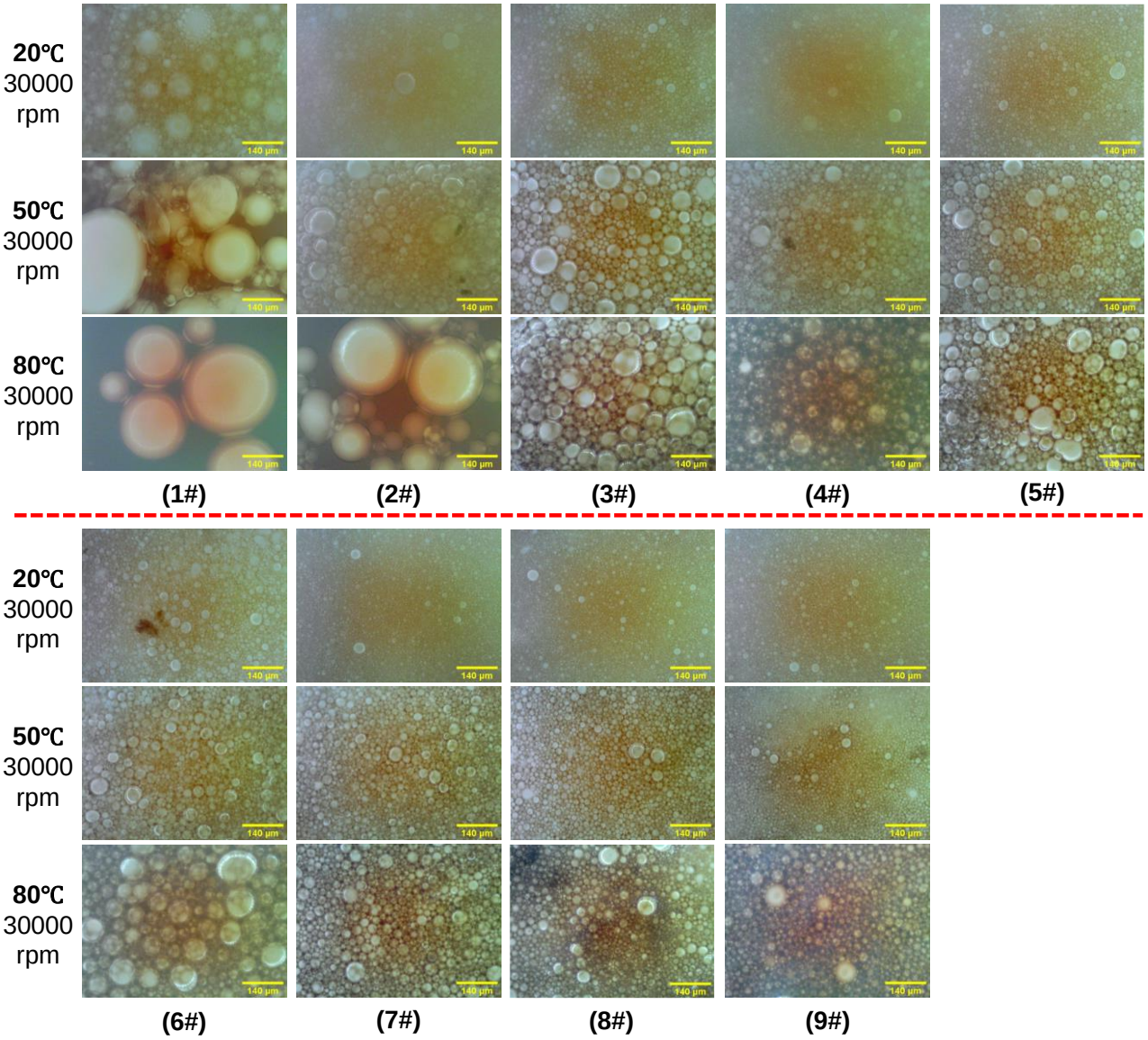


Figure 5. Microscope images of W/O emulsions for nine crude oils at 20 °C, 50 °C, and 80 °C

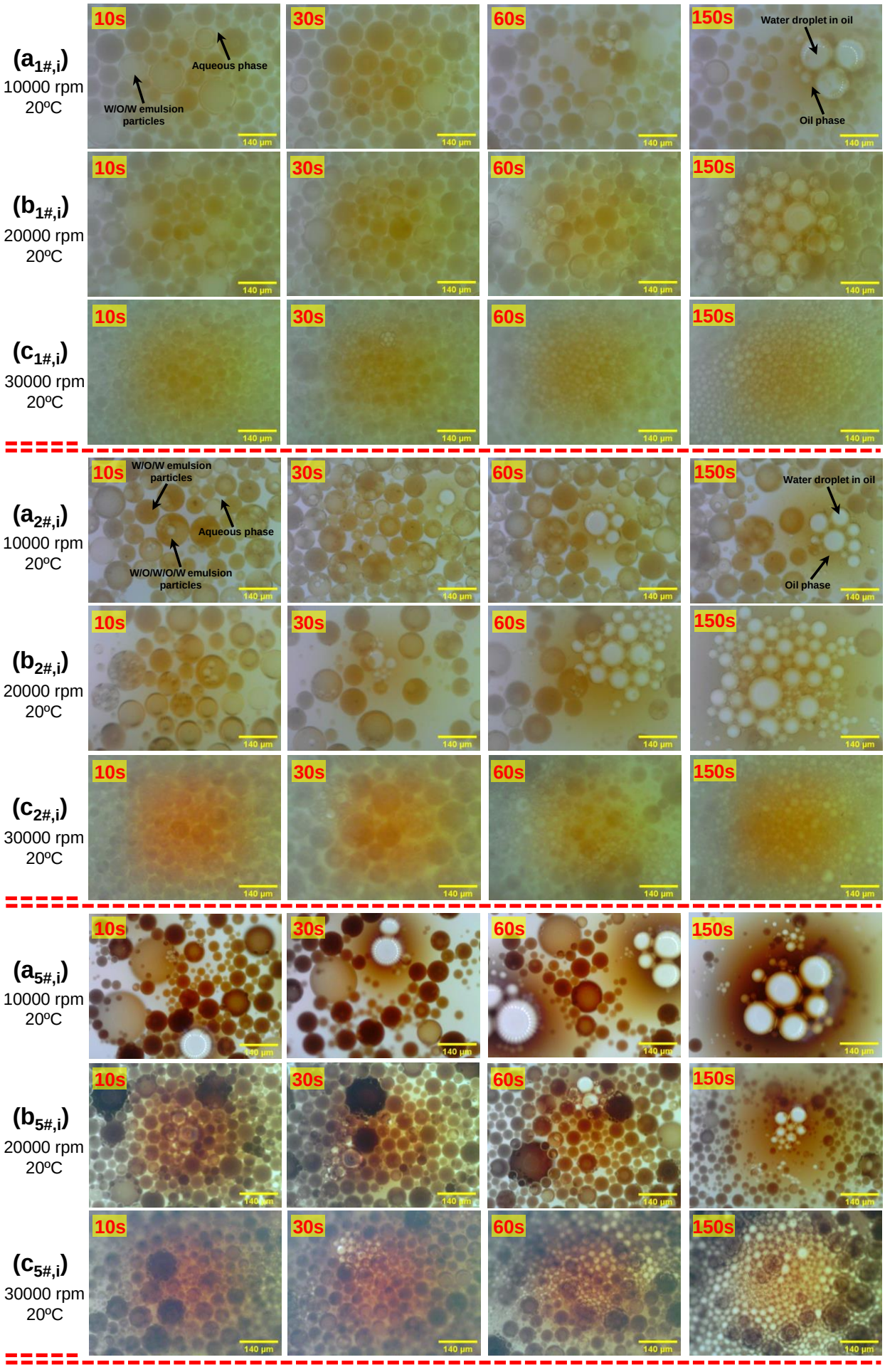
3.2 Effect of homogenizing conditions on emulsion formation and stability

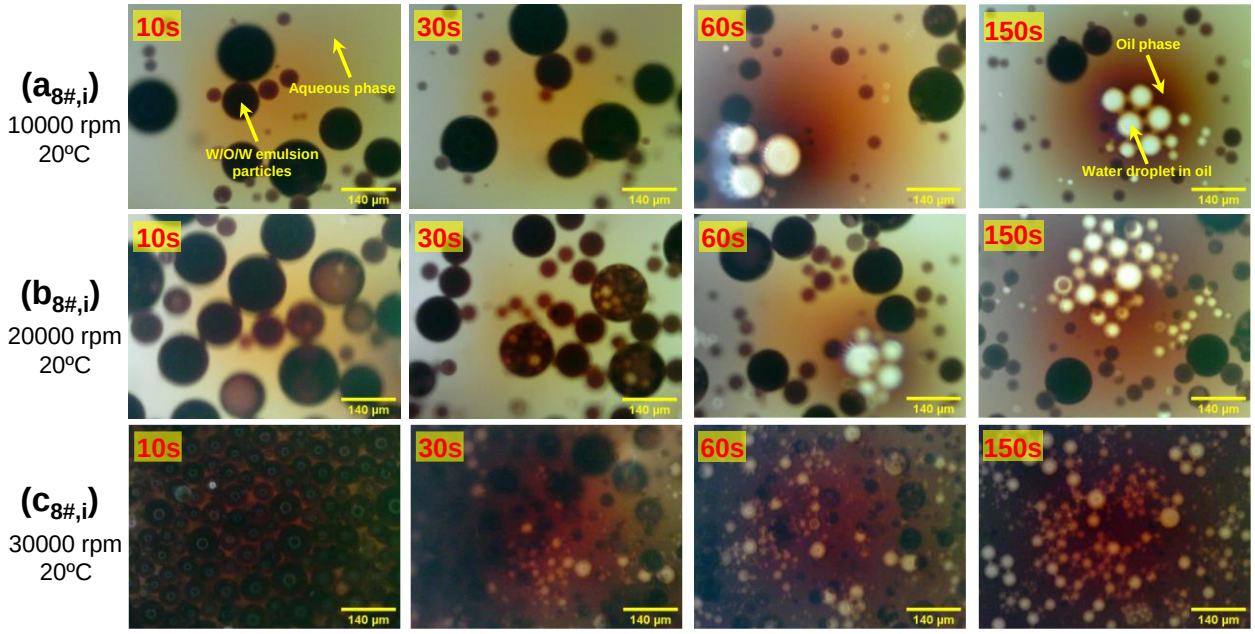
3.2.1 Homogenization speed

Figure 6 shows the emulsion formation processes for crude oils (1#, 2#, 5#, and 8#) after 5-second homogenization at a speed of 10000 rpm, 20000 rpm, or 30000 rpm. In the four crude oils, the W/O/W emulsion particles became smaller, and their quantity increased with an increase in speed due to the high shear forces and turbulence generated (**Figure 6 (i = 10 s)**). Another significant discovery is

that W/O/W/O/W emulsion particles were formed in crude oil 2# but not in the other three oils. Meanwhile, the W/O/W/O/W emulsion formed at 10000 rpm was stable, and its amount was sharply reduced at a speed of 30000 rpm (**Figure 6 ($a_{2\#,10s}$), ($b_{2\#,10s}$),** and **($c_{2\#,10s}$)**). This suggests that homogenization speed is not the dominant factor in W/O/W/O/W emulsion formation; instead, the structures and molecular weight of natural surfactants in crude oil determine viscosity, which is the key factor. Moreover, W/O emulsions were transformed from W/O/W or W/O/W/O/W emulsions in four oils (**Figure 6 ($i = 150$ s)**). Furthermore, high homogenization speed accelerated W/O emulsion formation, increased its quantity, and minimized its particle size, suggesting higher emulsion stability.

According to the emulsion formation process, different homogenization speeds produced multiple emulsions (W/O/W or W/O/W/O/W emulsions) with varying particle sizes. This variation can influence the dispersion and alignment of different surface-active substances from crude oil and affect their performance. Therefore, the ζ-potentials of multiple emulsion droplets prepared by homogenizing at three different speeds for 2 minutes were measured, as shown in **Figure 7**. The ζ-potentials of the four crude oil systems varied and even changed from positive to negative with changes in homogenization speed. This indicates differences in the charged surfaces of the multiple emulsions formed. The surface charges of W/O/W or W/O/W/O/W emulsion particles formed in DI water are primarily due to the ionization of surface-active components in crude oil. Carboxyl groups contribute to negative charges, while amidogen groups contribute to positive charges. It should be noted that the interaction between these functional groups and their performance influences the final surface charges. At 10,000 and 20,000 rpm, the negative ζ-potentials for the four oils suggested that TAN dominates the emulsion surface properties, even though TAN is smaller than TBN for crude oil 2#, 5#, and 8#. However, when the homogenization speed was increased to 30,000 rpm, TBN began to play a non-negligible role in determining the charged emulsion surface.


(a1#,i)
10000 rpm
20ºC
(b1#,i)
20000 rpm
20ºC
(c1#,i)
30000 rpm
20ºC
(a2#,i)
10000 rpm
20ºC
(b2#,i)
20000 rpm
20ºC
(c2#,i)
30000 rpm
20ºC
(a5#,i)
10000 rpm
20ºC
(b5#,i)
20000 rpm
20ºC
(c5#,i)
30000 rpm
20ºC
10s
30s
60s
150s
Aqueous phase
W/O/W emulsion particles
Water droplet in oil
Oil phase
W/O/W emulsion particles
Aqueous phase
W/O/W/O/W emulsion particles
Water droplet in oil
Oil phase
140 μm



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307 **Figure 6.** Micrographs of emulsion formed at different homogenization speeds ($a_{x,i}$: microscope

308 experimental image of emulsion formation process (x = crude oil 1#, 2#, 5#, and 8#; i = 10 s, 30 s,

309 60 s, and 150 s) after 5-second homogenization; where ($c_{1\#}$), ($c_{2\#}$), ($c_{5\#}$), and ($c_{8\#}$) in this figure are

310 the same as Figure 3 ($a_{1\#}$), ($a_{2\#}$), ($a_{5\#}$), and ($a_{8\#}$), respectively.)

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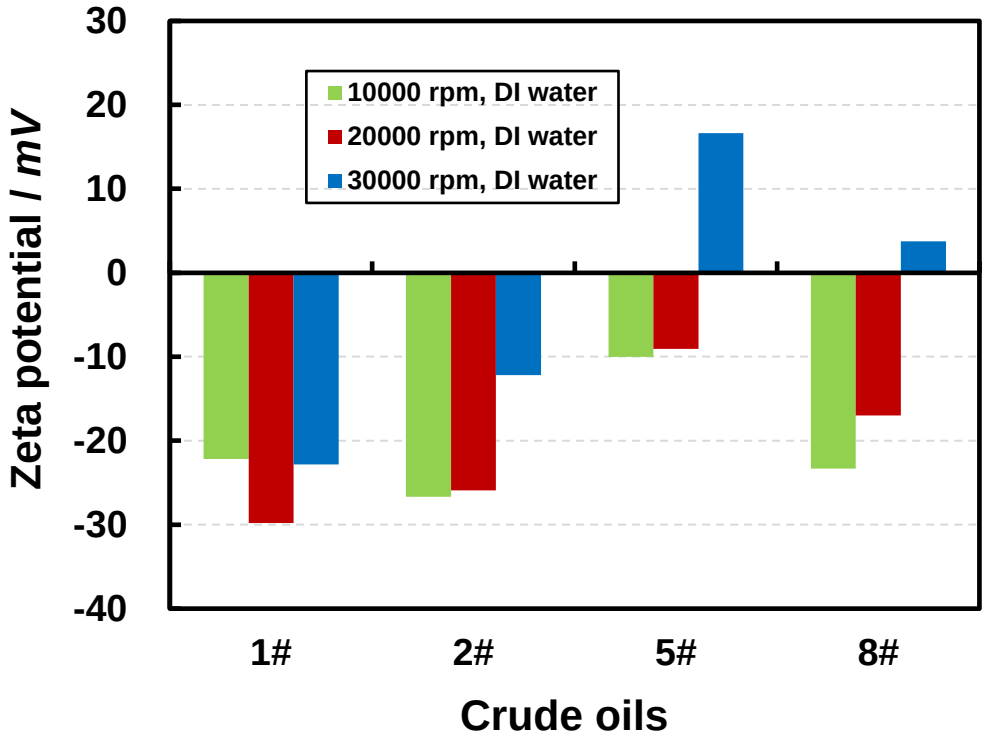

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313 **Figure 7.** Zeta potentials of crude oil emulsion particles formed at different homogenization speeds

Figure 8 depicts the effect of homogenization speed on W/O crude oil emulsions formed in DI water. There is a strong correlation between the changes in ζ-potential of multiple emulsion particles (formed by crude oil 1#, 2#, and 8#) and their corresponding variations in resolved water content. This suggests that electrokinetics significantly influences W/O emulsion transformation for extremely low or high-viscosity crude oils. When the homogenization speed was increased to 30,000 rpm, more resolved water was obtained, while there were no apparent changes at 10,000 and 20,000 rpm for all nine oils. High homogenization speeds above certain values can significantly enhance the production of W/O emulsions. **Figure 9** illustrates the size changes of W/O emulsion particles for all nine crude oils with increasing homogenization speed. As the homogenization speed increased, the size of W/O emulsion particles decreased for all oils, indicating that a lower homogenization speed is beneficial for destabilizing the W/O emulsions in crude oils. Additionally, the colour of W/O emulsions became lighter with increasing homogenization speed, indicating an increase in water content in the W/O emulsions. Comparing the W/O emulsions formed by different oils under the same conditions, it can be concluded that higher viscosity tends to increase the stability of W/O emulsions.

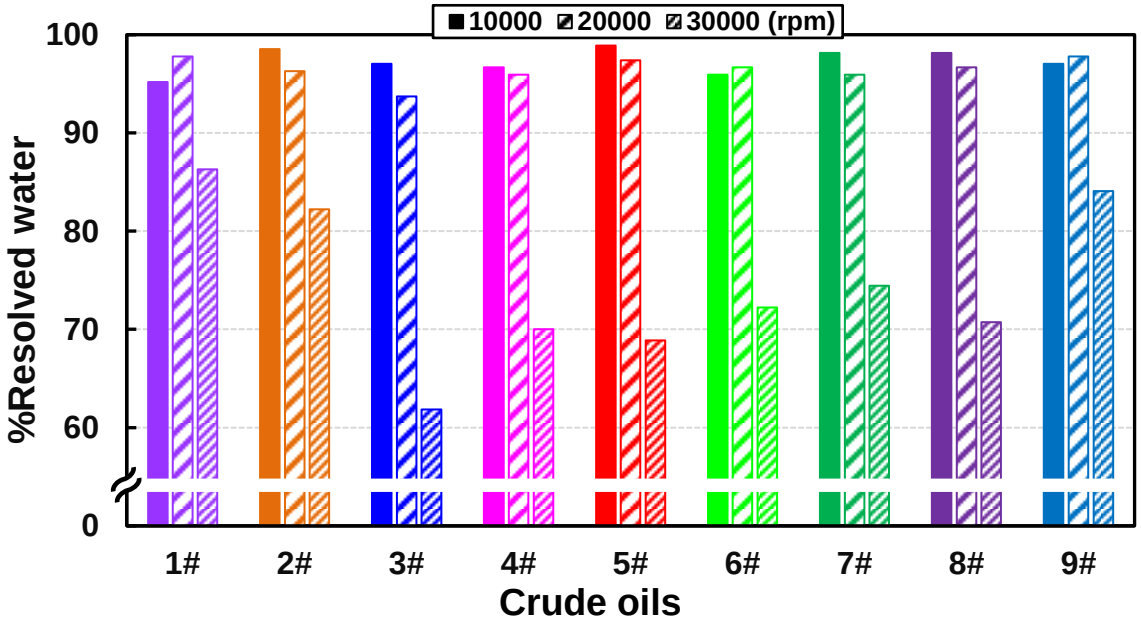


Figure 8. Effect of homogenization speed on the changes of resolved water

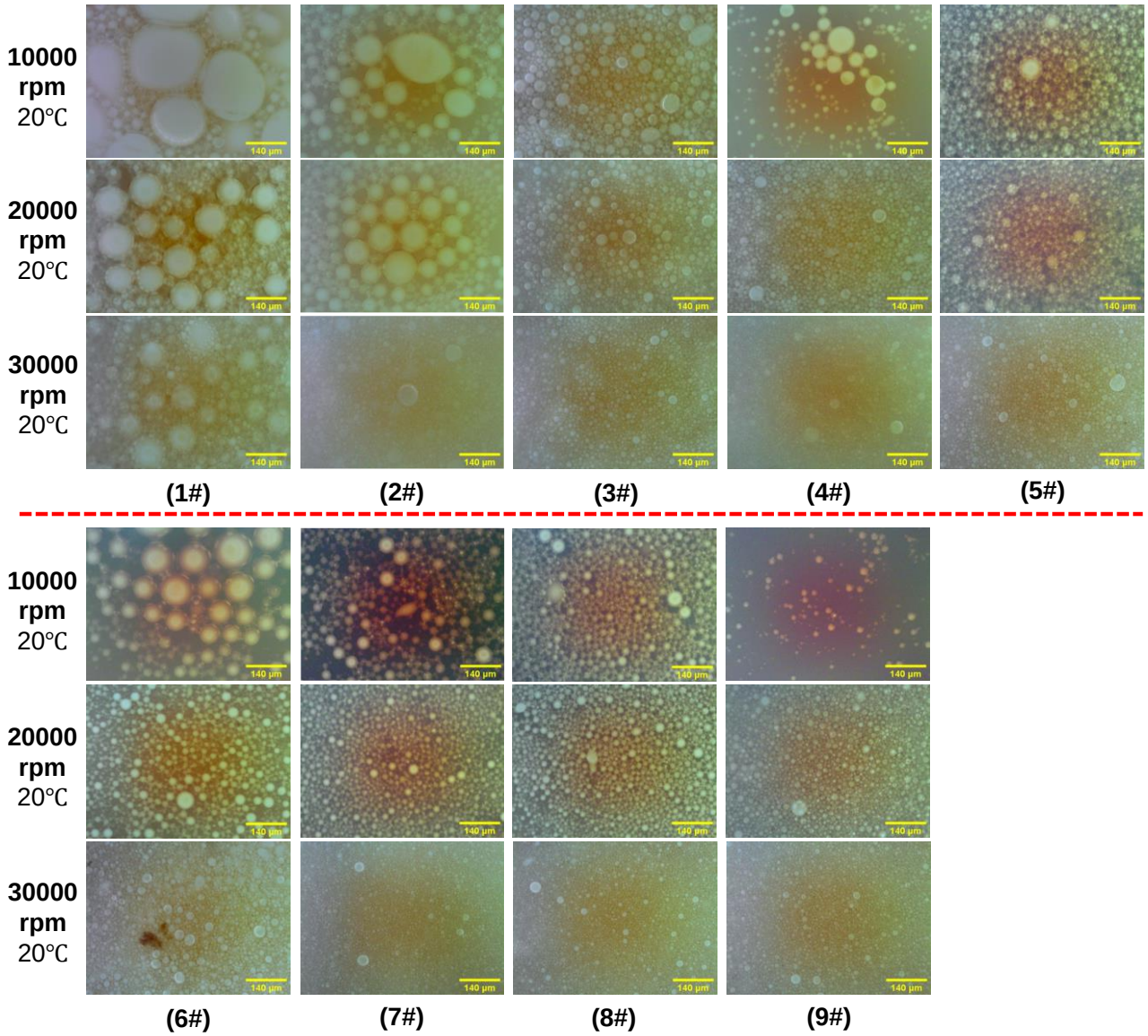
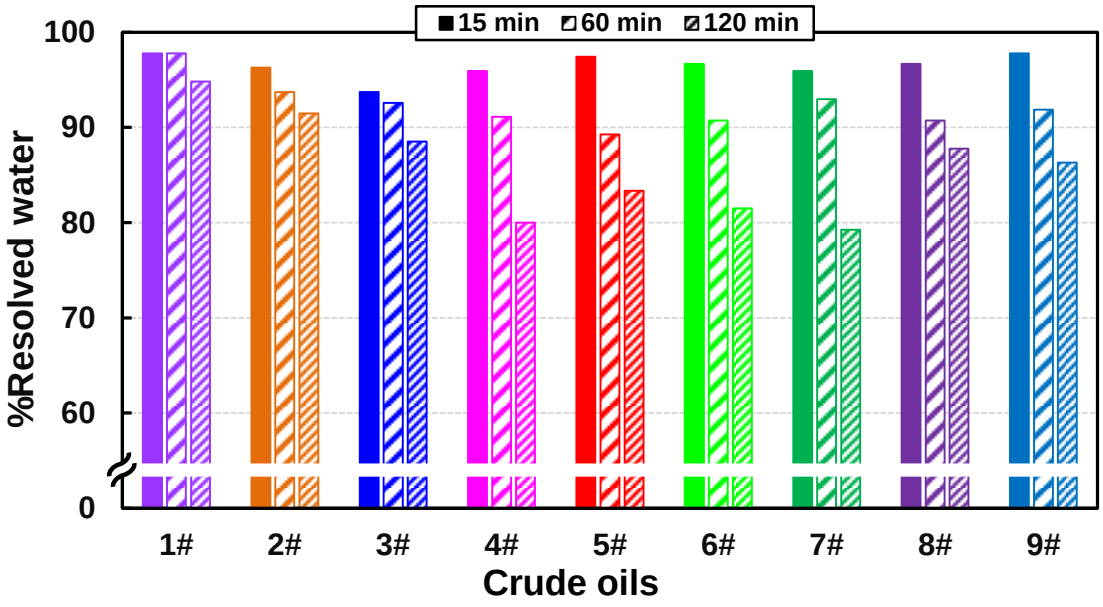


Figure 9. Microscope images of the second layer formed at the speed of 10000 rpm, 20000 rpm, and 30000 rpm

3.2.2 Homogenization time

The duration of homogenization is one of the factors affecting crude oil emulsions that rely on external energy support. As shown in **Figure 2 (c)**, resolved water was separated and measured under the following homogenization conditions: 20ºC; 20,000 rpm; and homogenization times of 15 minutes, 60 minutes, or 120 minutes. For nine different crude oils, the amount of resolved water decreased as the homogenization time increased (see **Figure 10**). Longer homogenization times

contributed to higher emulsification efficiency, forming more W/O emulsions. It is worth noting that the impact of homogenization duration on the amount of W/O emulsions formed was more pronounced for the other six oils when compared to crude oils 1#, 2#, and 3#. This could be attributed to the presence of natural surfactants with higher molecular weights in these crude oils. Longer homogenization times might enhance the activation of these surfactants, leading to the formation of more emulsions. To evaluate homogenization time on W/O emulsion stability, the observation of the second layer (W/O emulsion) was conducted, and the micrographs are presented in **Figure 11**. Longer homogenization times resulted in smaller particle sizes of W/O emulsions for all nine crude oils, indicating increased emulsion stability. Notably, there were significant stability changes in W/O emulsions formed by crude oils with lower viscosity (see **Figure 11** for 1# and 2#). Additionally, viscous solids, identified as asphaltenes, precipitated in the W/O emulsion for crude oil 6# with increasing homogenization duration (as shown in **Figure 11** for 6#). This behaviour might be attributed to the temperature-induced performance of asphaltenes in crude oil 6#. The homogenization process involves high shear forces, resulting in friction between the sample and the homogenizer. This friction generates thermal energy that is transferred to the sample system, effectively increasing the system's temperature. The asphaltenes, which are large molecules with little activity at 20 ºC, can act as surface-active substances during homogenization. However, these asphaltenes precipitate when the homogenized sample is allowed to rest at 20 ºC.



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363 **Figure 10.** Homogenization time effect on changes of %Resolved water for nine crude oils

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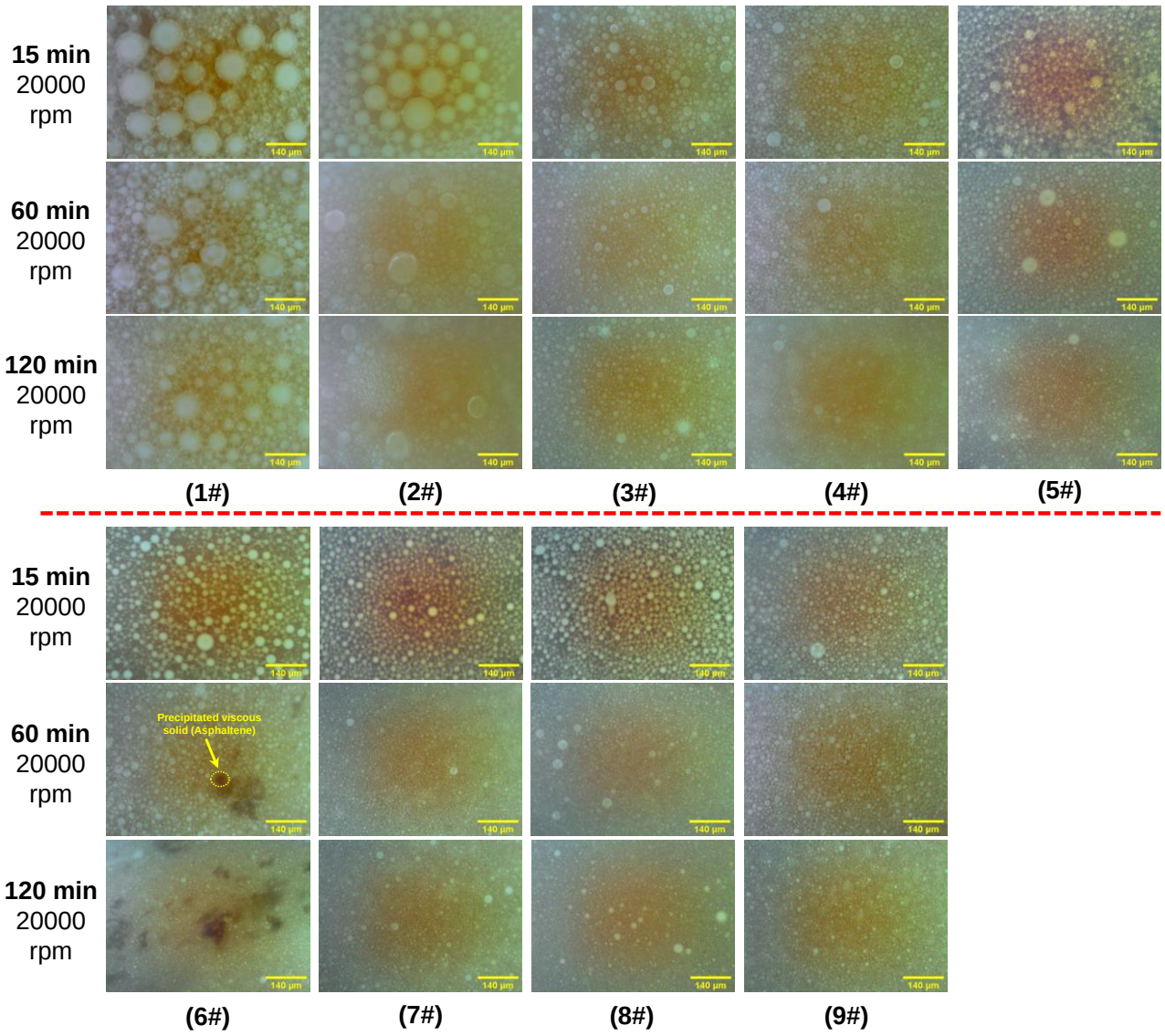

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Figure 11. Microscope images of the second layer for nine crude oils with homogenization time of 15 min, 60 min, and 120 min

3.2.3 Mechanism of homogenization effect on emulsification

As discussed in Section 3.2.1, the ζ-potential of crude oil emulsion particles (specifically, W/O/W emulsion droplets) exhibited variations with increasing homogenization speeds. In simpler terms, the active surface functional groups of these emulsion particles changed under different homogenization conditions. **Figure 12** illustrates the proposed mechanism, hypothesizing the impact of shear intensity on emulsification. After homogenization, W/O/W emulsion particles were formed, with an oil film acting as a barrier between the inner and outer water phases. This oil film primarily consisted of natural surfactants present in crude oil, comprising both active surfactants and inactive ones hidden within oil molecule aggregates. Low homogenization speed and short duration result in lower shear intensity, whereas the opposite holds true for high speed and extended duration. Strong shear forces can produce a larger quantity of smaller W/O/W emulsion particles (as shown in **Figure 6**). Consequently, the specific surface area of these W/O/W emulsion particles increases with higher shear intensity, raising the likelihood of hidden surfactants transitioning into active ones. Due to the higher free energy associated with W/O/W emulsion particles (characterized by two curved water-oil interfaces), their stability tends to be lower than that of W/O emulsion particles [9]. If there is a higher concentration of natural surfactants with activity, a larger quantity of W/O emulsion can be transformed from W/O/W emulsion.

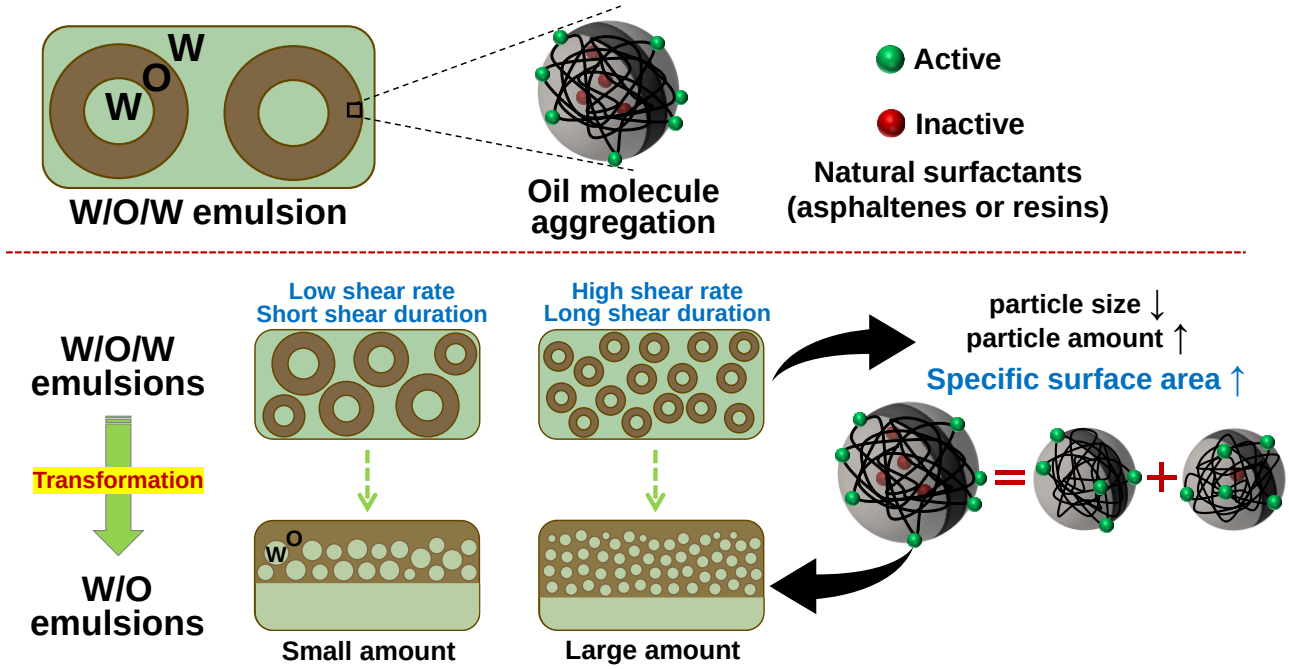


Figure 12. Proposed mechanism for the impact of homogenization conditions on emulsification

3.3 Effect of crude oil properties on W/O emulsion

Surface-active agents in crude oil play a crucial role in emulsion formation, particularly when there is no external energy influence or brine effect. The surface-active properties primarily stem from functional groups present in crude oil. FTIR spectra were obtained for nine crude oils, and their emulsions (the second layer) formed at 20 ºC under the homogenization condition of 30,000 rpm for 15 minutes, as shown in **Figure 13**. In the FTIR spectra, the peaks for crude oils were primarily located within the band regions of 2990~2700 cm^{-1}, 1550~1075 cm^{-1}, or below 1050 cm^{-1} (see **Figure 13 (a)**). In contrast, various peaks in crude oil emulsions were distributed across broader regions: 3770~2990 cm^{-1}, 2990~2800 cm^{-1}, 1800~1490 cm^{-1}, 1490~1300 cm^{-1}, or less than 1050 cm^{-1} (**Figure 13 (b)**). The wide range of band regions for each peak makes it challenging to extract detailed information directly. Therefore, using a Gaussian band shape selection, FTIR spectra curve fitting was carried out for four crude oils (1#, 2#, 5#, and 8#).

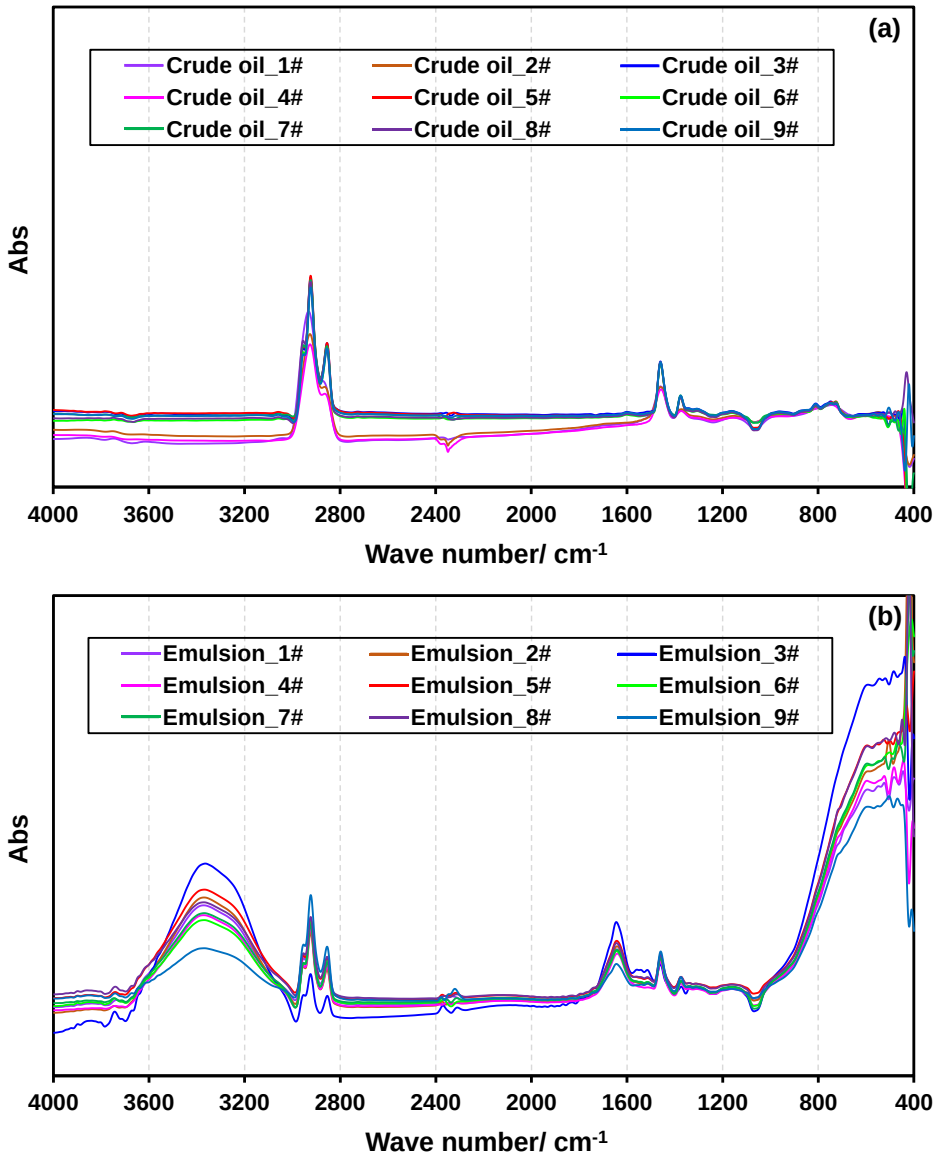


Figure 13. FTIR spectra of (a) crude oils and (b) corresponding W/O emulsions

Figure 14 displays the resolved spectral curves for crude oils 1#, 2#, 5#, and 8# in two regions: 1550-1075 cm^{-1} and 2990-2700 cm^{-1}. Oxygen/nitrogen-containing functional groups are typically found in the 1800-1000 cm^{-1} range, while peaks influenced by heteroatoms appear in the 2800-2900 cm^{-1} range [48]. A band within the 1570-1515 cm^{-1} range can be attributed to the N-H in-plane bending of secondary amides, with its C-N stretching occurring in the 1310-1230 cm^{-1} range [49]. Peak1, fitted for the four different crude oils around 1515 cm^{-1}, was identified as the N-H in-plane bending. The band near 1300 cm^{-1} (Peak9) corresponded to C-N stretching, with its corresponding band area being the smallest for crude oil 1#, equal to 0.017 (as shown in **Figure 14 (a)**). As per a previous study [48],

414 the bending of in-plane O-H in carboxylic acids falls within the 1440-1395 cm^{-1} region. The band
415 near 1425 cm^{-1} (Peak5) was associated with in-plane O-H bending, and crude oil 5# exhibited a
416 smaller band area, equal to 0.010. Supported by the findings that methyl asymmetric bending and
417 scissors-type vibration of methylene occur near 1440-1480 cm^{-1} [49], Peaks 2, 3, and 4 for all four
418 oils are related to these bending and vibrations (as depicted in **Figure 14 (a)**). Bands for C-O-H,
419 C-C-O, and O-C-C of different molecules typically appear in the 1400-1000 cm^{-1} range. The more
420 dispersed the peaks and the larger the bands in this region, the greater the presence of molecules with
421 these functional groups. In comparison to oil 2#, oil 1# may benefit from these functional groups
422 when forming emulsions. The stretching of aliphatic C-H bonds typically occurs in the 2990-2750
423 cm^{-1} range. Bands appearing at approximately 2954 cm^{-1} (identified as Peak2 for crude oil 1# and 2#,
424 and Peak1 for 5# and 8#) are attributed to CH3 asymmetric stretching (as shown in **Figure 14 (b)**).
425 Larger bands around 2930 cm^{-1} (Peak3 for crude oil 1# and 2#, and Peak2 for 5# and 8#) indicate
426 methylene asymmetric stretching. The stretching of CH3 groups attached to other saturated groups
427 results in bands at approximately 2970 cm^{-1} (Peak1 for crude oil 1# and 2#, and Peaks 7 and 8 for 8#)
428 and 2900 cm^{-1} (Peak4 for crude oil 1# and 2#, and Peak3 for 5# and 8#), with crude oil 1# and 2#
429 exhibiting larger band areas. Furthermore, bands around 2868 cm^{-1} (Peak4 for crude oil 5# and 8#)
430 are attributed to the attachment of aromatic rings to CH3 groups. Additionally, bands near 2855 cm^{-1}
431 are caused by heteroatoms, including O-CH3 and N-CH3 (Peak5 and Peak6) [48], with crude oil 1#
432 and 2# having band areas twice as large as those for the other two oils.
433

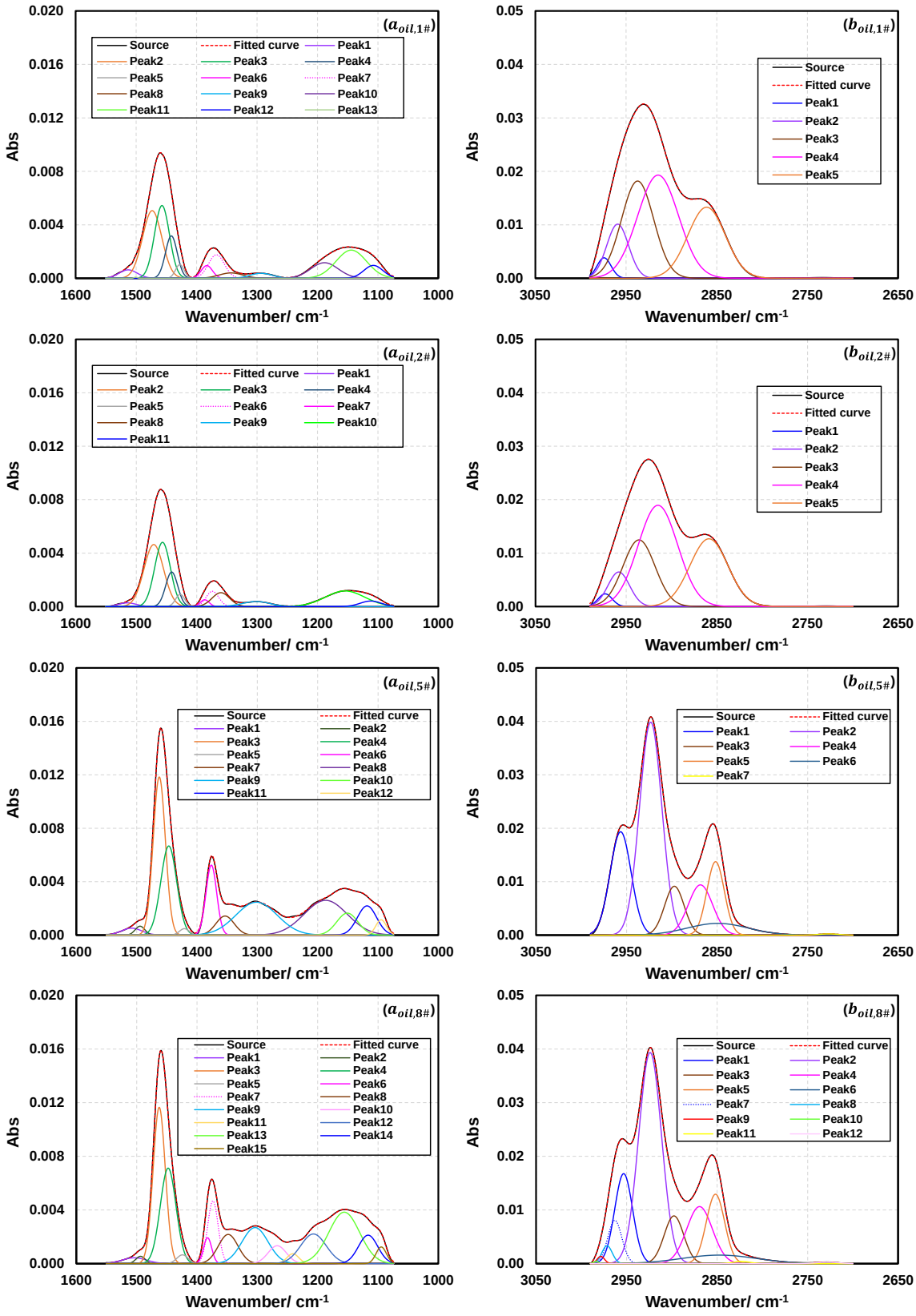
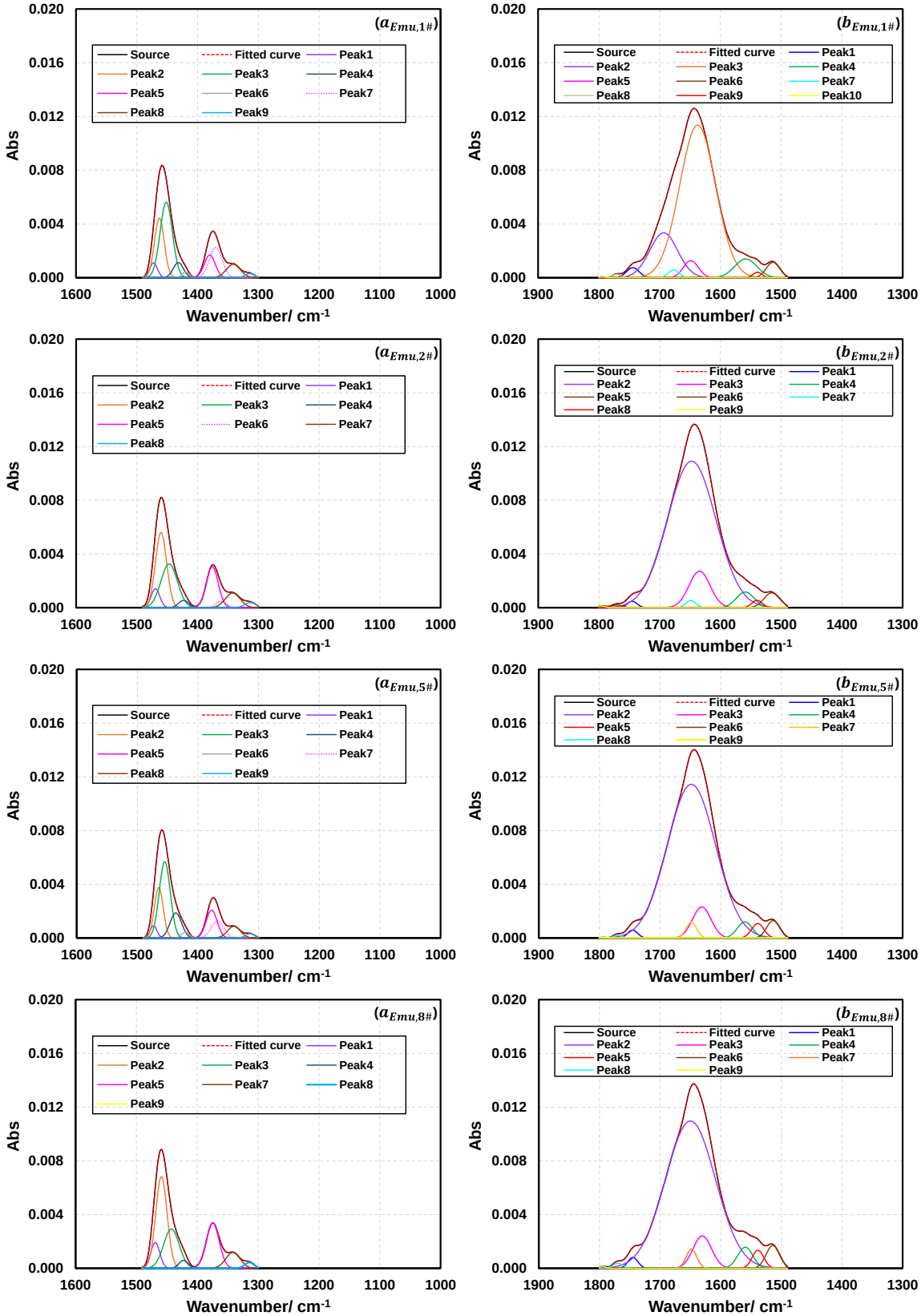


Figure 14. Curves resolved spectra of four oils at two different regions ($a_{oil,i}$ and $b_{oil,i}$: oil spectra at 1550-1075 cm^{-1} and 2990-2700 cm^{-1}, respectively; $i = oil\ 1\#, 2\#, 5\#, or\ 8\#$)

To further understand the effect of functional groups on crude oil emulsions, we studied the resolved spectra of four W/O emulsions at four different regions: 1490-1300 cm^{-1}, 1800-1490 cm^{-1}, 2990-2800 cm^{-1}, and 3770-2990 cm^{-1} (see **Figure 15**). Stronger NH···O hydrogen bonds can weaken and redshift the N-H bond of secondary amides, resulting in the appearance of a band at approximately 1470 cm^{-1} (Peak1 in **Figure 15 (a)**). A similar phenomenon occurred with the bending of in-plane O-H in carboxylic acids, where the formation of stronger OH···O hydrogen bonds caused the peak of O-H in carboxylic acids to shift from about 1425 cm^{-1} in crude oils to approximately 1375 cm^{-1} in their W/O emulsions (Peak5 in **Figure 15 (a)**). It is worth noting that peaks lower than 1375 cm^{-1} may be attributed to C-O-H, C-C-O, and O-C-C groups in various molecules. In the 1800-1490 cm^{-1} region, bands were observed at approximately 1795, 1770, 1745, 1650, 1630, 1560, 1540, and 1515 cm^{-1} (see **Figure 15 (b)**). The C=O bonds of carbonyl, ester, carboxylic acid, and ketone groups are associated with peaks at 1795, 1770, 1745, and 1650 cm^{-1}. Additionally, the spectra around 1630 cm^{-1} correspond to the H-O-H bending vibration in water [49]. The band at 1540 cm^{-1} may be attributed to the N-H of amine in W/O oil emulsions. Meanwhile, the bands at 1560 cm^{-1} and 1515 cm^{-1} could be caused by the C=C stretching of aromatic substances, as C=C aromatic bonds typically appear in the 1620-1400 cm^{-1} range [48]. In the 2990-2800 cm^{-1} region (**Figure 15 (c)**), bands observed at approximately 2967, 2955, 2924, 2898, and 2868 cm^{-1} correspond to C-H bonds present in aliphatic or aromatic compounds. These bands are indicative of the presence of these types of bonds. Additionally, bands shifted to 2852 and 2822 cm^{-1} are associated with O-CH3 and N-CH3 groups, respectively. The 3770-2990 cm^{-1} region contains bands related to O-H and N-H bonds. The band for the free O-H bond is typically found in the 3650-3500 cm^{-1} range, while the band for the hydrogen-bonded O-H is located around 3390 cm^{-1} (see Peak2 in **Figure 15 (d)**). The order of the band area ratio of the hydrogen-bonded OH to the free one is as follows: oil 5# (6.02) > oil 8# (5.54) > oil 1# (5.26) > oil 2# (5.01). Notably, the largest band area for the hydrogen-bonded O-H is found in crude oil 5#, with a value of 7.136. Additionally, the band areas of hydrogen-bonded N-H bonds at approximately 3218 cm^{-1} (Peak4 in **Figure 15 (d)**) for the four oils are as follows: 2.710 (1#), 4.099

(2#), 3.019 (5#), and 2.817 (8#). Furthermore, bands occurring at frequencies lower than 3060 cm^{-1} are associated with the C–H stretching vibration of substituted polynuclear aromatic compounds (as depicted in **Figure 15 (d)**).



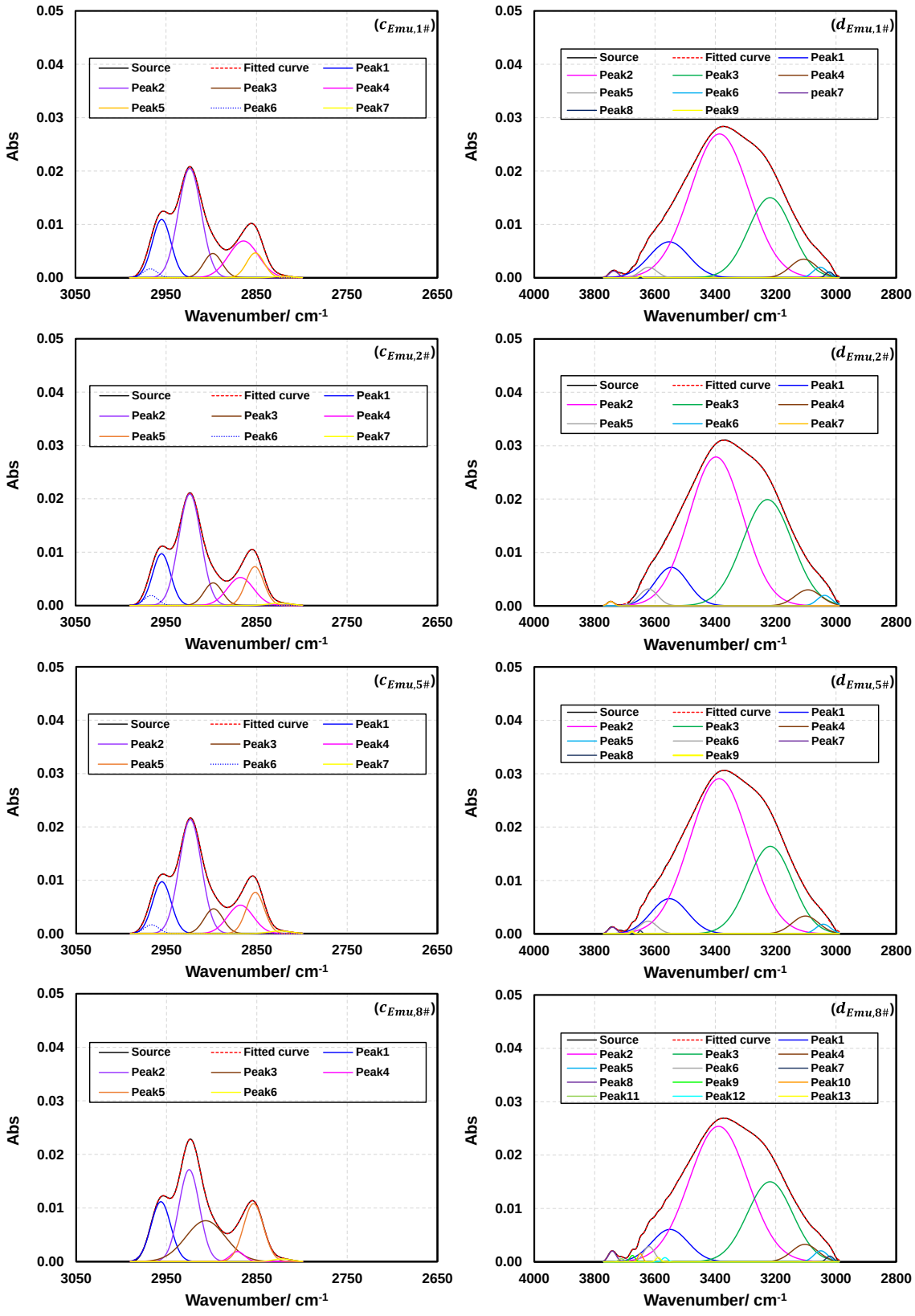


Figure 15. Curves resolved spectra of four oil emulsions at four different regions ($a_{Emu,i}$, $b_{Emu,i}$, $c_{Emu,i}$ and $d_{Emu,i}$: oil emulsion spectra at 1490-1300 cm^{-1}, 1800-1490 cm^{-1}, 2990-2800 cm^{-1} and 3770-2990 cm^{-1}, respectively; $i = oil\ 1\#, 2\#, 5\#, or\ 8\#$)

4. Conclusions

In this study, we observed the formation of W/O emulsions by various crude oils under different temperatures and homogenization conditions. It was found that, regardless of temperature and shear intensity, W/O emulsions transformed from W/O/W emulsions and W/O/W/O/W emulsions for various crude oils, except for crude oil 1# at 80 ºC. Notably, at 80 ºC, the W/O/W emulsion formed by the least viscous crude oil (crude oil 1#) exhibited the highest stability, attributed to the increased deprotonation of carboxyl groups at elevated temperatures. Although similar W/O emulsion particle sizes were observed for the same oil at different temperatures during the W/O emulsion formation process, the W/O emulsion amounts varied, and the shifts in W/O emulsion amounts with temperature differed depending on the type of oil. In contrast to the temperature effect, high homogenization speeds produced a larger quantity of smaller W/O emulsion particles, suggesting a more stable W/O emulsion transformation at higher shear rates. The shift in ζ-potentials of multiple (W/O/W or W/O/W/O/W) emulsion particles when increasing homogenization speed indicated changes in natural surfactants within oil films, which is a key factor in determining the effect of homogenization on emulsification. Furthermore, we evaluated the stability and amount of W/O emulsions obtained under different conditions. The results revealed four distinct patterns in the variations of W/O emulsion amounts for various oils under the influence of temperature. With increasing temperature, the coalescence of W/O emulsion particles after 24 hours became more pronounced due to the reduction in water viscosity, resulting in reduced stability. Conversely, high shear intensity increased W/O emulsion amounts and enhanced their stability, primarily influenced by the emulsion formation process. Moreover, W/O emulsion amounts were found to be mainly dependent on hydrogen-bonded O-H groups, followed by hydrogen-bonded N-H groups. Based on the findings presented in this study, strategies to reduce stable W/O emulsions can be devised, including lowering shear rates, reducing shear duration, and adjusting the temperature based on oil type or viscosity.

CRediT authorship contribution statement

Xingjuan Hao: Methodology, Investigation, Writing-original draft, Writing-review & editing. **Mai Shimokawara:** Supervision, Writing-review & editing, Funding acquisition. **Yoshitake Kato:** Supervision, Writing-review & editing, Funding acquisition. **Ryuta Kitamura:** Supervision, Writing-review & editing, Funding acquisition. **Naoki Hiroyoshi:** Writing-original draft, Supervision, Validation, Writing-review & editing. **Yogarajah Elakneswaran:** Writing-original draft, Supervision, Validation, Writing-review & editing, Funding acquisition.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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653 **TOC Graphic**

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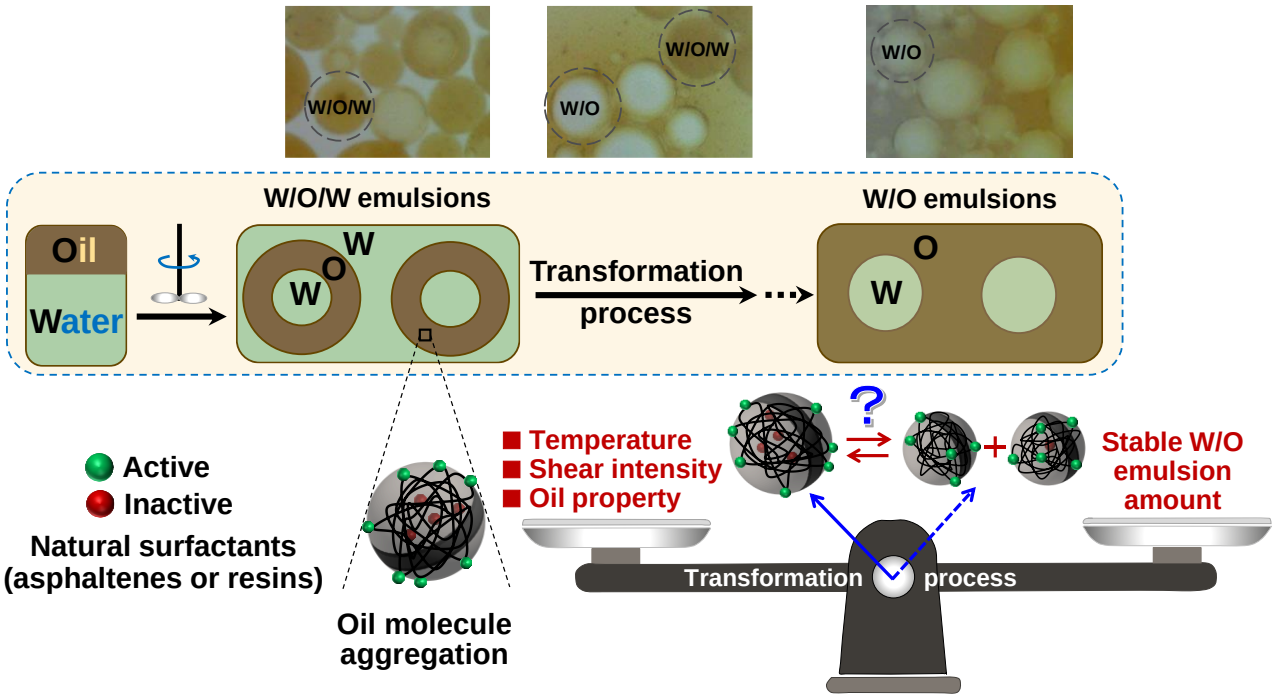

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