Influence of Inorganic Solid Particles on the Stability of Water-in-Crude Oil Emulsions: Evaluating the Role of Surface Charge

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Abstract

This study examines the effect of inorganic solid particles on the stability of water-in-oil (W/O) emulsions formed during the transportation, refining, and storage of crude oil. The surface properties of inorganic particles, such as kaolinite and calcite, can influence the interface between crude oil and water, affecting the stability of the emulsion. The study evaluates the quantitative effect of these particles on emulsion stability and investigates how surface properties affect the emulsions. Emulsions were prepared using crude oil and synthetic brine, with calcite and kaolinite added as inorganic solid particles. Adding inorganic solids increased the volume of released water and altered the emulsion stability, with high concentrations decreasing the formation of stable emulsions. The dissolution of inorganic solids increased the pH of the solution and promoted demulsification due to the high surface potential of crude oil. The solid particles enhanced the formation of oil-in-water-in-oil (O/W/O) emulsions, generating unstable emulsions. The study also found that increasing temperature and adding inorganic solids decreased the emulsion height over time, which was predicted by the emulsion layer growth model. The coagulation rate constant was a tuning parameter, with a higher value implying higher internal repulsion and stronger coagulation between water droplets, facilitating emulsion instability. It has been observed that elevating the storage temperature and introducing kaolinite accelerates the coagulation rate constant, whereas the addition of calcite decreases this value, ultimately contributing to the stabilisation of the emulsions.

Keywords: crude oil emulsion; stability; emulsion growth model; Zeta potential; coagulation rate

1. Introduction

Emulsions, mixtures of multiple liquids dispersed as fine droplets in another phase due to low interfacial tension, have wide-ranging applications in industries such as food, cosmetics, agricultural products, paints, coatings, and pharmaceuticals [1-2]. While emulsions can benefit viscosity control, transfer processes, and chemical reactions facilitated by the large interfacial area, their presence is

often undesirable in the petroleum industry. Stabilised water-in-oil emulsions can significantly increase the viscosity of a liquid, cause a pressure drop in the flow line, decrease production, result in pipeline corrosion, and cause pump malfunctions [3-8]. Moreover, emulsions in production wells are directly related to a lower oil recovery. The formation of a thick and viscous layer at the oil-water interface can pose significant challenges during separation [9]. Controlling production conditions and improving productivity are crucial in minimising emulsion formation. Successful implementation of these measures can lead to a significant reduction in the subsequent emulsion separation process. In order to address these emulsion-related issues, it is crucial to understand the mechanisms of emulsion formation and develop efficient solutions for reducing or breaking down these emulsions.

The mechanisms governing the formation and stability of emulsions remain incompletely understood, although four primary mechanisms have been proposed: electrostatic forces, the Marangoni-Gibbs effect, steric repulsion, and thin film stabilisation [10]. In the case of water-in-crude oil emulsions, electrostatic forces have a limited impact on emulsion stability due to the low dielectric constant of crude oil compared to water. The Marangoni-Gibbs effect refers to fluid movement caused by variations in surface tension across a liquid interface. When a gradient in surface tension exists, the liquid moves from areas of lower surface tension to areas of higher surface tension [11]. This phenomenon is unlikely to occur in crude oil emulsions because the interfacial viscosity increases due to the formation of the film [10]. Steric repulsion, which relates to the resistance between adsorbed species on the droplets, plays a significant role in stabilising asphaltene dispersion due to the high energy associated with asphaltene-resin interactions. The formation of a robust, viscoelastic, and stationary thin film around the droplets acts as a barrier against droplet-droplet coagulation, thereby stabilising the emulsion. This film primarily consists of asphaltenes and resins [1,7,8,12,13,14]. Asphaltenes are flat sheets made up of condensed polyaromatic hydrocarbons connected by sulfide, aliphatic chain, or naphthenic ring linkages [15,16]. Simultaneously, resins structurally resemble typical surface-active molecules, featuring one hydrophilic end with polar

functional groups and one hydrophobic end composed of alkyl chains. In the nonpolar oil environment, the polar end of the resins interacts with the exposed cores of asphaltenes, while the nonpolar end of the resins interacts with the crude oil medium. The polar cores of asphaltenes can also interact with polar cores from other asphaltene molecules, resulting in asphaltene aggregates solvated with resins [10]. Additionally, the interaction of these aggregates with the interface is energetically favoured over interactions with resins and aromatics in the oil phase. Consequently, an intermediate level of solvation exists at which the formation of a viscous, cross-linked interfacial network of asphaltenes takes place [17-21].

Various factors influence the formation and stability of emulsions in crude oil. These conditions comprise pH, ionic strength, ionic composition, and the ratio of crude oil to water [22]. A high or low pH can cause functional groups on asphaltene molecules to become charged or partially charged, increasing their hydrophilicity and surface activity. Ionic strength can impact the stability of emulsion by forming salts with monovalent cations, reducing the total number of -COOH groups and acid-base interactions. Divalent cations, on the other hand, can stabilise the emulsion in two ways: by adsorbing asphaltene at the brine-crude oil interface and by forming naphthenate soap. Additionally, as the percentage of crude oil increases, the number of oil components increases, leading to the formation of a stabilisation film and thin-film thickening.

Inorganic solid particles are recognised for their significant influence on emulsion stability. The presence of these particles can impact emulsion stability when they are sufficiently small to become interfacially active by adsorbing resin and asphaltene, thereby reinforcing the stability of the asphaltene-resin film [3,7,10]. Particle-stabilised emulsions, referred to as Pickering emulsions [23], generally offer superior stability over surfactant-stabilised emulsions because of the irreversible adsorption of particles at the interface. The size, wetting properties, and concentration of these particles also determine their effect on emulsion stability [24]. Smaller particles and higher particle

concentrations lead to smaller emulsion droplets and increased emulsion stability as the occurrences of droplet collisions become less frequent [1,10,25-28]. Coarse solids with diameters larger than 1 μm influence the stability of crude oil emulsions depending on their concentrations. They encourage droplet coalescence at low concentrations but hinder contact between droplets at high concentrations, consequently reducing coalescence. Hydrophilic particles have contact angles of less than 90°, which stabilise oil-in-water emulsions, while hydrophobic particles exhibit contact angles greater than 90°, leading to the stabilisation of water-in-oil emulsions [28-34].

It is well-established that the presence of asphaltenes and naturally occurring polar components soluble in crude oil are significant factors in altering the wettability of solid surfaces, making them more oil-wet [35-39]. The affinity of the molecules for the rock surface, driven by electrostatic and electrochemical interactions, is one of the primary mechanisms behind their adsorption on the rock [40]. Asphaltenes, which often carry negative charges, have a pronounced influence on the surface charge of crude oil. It has been observed that the zeta potential value, representing the potential difference between the dispersion medium and the stationary layer of fluid adhering to the dispersed particle, increases toward a negative value as the pH of the brine solution rises, affecting the oil droplets in emulsions [22]. On the other hand, rock minerals inherently possess surface charges [41-46], and these surface charges are contingent on the nature of the surface and the surrounding liquid. The principal mechanisms that determine surface charge include protonation/deprotonation, ionic adsorption, and the preferential dissolution of ions from the crystal lattice [47]. To promote interaction between crude oils and rock minerals, having opposite charges is desirable, as this induces electrostatic or electrochemical interactions. When evaluating the adsorption of crude oil on inorganic particles and its impact on emulsion stability, it is crucial to consider the surface charge of both the crude oil and the inorganic particles. However, research in this area is limited, and there is a lack of understanding regarding the impact of interface charge on emulsion stability. Comprehending the role of surface charge in the adsorption phenomenon is instrumental in gaining insight into the interactions

among oil, particles, and water. Thus, this study aims to assess the influence of inorganic particle surface properties, particularly surface charge, on emulsion stability using batch experiments and the emulsion layer growth model.

2. Materials and methods

2.1 Experimental

In this study, an emulsion was prepared using crude oil, and its properties are presented in **Table 1**. The chosen inorganic solids were kaolinite and calcite, commonly found in oilfield emulsions. Wettable aluminosilicate clays, specifically kaolinite, have been identified as typical solids associated with oilfield emulsions [48]. Additionally, carbonate rock is frequently encountered in reservoir rocks of oil fields. For this experiment, kaolinite and calcite were utilised in powdered form. The properties of inorganic particles, including their zeta potential as a function of pH, are reported in our previous study [41].

The zeta potential and weight of oil-adsorbed particles were measured to assess the surface charge of inorganic particles and their influence on oil adsorption. The crude oil to solution ratio and amount of inorganic particle addition were kept constant for each measurement: 2 mL of crude oil in 20 mL of a solution containing 1g of inorganic particles. The crude oil, solution and inorganic particles were mixed with the vortex mixer for 1 minute and then an ultrasonic cleaner for 2 minutes to emulsify the mixture. The emulsion was extracted to measure the zeta potentials (**Fig. 1**). Moreover, the crude oil to solution ratio was constant for the zeta potential measurement of crude oil: 0.1 mL (0.5%) of crude oil in 20 mL of solution. The zeta potential of the crude oil, calcite, kaolinite, oil-adsorbed inorganic particles and particle size were measured at 25 °C using Zeta-Potential & Particle size analyser ELSZ-1000, manufactured by Otsuka Electronics. Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particles. The particle

size and distribution were determined using the photon correlation method, which analyses the fluctuations of scattered light when light irradiates particles in Brownian motion within a solution.

The mass of oil-adsorbed particles was calculated by measuring the mass of precipitated particles through filtration of the water layer using the following formula.

$$M_{adsorbed} = 1 - M_{precipitatted} - M_{dissolved} \quad (1)$$

The weight of dissolution particles was obtained by performing the experiments at the same conditions without adding crude oil.

The emulsions were prepared by measuring 9 mL of solution with varying pH and adding it into a 15 mL centrifuge tube. Then, 1 mL of crude oil was added to the tube. The emulsion was created by homogenising the crude oil and solution at 30,000 rpm for 15 minutes, followed by 24 hours of ageing at room temperature. The emulsion was then centrifuged for 5 minutes at 10,000 rpm to separate the stable emulsion layer and released water. The crude oil-to-water volume ratio was chosen to ensure the formation of a stable emulsion after centrifugation and to facilitate the measurement of the zeta potential of the emulsion. The experimental procedures are shown in **Fig. 1**. In Procedure 1, the inorganic particles were added to the solution before emulsion preparation, while Procedure 2 involved preparing the emulsion without adding inorganic particles, followed by adding them after 24 hours of ageing. The centrifugation and separation process in Procedure 2 was the same as in Procedure 1. In Procedure 3, the emulsion was prepared using Procedure 1 but with a different ageing time. The volumetric ratio of crude oil to the solution was 1:9, and the sample was separated into three layers upon centrifugation: a water layer, an oil layer, and a highly stabilised water-in-oil emulsion layer. The volume of released water and the height of the stable water-in-oil emulsion layer were recorded after centrifugation.

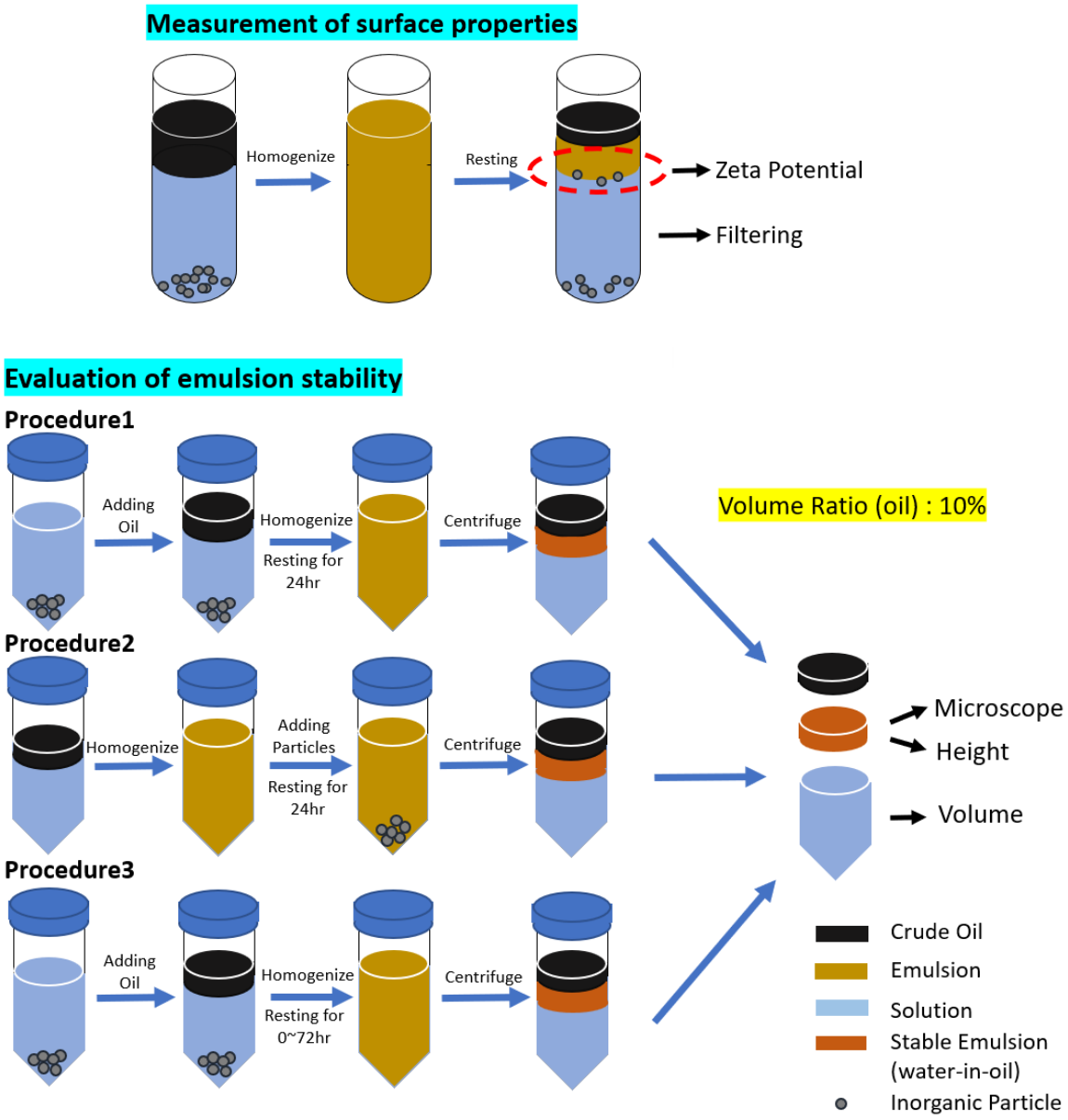


Fig. 1 Schematic diagram for emulsion preparation for zeta potential measurement and stability evaluation

Table 1. Properties of crude oil

Parameter	Value
Density (g/cm3) (15 ˚C)	0.87
API (60 ˚F)	31.3
Water content (Vol. %)	1.05
TAN (mgKOH/g)	0.07
TBN (mgKOH/g)	0.22
Composition (wt. %)	

Saturates	34.8
Aromatics	52.7
Resins	8.0
Asphaltenes	4.5

188

189

190 **2.2 Modelling approach**

191 This study employed the emulsion layer growth model [9,24] to evaluate the formation of emulsions
192 and their interaction with inorganic solid particles. This model considers the water-in-oil emulsion
193 layer to be a densely packed zone, with its volume changing due to the coalescence and compaction
194 of the dispersed phase. Equation (2) was used to express the accumulation of water and oil in the
195 emulsion layer. Additionally, the volume of the emulsion layer was found to change with the
196 liberation of the continuous phase, which is expressed using Equation (3).

197

198 $$\frac{dM_w}{dt} = -m_{w.out} \quad (2)$$

199 $$\frac{dM_o}{dt} = -m_{o.out} \quad (3)$$

200

201 M_w is the mass of water in the emulsion layer at time *t* and $m_{w.out}$ is the mass flow rate of free water
202 exiting the emulsion layer. Similarly, M_o is the mass of oil in the emulsion layer at time *t* and $m_{o.out}$
203 is the mass flow rate of free oil existing in the emulsion layer. Moreover, the mass of water and oil in
204 the emulsion layer are each given by the following formulas.

205

206 $$M_w = Ah\emptyset_w(t)\rho_w \quad (4)$$

207 $$M_o = Ah\emptyset_o(t)\rho_o \quad (5)$$

208

209 A is the cross-sectional area of the emulsion layer, h is the height of the emulsion layer, $\emptyset_w(t)$ and
210 $\emptyset_o(t)$ is the volume fraction of dispersed water and oil in the emulsion layer at time *t*, and ρ_w, ρ_o are

211 the density of water and oil, respectively. The volume fraction is calculated from the volume of
212 released water, which was determined by experiments.
213
214 $$\emptyset_w = \frac{V - V'}{Ah} \quad (6)$$
215
216 V is the volume of the total solution in the sample, V' is the volume of released water by centrifugation.
217 It is assumed that the mass flow rate of water in the emulsion layer equals the bulk coagulation rate
218 of water droplets within the emulsion layer. Assuming no direct contact or agglomeration between
219 the water phase and dispersed droplets, the coagulation rate is proportional to the number of collisions
220 between droplets. If the droplet size distribution is invariant, the coagulation rate is also proportional
221 to the volume of water in the emulsion layer. Therefore, the flow rate of coalesced water in the
222 emulsion layer can be expressed as follows.
223
224 $$m_{w,out} = kAh\emptyset_w(t)\rho_w \quad (7)$$
225
226 Additionally, it is assumed that the mass flow rate of oil existing in the emulsion layer to the oil phase
227 is equal to the bulk coagulation rate of oil in the emulsion layer. As the dispersed droplets separate,
228 oil is released, coagulates, and then rises to the surfaces of the emulsion layer. The coagulation rate
229 depends on the change in the number of water droplets, and if the droplet size distribution remains
230 constant, it is also proportional to the change in the volume of water in the emulsion layer. Therefore,
231 the oil flow rate in the emulsion layer can be expressed as follows.
232
233 $$m_{o,out} = k'Ah\frac{d\emptyset_w(t)}{dt}\rho_w \quad (8)$$
234

Where k is the bulk coagulation rate constant of water and *k'* is the bulk coagulation rate constant of oil. Equations (4) and (7) are substituted into Equation (2), and Equations (5) and (8) are substituted into Equation (3) to obtain the following equation for the change in emulsion layer height with time:

$$\frac{dh}{dt} = -kh - \frac{h}{\emptyset_w(t)}\frac{d\emptyset_w(t)}{dt} + (1 - k'\frac{\rho_w}{\rho_o})\frac{h}{1-\emptyset_w(t)}\frac{d\emptyset_w(t)}{dt} \quad (9)$$

The following equation gives the dimensionless form of equation (9).

$$\frac{d(\frac{h}{h_0})}{dt} = -k(\frac{h}{h_0}) - \frac{\frac{h}{h_0}}{\frac{\emptyset_w(t)}{\emptyset_w(0)}}\frac{d(\frac{\emptyset_w(t)}{\emptyset_w(0)})}{dt} + (1 - k'\frac{\rho_w}{\rho_o})\frac{\frac{h}{h_0}}{1-\frac{\emptyset_w(t)}{\emptyset_w(0)}}\frac{d(\frac{\emptyset_w(t)}{\emptyset_w(0)})}{dt} \quad (10)$$

To apply the above model for this study, h and $\emptyset_w(t)$ at time *t* were obtained by experiments (Procedure 3), and the coagulation rate was determined by the least-squares method.

3. Results and discussion

3.1 Surface properties of crude oil, inorganic particles, and crude oil-brine-solid system

Figure 2 illustrates the state of inorganic particles in crude oil emulsion, with both kaolinite and calcite present in precipitated, dissolved in the water phase, and adsorbed on the surface of oil (as depicted in **Fig. 3**). The results show that calcite adsorbs onto the oil droplet surface and exists as oil-adsorbed for approximately 9% of the total weight, while kaolinite is present in its oil-adsorbed state for around 4% of the total weight. This indicates that the surface properties of crude oil and inorganic particles influence their interaction. Moreover, the ratio of calcite in the dissolved state is slightly higher than that of kaolinite. Additionally, the size distribution of inorganic particles in solution varied depending on their types. Most of the kaolinite particles are around 10 μm in size, whereas the majority of calcite particles are approximately 100 nm. Notably, most calcite particles exist in the nanoscale due to their higher solubility than kaolinite.

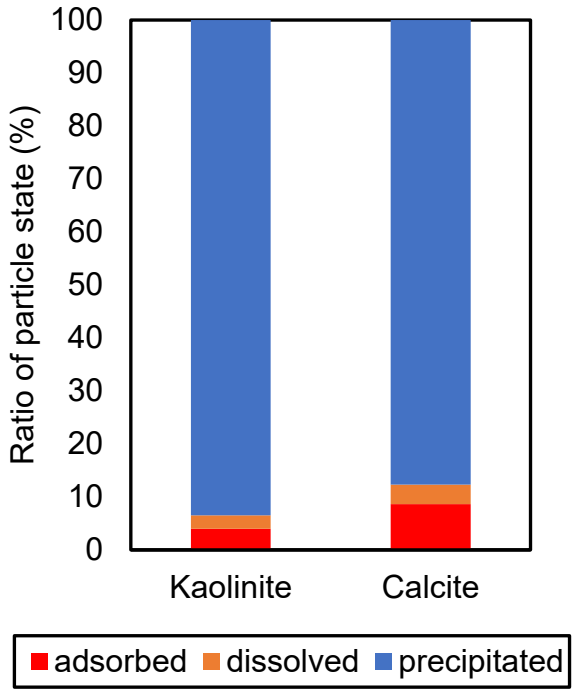


Fig. 2. Adsorption of inorganic particles on crude oil emulsion

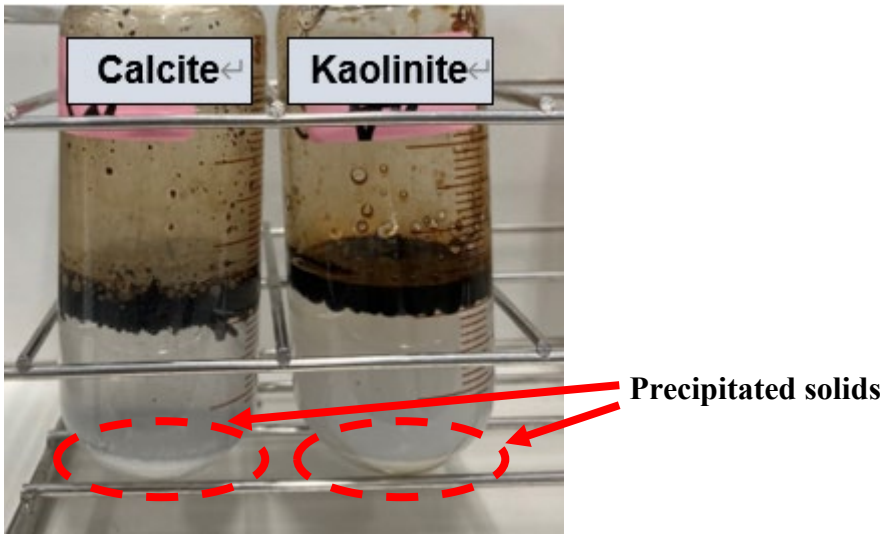


Fig. 3. Photos of an emulsion with inorganic particles

Figure 4 illustrates the alteration in zeta potential at the oil-water interface due to adsorption phenomena. The graph shows the zeta potential of crude oil emulsion without inorganic particles (referred to as "oil-solution"), which varies based on pH. At high pH, the surface charge of oil becomes more negative, and at low pH, it becomes positive due to the ionisation of functional groups

like carboxyl groups. The zeta potential of inorganic particles in solution (referred to as "particle-solution") is also shown. The addition of inorganic particles to the crude oil emulsion changes the potential to the value depicted as "oil-particle-solution," owing to the adsorption of inorganic particles on the crude oil surface. The surface of calcite is positively charged, while oil is negatively charged. Therefore, electrostatic adsorption can occur between oil and calcite. On the other hand, the kaolinite surface has a negative potential, which limits the oil adsorption. According to a previous study, basic nitrogen groups in crude oil play a significant role in asphaltene adsorption to montmorillonite, with π-bonding between the asphaltenes and the clay surface [49]. Kaolinite and montmorillonite share a crystal structure made up of overlapping aluminium and silicate [50-52], making this mechanism the primary method of kaolinite adsorption to asphaltenes. The adsorption of kaolinite particles onto the oil surface causes the potential of the oil-water interface to become more negative. This suggests that kaolinite adsorption onto the crude oil surface may not occur or may occur to a limited extent through a mechanism other than electrostatic attraction. However, when using a solution adjusted to pH 11, the result was a decrease in potential rather than an increase. In solutions with a high pH, both kaolinite and crude oil carry highly negative charges, making adsorption phenomena less likely due to unfavourable electrostatic interactions. As a result, the charge at the interface is approximately an intermediate value between the charge on the kaolinite particle surface and the charge on the crude oil surface. Conversely, positively charged calcite adsorbs onto the surface of negatively charged oil, neutralising its charge. When using a solution adjusted to pH 3, hardly any change in charge was observed. This is because the negative charge on the crude oil surface decreases under low pH conditions, making it less likely for calcite to adsorb onto it. In summary, inorganic particles in crude oil emulsions can modify the surface properties of crude oil through the following mechanisms: adsorption onto the crude oil surface and a change in oil's surface charge.

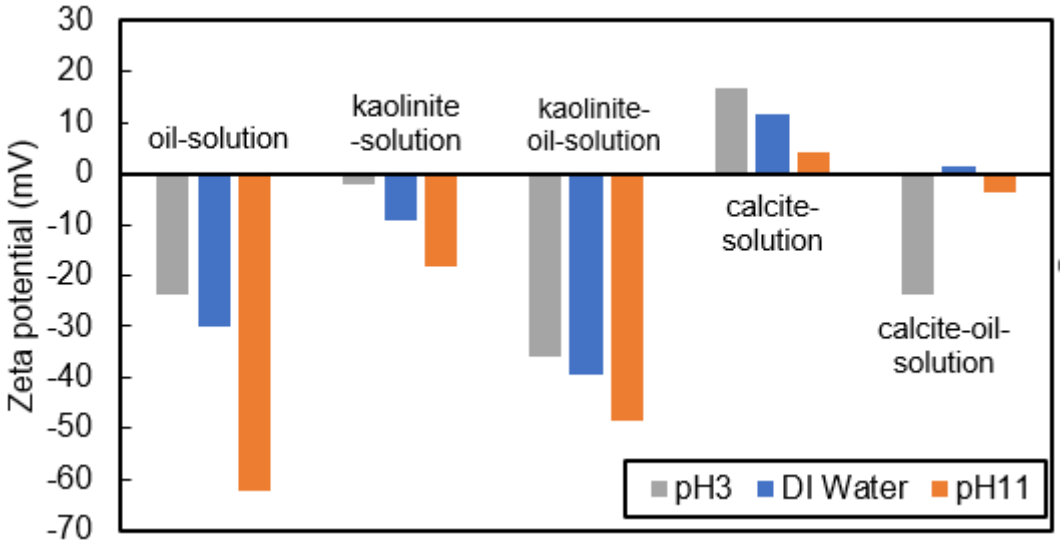


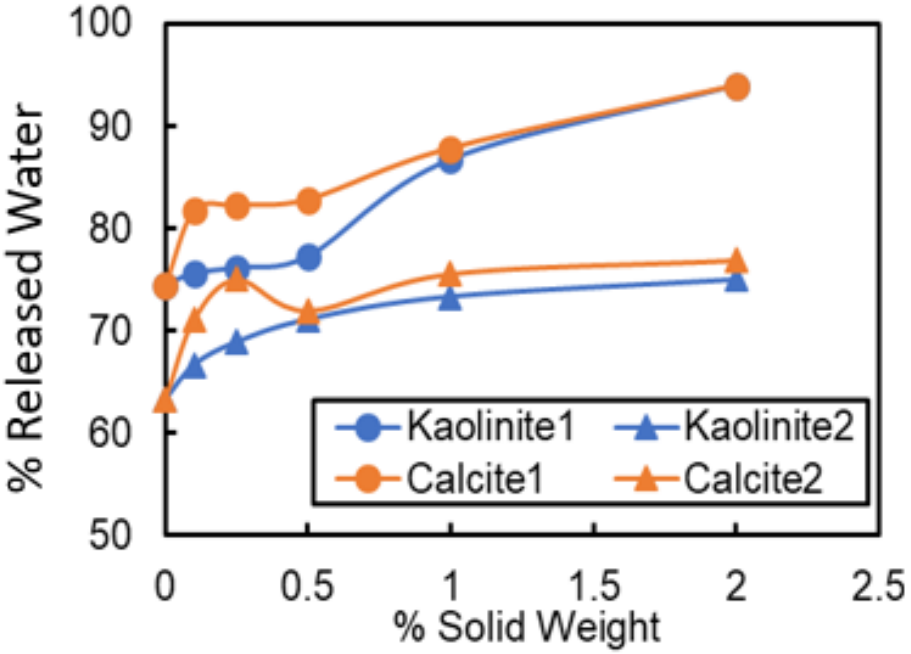
Fig. 4. Zeta potential of crude oil/brine, solid/brine and crude oil/brine/solid system

3.2 The stability of the emulsion in the presence of inorganic particles

Figure 5 illustrates the impact of adding calcite and kaolinite solid particles on water-in-oil emulsion stability. The emulsion was prepared using de-ionised water, and two procedures were followed to determine the volume of released water. In Procedure 1, the solid particles were added to the water before mixing with crude oil, while in Procedure 2, they were added to the emulsion after it was formed. The Released Water (%) in the graph shows the proportion of the separated solution in the water layer relative to the total volume of the solution. The findings suggest that the formation and stability of the emulsion, measured by the volume of released water, are influenced not only by the amount of solid but also by the timing of solid addition. Higher amounts of released water indicate less stable emulsion formation. Adding calcite and kaolinite particles reduces emulsion stability, especially in Procedure 1. The volume of released water is nearly identical for small amounts of addition (less than 0.5 wt. (%)), but it increases significantly for higher amounts (Procedure 1). Adding a large amount of calcite or kaolinite to the solution results in minimal emulsion formation.

Additionally, the addition of less than 0.5 wt. (%) calcite leads to an increase in released water, which is not observed with kaolinite. At high concentrations of both calcite and kaolinite, a similar decrease

in emulsion stability is observed in Procedure 1. On the other hand, in Procedure 2, there is only a slight difference in released water between calcite and kaolinite, which could be due to the dissolution of calcite increasing the pH of the released water to around 8. Experiments were conducted using Procedure 1 in a pH-adjusted solution to investigate the effect of pH on emulsion stability. **Fig. 6** shows the effect of initial pH on released water, while **Fig. 7** shows the pH shift. The concentration of solid particles was kept constant at 0.5 wt. (%). Both calcite and kaolinite significantly impact emulsion stability in the pH range of 5-8, with calcite having a more pronounced effect. Furthermore, calcite increases the pH of the released water due to its dissolution, while kaolinite and the sample without solids decrease the pH of the released water in basic solutions (**Fig. 7**). The deprotonation of carboxyl groups in crude oil at high pH reduces the solution's pH and increases the negative surface charge [53], resulting in stronger repulsion between oil droplets. Additionally, since the light crude oils are basic, adding a basic brine to the aqueous phase does not attract asphaltenes to the interfacial layer, leading to emulsion destabilisation [54]. This high surface charge or potential makes the emulsion formed under these conditions more susceptible to external disturbances, thus increasing the volume of released water [22]. However, adding kaolinite increases the volume of released water without affecting the initial pH in the range of 5-8, indicating that another mechanism may contribute to emulsion stability.



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332 **Fig. 5.** Released water changes with solid weight percentage

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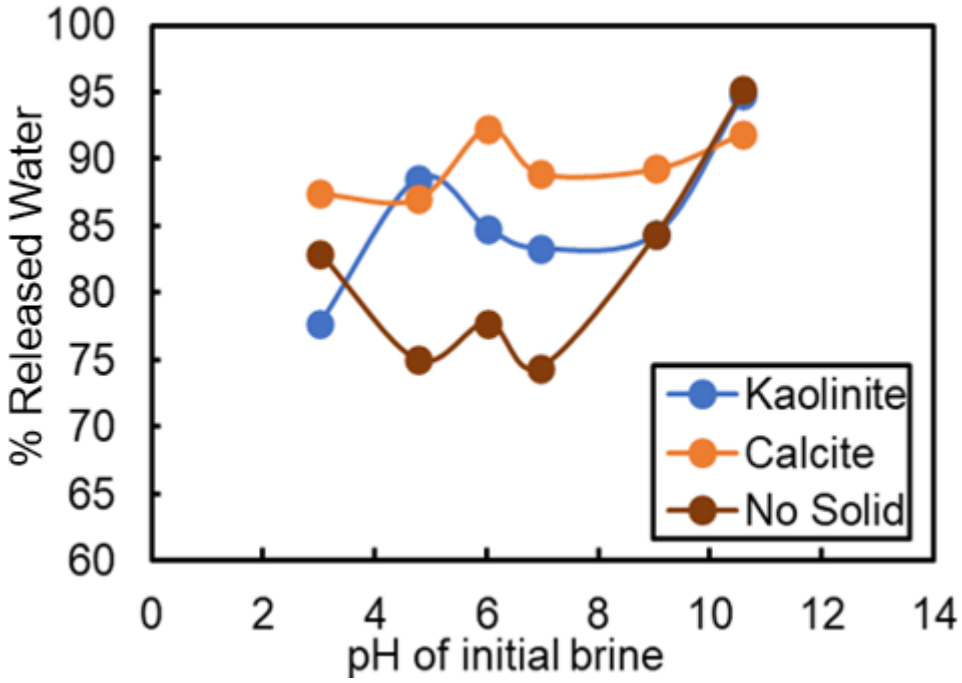

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335 **Fig. 6.** Released water changes with pH

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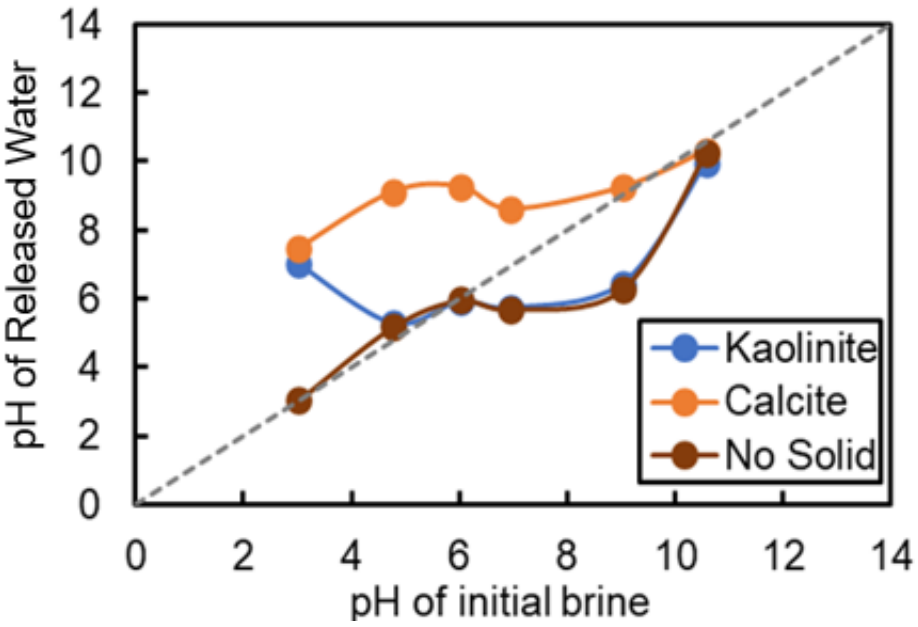

Fig. 7. pH shift in released water as a function of initial pH

Based on the experimental findings discussed above, it is apparent that the presence of inorganic particles adsorbed onto the surface of the oil can affect the emulsion stability by altering the surface properties (**Fig. 2**). Microscopic images of the emulsion before and after the addition of solid particles (**Fig. 8**) show that the morphology of the emulsion changes due to the addition of inorganic particles that act as hydrophilic surfactants. The lipophilic asphaltenes in the emulsion form water-in-oil emulsions without the addition of solid particles. However, the addition of inorganic particles leads to the formation of oil-in-water-in-oil emulsions (O/W/O) due to the presence of inorganic particles as hydrophilic surfactants with contact angles less than 90˚ (**Fig. 9**) [23, 28-33]. Multiple emulsions have inherent thermodynamic instability, and the formation of complex interfacial states due to the presence of inorganic particles could lead to a higher surface potential of crude oil [55,56]. This increased surface potential causes internal repulsion between oil droplets, making the emulsion more susceptible to external disturbances and demulsification. Consequently, the addition of inorganic particles results in a decrease in the stability of emulsions, and more separated water is observed. The effect of particle adsorption on emulsion stability depends on the surface potential of the inorganic particles. In samples containing kaolinite, a decrease in pH results in an increase in separated water,

except under high pH conditions. This is because the surface charge of kaolinite becomes relatively positive at acidic conditions, increasing its affinity for adsorption onto crude oil. In contrast, kaolinite exhibits behaviour similar to the "No Solid" condition at high pH, which is more strongly negatively charged, resulting in limited adsorption. Calcite, which has an opposite charge, shows a slight increase in separated water as the pH increases (**Fig. 6**). Thus, the stability of emulsions is influenced by the change in surface potential due to the adsorption of inorganic particles onto the oil-water interface.

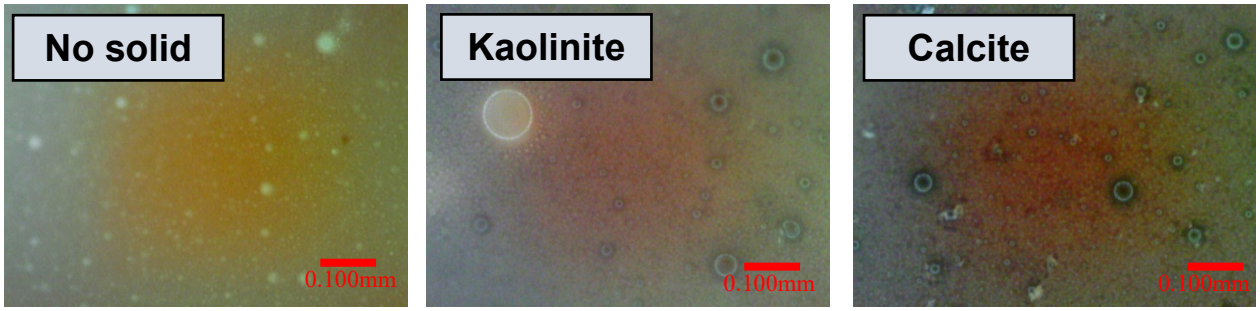

Fig. 8. Microscope image of the emulsion after homogenisation

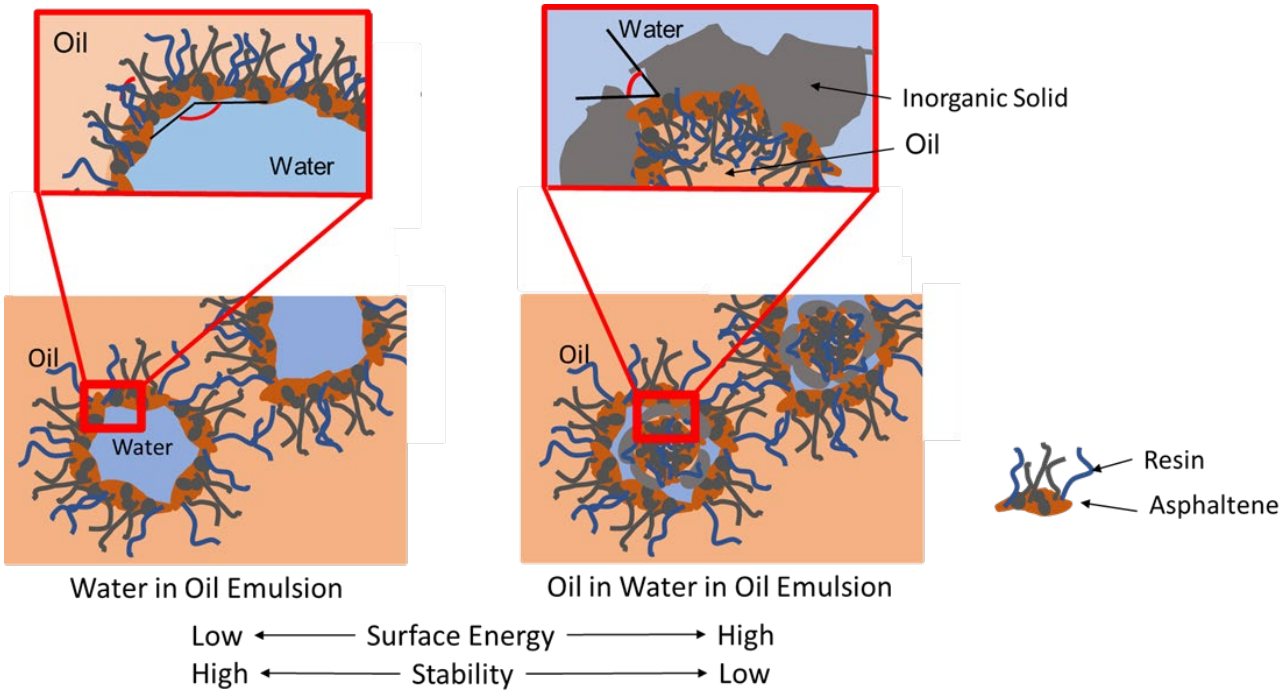

Fig. 9. A proposed mechanism for the formation of multiple emulsions

3.3 Model validation

To obtain the dimensionless height at time t, h and $\emptyset_w(t)$ were derived from the experimental results using Procedure 3, as presented in **Fig. 6**, and were then substituted into equation (9), as shown in **Fig. 10**. The experimental data were fitted to the model (Eq. (9)) by adjusting the bulk coagulation rate constants for water and oil (k and k'). The settling/creaming rate depends on the droplet size, phase densities, and viscosity of the continuous phase, while the coagulation rate is a function of droplet size and interfacial properties [57-60]. The emulsion containing kaolinite experiences the most substantial reduction in height. The coagulation rate constants play a pivotal role in emulsion stability since the mass flow rate of free water and oil within the emulsion layer is directly proportional to these constants. The estimated coagulation rate constants for the emulsion are depicted in **Fig. 11**, where each coagulation rate constant is normalised relative to the values at 20 ℃. It is observed that the coagulation rate constants for oil or water increase in the emulsion without solids at 50 ℃ and in the emulsion containing kaolinite at 20 ℃, respectively. The addition of inorganic particles does not significantly affect the coagulation rate of oil but does influence the coagulation rate of water. The change in stability is attributed to the presence of solid particles at the oil-water interface. It has been previously reported that the emulsion stability depends on the repulsive forces between droplets [61]. **Figure 12** reveals that kaolinite particles expedite the agglomeration of water droplets. Most kaolinite particles are found between water droplets, acting as a hydrophilic medium rather than a surfactant due to their size (10 μm~), while calcite reduces the coagulation rate and stabilises the emulsion. The measured size of calcite in the emulsion is approximately 100 nm, indicating that most calcite particles can become interfacially active through proper adsorption of resin and asphaltene [10].

As previously mentioned, the high surface potential of the crude oil results in internal repulsion at the oil and water interface. Introducing kaolinite to a crude oil emulsion not only promotes aggregation

between water droplets but also enhances the negative charge on the surface. This increase in surface charge leads to an elevated coagulation rate constant for water. Conversely, adding calcite particles reduces the coagulation rate constant for water by neutralising the surface charge through adsorption to the oil surface. Furthermore, the formation of a barrier at the oil-water interface by calcite, resulting from its adsorption to the oil surface, impedes coagulation.

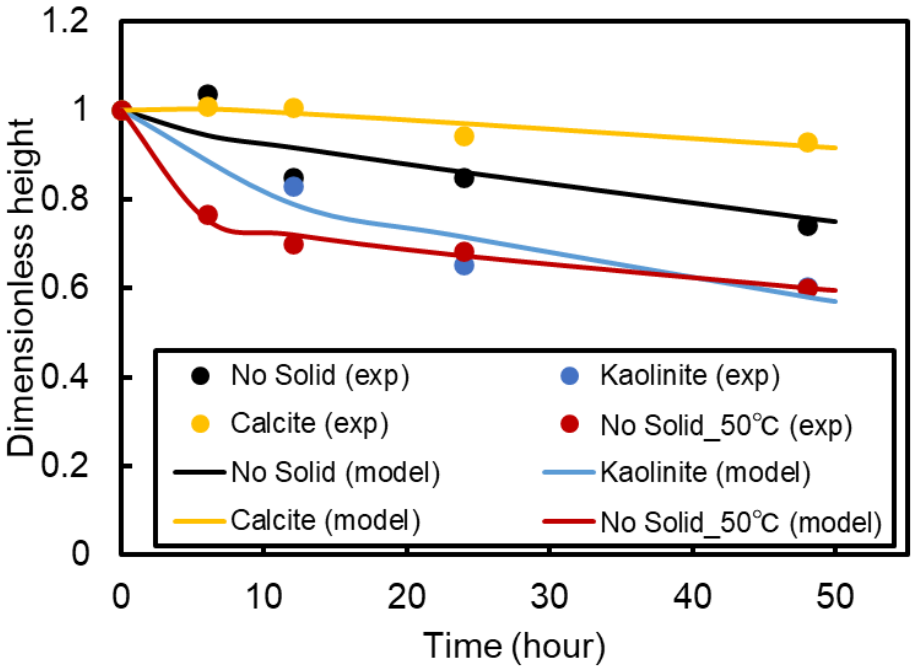

Fig. 10. Dimensionless height of emulsion layer as a function of time

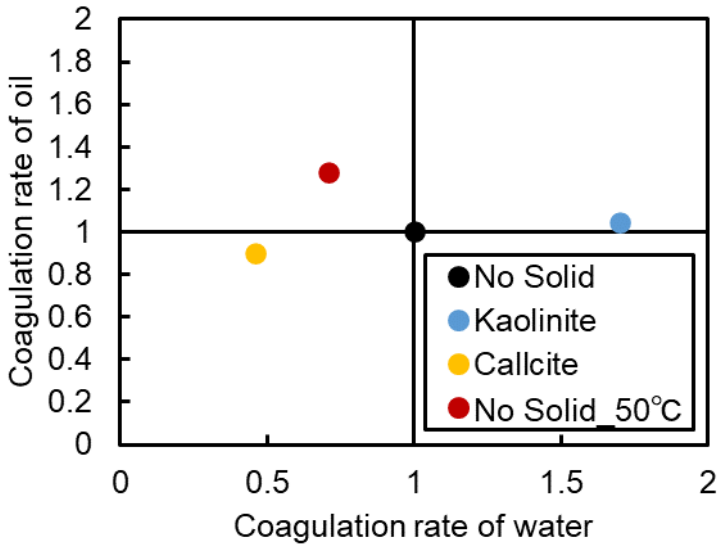

Fig. 11. Coagulation rate constant of oil and water normalised by the values at 20 ℃

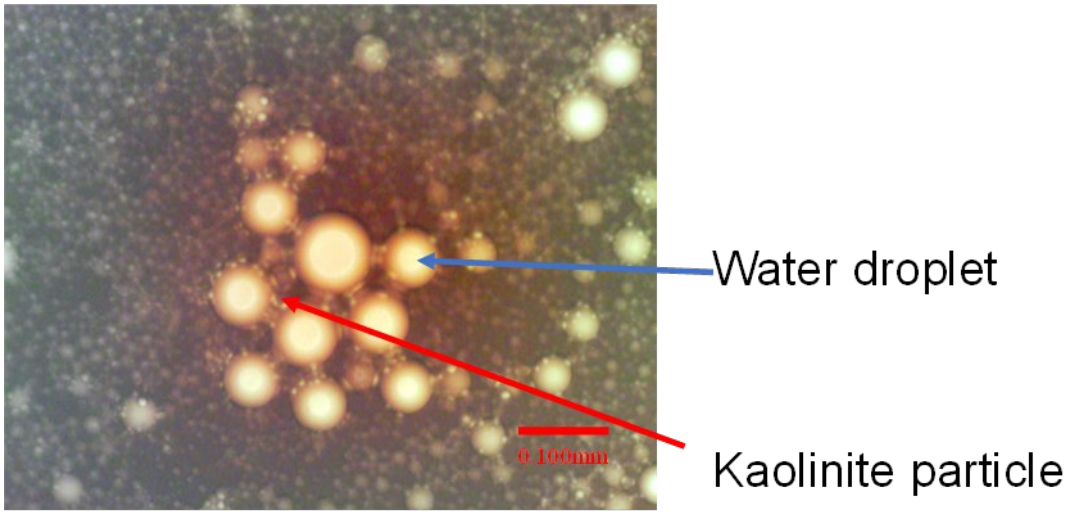

Fig. 12. Microscopy image of stable emulsion with kaolinite

4. Conclusions

This research investigated the impact of kaolinite and calcite solid particles on the stability of crude oil emulsions. Three different procedures were employed to create emulsions with added solid particles, and their stability was evaluated by measuring the released water and changes in the dimensionless height of the emulsion layer over time. The addition of solid particles during emulsion formation (Procedure 1) resulted in a more significant reduction in resistance to separation when subjected to external forces compared to the addition of solids to an already-formed emulsion (Procedure 2). Inorganic solid particles reduce the volume of stable emulsion by enhancing the surface potential of crude oil, making the emulsion more susceptible to demulsification by introducing internal repulsion. Within the stable emulsion, kaolinite promoted water droplet coagulation and destabilised the emulsion, whereas calcite created a barrier at the oil-water interface, impeding coagulation. The distinct behaviour of these two solid particles can be attributed to differences in particle size distribution resulting from dissolution and variations in surface charge. The layer growth model was utilised to quantify the emulsion's stability over time and forecast the volume of a stable emulsion. The coagulation rate constant was adjusted to match the experimental

data with the model, revealing higher values that indicated destabilisation over time for emulsions at elevated temperatures without added solids and with kaolinite.

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