

Coalescence behavior of stable pendent drop pairs held at different electric potentials

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Abstract

In this work we studied electrocoalescence behavior of stable pendent drop pairs and compared the results to the clean drops, where the interface is void of surface-active compounds. The drop phase is brine and the drop-oil interface is stabilized by aging into asphaltene and demulsifier solutions. The experiments involving asphaltene-laden drops required the bulk phase to be clear for visualization of the drops, which is realized by a procedure to replace the asphaltene-containing dark bulk phase by a pure solvent mixture. The narrowly spaced pendent drops, maintained at different electric potentials, acquire net surface charge of opposite polarity which leads to the Coulombic attraction in the drop-pair. After the application of voltage, a drop pair observed to be remained at a standstill, attracted or coalesced depending on the inter-drop separation, drop size, and potential difference. We systematically investigated the influence of different surface active compounds on interfacial stabilization and electrostatic drop-drop attraction and coalescence behavior. Interestingly, the experimental data shows that a drop pair coalesces at a lower potential (ΔV_{crit}) when the drop-oil interface is populated with the surface active molecules. Similarly, the minimum voltage (ΔV_m) needed to induce attraction between two stable drops and degree of the attraction is different than the clean drops. Furthermore, the demulsifier-laden drops exhibit dissimilar attraction, coalescence and non-coalescence characteristics to the drops stabilized in asphaltene solutions. Our analysis suggests that the asphaltenes and the commercial demulsifiers differently influence the drops' response to the applied electric potential. The contrasting coalescence nature of the stable drops can be attributed to a complex interplay between hydrodynamics, electrostatics, and interfacial reorganization of the molecules and charges.

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I. INTRODUCTION

In a crude oil emulsion the interface between dispersed aqueous phase and the organic bulk is always stable, thanks to a variety of indigenous compounds which crowd the water-oil interface. Asphaltenes are considered the most stabilizing among a vast array of surface active compounds including resins, naphthenates, clays, etc¹. Given the stability of the interface, water droplets do not coalesce easily upon their contact. When two water droplets collide their mechanically strong interfaces resist the film drainage and thin film breakage which could lead to coalescence. The interfacial stability helps in maintaining homogeneity of emulsions such as food and pharmaceutical emulsions; however, it is an obstacle in phase separation e.g. crude oil dewatering.

The electrocoalescence has been considered a very promising phase separation method in crude oil desalting and dewatering. The faster speed of separation, lower energy consumption and ability to handle a large spectrum of emulsions give it an edge over other methods such as gravity settling, centrifugation, membrane separation, chemical demulsification, etc². Applying an electric field to a stable emulsion facilitates segregation and merging of the droplets³. The method has also been used in a variety of other industrial applications involving emulsions with dielectric bulk phase. Cottrell's⁴ invention of electrostatic precipitator in the early 20th century and subsequent research resulted in a better understanding of the phenomenon. Its suitability in crude oil treatment and Taylor's seminal work on drop electrohydrodynamics^{5,6} encouraged fundamental research in the electrostatic phase separation.

The research in electrohydrodynamics kick-started after realization that a drop subjected to electric field can be investigated by dispersing it into a higher viscosity insulating liquid⁷. It also made easier to observe the coalescence of a dispersed pair of droplets under electric field^{8,9}. An experimental investigation of a clean drop pair, where the drop interface is void of surface active molecules, is easier as the time span between drop generation and field application can be very short. However, to study the electrocoalescence of stable droplets, they need to be held in a surfactant containing bulk phase for a long time, sometimes more than an hour. This poses difficulties in the systematic investigation of stability and coalescence of two droplets in a crude oil system under electric field. Because the asphaltenes are soluble in low viscosity organic solvents, it is near to impossible to stabilize and study

electrocoalescence of a freely suspended aqueous drop pair. Furthermore, the difficulty in visualization of the drops, surrounded by a dark crude oil, is a major constraint to study their coalescence mechanism.

The fundamental studied in the drop-drop electrocoalescence are predominantly done using clean drops and the observations are applied to the stable emulsions, where the drop interface is populated with surface active molecules. However, the molecules not only determine the interfacial properties, but also govern the electrostatic behavior drops in response to the applied electric field. The electrocoalescence literature lacks the understanding of how the electrostatics and a populated interface influence each other while two drops approach and merge.

The coalescence (and non-coalescence) of two charge bearing droplets has been extensively studied¹⁰⁻¹². The homo-polar drops in an emulsion make it stable; whereas, oppositely charged drops assist in phase separation. The Coulombic attraction between oppositely charged droplets in an emulsion leads to coalescence, increase in average drop size and faster sedimentation. However, recent studies have shown that although they draw together, the oppositely charged drops do not coalesce every time upon their contact. Ristenpart *et al.*¹² reported that two highly charged drops of opposite polarity may recoil after they touch. The subsequent theoretical studies attempted to elucidate the phenomenon^{13,14}. The experimental observations by Bird *et al.*¹³ and Wang *et al.*¹⁵ suggested that the non-coalescence is governed by Taylor angle made by drops upon contact, which is in turn dependent on conductivity of the drop phase.

When an emulsion is subjected to externally applied electric field, its uncharged droplets polarize in the direction of the field. An individual polarized droplet acts as a dipole and experiences dipolar attractive pull from the neighboring droplets. The droplets are always on the move in an emulsion under the action of electrostatic, colloidal, gravity or externally applied forces. Taylor¹¹ argued that to investigate the stability of narrowly spaced drops they need to be in equilibrium state. The freely suspended moving drops do not exhibit such an equilibrium, in contrast they accelerate when approach each other¹⁶. The stability of oil-drop interfaces plays a critical part in the film thinning and breakup; but, it prevails only when the coalescing drops are in the immediate vicinity.

In the present study we report experimental observations on the coalescence of two stable pendent drops raised to different constant DC electric potentials. The drops are stabilized

by aging into three surface active compounds- whole asphaltenes and two commercial demulsifiers used in crude oil desalting and dewatering- and their coalescence behavior is analyzed against the clean drops. The experiments involving asphaltenes need the dark bulk phase to be replaced (after the drops are aged for a specific time) with pure solvents in order to visualize the coalescing drops. A method is developed to replace the dark concentrated asphaltene solution. Here we elaborately discussed the role played by the surface active compounds in the coalescence of the narrowly spaced pendent drops maintained at an electric potential difference ΔV_0 . The drops are oppositely charged in the absence of externally imposed background electric field. The objective of this work is to demonstrate how the populated interfaces influence the film thinning and film rupture stages of electrocoalescence. Although, the dynamics of drop-drop electrocoalescence is not recorded, the critical conditions of coalescence of differently stabilized drops highlight the difference in coalescence mechanism between clean and populated interfaces.

Taylor's theoretical analysis showed that the maximum potential difference, two narrowly spaced drops can bear before their coalescence (ΔV_{crit}), is decided by the size (a) and minimum distance (s_0) between them¹¹. The expression for the critical potential difference was found to be in agreement with the experimental observations only when the ratio s_0/a is less than 0.24. As the critical potential of coalescence is governed by the separation and radius simultaneously, we present the drops' response and critical voltage of coalescence as a function of s_0/a ratio. Although, the drops studied in this work attract towards each other, being held at the tips of capillaries they are not freely moving. The minimum voltages of drop-drop attraction (ΔV_m) and coalescence are measured for the stable as well as clean drop pairs.

II. EXPERIMENTAL

The schematics of the experimental setup used to age drops and study electrocoalescence is shown in Figure 1. The pendent drops are generated at the tips of stainless steel capillaries (OD = 890 μm , ID = 500 μm) using dosing pumps. The PTFE tubings and fittings, connecting the capillaries to the pumps, are fitted with miniature two-way valves. The whole assembly is mounted on a high precision XYZ-manipulator to position the drops next to each other and set them in the camera focus. A CCD camera is used to capture the

drops at 24 frame per second and the images are analyzed by using an image analysis tool, ImageJ.

To apply the electric potential difference, one capillary is connected to a DC power source - a function generator (Agilent Technologies DSO-X 2022A) and an amplifier (Trek 609E-6) assembly - while the other is grounded. When the voltage is applied, one drop is raised to V_0 (V) keeping the other at 0 (V), therefore the voltage drop between the two drops is $\Delta V_0 = V_0$ (V).

A. Chemicals

In clean drops experiments the pendent drops (3.5 wt% brine) are surrounded by a solvent mixture containing 60 V/V % xylene (VWR) and 40 V/V % octane (Sigma Aldrich). In the experiments involving asphaltene-stabilized drops, the asphaltenes are dissolved in the solvent mixture. The drops are found to be unstable when aged in high concentration asphaltene solutions in pure xylene. The use of a xylene-octane mixture at the above-mentioned proportion helped to achieve stable drops which do not merge when brought in contact¹⁷. The asphaltenes are extracted from a heavy crude oil from Norwegian continental shelf and used without further fractionation. The method used to obtain the asphaltenes is described in detail by Subramanian *et al.*¹⁸. The two chemical demulsifiers are supplied each by Nalco Champion (henceforth called Demulsifier A) and Nouryon (Demulsifier B). The experiments with low concentration demulsifiers are done to see their effects in comparison with the asphaltenes. The relative solubility numbers (RSN) of the demulsifiers are provided by their suppliers.

B. Asphaltene-stabilization procedure

Achieving stable drops by raising molecular density at their interfaces is a crucial part of this study. Two clean drops instantaneously merge when brought into contact. The bulk concentration of asphaltenes (C_{a0}) and the time (t) for which the drops held in the solution (before the voltage is applied) determine stability of the interface. The C_{a0} and t in our experiments are high enough to obtain stable drops. The stability of the asphaltene-laden drops is tested by bringing them in contact and pressing against each other. The stabilized

drops do not merge by holding them in contact for long or unless pressed strongly. Achieving such stable drops needs a highly concentrated asphaltene solution and a long aging. To get differently stable drops we used 1 g/l and 5 g/l asphaltene solutions and aged the drops for 30 minute and 60 minute.

The asphaltene-containing bulk phase is a dark solution which makes visualization of the drops challenging. Moreover, the stabilization of the drop-oil interface needs a high concentration of the asphaltenes in the organic bulk phase. Therefore we developed a method to age the drops in asphaltene solution and replace the dark bulk phase with pure solvent mixture such that the asphaltene-stabilized drops can be clearly seen by the camera. We assume that the asphaltenes are irreversibly adsorbed to the water-oil interface and do not desorb during the bulk phase replacement¹⁹. The turbulence near the interface was avoided by keeping the tube openings away from the drops and using small flow rates of the pure solvent injection and asphaltene bulk drawing.

The method used to age the drops and subsequently replace the dark asphaltene-rich bulk phase is demonstrated in Figures 2(a) & 2(b). To begin with, the cell is partly filled with the pure solvent mixture. Two pendent brine drops of a desired size (radii a) are generated at the tip of the capillaries using a dosing system shown in Figure 1. The capillaries are fitted with valves which are closed, after the drops of desired size are generated, to eliminate possibilities of subsequent change in the drop volumes. A highly concentrated asphaltene solution is then pipetted to raise the concentration in the cell to C_{a0} and makeup the total volume of solution to 20 ml. The fluid system is left undisturbed to age the drop interface for time t .

At the end of aging, the dark asphaltene solution is pumped out and pure solvent mixture is pumped in simultaneously to the cell at constant flow rates (r). The procedure is similar to the one previously described by Svitova *et al.*²⁰. The pumping rates, amount of replacement solvents, resultant interfacial tensions(after bulk phase replacement) for the concentrations and aging times used are given in table I. A multichannel dispensing pump (Ismatec, Germany) is used to displace the asphaltene solution with the pure solvent mixture. The amount of the pure solvent mixture (M) for every asphaltene bulk concentration is decided, by trial and error, based on visibility in the resultant solution. The flow rates are kept small so as to avoid excessive flow field near the oil-water interface. The water-oil interfacial tension (γ) after the bulk phase replacement is measured using profile analysis tensiometer (PAT1,

TABLE I. Parameters in drop stabilization process and bulk replacement.

| Bulk phase | Aging time, t (min) | Replacement solvent, M (ml) | Pumping rate, r (ml/min) | Interfacial tension, γ (mN/m) |
|---|------------------------|--------------------------------|-----------------------------|---|
| Pure solvent mixture | | | | 38.07 |
| Asphaltene solution, $C_{a0} = 1 \text{ g/l}$ | 30 | 20 | 1 | 26.20 |
| $C_{a0} = 1 \text{ g/l}$ | 60 | 20 | 1 | 24.00 |
| $C_{a0} = 5 \text{ g/l}$ | 60 | 60 | 2 | 24.00 |
| Demulsifier A (RSN = 6.9) solution, $C_{DA} = 5 \text{ ppm}$ | 60 | - | - | 17.20 |
| Demulsifier B (RSN = 6.1) solution, $C_{DB} = 2 \text{ ppm}$ | 60 | - | - | 10.38 |
| $C_{DB} = 5 \text{ ppm}$ | 60 | - | - | 7.04 |

Sinterface, Germany). The interfacial tension is monitored over an hour (demonstrated in Figure 2(c)) and found to be remained constant, which supports the assumption that the asphaltenes are irreversibly adsorbed to the drop interface.

After the bulk phase replacement is over, the drops are moved closer by using a XYZ-manipulator. At their new position the drops are in a plane perpendicular to the camera and the smallest distance between their inner faces is s_0 .

In the experiments involving chemical demulsifiers, the bulk concentrations are low (2 ppm and 5 ppm) and the drops are aged for an hour. The demulsifiers are dissolved in solvents to the concentrations C_{DA} (Demulsifier A) and C_{DB} (Demulsifier B). Since the bulk phase is colorless, the drops are clearly visible and the procedure described above is not required. Therefore, the cell is filled with 20 ml demulsifier solution and the drops of desired size are generated and left to age for time t . After the aging is completed, they are brought closer to the separation s_0 and raised to electric potential difference, ΔV_0 .

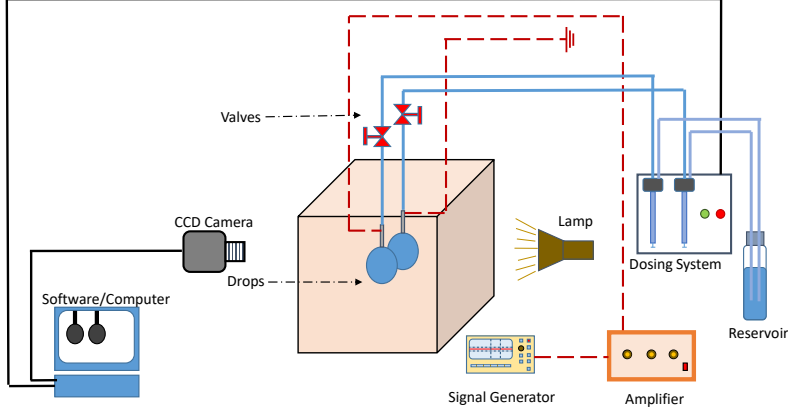


FIG. 1. Schematics of the experimental setup.

III. RESULTS AND DISCUSSION

In the present work, the pendent drops are approximately uniform in size and closely held such that the ratio of initial separation to drop radius (s_0/a) is less than 1.0. The brine drops acquire net charge when held at a potential difference, polarity of which is determined by the supply potential. One capillary is electrified with positive potential $+V_0$ and the other is kept at 0 V. Therefore, the charge acquired by the drop on the first is positive ($+Q_1$) while the induced charge on the latter is equal in magnitude but of negative polarity, $Q_2 = -Q_1$. The equal but opposite polarity charges trigger the attraction between the drops. The magnitude of the charge is a function of applied voltage, drop size, and electrical properties of the drop and its surrounding medium²¹⁻²³.

The reaction of the drops to the applied potential is evident from their shape and position. The plot in Figure 3(a) demonstrates a typical response of uniform size pendent drops, of radii a initially held at s_0 , to the applied potential difference ΔV_0 . The drop snapshots corresponding to the points denoted by letters are shown in Figure 3(b). When ΔV_0 is not large enough, the drops do not exhibit attraction; as shown by snapshot A in Figure 3(b) corresponding to point A in Figure 3(a). Further increase in the electric potential induces

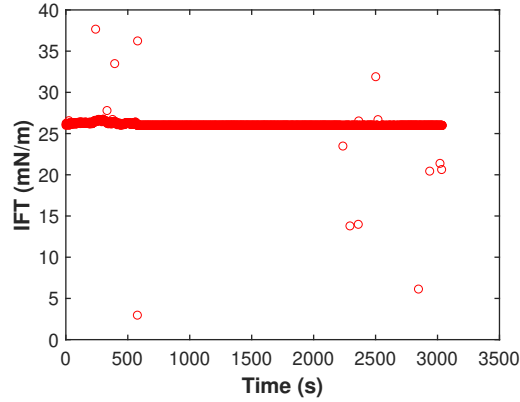
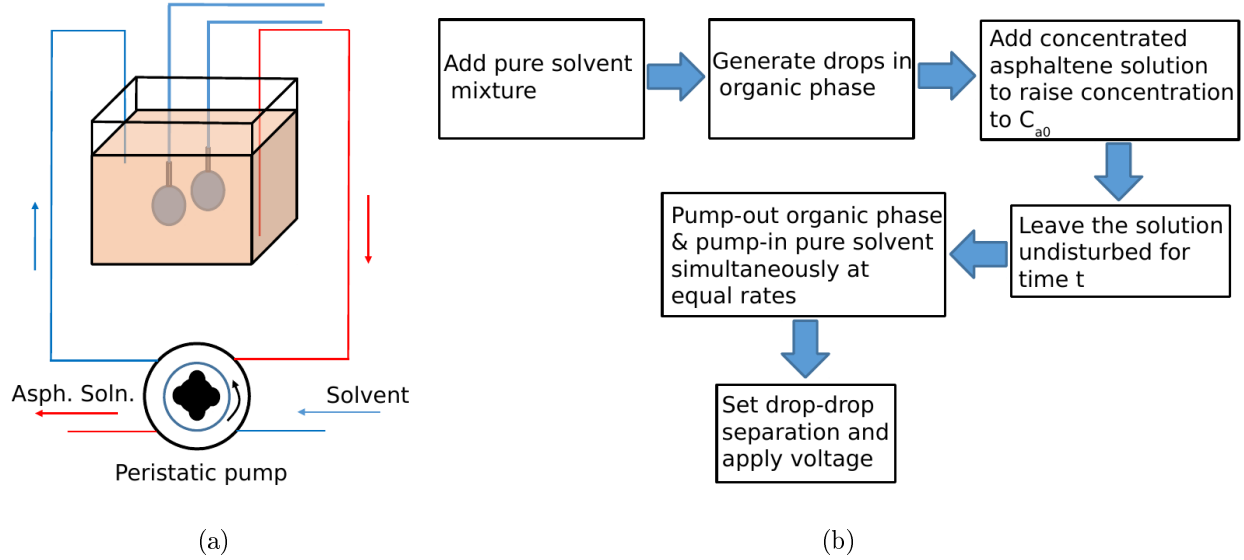


FIG. 2. (a) Schematics of the system used for pendant drop aging in an asphaltene solution and the bulk phase replacement. (b) Procedure to age brine drops in highly concentrated asphaltene solution and replace the bulk phase with pure solvent mixture. (c) Interfacial tension after the bulk phase replacement, where the drop is aged in $C_{a0} = 1$ g/l solution for $t = 30$ minute.

drop-drop attraction at $\Delta V_0 > \Delta V_m$. The drops instantaneously tilt inward reducing the distance between inner faces to $s < s_0$. The sketch in Figure 3(b) F depicts initial position of the drops and the new position after ΔV_0 is applied. The ordinate of the plot in Figure 3(a)- ratio $\frac{s_0-s}{s_0}$ - denotes reduced distance between the drops relative to the initial separation in response to the applied voltage, thus indicates the extent of attraction. The plot suggests the drop-drop pull linearly increases with ΔV_0 for a drop pair. The snapshots B, C and D

of Figure 3(b) show tilted drops denoted by the red bullet points in Figure 3(a) by the same letters.

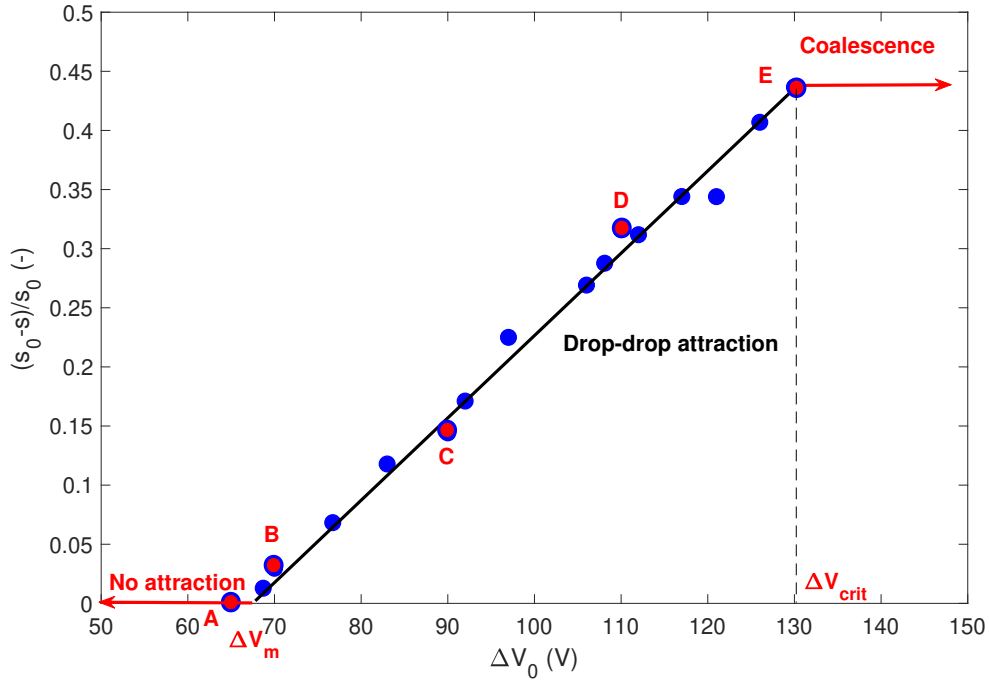
Briefly, a pair of drops, when held at a certain distance apart, does not attract when ΔV_0 is lower than the minimum voltage of attraction ΔV_m . When $\Delta V_0 > \Delta V_m$, inter-drop separation decreases linearly with increase in the applied voltage up to a critical voltage ΔV_{crit} . The inward tilting is instant and the drops do not move further unless ΔV_0 is changed. Above the critical voltage of coalescence the drops instantaneously merge upon application of the field.

Taylor¹¹ associated the coalescence of two closely spaced charged interfaces to the interfacial instability. The high speed imaging of neighboring drops maintained at opposite potentials by Wang *et al.*¹⁵ also suggested that the Coulombic instability might be responsible for the coalescence. In our experiments the maximum value of $\frac{s_0-s}{s_0}$ before a drop pair coalesces is found to be < 0.5 for clean drops. The value is lower for the stabilized drops: $\frac{s_0-s}{s_0} < 0.25$ for the asphaltene-laden drops, < 0.3 for the demulsifier A -laden drops at 5 ppm and < 0.35 for demulsifier B -laden drops at 2 ppm. However, for the drops in 5 ppm demulsifier B solution, $\frac{s_0-s}{s_0}$ can be as high as 0.55. The maximum $\frac{s_0-s}{s_0}$ at $\Delta V_0 < \Delta V_{crit}$ can be attributed to IFT of drop-oil interface. When the IFT is low the drops stretch and tilt more after ΔV_0 is applied. The critical conditions of drop-drop attraction and coalescence for the unstable and stable drop pairs are discussed in the following subsections.

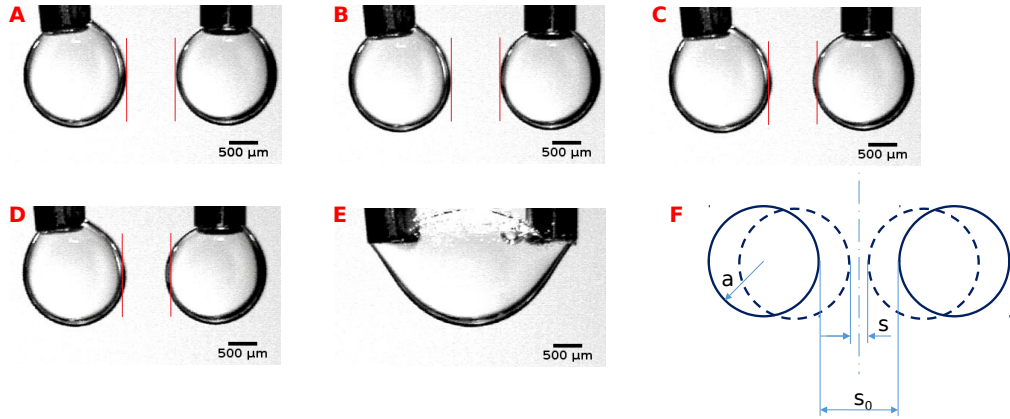
A. Critical potential difference

The minimum potential required for coalescence of a drop pair is dependent on drop size and initial separation between inner faces of the drops¹¹. The critical potential (ΔV_{crit}) is measured for drop pairs with different separation to size ratios (s_0/a). The data for clean drops plotted in Figure 4 indicates ΔV_{crit} is a strong function of s_0/a . When the drops are bigger or the inter-drop separation is smaller, they coalesce at a lower voltage.

The effect of drop size on the critical potential stems from the amount of interfacial charge acquired and consequently the Coulombic attraction. The charge acquired by a drop emitting from an electrified needle or upon contact with an electrode is a function of its size²²⁻²⁵. A larger drop gains more charge and experiences stronger pull towards the nearby charged interface. A drop can undergo instability when the charge exceeds Rayleigh



(a)



(b)

FIG. 3. Drop response to the applied electric potential. (a) No attraction, attraction and coalescence of a clean drop pair, $s_0/a = 0.274$. (b) A, B, C, D & E: drop positions corresponding to points on the curve in 3(a). Two vertical red lines between drops indicate initial inter-drop separation. F: sketch of positions of the attracting drops.

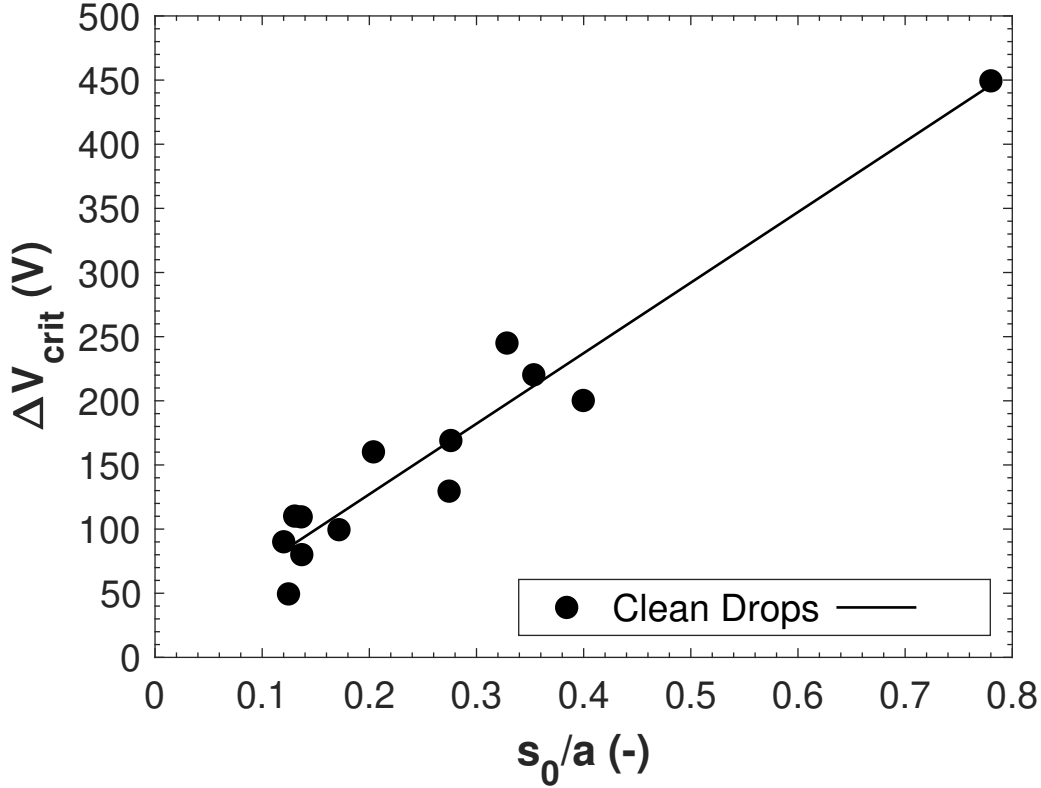


FIG. 4. The critical voltage of coalescence for clean brine drops surrounded by pure xylene-octane mixture. The continuous line is a fitting curve.

critical charge limit^{25,26}, $Q_{crit} = 8\pi\sqrt{\gamma\epsilon_0 a^3}$ (where γ and ϵ_0 are surface/interfacial tension and permittivity of vacuum, respectively). However, given the very small s_0 and low ΔV_0 , the presence of another charged drop induces attraction followed by coalescence, before the instability sets in.

The work by Ristenpart *et al.*¹² and subsequent studies¹⁵ reported the destabilization of highly charged droplets at the onset of their contact. The drop interactions either result into coalescence accompanied by generation of tiny droplets or recoil. Such progeny droplets or receding of about-to-coalesce drops is not observed in our experiments.

The critical voltage of asphaltene-stabilized drop-drop coalescence follows similar dependence (to the clean drop coalescence) on the size and separation. To demonstrate the effect of asphaltene stabilization, ΔV_{crit} data for the drops aged in two concentrations (1 g/l and 5 g/l) and for 30 and 60 minute duration is plotted in Figure 5. As evident from the plots, the

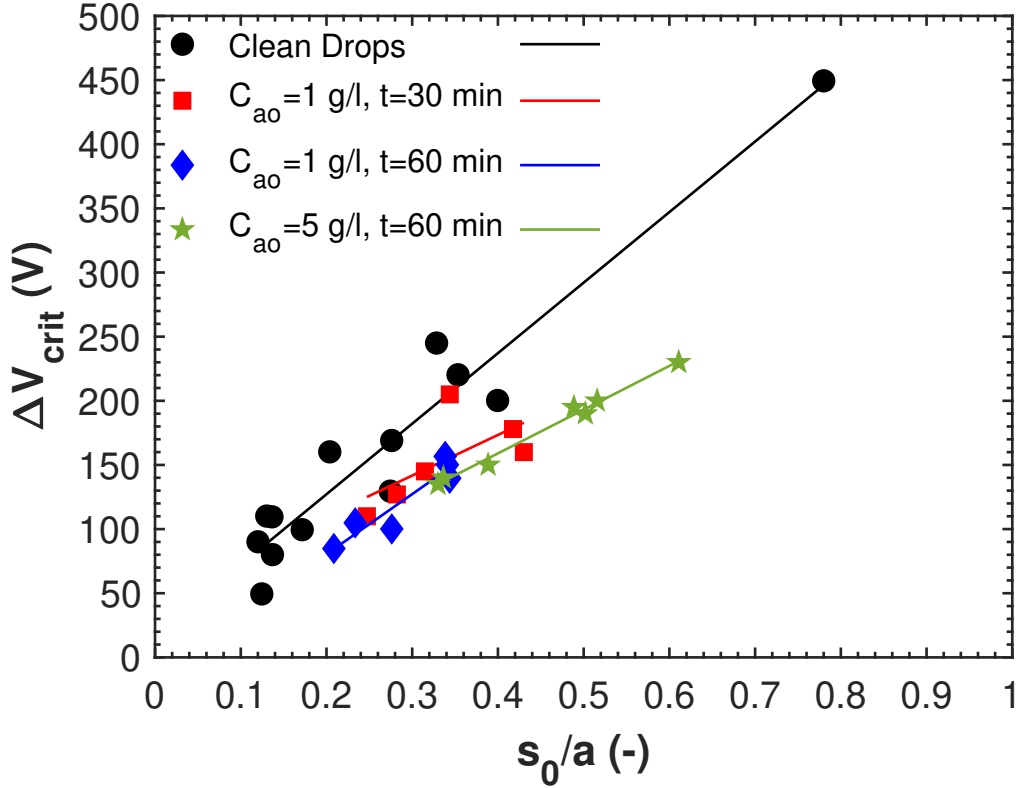


FIG. 5. The critical voltage of coalescence for clean and asphaltene-stabilized drops. The symbols are experimental data and the continuous lines are fitted curves. C_{a0} and t are the asphaltene concentration in the bulk phase and aging time, respectively.

asphaltene-laden drops have significantly lower critical voltage of coalescence in comparison with the ΔV_{crit} of the clean drops. The effect can also be seen on the differently aged drops in spite of a little intertwined data. The drops stabilized in 5 g/l asphaltene solution for 60 minute merge at lower potentials than those aged in 1 g/l solution for 30 and 60 minute. As noted in Table I, the interfacial tension in these three cases is comparable, but the slopes of the linear fits (Figure 5) indicate the applied voltage impacts the drops distinctly.

The presence of the demulsifier molecules at drop interface further reduces the critical voltage of coalescence. As shown in Figure 6 the difference is noticeable, where the ΔV_{crit} for demulsifiers A & B, and asphaltene ($C_{a0} = 5$ g/l, $t = 60$ minute)- stabilized drops is plotted along with the clean drops. The difference in their interfacial tension is significant, which is coherent with the ΔV_{crit} data. The presence of asphaltene molecules at and around

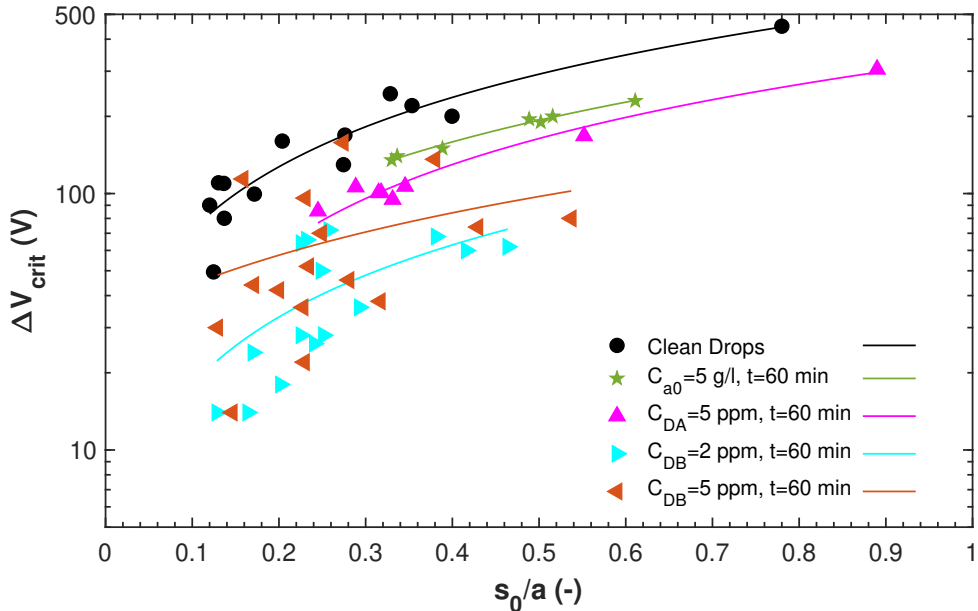


FIG. 6. The critical voltage of drop-drop coalescence of demulsifier stabilized drop pairs. The symbols are experimental data and the continuous lines are fitted curves. C_{a0} , C_{DA} , C_{DB} , and t are the asphaltenes, demulsifier A and demulsifier B concentrations in the bulk phase, and aging time, respectively.

the water-oil interface facilitates electrocoalescence of the charged drops. The demulsifier molecules further ease off the coalescence. Among the demulsifier stabilized drops, demulsifier B appears to be more effective in triggering drop-drop attraction and their coalescence. Upon increasing the demulsifier concentration, a drop pair coalesces at even lower electric potential.

As mentioned earlier the aged drops were tested for their stability by pressing them against each other while the voltage is off. They do not coalesce unless pressed hard and for long, unlike the clean drops which merge instantaneously upon mere contact. In the absence of electrostatic forces, if γ is low the colliding stable drops form a larger thin film which exerts stronger resistance to the coalescence²⁷. On the contrary, the reduced interfacial tension transforms the drop-drop interaction when subjected to the electrostatic forces. The effect is a result of altered charge dynamics at the drop interface. The complex interplay between charge density, interfacial tension and local curvature governs the coalescence dynamics of moderately charged neighboring drops. When the distance between their inner faces is small,

the interstitial electric field is way stronger compared to the field anywhere in the bulk phase. Also, the both charged interfaces induce mirror charges on each other. The strong electric field not only brings about dielectrophoretic attraction but also causes shape deformation due to the strong local electric stresses. The lower interfacial tension results in to larger deformation and higher curvature to the inner faces of the drop pair. The convection of charges to the high curvature part from rest of the drop interface ramps up the local charge density. As a result, the inner faces experience strong Coulombic attraction compared to rest of the drop, protrude inward to touch and coalesce easily.

Further investigations into convection of surface active molecules at a charged interface, when in vicinity of another charged interface, are needed to shed light on its contribution to the coalescence mechanics and dynamics. The asphaltenes are believed to be polar and carry charge, although its polarity has been disputed^{28,29}. However, the response of the asphaltene molecules and its nanoaggregates to the electric field is unclear. In addition to the interfacial rearrangement, orientation of asphaltenes under electric forces contribute to the drop-drop interaction. The asphaltenes believe to form a complex multilayer structure at water-oil interface. The fundamental studies elaborating such structures, when oppositely charged interfaces approach each other, and their part in draining and rupturing of the thin films are crucial.

Taylor derived a comprehensive expression for critical potential difference of coalescence for a drop pair¹¹,

$$\Delta V_{crit} = 0.38 \frac{s_0}{2a} \sqrt{\frac{2\gamma a}{\epsilon_0}}. \quad (1)$$

Equation (1) together with our experimental results are plotted in Figures 7 and 8 for asphaltenes and demulsifiers, respectively. Evidently, the data for clean and stabilized drop pairs crudely follow Equation (1). However, given the scatteredness of the data, the extent of deviation of each subset from the Taylor's expression is difficult to determine. The scattered data for Demulsifier B at both concentrations studied (2 ppm and 5 ppm) can be attributed to the very low interfacial tension. Although the drops studied at these conditions are small, they excessively sag under their weight. Moreover, the drops are prone to minute external vibrations.

Experiments in this study are done for a broader range of s_0/a between 0.1 and 0.9. Taylor found that Equation (1) is in fairly good agreement with experimental results for

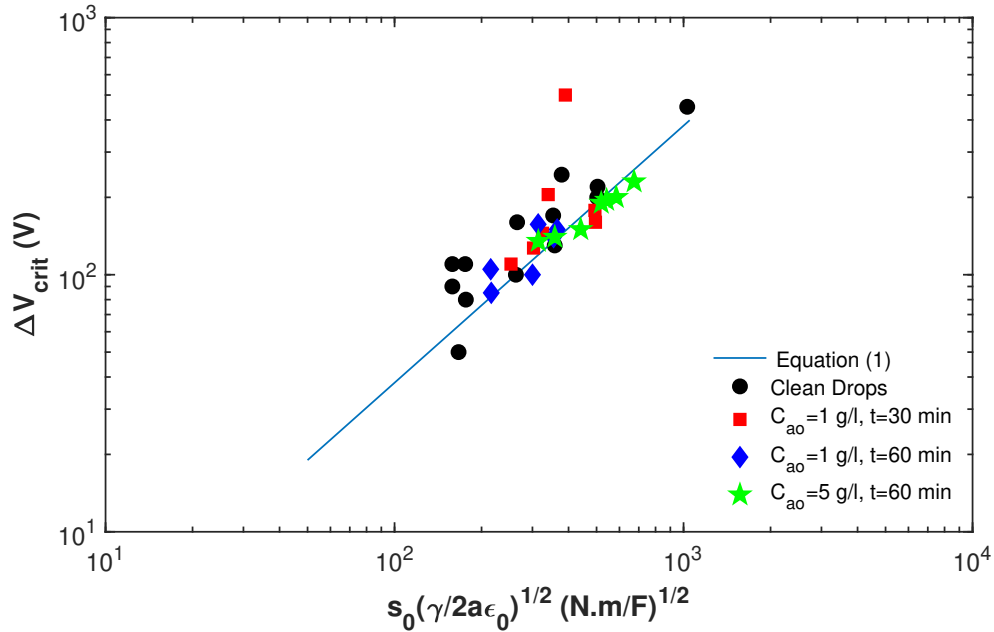


FIG. 7. Asphaltene stabilized drops: comparison with Taylor’s expression for maximum potential difference between closely held drops. The continuous line is Equation (1) and the symbols are experimental data. C_{ao} and t are the asphaltene concentration in the bulk phase and aging time, respectively.

clean drops when the ratio s_0/a is less than 0.24. The experimental results by Latham *et al.*³⁰, which Taylor compared Equation (1) with, were done on uncharged drops supported at the ends of teflon rods placed in an external uniform field. The drops were unstable with no surface active compounds at their interface. It was assumed that the displacement of the drops upon application of electric field which was applied parallel to the line of centers, was due to the different potentials at the drops. Whereas, the drops in our experiments are pendant, stable and charged, with no external electric field.

B. Drop-drop attraction

The extent to which a pendent drop pair tilts inward after electric potential is turned on is dependent on the magnitude of ΔV_0 . The scale of drop attraction can be demonstrated by the slope of $\frac{s_0-s}{s_0}$ versus ΔV_0 plot in Figure 3(a). The slope, denoted by factor $f = \frac{d[(s_0-s)/s_0]}{d(\Delta V_0)}$ is another indicator of how interfacial and electrical properties play a role in drops’ response

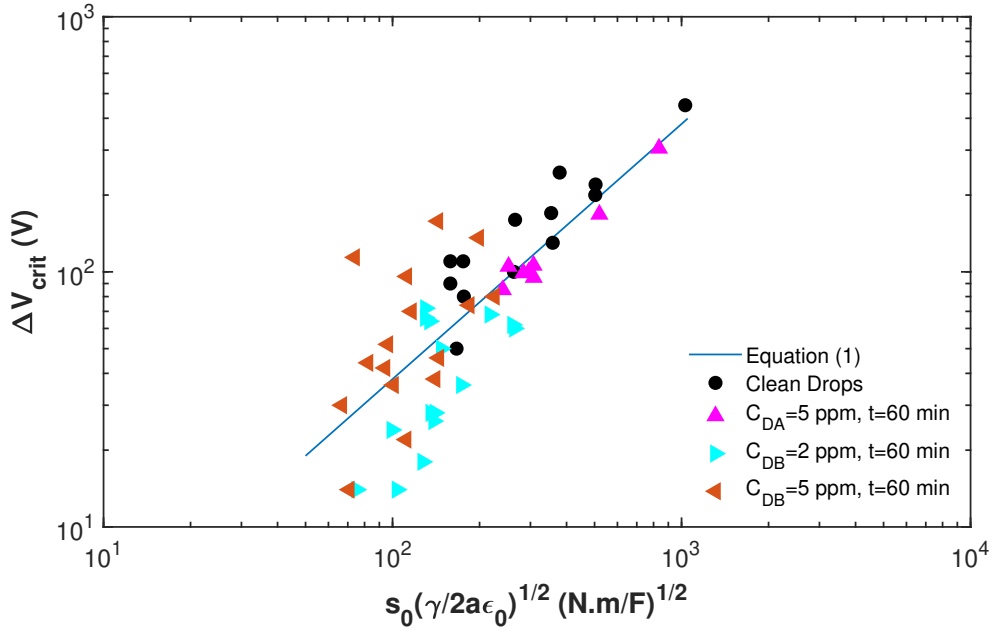


FIG. 8. Demulsifier stabilized drops: comparison with Taylor’s expression for maximum potential difference between closely held drops. The continuous line is Equation (1) and the symbols are experimental data. C_{DA} , C_{DB} , and t are the demulsifier A and demulsifier B concentrations in the bulk phase, and aging time, respectively.

during coalescence. The attraction is instantaneous and the restrained displaced drops do not show further stretching because ΔV_0 is constant and interfacial properties do not change dramatically after the electric potential is switched on³¹. The displacement is governed by balance between electrostatically induced pressure and capillary pressure. The electrical capillary number ($Ca_E = \frac{\epsilon_m a E^2}{\gamma}$) is expressed as ratio of these two pressures, where ϵ_m is electrical permittivity of bulk phase. As the drop fluid is highly conducting and the interfaces are very close, the electric field can be estimated as the ratio of the applied potential difference and minimum separation. Therefore, expressing the electric field in terms of f gives, $E = \frac{1}{fs_0}$, and thus Ca_E can be written as,

$$\frac{1}{f^2} = \frac{Ca_E}{\epsilon_m} \left[\frac{\gamma s_0^2}{a} \right], \quad (2)$$

The plots in Figure 9, $1/f^2$ versus factor $\gamma s_0^2/a$, illustrate the extent of response of the stable and unstable drop pairs to the applied voltage, when $\Delta V_m < \Delta V_0 < \Delta V_{crit}$. The scaling of f in terms of Ca_E collapses the data. Figure 9 suggests that the general trend

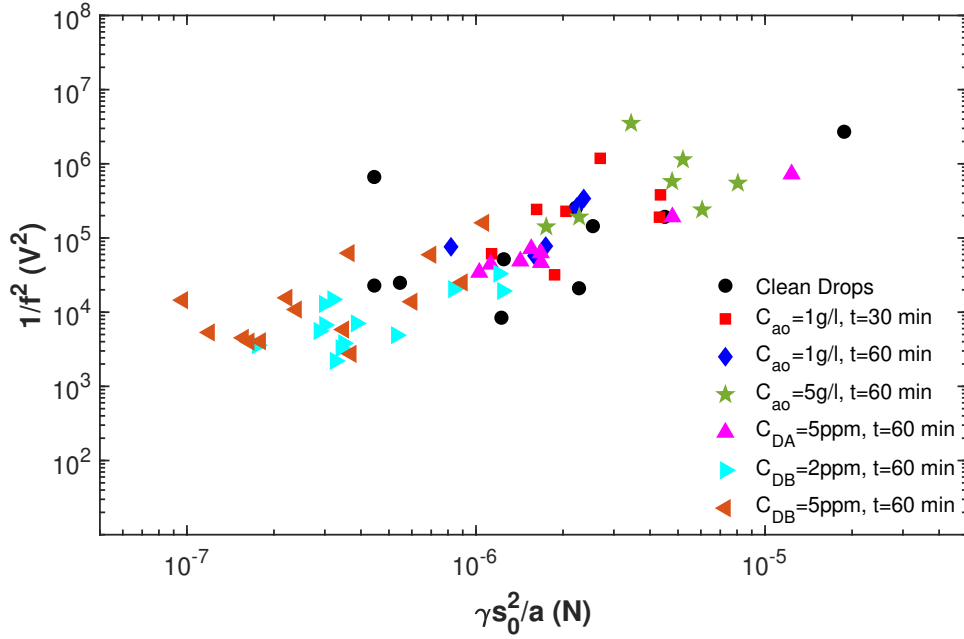


FIG. 9. Scaled degree of attraction between unstable and stable drop pairs (Equation 2). C_{a0} , C_{DA} , C_{DB} , and t are the asphaltenes, demulsifier A and demulsifier B concentrations in the bulk phase, and aging time, respectively.

is linear irrespective of drop stability. However, the slope of the plot (Ca_E/ϵ_m) is observed to be different for the differently stable drop pairs. It is highest in the absence of surface active compounds and lowest when the drop interface is populated with Demulsifier B. That implies a stronger reaction of stable drops when raise to a potential difference than the clean drop pairs. Moreover, the demulsifier-stabilized drop pairs attract more easily than the asphaltene-stabilized drops.

C. Minimum potential difference

The $\frac{s_0-s}{s_0}$ versus ΔV_0 plot in Figure 3(a) intersects the x-axis at ΔV_m , the minimum voltage needed to trigger inward drift of the drops. The opposite charges induced due to the potential difference bring about Coulombic attraction by overcoming gravity and drag. Although the movement of pendent drops in our experiments is restricted, when the electric potential difference raised above ΔV_m , the freely suspended drops start attracting followed by collision and coalescence. The beginning of tilting in pendent drops marks the

manifestation of coalescence. At $\Delta V_0 < \Delta V_m$, the drops do not experience any attraction and stay stationary.

The net charge a liquid drop acquires upon contact with an electrode is directly proportional to a^2 and strength of the electric field^{23,24,32}. We estimated the amount of charge a drop in the pair holds when it starts tilting towards the other drop as, $Q_1 = \kappa a^2 (\Delta V_m / s_0)$, here κ is a constant. As the drop phase is highly conducting, the electric field is expressed as the ratio of minimum potential of coalescence and initial interdrop separation. Therefore the minimum Coulombic force that induces attraction in a drop pair can be written as,

$$F_C = \frac{-\kappa^2 a^4 (\Delta V_m / s_0)^2}{s_0^2} \quad (3)$$

The factor $\frac{a^4 (\Delta V_m / s_0)^2}{s_0^2}$ for stable and unstable drop pairs is plotted in Figure 10. Apparently the clean drops need significantly stronger force to induce drop-drop attraction. The plots suggest that the stable drops with populated interfaces acquire more charge and a drop pair tends to pull inward at fairly lower electric potential. The trend is coherent with the previously discussed critical potential of coalescence and degree of inter-drop attraction. However, the data for Demulsifier B is still mixed and suggests that the drops aged in $C_{DB} = 2$ ppm solution gain more charge in comparison with $C_{DB} = 5$ ppm.

The data presented here suggest that the minimum voltage to induced coalescence, drop-drop attraction, and the critical voltage of coalescence are distinctively different for differently stable drops. In general the asphaltene-laden drops attract and coalesce at lower potentials than the clean drops, while the drops aged in demulsifier solutions show better response to the applied voltage than the asphaltene-stabilized drops. The trends can be attributed to following aspects: (i) The changed mechanical properties of the water-oil interface due to the presence of surface active molecules. (ii) The polarity of the molecules add to the interfacial charge acquired due to the electric potential. (iii) The interfacial convection of the charges and the molecules. They both have tendency to migrate towards a high curvature region. Being in close proximity, the inner faces of the drops have stronger electric stress density which protrude them inward as can be seen in Figure 3. The charges and molecules convect to the inner faces, which in turn, further increases the curvature. (iv) The multiple mirror charges induced by the drops on each other's interfaces. (v) The strong electric field in the space between drops due to the high potential gradient and high interfacial charge density. The non-uniformity of the electric field - strong field between

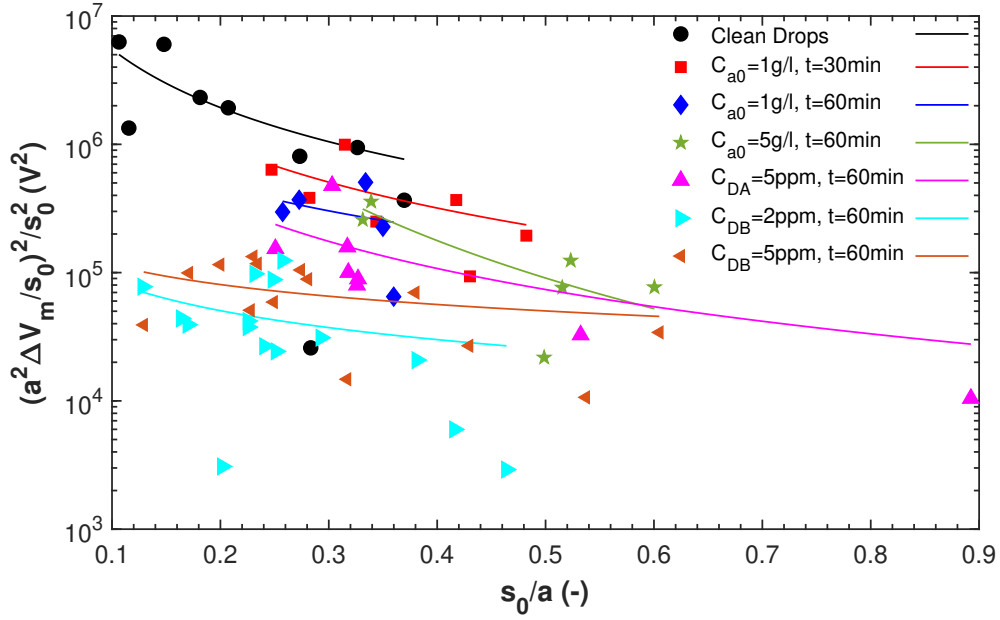


FIG. 10. The Coulombic attraction at the onset of tilting. C_{a0} , C_{DA} , C_{DB} , and t are the asphaltenes, demulsifier A and demulsifier B concentrations in the bulk phase, and aging time, respectively. The symbols are experimental data and the continuous lines are fitted curves.

inner faces than the remaining bulk- brings about dielectrophoretic attraction. The above mentioned factors are interdependent.

CONCLUSIONS

The clean and stable drop pairs held at narrow separations and raised to electric potential difference are investigated for their coalescence mechanism. In the absence of electrostatic forces the clean drops merge instantaneously upon their contact while the stabilized drops do not coalesce unless pressed together. A procedure is developed for aging of a pendent drop pair in asphaltene solution and visualizing its electrocoalescence. The drops covered with asphaltene and demulsifier molecules are turned out to be attracted and coalesce at lower voltages than the clean drops when raised to a potential difference. The drops can be irresponsive, attracted or coalesced depending on the voltage, drop size and separation. The minimum voltage to induce drop-drop attraction, degree of attraction and critical voltage of coalescence are distinct for clean drops, asphaltene, and demulsifier-stabilized drops. ΔV_{crit}

and ΔV_m are observed to be lowest when the drop-oil interface is populated with demulsifiers and largest when it is void of surface active compounds. The results presented here evident the interplay between hydrodynamics, electrostatics, and molecular and charge convection at the oil-drop interface during drop-drop approach and coalescence. The mechanism of electrocoalescence of stable drops can be rather different than a clean drop pair. Furthermore, the different surface active compounds contribute to the electrostatic and mechanical properties of the drop interface to a unique degree, which in turn differently influences the drop-drop attraction and merging. Further investigations on the interplay between polar surface-active molecules at a liquid interface and externally applied electrostatic force are necessary to elucidate the stable drop electrocoalescence mechanism and dynamics.

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