

## Demulsifier Assisted Electrocoalescence in Crude Oil Emulsions

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Electrocoalescence has been considered a most efficient method of crude oil dewatering; however, just electric fields are not enough when dealing with heavy crude oils. In this work we studied effect of asphaltenes flocculation and effectiveness of variety of demulsifiers in electrocoalescence of water-in-crude oil emulsions. A parallel plate electrodes cell was used to apply a uniform, linearly rising DC electric field to a thin layer of emulsion and the current running through the emulsion was monitored as an indicator of progress in the coalescence. In the first part of the study, model crude oils were used to investigate the role of flocculated asphaltenes and flocculation inhibitor on electrocoalescence. It was observed that the asphaltenes flocculation adversely affects the rate of electrocoalescence. Second part compares effectiveness of different demulsifiers in breaking water-in-crude oil emulsions under electric field. The experimental observations suggest that there exist a threshold demulsifier concentration limit and increasing concentration further does not improve electrocoalescence rate. The addition of a demulsifier before dispersion of water results into faster separation as compared to the electrocoalescence in emulsion where the demulsifier was added later. Further, we devised a model for qualitative prediction of film drainage between two demulsifier-laden water-crude oil interfaces under an electric field. The model predicted film thinning rates are consistent with the experimentally measured critical electric fields which are used as an indicator of progress in electrocoalescence.

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## I. INTRODUCTION

Crude oil drilled from an oil well contains a large amount of water in the form of tiny dispersed droplets as well as some dissolved and undissolved components<sup>1</sup>. Moreover, addition of relatively fresh water helps to get rid of water-soluble impurities in refinery operations. The water is difficult to separate due to very small droplet size and stable water-oil interface. The separation through sedimentation takes a great amount of time as average droplet size in a crude oil is less than  $50 \mu\text{m}$ <sup>2</sup>. Therefore, expediting local droplet merger and allowing resulting bigger drops to sediment are the key to enhance phase separation. The indigenous surfactants including asphaltenes, resins and some naphthenates are water-insoluble; which make a stable layer around a droplet<sup>3</sup> and consequently making drop-drop coalescence challenging<sup>1,4</sup>. A variety of methods have been employed to separate water from crude oil before its fractionation, including gravity settling, centrifugation, electrocoalescence, chemical demulsification, etc.; each having its own pros and cons<sup>5,6</sup>. Although electrostatic method of phase separation is considered the most efficient, further enhancement in its separation capabilities is crucial, which can be achieved by coupling with another method. Heavy crude oils, for instance, contain very stable droplets surrounded by viscous oils and therefore are tough to break by just electrostatic forces.

Numerous studies addressing coalescence rate by the individual methods exist in the literature<sup>4</sup>. Moreover, separation in coupled methods is also studied e.g. emulsion under shear in electric field<sup>7</sup>, centrifugation or gravitational settling in electric fields<sup>8,9</sup>, etc. However, there are only a few studies wherein combined action of chemical and electric fields<sup>10</sup> in enhancement of the phase separation is investigated. Nonetheless, applications of the combinations have some limitations. Therefore developing new combinations of methods that can break water-in-heavy and/or naturally stable crude oils is essential. In view of that we investigated the role of some commercial demulsifiers in dewatering of crude oil emulsions in the presence of DC electric fields.

Droplets in an emulsion, when exposed to an electric field, experience dipolar attraction which is the driving force in the drop approach stage of electrocoalescence<sup>2,11</sup>. The separation between the attracting drops' leading faces reduces so much so that the thin liquid film separating them squeezes at the plateau borders. The film subsequently breaks, leading to the coalescence of the drops. Use of demulsifiers decreases interfacial tension of

water-oil interface in a water-in-oil emulsion. Thanks to their high diffusivity in crude oils, the demulsifiers easily migrate to the water-oil interface and compete with the stabilizing compounds, mainly asphaltenes which are already there<sup>12</sup>. Different mechanisms to explain demulsifier action at the asphaltene stabilized water-oil interface have been proposed. At a high demulsifier concentration asphaltanes might be replaced or displaced upon demulsifier triggered change in elasticity or viscosity of the interface<sup>13</sup>. Another hypothesis states that the formation of asphaltene-demulsifier complexes is responsible for the reduction in interfacial tension<sup>14</sup>. The reduction in interfacial tension plays a critical role in the film drainage and film rupture stages of the coalescence. Although, the presence of demulsifiers does not explicitly alter the electrostatic force, it determines the capillary and lubrication forces in the film between electrocoalescing droplets.

In the present work we investigated role of asphaltenes flocculation as well as the effects of five different demulsifiers on the electrocoalescence dynamics in water-in-crude oil emulsions. We used an electrode setup wherein a thin layer of a water-in-oil emulsion was exposed to a linearly increasing electric field ( $E_0$ ) with time. Effectiveness of the demulsifiers in the electrocoalescence was determined by monitoring the current passing through the emulsion. The field, termed critical electric field ( $E_c$ ) at which initially constant current shows a steep rise due to appearance of bridges facilitating the charge flow, is considered as an indicator of the coalescence rate. The study was divided into two parts: first we analyzed the role of asphaltene flocs and a flocculation inhibitor on electrocoalescence in model crude oil emulsions; followed by investigation on the combine effect of demulsifiers and electric field during coalescence in water-in-crude oil emulsions. Every experimental measurement is repeated at least five times. We also developed a theoretical model to estimate the rate of thin film drainage between two rigid uniform electrocoalescing water droplets as well as two planar bitumen emulsion films. The rates determined as such were compared with the experimental  $E_c$  values to check the consistency of demulsifier performance.

## II. EXPERIMENTAL

### Emulsion Preparation

#### 1. Model Emulsions

We used model crude oil emulsions, prepared in heptane (99 %, Merck) and toluene (100 %, VWR), to study water separation dynamics at the asphaltene flocculation limits. A heavy crude oil from Norwegian continental shelf mixed with solvents was used as a medium phase while Milli-Q water containing 3.5 wt% NaCl (99.5%, Merck) was the dispersed phase. 4-Dodecylbenzenesulfonic acid, DBSA (99 %, Sigma Aldrich) at different concentrations was used as a asphaltene flocculation inhibitor. The solvent to crude oil ratio was fixed at 3.5 ml/g based on NIR measurements for asphaltene flocculation limit. The asphaltene flocculation onset for the emulsions prepared in heptane (Emulsions A1 and A2) was found to be  $3.4 \pm 0.3$  ml/g. Whereas in the emulsions containing toluene (Emulsion B) at the same ratio asphaltenes were completely dissolved. The emulsions were made using UltraTurax(IKA) homogenizer at 24000 rpm for 2 minutes. In Emulsions A1 and B, DBSA was added in model crude oil before water was homogenized while in Emulsion A2 it was added later.

#### 2. Crude Oil Emulsions

In addition to the model emulsions mentioned in the previous subsection, we used crude oil emulsions to study the coupled effect of electric field and demulsifier. Medium phase in the crude oil emulsions was a heavy crude oil of the Norwegian continental shelf without additional solvents. The composition of the emulsions and demulsifier solutions used are tabulated in Table I. Dispersed phase in all the emulsions was Milli-Q water. Method of emulsion preparation was the same as described in the previous subsection, i.e., 30 ml of the mixture was stirred by UltraTurax at 24000 rpm for 2 minutes. Different solvents and solvent combinations mentioned in Table I were used to mix demulsifiers and the solutions were added in small concentrations to the oil phase before water was dispersed. Although xylene was used as a solvent at majority of demulsifier concentrations, at higher concentrations xylene-methanol mixture (3:1 v/v) was used. Ring tensiometer was used to measure the interfacial tension of water-crude oil interface at different demulsifier concentrations in the bulk. The emulsions

containing five different demulsifiers, all supplied by AkzoNobel, are denoted as C, D, E, F and G, respectively and will be referred henceforth by these names.

## Electrode Setup

The schematic diagram of electrode setup used in the current study is shown in Figure 1 and was similar to the one used previously by Aske *et al.*<sup>15</sup>. The setup consists of two parallel brass electrodes sandwiching a 250  $\mu\text{m}$  thick PTFE plate. A cavity formed due to an 11 mm hole at the center of the PTFE plate was used to contain an emulsion layer between the electrodes. The emulsion was introduced into the cavity in such a way that no air bubble was entrapped in the layer. The electrodes were connected to a DC power source and the current flowing through the emulsion was measured while field was on. Linearly increasing DC electric potential (V) was applied at the rate  $\frac{dV}{dt} = 0.2 \text{ V/s}$  with initial potential set at  $V_0 = 0$ ,  $t$  is time.

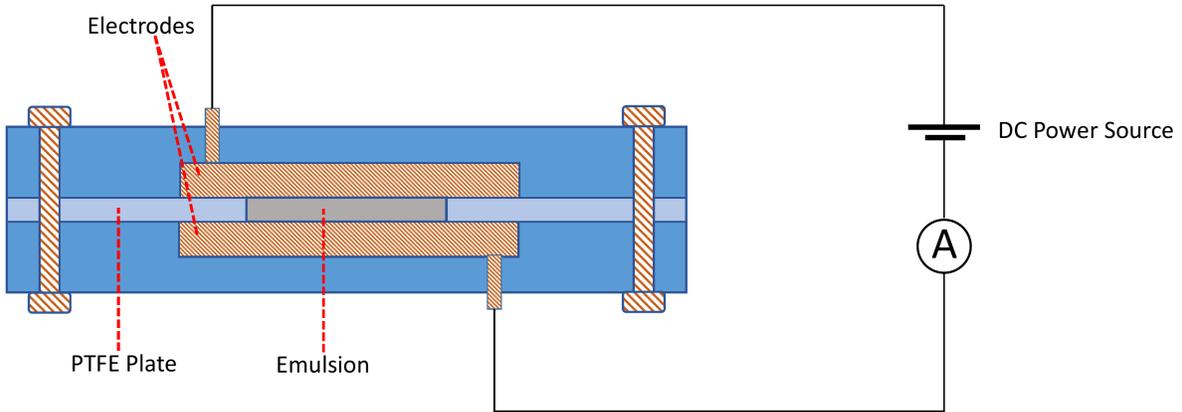


FIG. 1. Electrocoalescence cell to apply an electric field to, and monitor current through, a layer of an emulsion. Linearly increasing ( $dV/dt = 0.2 \text{ V/s}$ ) DC uniform electric field ( $E_0 \leq 4 \text{ kV/cm}$ ) was applied to the emulsion layer of thickness 250  $\mu\text{m}$ .

TABLE I. Composition of crude oil emulsions containing dispersed Milli-Q water prepared using UltraTurax at 24000 rpm for 2 minute. The solvents mentioned were used to mix with demulsifiers and just 20  $\mu$ l of the resulting solutions were added in the emulsions. In all the emulsions demulsifiers were added after dispersion of water and  $C_0$  is demulsifier concentration in an emulsion.

| Emulsion/<br>Demulsifier     | 15 % Water cut |                      | 30 % Water cut |                      | 50 % Water cut |         |
|------------------------------|----------------|----------------------|----------------|----------------------|----------------|---------|
|                              | $C_0$ (ppm)    | Solvent              | $C_0$ (ppm)    | Solvent              | $C_0$ (ppm)    | Solvent |
| Emulsion C/<br>Demulsifier C | 0              | Xylene               | 0              | Xylene               | 0              | Xylene  |
|                              | 47             | Xylene               | 89             | Xylene               | 172            | Xylene  |
|                              | 88             | Xylene               | 163            | Xylene               | 280            | Xylene  |
|                              | 156            | Xylene               | 222            | Xylene-Methanol(3:1) |                |         |
|                              | 258            | Xylene               |                |                      |                |         |
|                              | 325            | Xylene-Methanol(3:1) |                |                      |                |         |
| Emulsion D/<br>Demulsifier D | 0              | Xylene               | 0              | Xylene               | 0              | Xylene  |
|                              | 47             | Xylene               | 89             | Xylene               | 172            | Xylene  |
|                              | 88             | Xylene               | 163            | Xylene               |                |         |
|                              | 156            | Xylene               | 222            | Xylene-Methanol(3:1) |                |         |
|                              | 258            | Xylene-Methanol(3:1) |                |                      |                |         |
|                              | 325            | Xylene-Methanol(3:1) |                |                      |                |         |
| Emulsion E/<br>Demulsifier E | 0              | Xylene               | 0              | Xylene               | 0              | Xylene  |
|                              | 47             | Xylene               | 89             | Xylene               | 172            | Xylene  |
|                              | 88             | Xylene               | 163            | Xylene               |                |         |
|                              | 156            | Xylene               | 222            | Xylene-Methanol(3:1) |                |         |
|                              | 258            | Xylene-Methanol(3:1) |                |                      |                |         |
|                              | 325            | Xylene-Methanol(3:1) |                |                      |                |         |
| Emulsion F/<br>Demulsifier F | 0              | Xylene               | 0              | Xylene               |                |         |
|                              | 47             | Xylene               | 89             | Xylene               |                |         |
|                              | 88             | Xylene               | 163            | Xylene-Methanol(3:1) |                |         |
|                              | 156            | Xylene-Methanol(3:1) | 222            | Xylene-Methanol(3:1) |                |         |
|                              | 258            | Xylene-Methanol(3:1) |                |                      |                |         |
|                              | 325            | Xylene-Methanol(3:1) |                |                      |                |         |
| Emulsion G/<br>Demulsifier G | 0              | Xylene               | 0              | Xylene               |                |         |
|                              | 47             | Xylene               | 89             | Xylene               |                |         |
|                              | 88             | Xylene               | 163            | Xylene-Methanol(3:1) |                |         |
|                              | 156            | Xylene-Methanol(3:1) | 222            | Xylene-Methanol(3:1) |                |         |
|                              | 258            | Xylene-Methanol(3:1) |                |                      |                |         |
|                              | 325            | Xylene-Methanol(3:1) |                |                      |                |         |

### III. RESULTS AND DISCUSSION

#### A. Critical Electric Field

In a water-in-oil emulsion tiny water droplets are surrounded by the low conductivity oil. When a weak electric field is applied to a thin emulsion layer, no current is expected to flow through the electrode system. Figure 2(a) is a typical voltage-current variation after field is applied to an emulsion layer in the cell and Figure 2(b) is schematic depiction of droplet arrangements in the emulsion as the field builds-up (denoted by letters on the curve in Figure 2(a)). When an electric field is applied to an emulsion in the electrode cell, initially evenly distributed droplets (A, Figure 2(b)) start to get polarized and stretch in the direction of the field. The dipolar force of attraction between neighboring droplets induces motion and the droplets begin to arrange along the field direction (B, Figure 2(b)). Coalescence of the droplets starts as the electric field builds up. Over this period, a small constant current flowing through the electrode system was entirely due to the conductivity of the crude oil imparted by its indigenous impurities<sup>16</sup>. The rate of coalescence is governed by physical and electrical properties of the emulsion in addition to the applied electric field.

The rise in current at point C upon further increase in the electric field suggests a sudden appearance of paths for charges to flow. As previously reported in the literature, chains of droplets form in an electrocoalescing emulsion wherein individual droplets are separated by a stable non-rupturing film<sup>17,18</sup>. Since the film is stable and impermeable, electric charges are not allowed to travel across; moreover, it does not allow droplets to merge. Between two electrocoalescing droplets the charge transfer occurs through a liquid bridge; which depending upon electric field strength widens, leading to coalescence of the droplets<sup>19</sup>. Therefore the paths responsible for current flow could be droplet structures involving trains of interacting droplets<sup>20</sup> and/or grown large single droplets stretched to the electrodes due to electric stresses. As reported earlier by Ristenpart *et al.*<sup>20</sup> when a strong DC electric field is applied to multiple water droplets in silicone oil, the droplets do not coalesce but arrange in a string and oscillate between the electrodes. The charge transfer in such strings occurs through the transitory microscopic jets formed between neighboring droplets as well as between a drop and an electrode<sup>20,21</sup>. The bridge formation and exchange of charges between droplets in the string connecting electrodes through its ends is possible only in very strong

electric fields. Moreover, likeliness of forming such bridges in the presence of stable films around an interface, such as asphaltenes films in crude oil emulsions, is unknown. Therefore the only plausible reason for the sharp rise in current is the free path for charge transfer due to the coalesced big drops deformed and extended to the electrodes.

A merged drop, when grown big enough, extends to the electrodes to become a route for charge transfer. The drop exchanges charge through microscopic/nanoscale jets which emerge from its polar ends and touch the electrodes<sup>22,23</sup>. At electric fields  $E_0 > E_c$ , simultaneous formation and breaking of the charge routes is evident by the exponential but bumpy growth of the current in Figure 2(a). The intermittent fall in the current (e.g. at point D) can be attributed to breaking of the microscopic/nanoscale jets or breakup of the bridging drops. Various mechanisms of the jet breakup are proposed in the literature<sup>21-23</sup>. If the current fluctuations are due to drop breakup, the breakup by tip streaming or catastrophic breakup in the present system, where medium phase is highly viscous and drop phase is very conducting, is unlikely<sup>24</sup>. Also the constant fall and rise of current suggest the unlikeliness of these modes of drop-breakup as they drastically reduce the average emulsion size<sup>25</sup>. However, instant recovery of the current suggests immediate buildup of big drops; which is difficult to happen if there is generation of large number of tiny droplets in the emulsion.

The electrodes separation ( $250 \mu\text{m}$ ) is just an order of magnitude larger than the average drop size ( $\approx 10 \mu\text{m}$ ) of the fresh emulsion. Therefore microscopic irregularities at the electrode surface greatly influence the electrocoalescence rate. However, relative performance of the demulsifiers to the electrocoalescence dynamics can be interpreted in terms of the pace and consequently the field at which the grown drops reach the electrodes and the current flowing through the circuit shows a ramp-up. The electric field is referred to as critical electric field ( $E_c$ ) in this paper.

## B. Film Drainage in Electric Field

Resistance to the drop-drop coalescence by the film entrapped between them is governed by its geometry, which is essentially defined by the interfacial properties. When stable interfaces are involved, as in the coalescence in a stable emulsion, the film is planar and the film radius can be as large as drop radii (Figure 3(a) A). Such a large film takes longer to drain before the droplets merge. However, application of an electric field not only induces

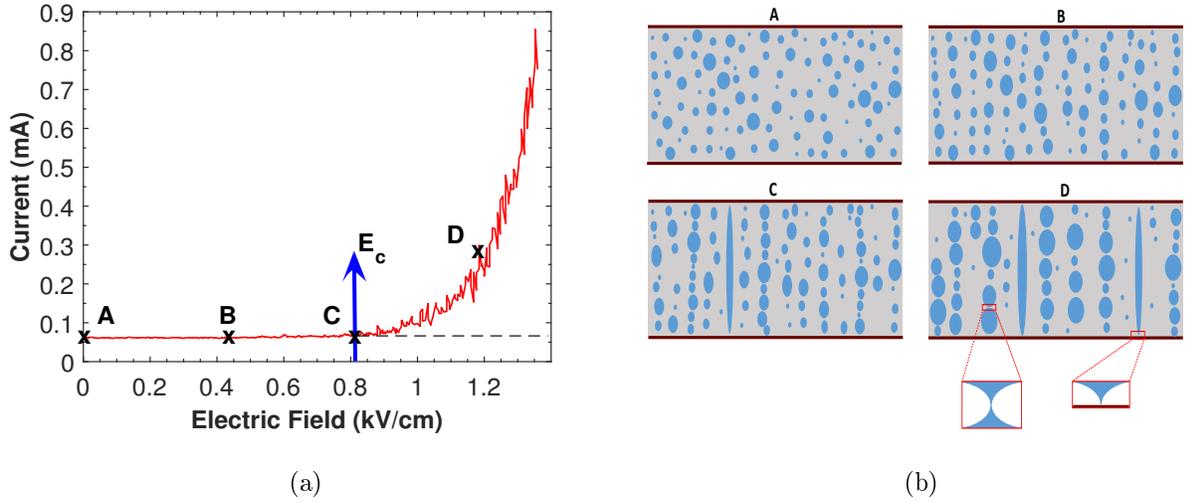


FIG. 2. (a) A typical current-voltage plot for an emulsion layer under linearly increasing electric field with time. (b) Schematics of droplet arrangements at stages shown by capital letters in (a). Above the electric field  $E_c$  merged drops stretch to the electrodes and drops start charge exchange causing sudden rise in the current. Insets: liquid bridges in drop-drop and drop-electrode charge exchange.

dipolar attraction but also deforms the coalescing droplets. As the droplets approach the electric stresses at their inner faces build up and the faces assume conical shape as shown in Figure 3(a) B.

Here we demonstrate the effect of electric field on thinning kinetics of the asphaltene-stabilized planar films. The kinetics of stable planar films in crude oil emulsions has been extensively studied<sup>26,27</sup>. In the absence of external forces the thinning rate can be predicted using Stefan-Reynolds equation<sup>28</sup> and Tchoukov *et al.*<sup>26</sup> reported that the predictions can be in reasonably good agreement with the experimental measurements for crude oil emulsions. The Stefan-Reynolds equation for the thinning kinetics of a planar film reads,

$$\frac{dh}{dt} = -\frac{4\gamma}{3\mu} \left(\frac{h}{a}\right)^3 \frac{s^2}{a^2 - s^2}. \quad (1)$$

We modified the Stefan-Reynolds equation to include the electrostatic effects on the thinning kinetics where the electric field is applied across the film. The modified Stefan-Reynolds equation is,

$$\frac{dh}{dt} = -\frac{2h^3s^2}{3\mu a^4} \left[ \epsilon_m E_0^2 + \frac{2\gamma a}{(a^2 - s^2)} \right]. \quad (2)$$

The second term in Equation 2 represents external electric force on the film. Tchoukov *et al.*<sup>26</sup> systematically studied thinning of the planar films in bitumen emulsions. We used their experimental data to theoretically show the effect of electric fields on thinning kinetics of the stable planar films. The experimental data for thinning of a 100 nm thick film, of bitumen diluted in toluene at 59 g/l (Figure 3(b)) and 217 g/l (Figure 3(c)), is plotted along with the theoretical predictions by Equation 1 and the Equation 2 for thinning under an electric field. The film of radius of 100  $\mu\text{m}$  is assumed to be planar throughout its squeezing. Apparently the application of very small voltages helps the film to drain faster. The results plotted for the film-thinning at 1 V applied across the film suggest that the thinning takes less than half the time under the electric field for complete drainage. However, it should be noted that the electric field even at a small applied voltage is high due to very small thickness of the film.

To qualitatively demonstrate the action of different demulsifiers in the presence of electric field we calculated coalescence kinetics of two uniform droplets in a small separation limit (Figure 4). Since the effects of demulsifier molecules start to appear in the film drainage stage of electrocoalescence, our model predicts the film thickness evolution under constant uniform DC electric field. The droplets are assumed to be spherical with uniform interfacial tension and Marangoni effects are considered to be negligible. Since the mechanism of demulsifier-induced destabilization of a thin film is unestablished, the reduction in interfacial tension is taken into account in the model. Electrohydrodynamic flows generate near the interface of a drop when exposed to an electric field and in case of a conducting drop, the flows are from its equator to poles<sup>31</sup>. The effect of the flows is assumed to be small for the sake of simplicity and since the crude oil is very viscous compared to the dispersed water phase ( $\lambda = \mu_m/\mu_d \gg 1$ ) the water-oil interface is considered to be fully mobile<sup>32</sup>. Here  $\mu_m$  and  $\mu_d$  are viscosities of medium and drop phases, respectively. The resisting lubrication force for a fully mobile interface is given by<sup>32</sup>,

$$F_l = 16.5\mu_d a \frac{dh}{dt} \sqrt{a/h_0}, \quad (3)$$

where  $a$  is radii of the coalescing drops,  $h$  is film thickness,  $t$  is time and  $h_0$  is the initial thickness of the film. The capillary force in the film is written as,

$$F_c = 4\pi\gamma(a - \sqrt{a^2 - s^2}), \quad (4)$$

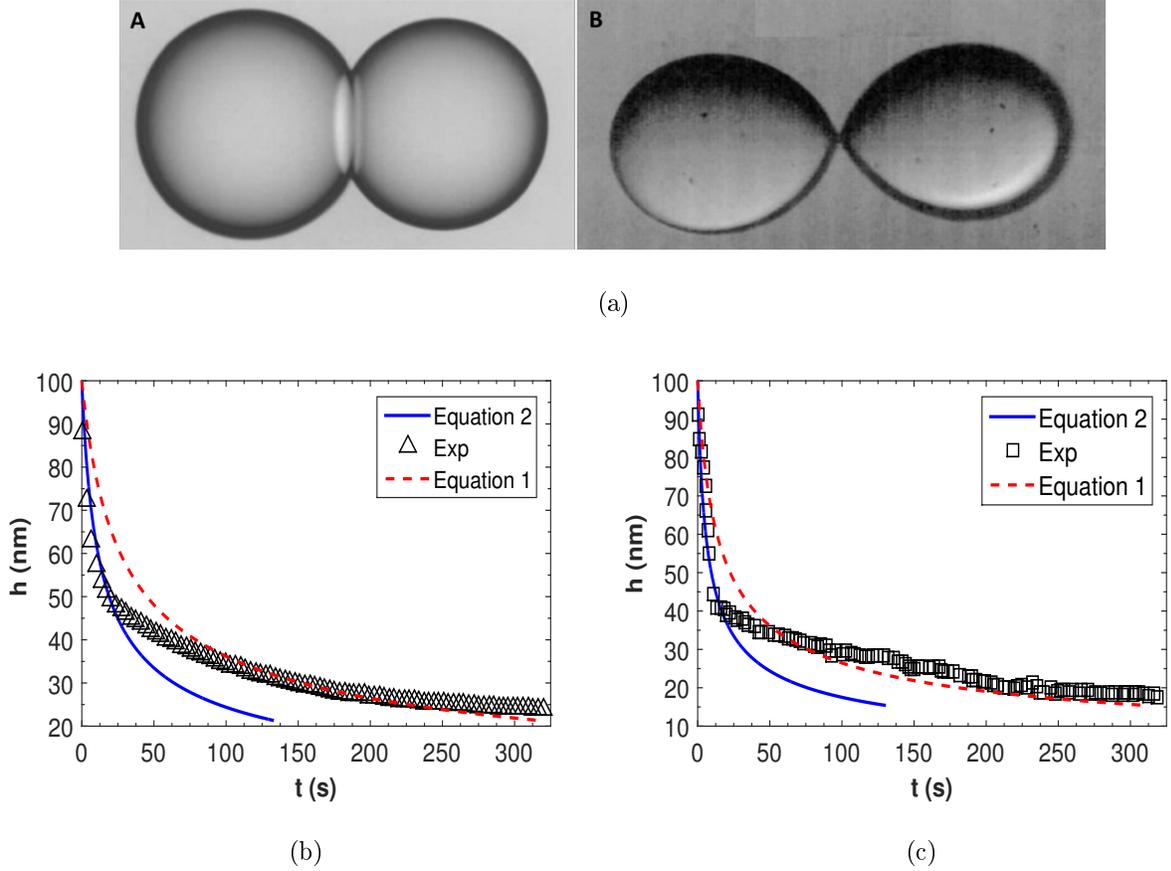


FIG. 3. (a) A. Coalescence of stable water droplets, surrounded by silicone oil containing phospholipids, in the absence of electric field (after Thiam *et al.*<sup>29</sup>) B. Water droplets coalescing in constant DC electric field (after Mhatre *et al.*<sup>30</sup>). (b,c) Thinning kinetics of planar bitumen emulsion films in solutions containing 59 g/l (b) and 217 g/l (c) bitumen. Thinning under electric field estimated by Equation 2 (—) and in the absence of electric field: experimental measurements  $\triangle$   $\square$  (after Tchoukov *et al.*<sup>26</sup>) and by Stefan-Reynolds equation (---).

here  $s$  is radius of the film which is assumed to be constant during its complete drainage and  $\gamma$  is interfacial tension. In the small separation limit electrostatic force of attraction between two drops can be accurately predicted by assuming dipole-induced-dipole interactions. The electrostatic force of attraction between two uniform drops of radii  $a$  aligned in the direction of a constant electric field can be written as<sup>2</sup>,

$$F_E = -12\pi\epsilon_m E_0^2 \frac{a^6}{(h + 2a)^4} (3M - 1). \quad (5)$$

Here  $E_0$  and  $\epsilon_m$  are applied electric field and permittivity of the medium phase, respectively.

Coefficient  $M$  in Equation (5) is<sup>30</sup>,

$$M = 1 + 2 \frac{a^3(h+2a)^5}{((h+2a)^2 - a^2)^4} + \frac{3a^3b^3(3(h+2a)^2 - 2a^2)}{((h+2a)^2 - 2a^2)^4}. \quad (6)$$

Forces in (3), (4) and (5) govern the rate of film drainage which can be expressed as,

$$\frac{dh}{dt} = \frac{8\pi \left( \frac{3\epsilon_m E_0^2 a^6 (3M-1)}{(h+2a)^4} + \gamma(a - \sqrt{a^2 - s^2}) \right)}{16.5\mu_d a \sqrt{a/h_0}}. \quad (7)$$

Equation (7) is solved for time evolution of  $h$  from initial thickness of the film,  $h_0 = 0.1a$  to the critical thickness of film breakup<sup>33</sup>,  $h_f = \left(\frac{Aa}{8\pi\gamma}\right)^{1/3}$ , where  $A$  is Hamaker constant which is assumed to be  $7 \times 10^{-21} \text{ J}^{34}$ .

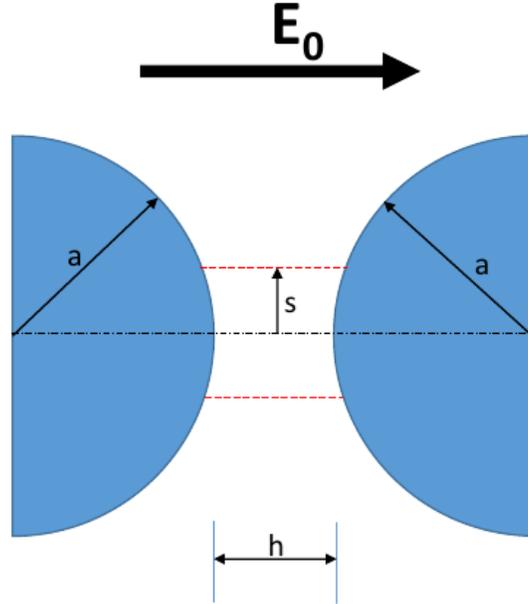


FIG. 4. Schematics of two uniform water drops of radii  $a$  in a crude oil approaching under a constant DC electric field  $E_0$ . Thin film between the drops, of thickness  $h$  and radius  $s$ , drains before it breaks and the drops merge.

### C. Effect of Asphaltenes Flocculation

Although the amount of asphaltenes was constant into three emulsions used to study the role of asphaltene flocculation on the electrocoalescence rate, asphaltenes concentration in Emulsions A1 and A2 was just above the flocculation bulk onset while in Emulsion B asphaltenes were completely dissolved. Note that both Emulsions A1 and A2 contained

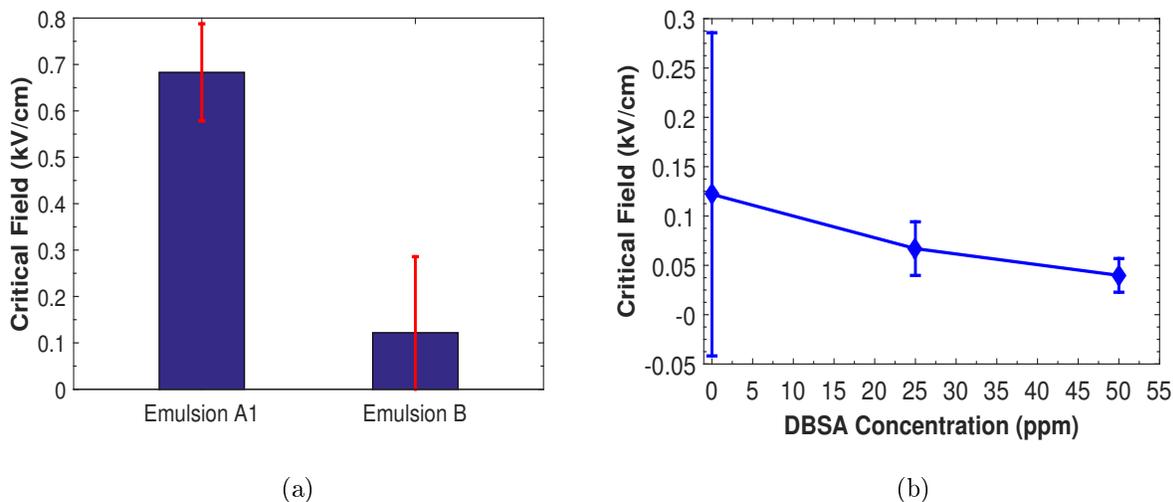


FIG. 5. Effect of asphaltene flocculation; (a) Critical electric fields in Emulsions A1 and B in the absence of asphaltene flocculation inhibitor. The emulsions contain 30 volume % brine (3.5 wt %). (b)  $E_c$  in Emulsion B at different demulsifier concentrations.

asphaltene flocs but the flocculation inhibitor (DBSA) in Emulsion A2 was added after dispersing water while in Emulsions A1 and B it was mixed before homogenization. Figure 5(a) shows critical electric fields ( $E_c$ ) at which current ( $I$ ) starts to ramp up during electrocoalescence in emulsions A1 and B. Both emulsions contained 30 % V/V dispersed water. The  $E_c$  value for the emulsion containing asphaltene flocs is apparently approximately 6 times higher than that for the emulsion containing dissolved asphaltenes; suggesting that the electrocoalescence is significantly slower in the presence of asphaltene flocs. As mentioned earlier, the critical electric field  $E_c$  is used as an indicator of electrocoalescence rate and higher values of  $E_c$  signify lower rate of electrocoalescence. The electrical conductivity of crude oils containing asphaltene flocs is lower compared to the oils having dissolved asphaltenes of the same amount<sup>16</sup>. However, the reduction is not enough to influence the electrostatic force as the drop to medium conductivity ratio is still high.

To demonstrate the role of flocculation inhibitor we measured  $E_c$  values in Emulsions A1, A2 and B at different DBSA concentrations. Therefore the slower electrocoalescence in Emulsion B can be attributed to stabilization of droplets due to the presence of asphaltene flocs in the surrounding oil phase. The data is plotted in Figures 5(b) and 6. In Emulsion B, water appears to separate faster on increasing the DBSA concentration over the limited

range of  $C_0$  studied (Figure 5(b)). At concentrations  $C_0 > 50$  ppm Emulsion B was unstable and broke without application of an electric field. Similar to Emulsion B, in Emulsion A1 separation occurred faster on increasing  $C_0$ , which is evident by decreasing  $E_c$  (Curve  $-\bullet-$  Figure 6). However, at concentrations  $C_0 > 200$  ppm further reduction in critical electric field upon increasing  $C_0$  was not observed.

The addition of DBSA influences the coalescence rate in a crude oil emulsion in two ways: first by increasing the flocculation onset of asphaltenes and second by reduction in water-oil interfacial tension. Therefore, DBSA in the present system acts as an asphaltene flocculation inhibitor as well as a demulsifier, as DBSA is an anionic surfactant<sup>35,36</sup>. The increase in the flocculation onset occurs by adsorption of DBSA molecules on to positively charged asphaltene particles and reduction in their electrophoretic mobility<sup>35</sup>. However, as the number of sites for adsorption of DBSA molecules on to an asphaltene floc is limited, the effect of DBSA bulk concentration on the mobility stops to appear above a threshold concentration. The addition of DBSA influences interfacial properties of the water-in-oil emulsion. However, we believe that the presence of such a small amount of DBSA does not significantly modify electrical and other physical properties of the bulk. The adsorption and competition of the DBSA molecules with the native asphaltene molecules at water-oil interface reduce the interfacial tension, making the emulsion less stable. However, as reported in the demulsification literature, an equilibrium between adsorption and desorption of the molecules at water-oil interface appears when concentration of demulsifier increased above a threshold limit<sup>37</sup>. Above this limit, the number of demulsifier molecules adsorbing to the interface equals to those leaving as the sites for new molecules to rest at the interface are limited owing to irreversibly adsorbed asphaltene molecules already there.

The applied electric field adds an extra effect to the adsorption dynamics of demulsifier molecules. In addition to dipolar attraction and segregation of droplets, the externally applied electric field induces electrohydrodynamic flows in an emulsion. As illustrated in Figure 7 the flows are limited to the region close to a water-oil interface. In a water-in-crude oil emulsion where  $\frac{\sigma_m \epsilon_d}{\sigma_d \epsilon_m} < 1$  the electrohydrodynamic flows occur from drop's equator to its poles<sup>30,31</sup>, here  $\sigma$  and  $\epsilon$  are electrical conductivity and permittivity and subscripts  $m$  and  $d$  denote medium and drop phases. In the case of approaching droplets, the flow currents are always stronger at their inner faces, leading to convection of the molecules to the inner poles while making equatorial region (and to a certain extent the outer poles) continuously avail-

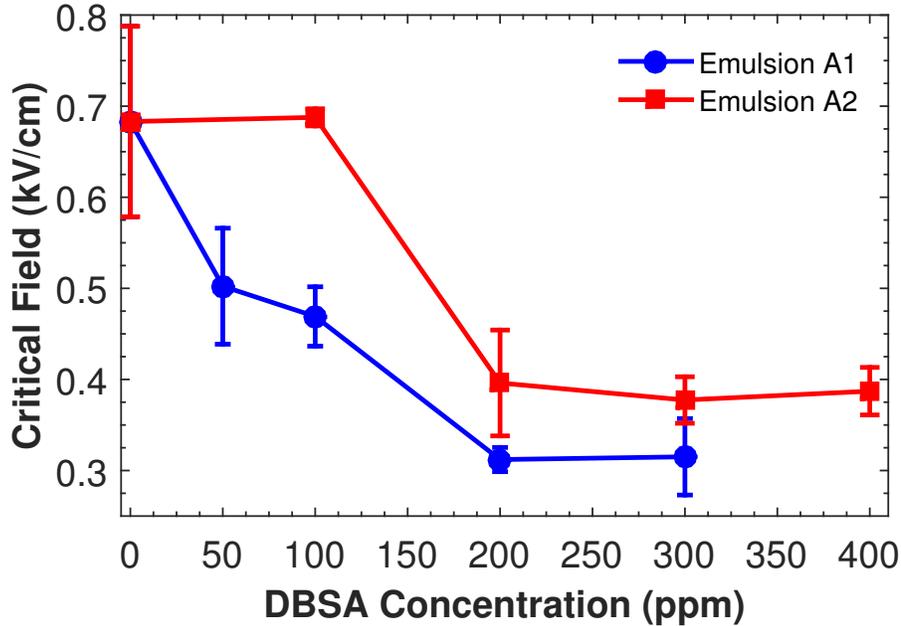


FIG. 6. Critical electric field as a function of demulsifier concentration. In Emulsions A1 and A2 demulsifier was added before and after water was dispersed, respectively.

able for new adsorptions. The distribution of molecules at the water-oil interface is always nonuniform with higher concentration at the inner poles. At higher  $C_0$  such a migration may result in stagnant caps at the leading edge of a merging drop<sup>38,39</sup>, which in turn makes that part of the interface stable and resistant to the coalescence. The complex combination of the DBSA adsorption dynamics on asphaltenes flocs as well as on the drop interface and interfacial convection of the surface active molecules due to electrohydrodynamic flows is responsible for the plateau in  $E_c$  vs  $C_0$  curve at higher concentrations.

#### D. DBSA-Asphaltenes Interaction at Drop Interface

To further demonstrate the DBSA-asphaltenes interaction at oil-water interface we used two emulsions containing dissolved asphaltenes. In one DBSA was mixed before dispersion of water (Emulsion A1) while the other already contained water droplets and asphaltenes at the time of DBSA addition. Mixing a demulsifier (DBSA) in medium phase before dispersion of water helps the demulsifier molecules to adsorb before oil-water interface is completely occupied by asphaltene molecules. The effect can be seen in Figure 6 where the  $E_c$  curves

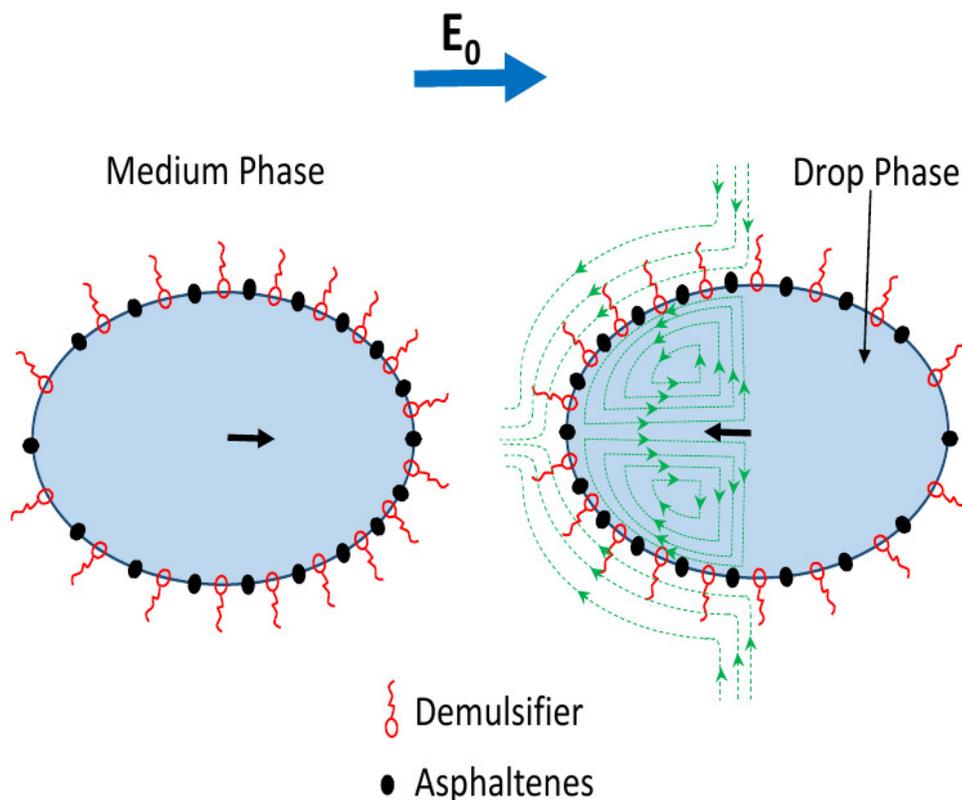


FIG. 7. Schematic of the electrohydrodynamic flow streamlines around asphaltene-stabilized electrocoalescing droplets in the presence of demulsifier.

for emulsions A1 and A2 suggest a notable difference in the rate of electrocoalescence. In Emulsion A2, emulsification in the absence of a demulsifier allows asphaltene molecules to occupy the clean water-oil interface. The demulsifier molecules added later are compelled to diffuse and fight their way through asphaltenes multilayer structures to the interface, resulting in a higher interfacial tension. On the other hand, as reported earlier by Pradilla *et al.*<sup>40</sup> in the presence of multiple surface active compounds during a fresh interface formation, the compound with more surface activity adsorbs first. During preparation of Emulsion A1, since initially interface was clean and free of either asphaltenes or demulsifiers, both compounds needed to compete to adsorb to the interface. Therefore, Emulsion A2 has higher interfacial tension compared to Emulsion A1 having same demulsifier concentration. Consequently the  $E_c$  values in Emulsion A2 are higher than that in Emulsion A1 at all the concentrations studied.

## E. Demulsifiers in Electrocoalescing Crude Oil Emulsions

We used critical electric field to compare effectiveness of variety of demulsifiers in electrostatic dewatering of crude oil emulsions. The performance is studied with reference to demulsifier concentration as well as water cut and consequently to the droplet size and inter-drop separation. In Figure 8, experimentally measured  $E_c$  values for Emulsions C, D, E, F and G, containing 15 % dispersed water, are plotted against demulsifier concentrations. Similar to the emulsions studied in the previous sections,  $E_c$  decreases with increasing  $C_0$ . Interestingly the threshold demulsifier concentrations above which  $E_c$  ceases to reduce is different for different demulsifiers. The  $E_c$  trends suggest that in Emulsions C, D and E, the rate of separation steadily increases upon increasing  $C_0$ , but at  $C_0 \geq 250$  ppm it starts decreasing. For remaining two emulsions (Emulsions F and G), the threshold limit is lower. Emulsion F shows the enhancement in electrocoalescence at very low concentration of demulsifier; however, on increasing  $C_0$  above 89 ppm, rate of coalescence does not improve significantly. In Emulsions F and G, demulsifiers bring about a minor reduction in  $E_c$  and even upon increasing  $C_0$ ,  $E_c$  remains high. The data suggests that increasing  $C_0$  of Demulsifiers C, D and E to a threshold limit boosts the water separation; however, the use of Demulsifiers F and G is unproductive over a wide range of  $C_0$  studied.

Addition of a demulsifier to a certain limit clearly enhances the rate of coalescence in the presence of electric field; however, the separation ceases to improve upon further increase in demulsifier concentration in the bulk. The behavior can be attributed to two competing kinetics; namely, diffusion and adsorption of demulsifier molecules, and interfacial convection of the surface active molecules in the presence of an electric field. Increasing concentration of a demulsifier as well as asphaltenes in a solution decreases their diffusivity<sup>37</sup>. At higher concentrations, effect of electrohydrodynamic flow-induced formation of new sites for molecular adsorption is counterbalanced by the reduction in diffusivity of the demulsifier molecules. On the other hand, asphaltene adsorption is not diffusion controlled and also irreversible<sup>37</sup>. Moreover, at the higher concentrations, formation of stagnant caps makes leading faces of the electrocoalescing droplets rigid, which not only increases the drag force<sup>39</sup> but also resists the film drainage and film breakup.

Figure 9(a) demonstrates the rates of electrostatically assisted squeezing of the interstitial film estimated using Equation (7) between two 10  $\mu\text{m}$  water droplets in Emulsion E.

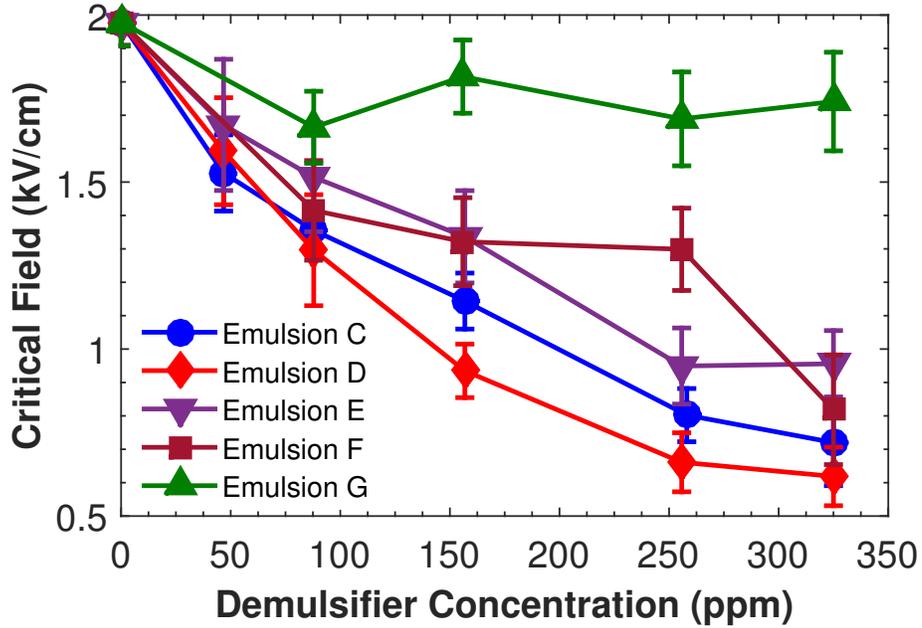


FIG. 8. Change in critical electric field with demulsifier concentrations in crude oil emulsions containing 15 volume % dispersed Milli Q water.

Since the applied electric field in Equation (7) is constant, the curves suggest that the film thins faster as demulsifier concentration is increased. However, the predicted rate of film thinning is higher at the lower concentrations ( $C_0 \leq 95$  ppm) and it slows down upon further increasing the concentration. The time required to drain the film to breakup ( $t_f$ ) at different concentrations is plotted along with  $E_c$  in Figure 9(b). Although the threshold  $C_0$  limit for measured  $E_c$  is higher ( $\approx 250$  ppm), both parameters - $E_c$  and  $t_f$ - follow a similar trend; a sharp reduction at the lower concentrations, followed by a small decline in the rate. The coherence suggests that a demulsifier assists the film thinning during electrocoalescence of two droplets, however above a limit further increase in demulsifier concentration does not speed up the coalescence. This also affirms suitability of critical electric field to investigate the merits of a demulsifier in electrocoalescence as well as to compare the effectiveness of different demulsifiers.

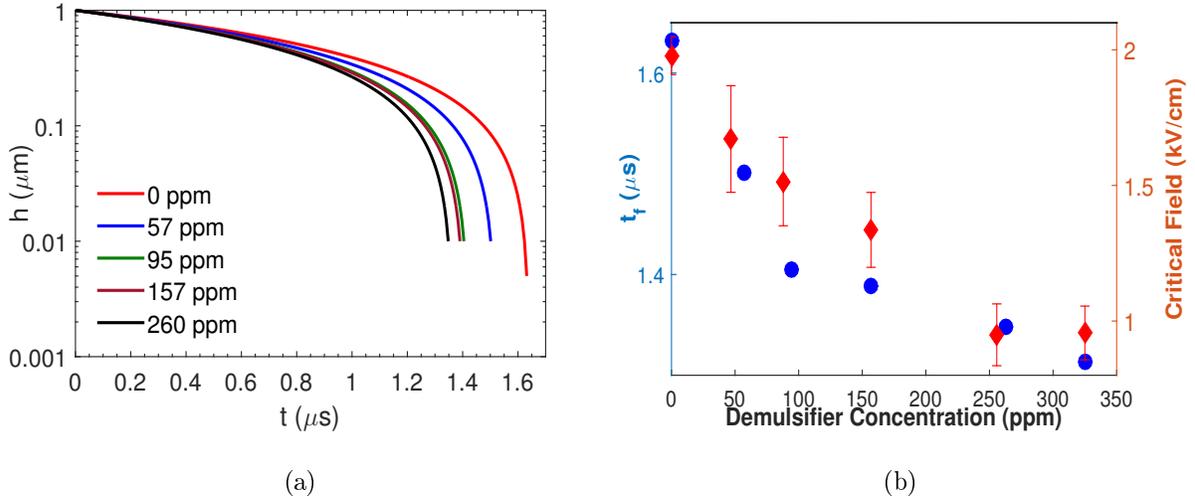


FIG. 9. Effect of a demulsifier on thinning of a film between two uniform electrocoalescing water droplets in Emulsion E. (a) Film thickness evolution at different demulsifier concentrations. (b) Theoretically predicted time for film thinning and breakup ( $\bullet$ ) and experimentally measured critical electric fields ( $\blacksquare$ ) at 15 % water cut.  $a=10 \mu\text{m}$ ,  $h_0=0.1a$ ,  $s=0.5a$  and  $E_0=2.4 \text{ kV/cm}$ .

As discussed in section III A and demonstrated in Figure 2(a) the current passing through the cell grows exponentially as electric field raised above  $E_c$ . The small fluctuations in the curve suggest simultaneous breaking and building of the charge routes across the emulsion layer. Here we introduce a parameter which is analogous to mutual capacitance and indicator formation of the charge routes and drop coalescence. The parameter,  $P = \frac{\int_0^\tau I(t)dt}{\Delta V}$  is plotted against demulsifier concentrations in Figure 10. Here  $\tau$  is total time of field application,  $\Delta V = V_\tau - V_0$  and  $V_\tau$  is the voltage at time  $\tau$ . In all the emulsions the amount of dispersed water is 15 volume % and discounting the negligible effect of demulsifiers on conductivity of oil, flow of the current is facilitated by water structures connecting the electrodes. The parameter  $P$  characterizes the flow of current through the electrode system due to the charge routes and their sustenance. Higher  $P$  signifies existence of more water bridges and larger amount of current flowing through the emulsion layer. In Figure 10 the trends in  $P$  values are consistent with the  $E_c$  data in Figure 8. In Emulsions C, D, E and F,  $P$  rises exponentially on increasing  $C_0$ , at 325 ppm it falls in emulsions C and D though; which suggests faster build up and restoration of the charge routes in Emulsions C, D and E up on increasing  $C_0$  to a certain limit. On the other hand  $P$  for Emulsion G falls at lower  $C_0$  and recovers

marginally thereafter, suggesting a slower drop growth.

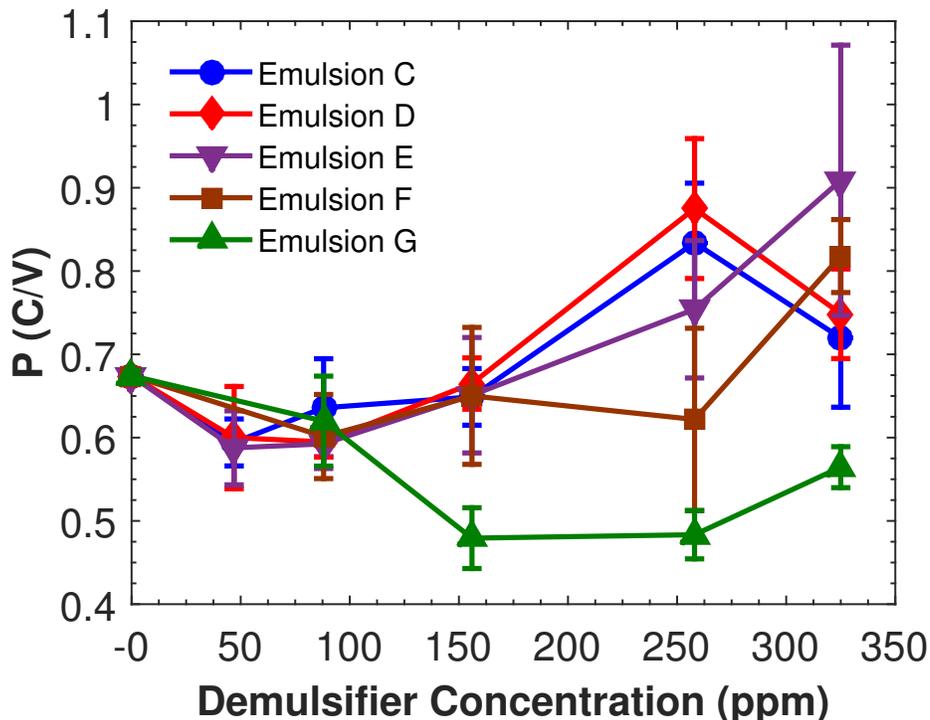


FIG. 10. Variation of  $P = \frac{\int_0^\tau I(t)dt}{\Delta V}$  with demulsifier concentrations in crude oil emulsions containing 15 volume % dispersed Milli Q water.

### *Role of Water Cut*

Varying fraction of dispersed phase in an emulsion not only varies the droplet size distribution but also the surface-to-surface separation. To investigate the influence of these effects on phase separation in the presence of demulsifiers and electric field we repeated the experiments discussed in the previous section with 30 % and 50 % water loadings. Critical electric field measurements for emulsion with 30 % water cut are plotted in Figure 11. The  $E_c$  values fall marginally but steadily over the range of demulsifier concentrations studied. Furthermore, the overall  $E_c$  values for 30 % water cut are much smaller than that for 15 % water cut at the respective concentrations. As lower  $E_c$  indicates faster coalescence, understandably the lower drop-drop separation or larger drop size as well as larger Taylor deformation and stronger electrohydrodynamic flows for larger drops amplifies the adsorption of surface active compounds accelerating the electrocoalescence in the high water cut

emulsions.

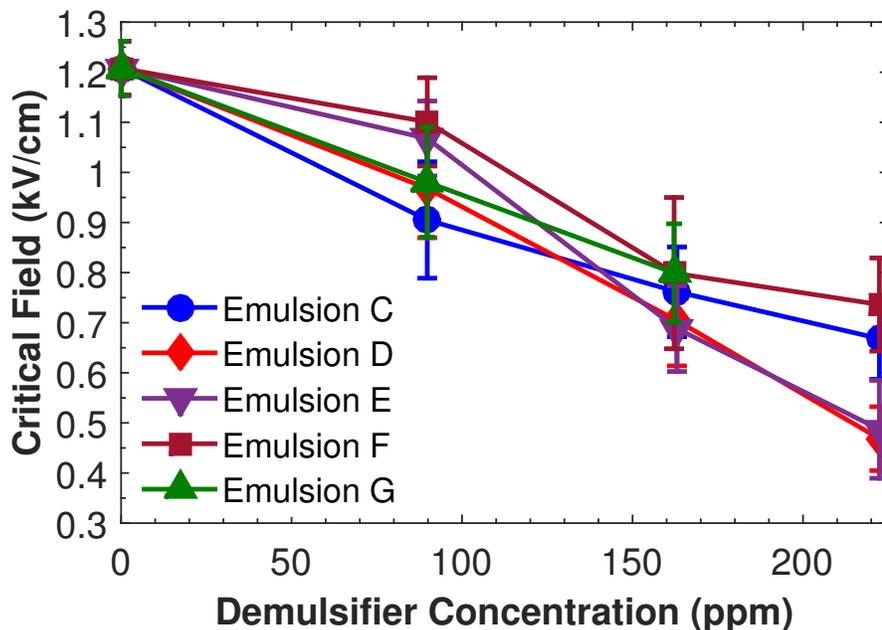


FIG. 11. Critical electric field variation as a function of demulsifier concentrations in crude oil emulsions containing 30 volume % dispersed Milli Q water.

Similar trends were observed in emulsions containing 50 volume % dispersed water. As shown in Figure 12 where water cut was varied in Emulsion C,  $E_c$  values are significantly different for the three water cuts studied. However, the effect of the demulsifiers on coalescence rate was found to be diminished as water cut was increased. Emulsions having larger amount of dispersed water are prone to coalesce faster, even at lower electric fields, owing to larger drop sizes or lower inter-drop separations. Furthermore, we studied the effects of water cuts on the rate of dewatering at a fix concentration of demulsifiers. Figure 13 shows  $E_c$  for Emulsions C, D and E with  $C_0 = 164 \pm 8$  ppm as well as for a plain emulsion without demulsifier. The critical field linearly drops with water cut in all the emulsions and  $E_c$  of the plain emulsion is significantly higher than that of emulsions containing demulsifiers at all the water cuts. The data in Figures 12 and 13 signify weakened stability of a crude oil emulsion at a higher water loading which easily leads the emulsion to breakup even in a weaker electric field.

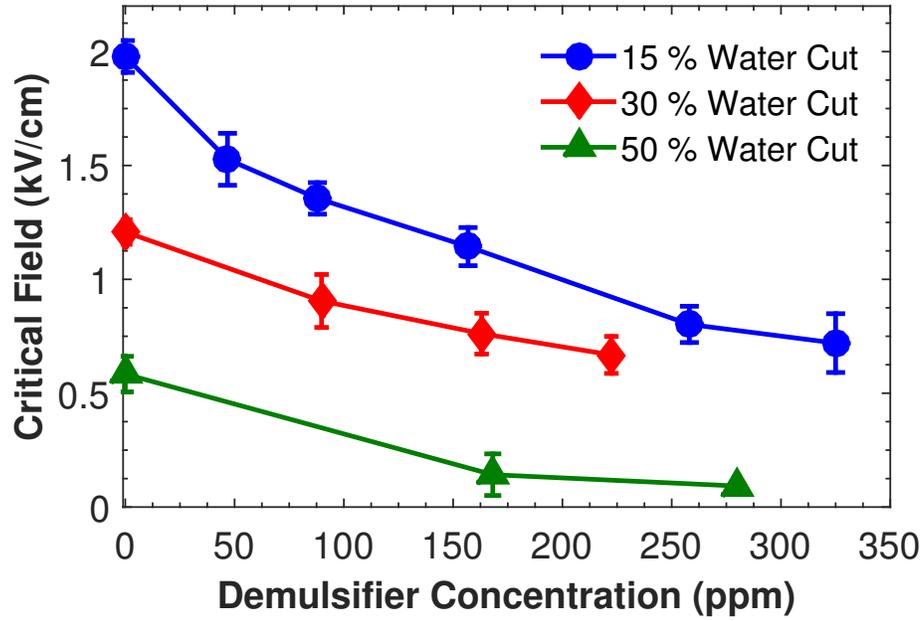


FIG. 12. Influence of varying demulsifier concentration on critical electric field in Emulsion C containing 15, 30 and 50 volume % dispersed water.

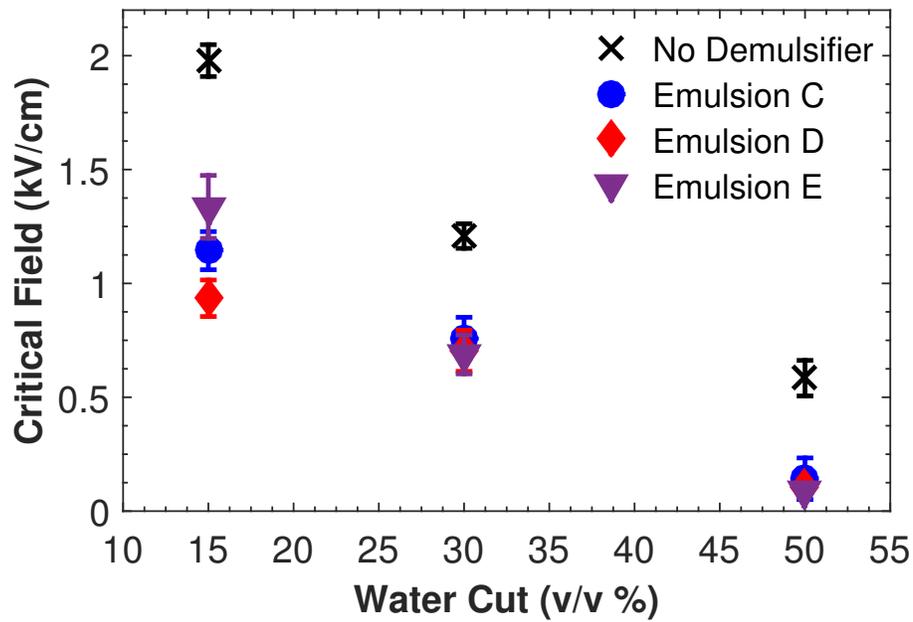


FIG. 13. Critical electric field as a function of water loading at a fix  $C_0$  in the emulsions containing different demulsifiers. The demulsifier concentration was constant  $164 \pm 8$  ppm in all the emulsions.

## F. Conclusions

Primarily two aspects are studied to investigate the role of a demulsifier in an electrocoalescing crude oil emulsion: (1) asphaltene flocculation state, and (2) demulsifier concentrations. A linearly increasing DC electric field was applied to a 250  $\mu\text{m}$  thin layer of an emulsion sandwiched between two parallel plate electrodes. Current passing through the emulsion was monitored and electric field at sudden rise in current when droplet growth reached the scale of the emulsion layer thickness was considered as an indicator of the coalescence rate. The coalesced big drops, stretching under electric stresses to the electrodes, facilitate the routes for current flow. The role of stable droplet chains or existence of interacting droplet strings for the current flow is ruled out as charges can not travel across a stable film separating two drops in the droplet chains. Further, interacting droplet strings exist only when emulsion is exposed to a very strong electric field in the absence surface active compounds.

The presence of asphaltene flocs in an emulsions has a detrimental effect on the rate of electrocoalescence; chiefly because of increased stability of the oil-water interface and partly because of reduced conductivity of oil. Addition of a flocculation inhibitor was turn out to be useful and increasing its concentration found to increase the rate of electrocoalescence; however, the concentration has a threshold limit above which the rate stops to grow further. The similar effect was observed in the demulsifier assisted electrocoalescence where the addition of a demulsifier enhances the coalescence rate below a threshold concentration limit. Two competing mechanisms are responsible for the threshold limit; the rate of diffusion and adsorption of demulsifier molecules to the water interface, and the interfacial convections due to electrohydrodynamic flows. Our analytical model for squeezing of a thin film between two electrocoalescing droplets suggests that the time required to break the film in the presence of a demulsifier shows trends similar to experimentally observed critical electric field. This fact validates our hypothesis of the current flow due to grown large drop/s at electric fields  $E_0 \geq E_c$  and also suggests  $E_c$  to be a good parameter to compare effectiveness of different demulsifiers in the electrostatic phase separation.

The findings reported here are crucial in industrial crude oil dewatering using coupled electric and chemical methods. Our results suggest mitigation of asphaltene flocculation significantly increases the rate of electrocoalescence. Moreover, the critical electric field data

over a range of demulsifier concentrations indicate there exists an optimum concentration above which addition of more demulsifier is unproductive. The observations are key to selection of demulsifiers and deciding their concentration for maximum separation of water from crude oil emulsions.

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