Shape evolution of a water drop in asphaltene solution under weak DC electric fields

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The microscopic shape change of a pendent water drop, surrounded by an organic solution containing asphaltenes extracted from heavy crude oil, under electric field is investigated. Weak constant DC electric fields were applied in the direction perpendicular to gravity. the asphaltenes extracted from a heavy crude oil from Norwegian continental shelf were mixed in xylene at low concentrations. The simultaneous action of electric field and the asphaltene adsorption at the drop interface determines the shape of drop. Upon application of the electric field the drop exhibits instantaneous deformation in the direction of the field. Interestingly, the subsequent shape change occurs perpendicular to the field direction. The drop shape is observed to be asymmetric about both axes and the asymmetry intensifies with magnitude of the applied field and the concentration of asphaltenes in the surrounding medium. We thoroughly analyzed the temporal changes in shape features of the drop, which was held in the asphaltene solution for an hour. The influence of a range of concentrations and electric field strengths is investigated. The counter-intuitive shape development and the asymmetry are attributed to the electric field-reinforced asphaltene mass transport at the drop interface and the resultant interfacial properties.

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I. INTRODUCTION

The behavior of a liquid drop, surrounded by another immiscible liquid of different properties and exposed to an electric field, has been extensively studied in the literature[1-4]. The scientific research activity in the field received a boost after it was found that a drop can be levitated into another electrically less conducting liquid and subjected to an electric field[5]. The dynamics, shape and instability of the drop is still an active field of research[6-8]. The shape of such a drop is of particularly important due to its relevance in the industrial applications such as microfluidics, mass spectroscopy, crude oil dewatering, electrostatic emulsification, etc[9-11]. The drop, when put into electric field, experiences electric stresses, magnitude and direction of which are governed by electrical properties of the two liquid phases. The electric stresses at the interface are balanced by interfacial tension forces where the drop attains a new equilibrium shape.

The recent studies in enhanced interfacial mass and heat transfer in the presence of electric field received attention due to the applications in microelectronic circuit cooling and microreactor technology. Majority of the studies are numerical investigations as the measurement of such an enhancement involves technical difficulties[4,12]. Taylor demonstrated the occurrence of quadrupole circulation inside a stagnant drop due to the electric stresses at its interface[13]. The circulation consists of two toroidal swirls in each hemisphere separated at the equator by a stagnant disk. Lee *et al*[14] and Ward and Homsy[15,16] showed that the stagnation disk can be shifted by tuning the externally applied electric field which leads to the intense mixing inside the drop. Jog and group[17-20] extensively studied the enhancement in heat and mass transfer across the drop interface due to the electrohydrodynamic phenomenon. Similarly, comprehensive studies by Di Marco and group demonstrated effects of applied electric fields on heat transfer in the multiphase systems[21-23]. Degen *et al*[24] demonstrated, through the shape analysis of a pendant drop surrounded by octadecyltrichlorosilane (OTS) solution, that the externally applied electric field enhances the polymerization process. The direction of the applied electric field in their experiments was parallel to gravity.

Use of electric field for the phase separation in crude oil treatment has a long history[25,26]. A naturally occurring water-in-crude oil emulsion can be speedily separated by electrostatic means as compared to the other methods of phase separation[11]. The technique has been constantly investigated in order to further enhance the coalescence capabilities[27,28]. However,

certain ill effects during the drop-drop electrocoalescence, such as partial coalescence, chain formation, etc., are still not fully understood[29–32]. These effects are essentially ascribed to the interfacial properties of the water-oil interface and may hamper the rate of phase separation if not alleviated. The current research activities in the field are mainly concerned with understanding and mitigating these effects[33,34].

The presence of various surface active components such as asphaltenes, resins, clays, etc. in a crude oil makes the water-oil interface stable[35]. The stabilization not only slows down drainage of the thin film between two electrocoalescing droplets but also can result into formation of tiny daughter droplets after the coalescence. The phenomenon is known as partial coalescence and it makes the use of electric field in the phase separation counter productive as it decreases the average droplet size of the emulsion. Another effect, known as chain formation, is characterized by the arrangement of droplets along the electric field direction. The chain-like structures formed in an electrocoalescing emulsion do not break when the individual droplets are separated by stable films. Additional measures such as chemical demulsifiers are needed to drain the films faster[36].

In this paper we present the microscopic changes in shape of a drop held pendent in a solution containing asphaltenes and exposed to a low strength DC electric field. The objective of the study is to investigate in detail the combined role played by electric field and indigenous surface active components of a crude oil i.e. asphaltenes. The study has implications in electrostatic crude oil dewatering wherein the shape and stability of the coalescing droplets play a paramount role in kinetics of film thinning and droplet merging. The low magnitude DC electric fields are chosen in order to keep the electrostatic deformation marginal. Therefore, any shape change occurring after the field is applied can be attributed to the developing properties of the drop interface. The externally applied electric field was perpendicular to the direction of gravity. The tangential electric stresses exerted at the interface are balanced by hydrodynamic stresses[13]. However, in the case of a drop held at the tip of a needle, such stresses are asymmetrically distributed. Also the different curvature of the drop interface near the needle tip contributes to asymmetric stress distribution[37]. The stress due to inertia is zero in the case of a pendent drop and it can be observed for a quite long period. To best of our knowledge this is the first detailed study wherein the changing shape of a water drop, surrounded by an asphaltene solution in electric field, is monitored over a long period of time. The shape evolution of such a drop implicitly indicates the

revised hydrodynamics and mass transport at the drop interface.

The observations reported in this study are important in a variety of multiphase applications where stability of the interface is critical. Crude oil emulsions are characterized by very stable interfaces thanks to the indigenous components of the oil[36]. In electrostatic coalescence of two droplets in a water-in-oil emulsion, the film thinning is a time limiting stage[33]. The curvature of the thinning interfaces which is determined by its interfacial tension governs the rate of the film drainage and coalescence. In the formation of pickering emulsions, use of electric field influences density of particles at the drop interface which in turn determines the stability of the emulsion[38]. The electrostatic emulsion-phase contactor is remarkably energy efficient compared to the conventional liquid-liquid extractors[39]. The electric field in the contactor can be fine tuned to optimize the mass transfer. Similar setup was used by Tsouris et al[40] as a bioreactor for oil desulfurization using a biocatalyst.

II. EXPERIMENTAL

A. Chemicals

The asphaltenes used in this study were extracted from a heavy crude oil from Norwegian continental shelf, the detail extraction procedure is described in reference[41]. The asphaltenes dissolved in xylene (98.5 %, VWR), at different concentrations ranging from 0.043 to 0.103 kg/m^3, was the medium phase while the drop was made of Milli-Q water. The maximum concentration was decided based on visibility of the drop as the high concentration solutions are dark and a CCD camera, used in this study to capture the drop profile, can not clearly visualize the drop. All the experiments were conducted at room temperature ($\approx 22^o$ C).

B. Electric field

The schematics of the experimental system in Figure 1(a) shows a pendent water drop surrounded by an oil medium held between two parallel electrodes. The drop was formed at the end of a capillary which was placed between two stainless steel electrodes (20 mm $\times$ 20 mm $\times$ 1 mm). A steady uniform DC electric potential ranging from 50 V to 400 V was applied across the electrodes which were fixed 1 cm apart. A function generator (Agilent Technologies DSO-X 2022A) and an amplifier (Trek 609E-6) were used to apply the electric

field. The strength of electric field selected such that the drop does not experience a large shape deformations. The distortion of the electric field due to the presence of drop itself was neglected.

C. Drop shape analysis

We used Profile Analysis Tensiometer (PAT 1, Sinterface Technologies, Germany) to generate a drop of the desired size and continuously capture its profile. PAT 1 has IMAQ PCI-1408 acquisition board which can acquire frames at 25 images per second and detect the edge of the image.The dosing system of the unit precisely controls the drop volume. The volume of the drop was maintained at 30 μl throughout the experiment. The drop was surrounded by 20 ml asphaltene solution in a glass cuvette. The minute changes in drop shape were continuously captured by a CCD camera, which was fitted with a Schneider-Kreuznach Componon-S 2.8/50 enlarging lens, at 1 frame per second. The cartesian coordinate data of the drop profile was then processed independently for the shape analysis. Every experiment was repeated for at least 4 times to establish repeatability of the results.

III. RESULTS AND DISCUSSION

A freely suspended drop when exposed to an electric field assumes a new equilibrium shape. The shape is a result of balance between Maxwell stresses at drop interface and the stabilizing surface tension forces. Taylor's discrimination function[13] $K = \frac{\epsilon}{\tilde{\epsilon}}\left((\frac{\tilde{\sigma}}{\sigma})^2 + 1\right) - 2 + 3\left(\frac{\epsilon}{\tilde{\epsilon}}\frac{\tilde{\sigma}}{\sigma} - 1\right)\left(\frac{5\frac{\mu}{\tilde{\mu}}+3}{5\frac{\mu}{\tilde{\mu}}+5}\right)$, which is independent of the electric field and drop size, determines the resultant shape. Where ϵ, σ and μ denote resistivity, conductivity and viscosity, respectively. The physical and electrical properties of drop phase are denoted with a tilde ($\sim$) while the notations without $\sim$ denote the medium phase properties. A polar drop in a non-polar medium deforms in the direction of electric field assuming a prolate shape. Such a spheroidal deformation of a levitated drop has been commonly defined by Taylor deformation D $= \frac{l-b}{l+b}$, where l and b are lengths of polar and equatorial axes, respectively.

A pendent drop is symmetric about its vertical axis but the shape irregularities at its neck, close to the tip of capillary from where drop is generated, introduce an up-down asymmetry. The pendent water drop, when exposed to an electric field, deforms in the direction of the
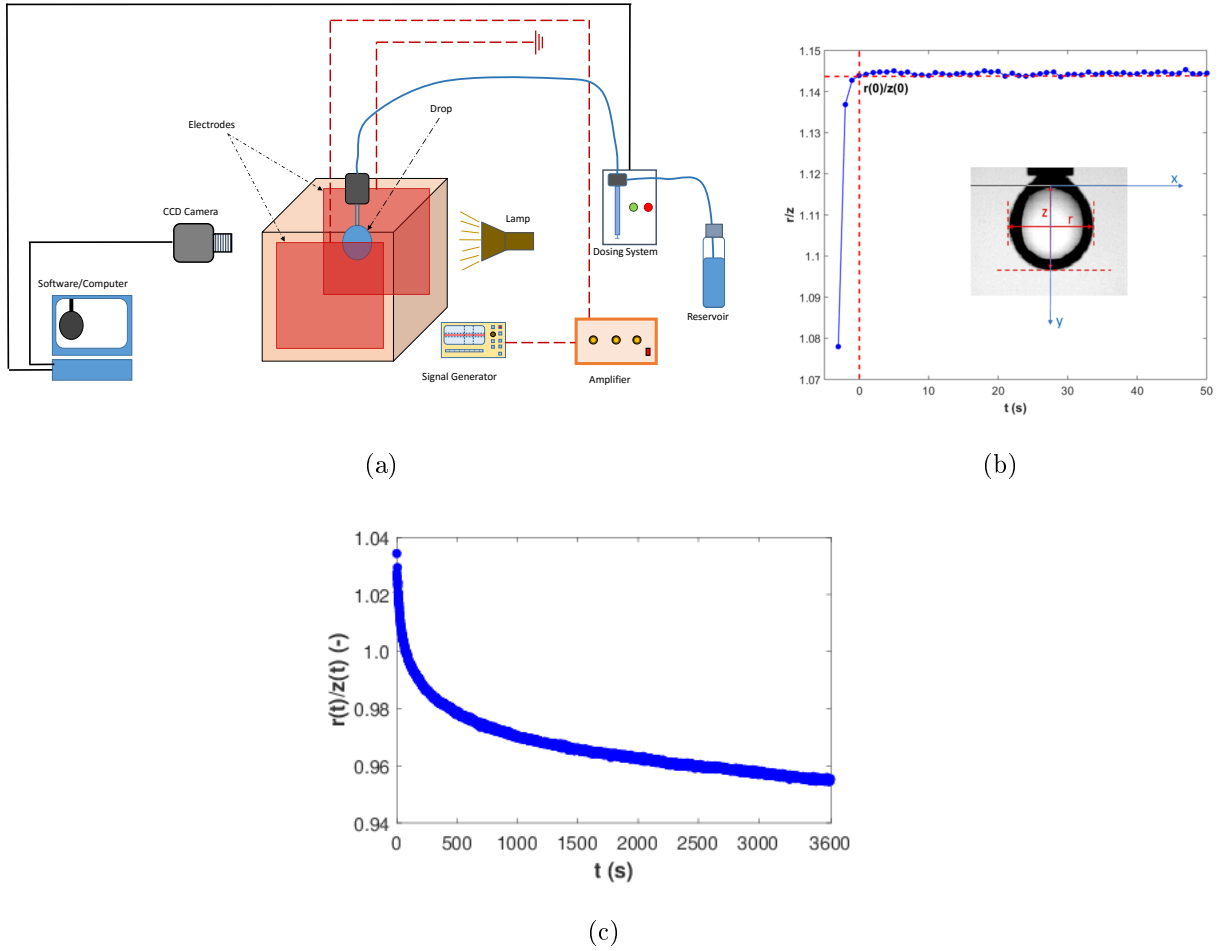
FIG. 1: (a) Experimental setup used to capture the profile of a pendent water drop in asphaltene solution and to apply electric field perpendicular to the drop's axis of symmetry. (b) The lengths of drop's axes (inset) and instantaneous stretching of the drop in response to the electric field. (c) The temporal aspect ratio of a pendent drop in 0.103 kg/m^3 solution under 0.2 kV/cm.

field. As the externally applied electric field in the present study is perpendicular to gravity, the electrostatic deformation breaks the symmetry about the vertical axis.

The new shape is asymmetric about drop's both axes. We characterized such an asymmetric shape of the pendant drop in an electric field using shape deformation factor,

$$DD = \frac{r(t)/z(t)}{r(0)/z(0)} - 1. \tag{1}$$

The lengths r and z are measured in the plane passing through the drop's vertical axis and

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parallel to the direction of the field. $r(0)/z(0)$ in (1) is the r/z ratio immediately after the electric field is applied. The definition of DD is similar to that used by Degen *et al.*[24] in their experiments. As shown in Figure 1(b), r/z rises sharply after the field is applied, attaining a new stable value at $t = 0$ s. The rise in $r(t)/z(t)$ upon application of the electric field suggests drop deformation in the direction of the field. We monitored the r/z ratio at times $t > 0$ s. The typical development in r/z when the bulk phase contains asphaltenes in shown in Figure 1(c). The factor DD represents the change in shape of the drop after initial sudden deformation which was purely due to the electric stresses. However, the changes in DD thereafter can be implicitly credited to the electric field driven phenomena. Note that we characterize electrostatically deformed shapes of levitated and pendent drops using different factors D and DD respectively.

A. Deformation of a clean drop

The clean drop system was realized by suspending a Milli-Q water drop in pure xylene. Figure 2 shows DD of the drop under different strengths of the electric field in the absence of surface active compounds in the medium phase. As the perfectly conducting (PC) drop phase (i.e. water) is surrounded by the less conducting oil phase, immediately after application of electric field the drop undergoes shape deformation in the field direction and the $r(t)/z(t)$ ratio shows a sudden rise (as demonstrated in Figure 1(b)). However, subsequently the DD remains constant over the period of electric field application, suggesting unchanged shape of the drop at t> 0 s. The DD measured at the range of electric field, $E_0 = 0$ - 0.4 kV/cm, is negligibly small and remains so while the field is on.

To make certain the unvarying shape of the drop, we applied electric field for an hour and recorded x-y coordinates of the drop contour. The lengths of both axes scaled with their lengths immediately after switching on the electric field. The resulting r(t)/r(0) and z(t)/z(0) ratios plotted in Figures 3 (a) and 3 (b) indicate that any change in the drop profile is limited to the period of electric stress appearance i.e. instantaneously after the electric field is switched on, but the drop maintains its shape subsequently. The unvarying shape of the drop, after the initial sudden stretching, is a characteristic of nonexistent surface active compounds which would alter the interfacial properties over the course of field application. However, the deformation of the drop is asymmetric about vertical axis as
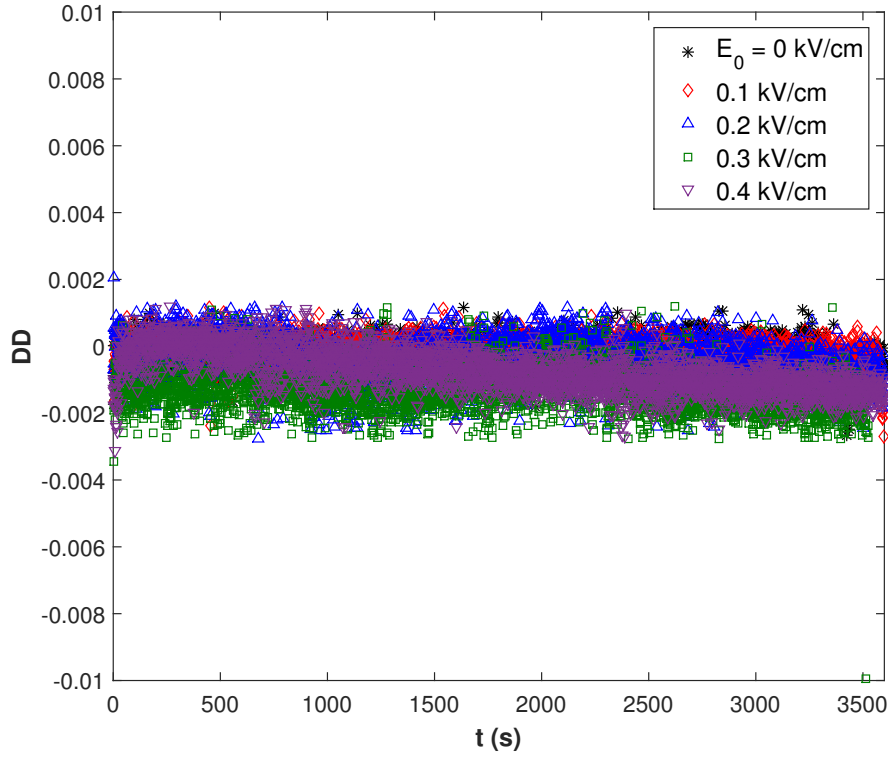
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FIG. 2: Shape deformation factor of a pendant water drop in pure xylene under constant DC electric field for one hour.

the electrostatic stresses stretch the drop surface in the horizontal plane while gravity pulls the drop downward.

The strength of the externally applied electric field (E_0) in our experiments is selected such that the observed shape distortions remain low. Moreover, a stronger field could drift the drop horizontally as the gap between the electrodes is only one order of magnitude greater than the drop diameter. The electric field strengths are just enough to alter the hydrodynamics in and around the drop.
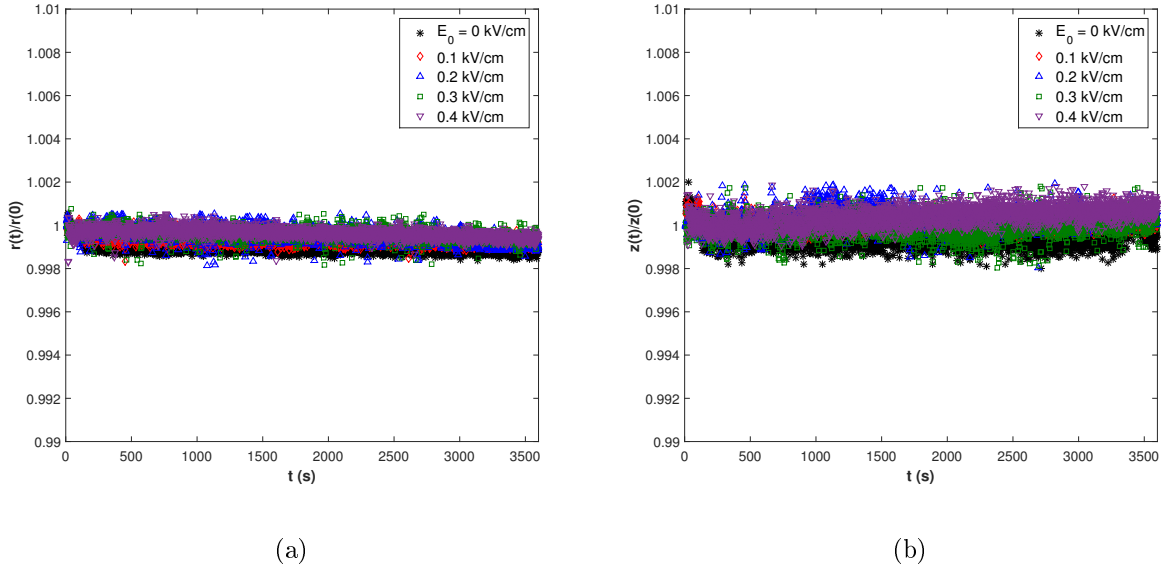
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FIG. 3: Temporal evolution of (a) horizontal axis and (b) vertical axis of a water drop in pure xylene under different strengths of the applied DC electric field.

B. Deformation of an asphaltene-laden drop

1. No electric field

The previous axisymmetric drop shape analysis (ADSA) studies of an asphaltene-laden pendant drop, in the absence of electric field, suggested the reduction in the interfacial tension (γ) over time[35,42]. The ADSA literature lacks the deliberation on shape evolution of such a drop where the growing population of asphaltene molecules at the interface imparts new shape to the drop. Figure 4 shows evolution of such a shape and corresponding interfacial tension.

When the drop interface is not experiencing any external forces except gravity, the interfacial tension reduces with the concentration of asphaltenes in the medium phase. We measured the interfacial tension of a water drop in asphaltene solutions at concentrations used in this study, which is plotted in Figure 5(a). The interfacial tension is a function of asphaltene concentration. The DD attained by a drop in these solution after an hour shows the similar trend with concentration as shown in Figure 5(b). The Figures 5(a) and 5(b) suggest that a drop undergoes a minute shape change as its interfacial tension reduces as a
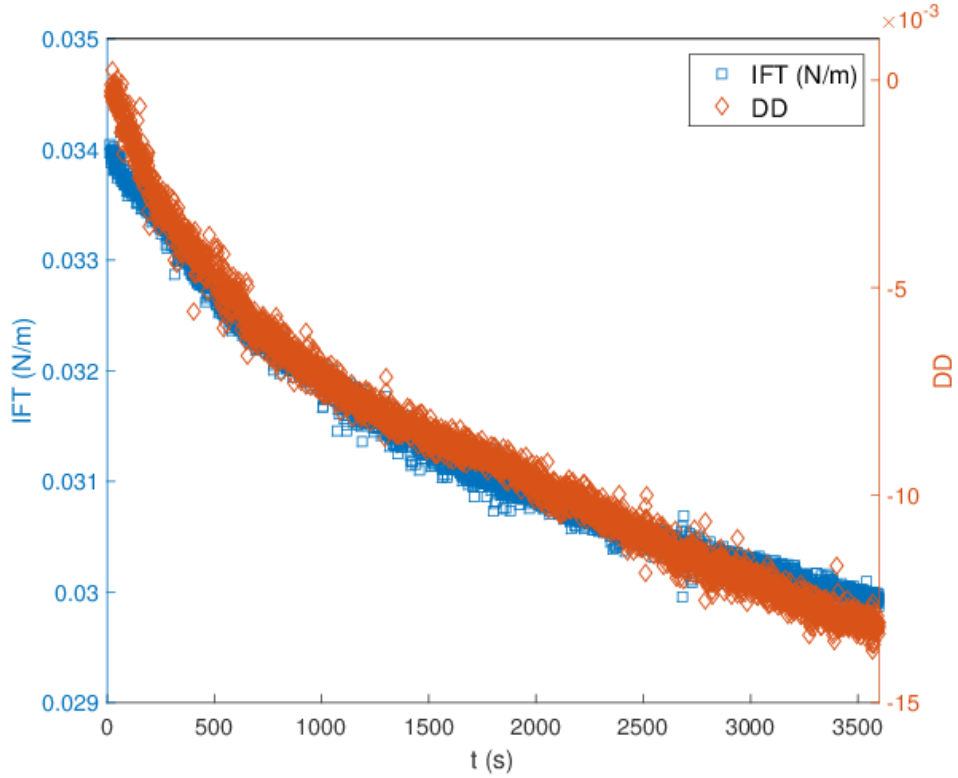
FIG. 4: Interfacial tension and deformation of a water drop in an asphaltene solution $C_0 = 0.064$ kg/m^3 in the absence of electric field.

result of increased asphaltene population at the interface.

2. Effects of electric field

A drop surrounded by the bulk phase containing asphaltenes was subjected to the electric field for an hour. In this case the drop shape evolution is determined by phenomena implicitly triggered by a combined action of asphaltene adsorption to the drop interface and the electric field. The changing DD of the drop in electric field at different concentrations of the asphaltenes (C_0) is plotted in Figure 6. Given the dark color of the asphaltene solution, the concentrations used in this study were chosen in such a way that the drop can be clearly seen by the camera. Four asphaltene solutions with concentrations ranging from 0.043 kg/m^3 to 0.103 kg/m^3 were used.

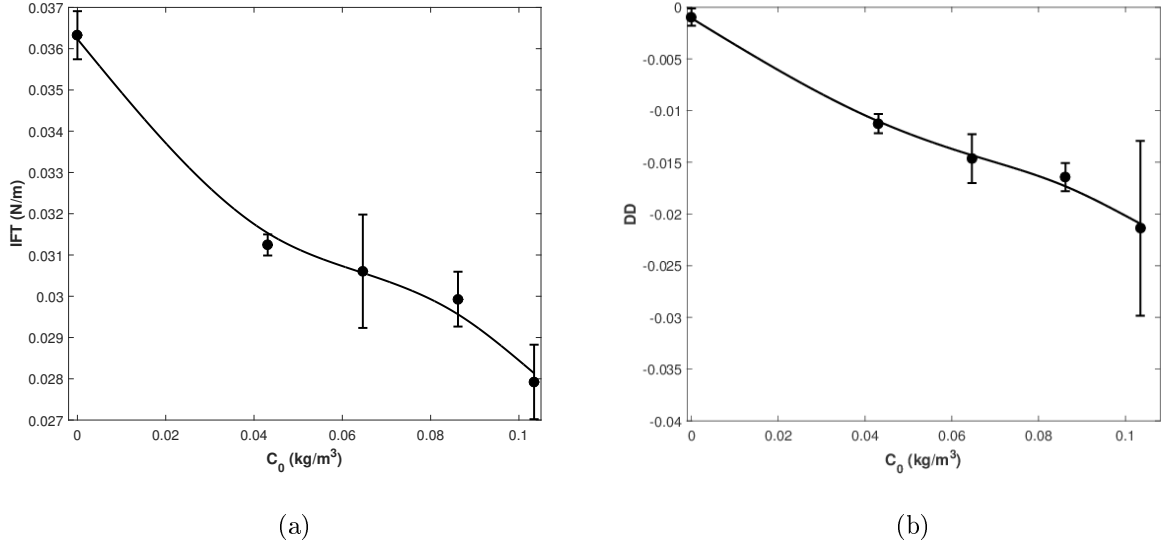Unlike the drop in pure xylene, DD of the asphaltene-laden drop shows variation over

FIG. 5: (a) Interfacial tension of a water drop after 1 hour as a function of asphaltene concentration in the absence of external forces. (b) DD of the drop at the different asphaltene concentrations.

time. Figure 6(a) shows that the DD of a drop in C_0=0.043 kg/m^3 solution fell marginally in an hour when the electric field was off. The initially steady reduction becomes sluggish subsequently. Similar trend was observed at the higher concentrations in Figures 6(b)-6(d). However, when the drop was exposed to the electric field, the reduction in DD was amplified. At all the asphaltene concentrations studied the reduction was observed to be augmented up on increasing the strength of the electric field. Furthermore, the shape of drop follows similar trend irrespective of strength of the electric field, initial steep fall followed by a shallow reduction in DD. However, the extent of the initial fall is determined by magnitude of the electric field. Subsequent difference in the DD descend remains constant as the DD shows a little change at the longer times. The trends suggest the drop does not attain an absolute equilibrium shape after 1 hour.

Apparently the DD reduces over time irrespective of the strength of the applied electric field. Unlike the clean water-oil system the drop continues changing shape after the initial sudden stretching in the electric field direction. Interestingly the stretching is in the vertical direction although electrostatic stresses exist in the direction perpendicular to gravity. The instantaneous shape deformation in the electric field direction is due to the sudden appear-
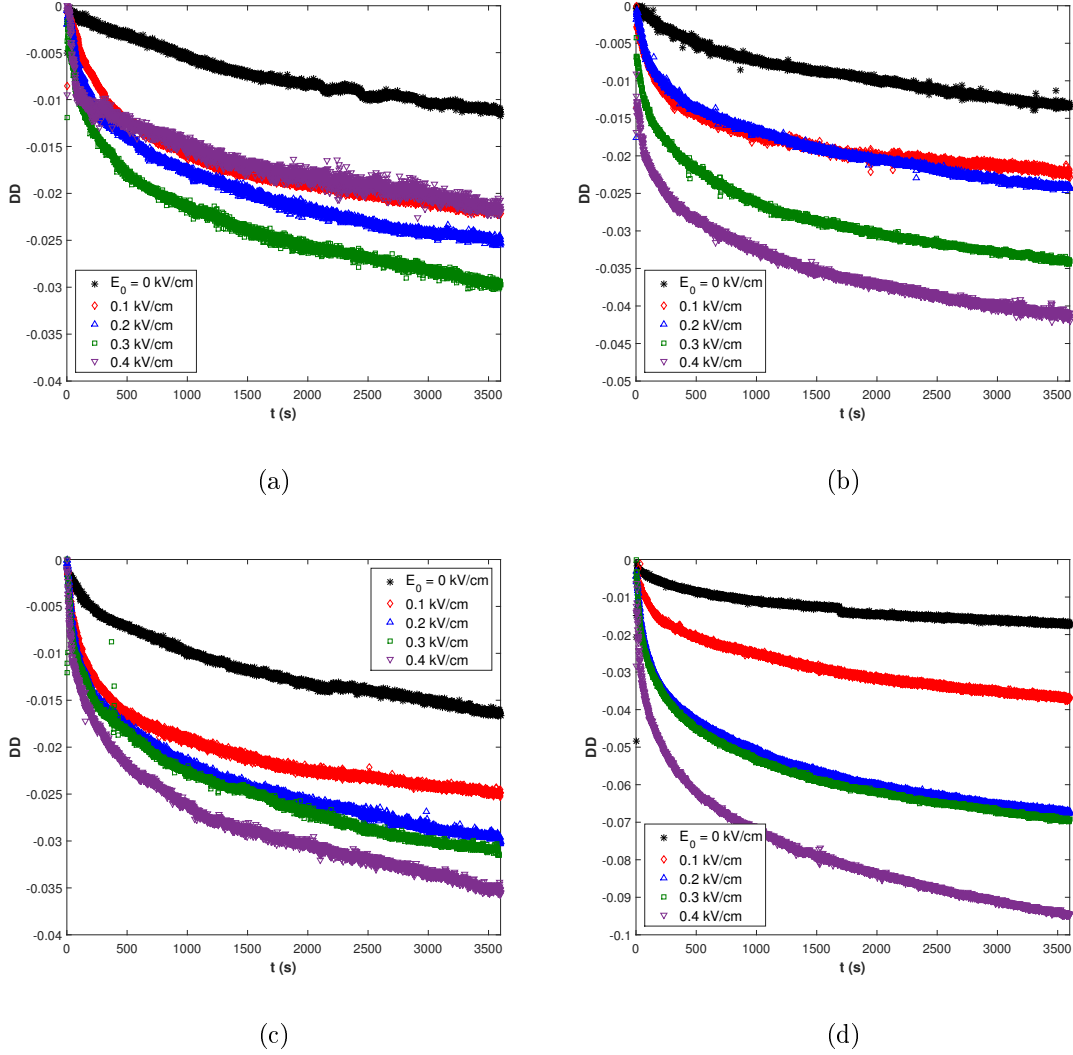
FIG. 6: Degree of deformation of a pendant water drop in asphaltene solutions of concentrations (a)0.043 kg/m^3 (b)0.064 kg/m^3 (c)0.086 kg/m^3 and (d)0.103 kg/m^3.

ance of the electric stresses upon application of the electric field. The subsequent change in the drop shape is a result of the modifying interfacial mass transport under the electric field.

The plots in Figure 6 suggest that although the drop does not completely stop deforming, it attains a near-equilibrium shape at t = 3600 s. The DD of a drop attained after 1 hr at different asphaltene concentrations is plotted in Figure 7. In the absence of asphaltenes at the interface, the drop shape remains unchanged at all the applied electric fields after initial sudden stretching. However, the equilibrium DD of a drop held in an asphaltene solution
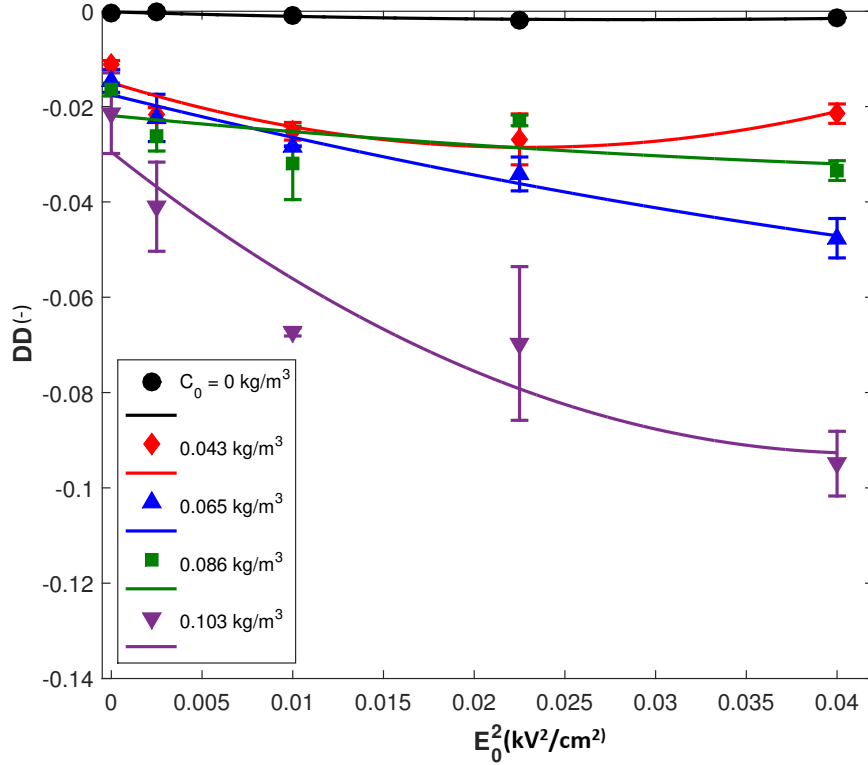
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FIG. 7: Shapes attained by a water drop, after suspending for an hour, in asphaltene solutions of different concentrations under electric field.

decreases upon increasing the magnitude of the field. Furthermore, the equilibrium shape of a drop is a function of asphaltene concentration and the effect is significant when the asphaltene concentration is high.

The increased reduction in DD under electric field in Figures 6 and 7 suggests the intensified alteration of interfacial properties due to the electrostatic effects. In addition to the electrical and physical properties of the fluids, shape of a spheroidal drop in an electric field is considered to be a function of electric capillary number (Ca_E) such that[3],

$$D = f(S, R, M)Ca_E. \tag{2}$$

The electric capillary number is a dimensionless number and defined as, $Ca_E = \frac{\epsilon\epsilon_0 aE_0^2}{\gamma}$ and the property ratios S = $\tilde{\epsilon}/\epsilon$, R = $\sigma/\tilde{\sigma}$, and M = $\tilde{\mu}/\mu$. Discounting the changes in electrical properties of the bulk phase due to the presence of asphaltenes as the concentrations used were small, we calculated the factor $\epsilon\epsilon_0 aE_0^2/DD$ to demonstrate the combined effect of the

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electric field and altered interfacial properties on the drop shape.

After the instantaneous deformation upon electric field is switched on, the factor $\epsilon\epsilon_0 aE_0^2/DD$ decreases continuously. Figure 8 shows the factor $\epsilon\epsilon_0 aE_0^2/DD$ plotted as a function of time in different asphaltene solutions. At all the concentrations the factor reduces over time and the reduction is maximum under strongest field and at the maximum concentration. Note that the higher magnitude of the factor $\epsilon\epsilon_0 aE_0^2/DD$ is an indicator of the stronger stabilizing forces. The reduction in $\epsilon\epsilon_0 aE_0^2/DD$ suggests the interface becomes more stable with time. When a larger number of molecules are present near the interface under stronger electric field, the increased adsorption dynamics leads to the stable interface. Equation (2), which is valid for a drop free from surface active molecules at its interface, indicates that the reduction in interfacial tension is responsible for such a stabilization. However, for asphaltene-laden interfaces it is difficult to point to only interfacial tension as the asphaltene adsorption alter mechanical properties as well[35].

C.   Asymmetry of the drop shape

The recorded drop profiles suggest that the new shape attained by the drop after application of the electric field is asymmetric about its vertical axis. Moreover, the asymmetry continues increasing with time under the constant external electric field. To further analyze the drop shape and investigate the growth in shape asymmetry, we measured the change in lengths of drop's individual axes at times $t > 0$ s.

In Figure 9(a) we plotted diameter (r) of the drop in the direction of the applied field scaled by the r at t = 0 s when the oil phase contained 0.103 kg/m^3 asphaltenes. The reduction in the $r(t)/r(0)$ ratio after 1 hour in the absence of electric field was approximately 1.5 % . However, when the drop was exposed to field E_0=0.1 kV/cm, the ratio reduced by ≈ 2.7 % and by ≈ 3.3 % at $E_0 = 0.4$ kV/cm. On the other hand the reduction in $z(t)/z(0)$ ratio of these drops (plotted in 9(b)) is found to be significantly higher. In the absence of electric field the ratio was reduced by ≈ 2.7 %; but the reduction was ≈ 4.7 % and 6.8% at the fields E_0=0.1 kV/cm and 0.4 kV/cm, respectively.

The disproportionate changes in $z(t)/z(0)$ and $r(t)/r(0)$ ratios are responsible for the growing asymmetry of the drop shape with time. Furthermore, Figures 9 (a) and 9 (b) suggest that the drop is more asymmetric at the higher electric field. Given the fact that the
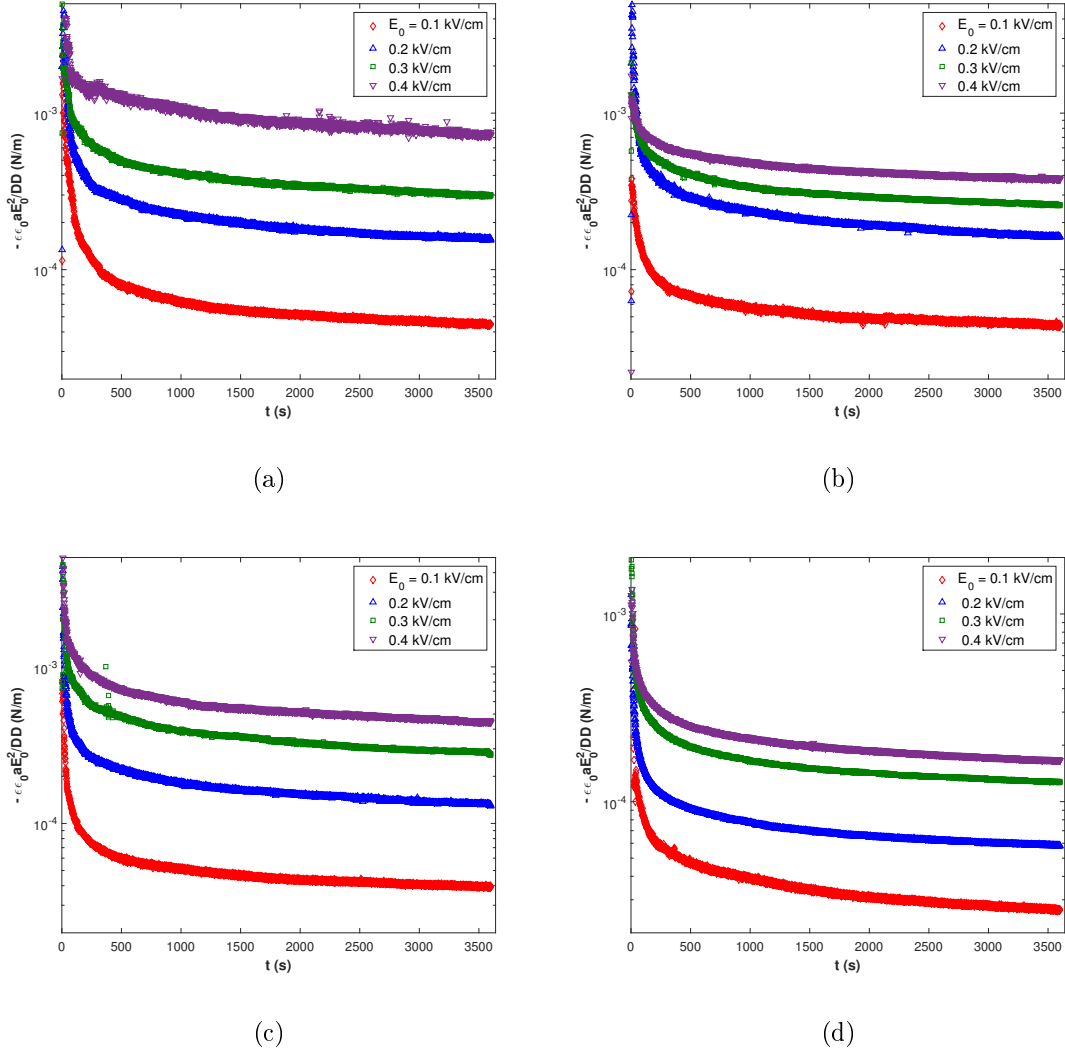
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FIG. 8: The factor $\epsilon\epsilon_0 a E_0^2/DD$ for a pendant water drop in asphaltene solutions of concentrations (a)0.043 kg/m^3 (b)0.064 kg/m^3 (c)0.086 kg/m^3 and (d)0.103 kg/m^3.

applied electric field is horizontal, the observed shape evolution- increasing z and decreasing r - is counter-intuitive. However, the varying extent of the ratio change occurs even when the electric field was off. Evidently the presence of an external force multiplies the asymmetry.

The $z(t)/z(0)$ and $r(t)/r(0)$ ratios of a drop after 1 hour in solutions $C_0 = 0.065$ kg/m^3 and 0.103 kg/m^3 under electric field are plotted in Figure 10. The big difference in the ratios at two concentrations indicates that in addition to the strength of the electric field, the number of asphaltene molecules in the medium phase play a major role in molecular adsorption dynamics, which in turn determines the interfacial properties and drop's temporal shape.
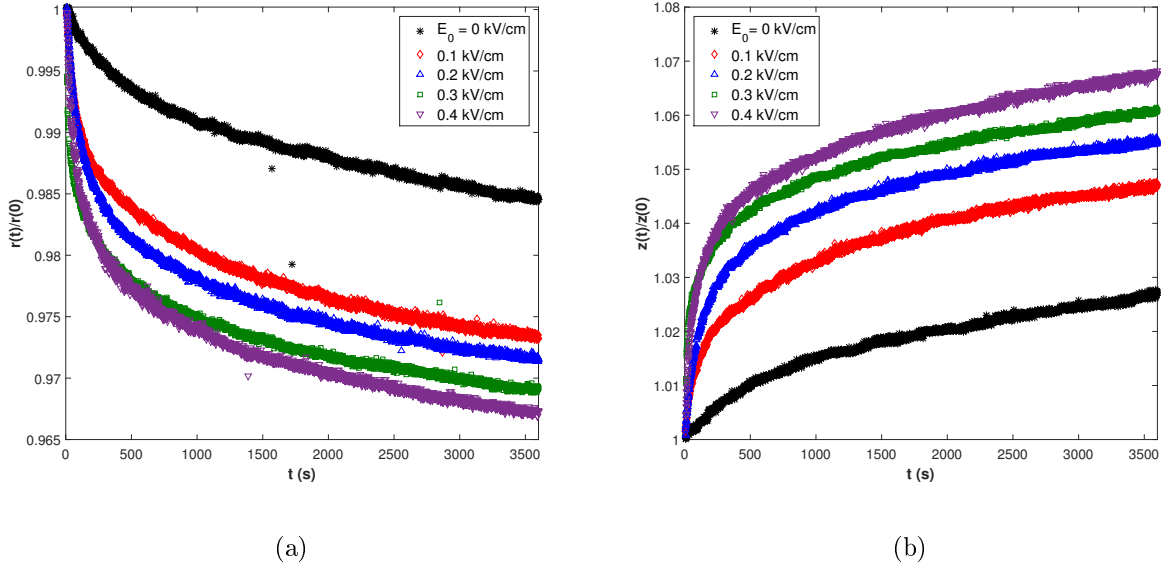
(a)   (b)

FIG. 9: Evolution of the lengths of axes of a pendent drop in 0.103 kg/m^3 asphaltene solution under electric field; (a) scaled horizontal axis $r(t)/r(0)$ and (b) scaled vertical axis $z(t)/z(0)$.

Also, the change in the ratios is apparently larger at a higher concentration. However, the plots suggest the electrostatic effects are limited to the lower strength of the applied electric field. The both ratios level off at higher strengths of the electric field.

Previously Alvarez *et al.* showed that the time scale for diffusion decreases on increasing the curvature of the interface[43] and flow in the bulk phase as long as the Reynolds number is low[44]. When a freely suspended spherical drop is subjected to a steady electric field it assumes a equilibrium spheroidal shape. The new shape is a result of balance between surface tension and stresses exerted by the applied electric field. In the case of a drop held pendent between two parallel electrodes, the fluid motion induced by electric field is limited to the parts of the drop interface facing the electrodes. The flows induce molecular convection towards the high curvature apex part which is relatively undisturbed when the applied electric fields are weaker. Under the stronger electric fields the flows reach the apex leading to the disappearance of the effect on the equilibrium r and z ratios.
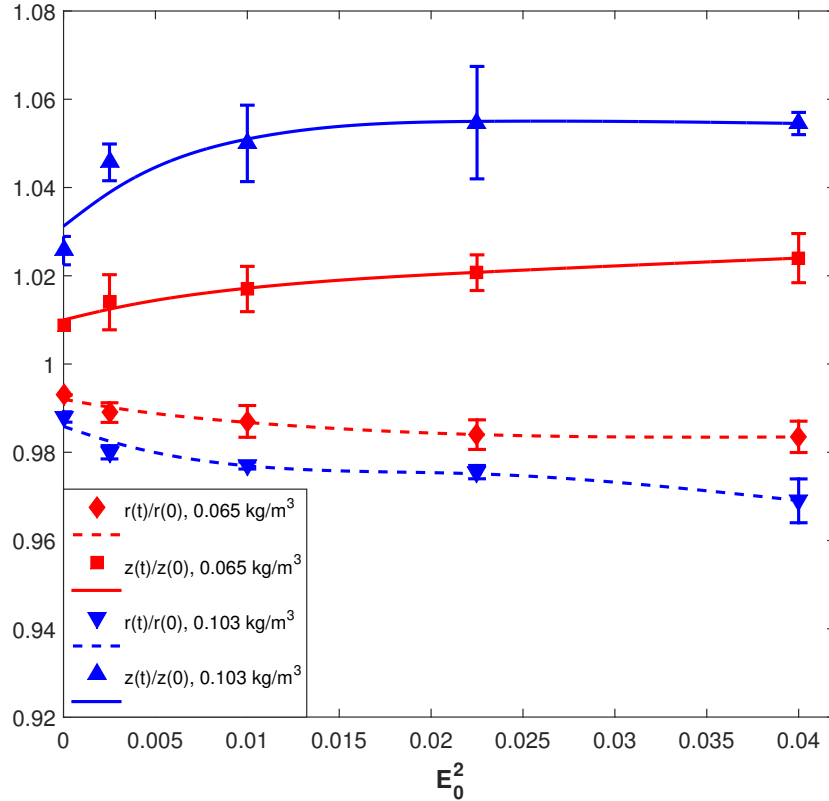
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FIG. 10: Disproportionate change in axes length: $r(t)/r(0)$ and $z(t)/z(0)$ ratios of a water drop after one hour under electric field in 0.064 kg/m^3 and 0.103 kg/m^3 asphaltene solutions.

D.   Shape of an aged drop

As discussed earlier the interfacial properties of a drop, surrounded by a liquid containing surface active molecules, change over time. The previous subsections discussed the shape analysis where the electric field was applied instantly after the drop was generated. The drop interface, to a certain extent, was void of asphaltene molecules at the time of electric field application. In the next set of experiments we aged the drop in an asphaltene solution for an hour before switching on the field. Figure 11 shows effect of electric field on the length of vertical axis of a drop aged in a solution with $C_0 = 0.103$ kg/m^3 before putting it in to the electric field. During the aging $z(t)/z(0)$ ratio increases steeply in the beginning before attaining an asymptote. When a very weak electric field (E_0=0.05 kV/cm) applied

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at t = 3600 s, the ratio showed a substantial rise from its steady value. Although, $E_0 = 0.1$ kV/cm did not further lift the $z(t)/z(0)$ ratio, increasing the electric field to $E_0 = 0.2$ kV/cm resulted into a notable increase. Akin to the trend at $t < 3600$ s, upon application of an electric field the z-ratio of the aged drop was observed to increase sharply, the growth slows down subsequently.

The aged drop and freshly generated drop in 0.103 kg/m^3 asphaltene solution attain different shapes after 1 hour in an electric field. The data plotted in Figure 9(b) shows that the vertical stretching of the fresh drop is 4.7 % at E$_0$=0.1 kV/cm and 5.5 % at E$_0$=0.2 kV/cm. On the other hand, the extent of the aged drop's vertical stretching is quite low; 0.5 % and 1.3 % at E$_0$=0.1 kV/cm and 0.2 kV/cm, respectively. The results suggest that even a weaker electric field triggers rearrangement of the molecules at the already populated interface. The electric field induced flows assist the convection towards high curvature apex. However, the crowded interface limits further molecular adsorption.

The drop shape analysis in this study confirms that the interfacial properties change over the time in the presence of surface active compounds even in the absence of external forces. The adsorption dynamics is faster in the beginning when the interface is free from the molecules and slows down after the interface becomes populated. A polar drop surrounded by a nonpolar phase undergoes a shape deformation in the direction of applied electric field irrespective of its interfacial properties at the time of the field application. The pendent drop in asphaltene solution shows a similar deformation. However, the negative growth of DD with time in Figure 6 is an indication of the changed direction of drop deformation and its intensification with the strength of electric field. Since the every external parameter is kept unchanged after the field is switched on, the only plausible reason for the changing shape is the evolving interfacial properties. The change in factor $\epsilon\epsilon_0 a E_0^2/DD$ with time, electric field and asphaltene concentration (Figure 8) is a clear sign that the interface stabilizes upon increasing these parameters. The previous studies involving a water drop in asphaltene solution in the absence of external forces pointed to the similar effects through the temporal intefacial tension data[35,42]. Given the asymmetry of the drop shape, extraction of such interfacial attributes is not possible in the case studied here. However, the observations are significant to point to the fact that the externally applied electric field enhances mass transport at the drop interface leading to the transformed interfacial properties and a more stable interface. Our observations (to be published) on a vertically applied electric field
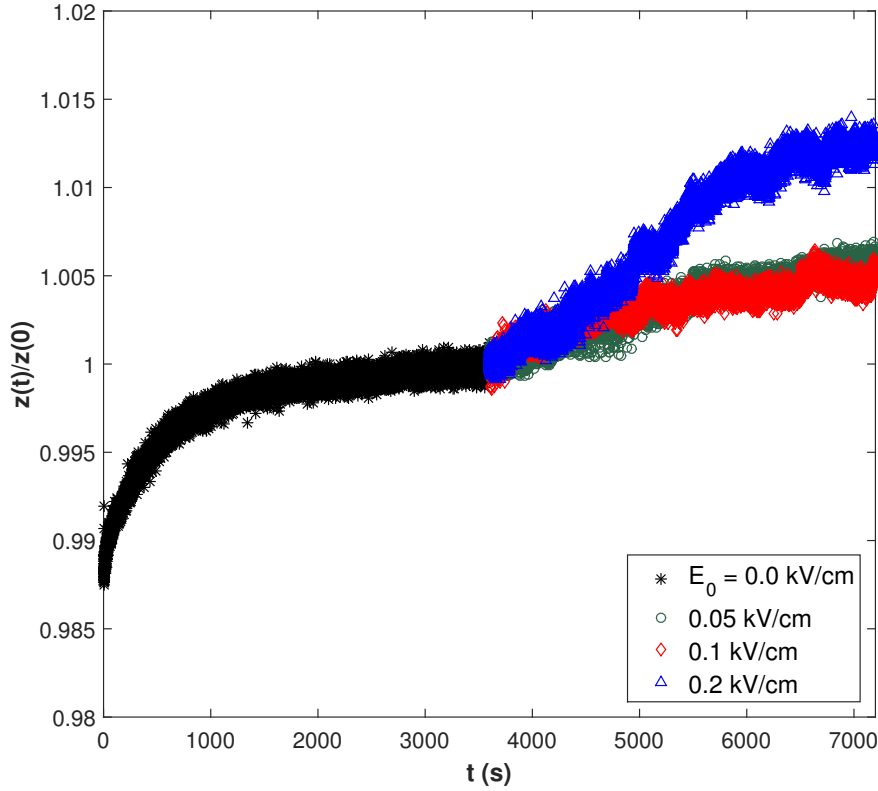
FIG. 11: Effect of the electric field on shape evolution of a drop aged in asphaltene
solution ($C_0 = 0.103$ kg/m³) for one hour.

suggest that the drop deforms symmetrically about y-axis and such shapes can be used to evaluate properties of asphaltene-laden interfaces.

CONCLUSIONS

The present study discusses microscopic shape change of a pendent drop held in an asphaltene solution and effects of externally applied electric field. The drop shape evolves over time as the molecular adsorption progresses irrespective of the external forces. We analyzed the shape of a pendent drop for an hour which undergoes minute changes in the shape and studied the role of asphaltene concentration and electric fields. The low strength DC electric fields are applied in the direction perpendicular to gravity. Instantaneously after the field is switched on, the drop deforms in the direction of the field due to the sudden

appearance of Maxwell stresses. However, as the time progresses drop starts stretching in the direction perpendicular to the field which is not observed when asphaltenes are absent in the bulk medium. The latter shape variations are attributed to the electric field- induced modification in the interfacial properties. The shape evolution occurs as the asphaltene adsorption progresses irrespective of the strength of the field. However, the presence of electric field found to intensify the deformation.

Our analysis of drop geometry highlights the disproportionate variation of drop's major axes following the initial deformation. The striking outcome of the analysis is that the drop shrinks in the direction of applied electric field while stretching vertically. The larger extent of the stretching relative to the shrinking adds up the asymmetry of the drop shape. The drop turns out to be more asymmetric at higher asphaltene concentrations and under stronger electric fields. Additionally, the shape of an aged drop implies that the applied electric field triggers rearrangement of a crowded interface. The phenomenon is more profound when the interface is void of asphaltene molecules as a freshly formed drop is found to be deformed more compared to the aged drop in an electric field.

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