

Forecasting the Problem of Excessive Oil Entrainment in a Desalter Using Spinning Drop Method

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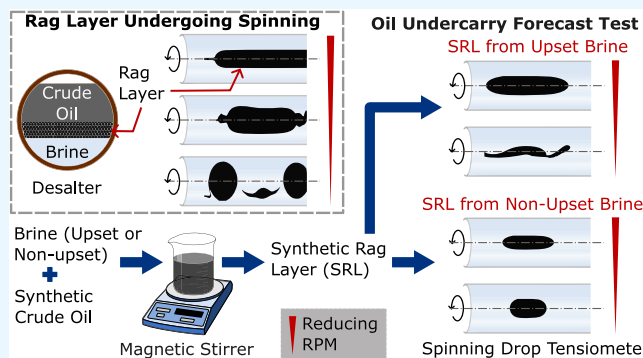
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ABSTRACT: Frequent desalter upsets in the refineries processing opportunity crude oils are often triggered by a rapid and uncontrollable buildup of the rag layer, a thick water-in-oil emulsion, at the oil–brine interface. This is caused by spontaneous emulsification of brine in oil. This study investigates a unique observation from a spinning drop (SD) tensiometer, revealing the low apparent interfacial tension and rigidity of SD caused by spontaneous emulsification. Fine droplets of brine generated through spontaneous emulsification decorate the SD surface and form a stable, low-energy bilayer. Simulated rag layers using the brines from upset incidences exhibit similar behavior, indicating that spontaneous emulsification is driven by chemical species in brine, which promote osmotic water transport. The rate of rag layer buildup correlates with the rate of spontaneous emulsification, with the temperature coefficient of interfacial tension reduction serving as a sensitive indicator. An imminent upset in the operation can be forecasted by measuring this temperature coefficient, enabling preventive measures.



1. INTRODUCTION

Crude oil received in the refinery contains well-dispersed brine droplets. If these droplets are not removed from the crude oil, several problems arise in downstream refining operations. These include corrosion and fouling of distillation columns, pipelines, and heat exchangers, deactivation of catalysts, etc. An electrostatic desalter is a unit used in refineries to remove brine from crude oil before processing it further. In a typical desalter, crude oil is preheated to a temperature ranging from 100 to 150 °C, mixed first with a demulsifier and then with wash water. The crude oil–brine dispersion enters the desalter, where it is subjected to an electric field. The electrostatic attraction among the droplets polarized by the electric field helps them coalesce and grow bigger. The bigger drops settle down due to gravity, and the settled brine is taken out from the bottom of the desalter.¹

The interface between the crude oil and the pool of the separated brine in a desalter unit usually consists of a buffer layer where large drops undergo hindered settling. The water drops must pass through this layer before they coalesce with the interface. In some situations, a thick viscous layer is formed at the interface. This layer is customarily known as a rag layer.² Figure 1 shows a schematic of an electrocoalescer exhibiting a rag layer.

In order to restore normal operations, the rag layer needs to be removed along with the brine, which causes entrainment of

oil along with the brine. Usually, this entrainment is small and manageable. However, under certain circumstances, the rag layer builds up rapidly with time. The rag layer removed from the desalter carries a significant amount of oil with it. This phenomenon is therefore termed “oil undercarry”. In extreme cases, the entire desalter unit must be drained, thus necessitating a complete shutdown of the refinery operation. This condition is also termed a “desalter upset event”. In such a case, disposal of the rag layer may have a harmful impact on the environment and is a great concern globally.³ Understanding the root cause, the mechanism responsible and the parameters that influence the rapid buildup of the rag layer will be critical in mitigating this issue in refineries.

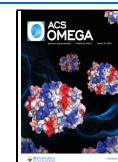
As the crude oil resources continue to deplete, refineries resort to processing crude oils with higher concentrations of asphaltenes and naphthenic acids. These crude oils are called opportunity crude oils, and although usually low-priced, they demand a comparatively higher processing cost. Moreover, modern refineries nowadays process blends of crudes prepared

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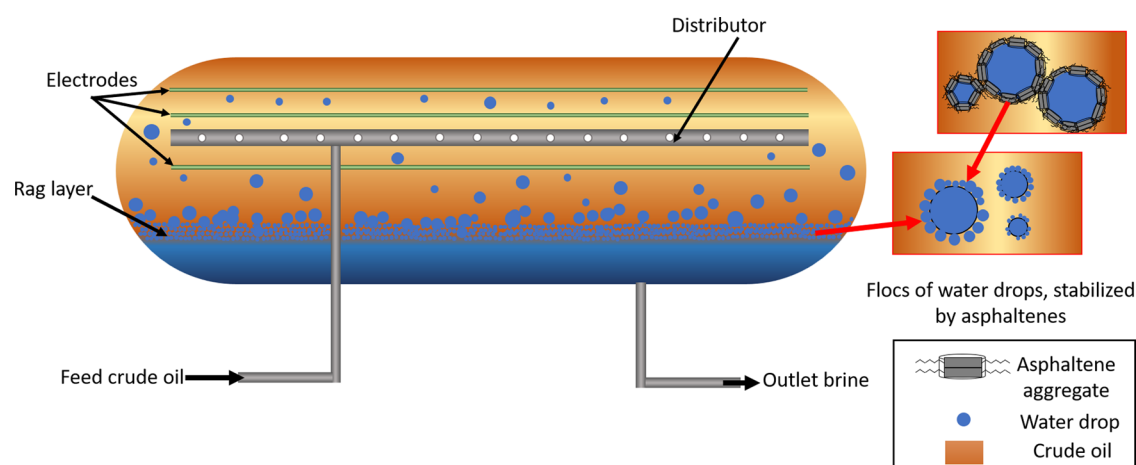


Figure 1. Schematic of a desalter having a rag layer. Flocs of water droplets formed in the rag layer are shown in the enlarged view.

by mixing a vast array of feedstocks with different API gravity, asphaltene and resin contents, total acid numbers (TANs), paraffin contents, and contaminants. Oil entrainment problems are more frequent and severe while processing such crude oils. Frequent upsets in processing the opportunity crude oils can tilt the balance unfavorably, such that higher operating costs could counterbalance the benefits of the low-priced feedstock. Significant research has been done recently to understand the compatibility of crudes in a blend of crude oils, using principles based on colloidal stability.^{4–6} The studies performed on crude oil compatibility do not provide sufficient information that can facilitate the prevention of a rapid buildup of the rag layer in desalters, and the problem still persists.

Rag layers are usually generated during enhanced oil recovery. They are either oil-in-water or water-in-oil emulsions and may also contain fine solid particles. For example, water-in-oil emulsions are generated during water/steam flooding of porous rocks for heavy oil recovery.^{7,8} They are also formed when bitumen is extracted from bitumen-carrying sand using water.⁹ On the other hand, oil-in-water emulsions are generated during surfactant flooding of rocks carrying heavy oils^{10–13} and flooding of anionic surfactant solutions containing silica nanoparticles.¹⁴

The existing literature contains various studies aimed at characterizing the rag layers and determining the causes for their stability. Varadaraj and Brons¹⁵ observed that the rag layer is a complex fluid composed of flocs of water droplets in oil, water droplets stabilized by submicron-sized sediments, double emulsions of oil–water–oil type, etc. They also observed that the elastic and viscous moduli of the rag layer were higher than those of water-in-oil emulsion, indicating a complex microstructure at the interface. Evdokimov et al.¹⁶ observed that the drops of water in the rag layer follow a bimodal distribution, with larger droplets following a log-normal distribution and smaller droplets following an exponential distribution. The exponential distribution of the smaller droplets led these authors to suggest spontaneous emulsification as a possible origin for the nucleation of drops. Bochner de Araujo et al.^{17,18} reported the spontaneous formation of water droplets when asphaltene dissolved in toluene or Heptol was brought into contact with water. Saadatmand et al.⁹ proposed that factors such as hindered settling, noncoalescence or slow coalescence of the droplets, and accumulation of asphaltene-coated water droplets at the

oil–water interface contribute to the thickening of the rag layer.

Attempts have also been made to reduce the extent of rag layer generation. Jiang et al.¹⁹ showed that adjusting pH and the addition of silicate can be helpful in the removal of the rag layer. Sellman and Mandewalkar²⁰ suggested the use of intermittent voltage spikes to reduce the buildup of the rag layer. Stark and Asomaning²¹ performed bottle tests and proposed the use of chemical demulsifiers along with asphaltene stabilizers to achieve better demulsification. Khan et al.²² used supercritical water and fine-tuned the effect of temperature (350–400 °C), pressure (25–35 MPa), and emulsion concentration (10–100 wt %). They observed that, at 400 °C, interfacially active species decreased and the naphtha-to-diesel fraction increased, achieving a clear oil–water separation in supercritical water. Balsamo et al.²³ examined the stability of oil–water emulsions at high temperatures for demulsifier screening, correlating results with factors like compressibility, film crumpling, drop detachment ratios, and interfacial tension. Adeyanju and Oyekunle²⁴ performed stability tests on crude oil–water emulsions, varying parameters like temperature, demulsifier concentration, mixing time, salt content, pH values, and modifier concentration. They also derived empirical model equations for both emulsions and optimized parameters for maximal separation. Hajivand and Vaziri²⁵ screened nearly 25 water-soluble and oil-soluble demulsifiers for water separation efficiency, considering factors such as temperature, concentration, pH, salinity, and modifiers.

It is worth noticing that a significant portion of the research in the literature is on the rag layers generated during the extraction of heavy oils (having a high asphaltene content) from the oil-bearing rocks/sands using either water/stream or surfactant solutions. Emulsification in these cases occurs under the action of shear. The rag layers in the electrostatic desalter are different. First, the feed to the desalter is obtained by blending heavy oils with light oils so as to keep the asphaltene content of the feed low. Second, the dispersion of brine drops at the inlet of the desalter is resolved under the action of an electric field so that the brine drops arriving at the interface are much larger in size. Third, the hydrodynamic condition at the oil–water interface is nearly quiescent and hence is not conducive to emulsification. This leads us to believe that the rag layer is generated in these desalters through spontaneous emulsification. Spontaneous emulsification occurs in the absence of an external input of mechanical energy. Hence, it

has been termed autoemulsification by Duboué et al.²⁶ These authors observed spontaneous emulsification in several crude oil–water systems as well as asphaltene-laden toluene–water systems. Silva et al.²⁷ observed spontaneous w/o emulsification at a heavy hydrocarbon–water interface in the presence of an oil-soluble nonionic surfactant, Span 80, and found that the rate of emulsification increases with a decrease in salinity of the aqueous phase. This led them to suggest that the emulsification is caused by the transport of water from the aqueous phase to the oil phase by Span 80. The steps involve the initial formation of reverse micelles of the surfactant in the oil phase, which undergo swelling with time to form water drops. Emadi and Sohrabi²⁸ observed that the interaction between crude oil and low-salinity brine results in microdispersion of brine in the oil phase. Such a fine dispersion is absent in high-salinity brine. Duboué et al.²⁶ reported spontaneous emulsification when water and crude oil were contacted. They also observed that the rate of spontaneous emulsification decreases with increasing salt concentration. Hence, they concluded that spontaneous emulsification is an osmotically driven phenomenon and is induced by “osmogeneous” species (species having a high affinity for water), which transport water from the brine phase into the oil phase, where nucleation of water occurs. These nuclei grow with time, forming drops. High salinity reduces the osmotic driving force, thereby slowing the rate of nucleation and the rate of subsequent generation of water drops.

The present study was performed on samples received from a two-stage desalter operated in a refinery. Occasional desalter upset events were experienced with the desalter. The salinity of the brine in the desalter is kept low so that the salt content of the treated oil is below the set limit. Hence, one of the conditions needed for spontaneous emulsification is satisfied. The second condition is that the osmogeneous species need to build up to a critical level to induce rapid spontaneous emulsification. Unfortunately, there is no way to assess both the concentration and osmogenicity of the species present in the desalter. This refinery processes blends of several crude oils, among which some are opportunity crude oils. The feed composition varies depending on the constituents of the blend. Identifying the components in feed crude oil is extremely difficult. Additional complexity arises because of possible synergies between the different components of the crude oil in stabilizing the emulsion. Hence, it is difficult to forecast whether a particular crude oil would cause an upset and how long the operation can be sustained with such crude oil without causing an upset. Recognizing the path that will lead to the upset conditions in a desalter operation at a later time would help forecast an impending upset. This would prompt the operator to take necessary measures, allowing the desalter operation to follow a stable path, thereby preventing its upset.

In this work, we developed a test to forecast the impending desalter upset using the spinning drop (SD) technique. W/O emulsion is prepared using crude oil and brine samples withdrawn periodically from the desalter. A drop of emulsion is spun in the capillary of the tensiometer. Due to the centrifugal action, water drops in the emulsion are forced against the boundary of SD. If the crude has a tendency toward spontaneous emulsification, then parent emulsion drops generate much finer droplets that pack closely and tightly on the inner surface of SD. This causes the SD surface to become rigid. On stepping down the spinning speed, buckling and disintegration of SD are observed. This behavior is a sign of a

tendency toward spontaneous emulsification. Moreover, a bilayer with a very low interfacial tension is developed in the region of contact between the attached brine droplets and the SD surface. With an increase in temperature, the rate of spontaneous emulsification increases and the fraction of the surface area of SD, which is covered by the bilayer region, increases. We have shown that the dependence of the interfacial tension on temperature can be used as a very sensitive measure for forecasting desalter upset.

2. BRIEF DESCRIPTION OF THE DESALTER OPERATION

A schematic diagram of the two-stage desalter is shown in Figure 2. The operating temperature of the desalter is about

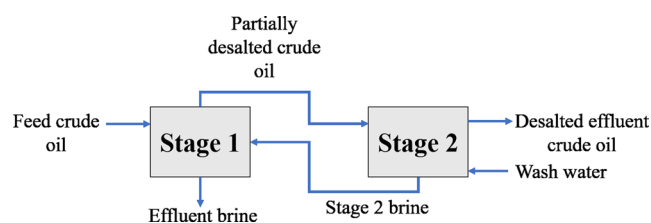


Figure 2. Schematic representation of a two-stage desalter.

150 °C. Crude oil containing very fine droplets of concentrated brine at a holdup of the order of 0.5% v/v flows in the direction counter-current to the wash water. The feed crude oil to the desalter enters stage 1, whereas the wash water enters stage 2. The wash water extracts brine from the crude oil in two stages so that the crude oil containing a low volume fraction of dilute brine exits stage 2, whereas the wash water containing the extracted salt exits stage 1. Wash water flowing from stage 2 to stage 1 carries with it water-soluble surface-active components extracted from stage 2. A further buildup of surface-active components occurs in stage 1. Sand also accumulates at the bottom of stage 1 and adsorbs the impurities from the wash water. These stored adsorbed impurities act as a reservoir of surface-active and osmogeneous impurities, changing the composition of wash water at later times. Desalter upset can occur when the critical concentration of the impurities is attained in the first stage of the desalter. Therefore, the upsets were invariably observed in stage 1 of the desalter.

3. MATERIALS AND METHODS

To study the characteristics of the rag layer, samples from the oil–brine interfacial layer from stage 1 of the desalter were collected. Table 1 lists the samples obtained for the desalter upset incidences of different severities, along with the samples from normal operations. The extent of the desalter upset is

Table 1. Samples from Desalter Upset and Nonupset Incidences

case	the extent of upset (%)	phases present in the sample
A	21.1	feed crude oil, brine, rag layer
B	10.7	feed crude oil, brine, rag layer
C	0.035	feed crude oil, brine
D	<0.03	feed crude oil, brine
E	<0.03	feed crude oil, brine

measured in terms of the entrainment of oil along with the brine stream drained from the desalter and is given in Table 1.

The extent of the upset was high for cases A and B; therefore, samples of the rag layer could be isolated for these two cases (see Figure 3). For case C, as the upset was very

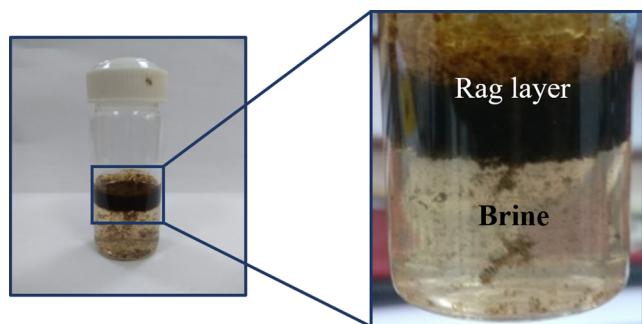


Figure 3. Brine from the upset incidence consisting of pure brine and rag layer.

mild, it was not possible to isolate the rag layer from the dispersion. For normal cases D and E, the rag layer was absent. Properties of crude oils that were fed to the desalter and effluent brine from stage 1 of the desalter are given in Tables 2 and 3, respectively. Cases D and E were regular operations, showing no upset. All of these feed crude oils were a blend of crude oils recovered from several wells.

Table 2. Properties of Feed Crude Oils to the Desalter for Cases A–C

crude oil of case	density (g/cm ³ at 15 °C)	viscosity (cSt at 40 °C)	TAN	asphaltene	salt (ptb)
A	0.899	28.44	1.072	5.58	
B	0.901	23	0.74	5.34	45
C	0.884	11.9	1.2	6.4	38.8

Table 3. Properties of Brines of Cases A–C

brine of Case	pH	conductivity (μS/cm)	TDS (ppm)	surface tension (mN/m at 20 °C)
A	8.1	4890	2340	43.6
B	8.7	4780	1805	42.4
C	7.4	3910	2275	45.7

Each of the samples, A and B, was allowed to separate into a rag layer and brine layer under gravity settling, as shown in Figure 3.

Some studies were also performed using simulated mixed crude oils, prepared by mixing three crude oils with different APIs in equal volumes. These three crude oils were recovered from three separate oil fields. The samples were provided to us by the refinery. The properties of these crude oils are shown in Table 4. Among these, the heavy crude oil was comparable to

Maya crude oil, which has a 12.3% asphaltene content and a viscosity of 175 cSt at temperatures around 25 °C.²⁹

Experiments were performed using the spinning drop tensiometer (SDT, model: SVT20, DataPhysics Instruments, GmbH), which could safely operate up to 100 °C for samples analyzed in our study. In a typical experiment, a capillary containing a drop of oil (lighter phase) in the brine (heavier continuous phase) was rotated. The drop deforms due to centrifugal force and takes an elongated shape. The steady-state drop shape is attained when the centrifugal force is balanced by force due to interfacial tension (IFT). The IFT can then be estimated from the shape of the drop at the equilibrium. A simplified formula known as the Vonnegut formula, as expressed in eq 1, was used when the drop had a cylindrical shape

$$\text{IFT} = \frac{\Delta\rho\omega^2b^3}{4} \quad (1)$$

Here, $\Delta\rho$ is the density difference between the two phases, ω is the spinning speed, and b is the radius of the drop rotating about its central axis. The instrument was validated by measuring the surface tension of absolute ethanol at different spinning speeds of the capillary and comparing the measured value of the interfacial tension to that reported in the literature. The following experiments were performed using the samples listed in Tables 1 and 4:

1. The interface can become unstable when the IFT becomes very low. To check this possibility, steady-state IFT of feed crude oil was measured with the respective brine at different temperatures. Since the highest operating temperature of measurement is limited to 100 °C, whereas the desalter operates at 150 °C, the interfacial tension at the operating temperature of the desalter was estimated by extrapolation using the Arrhenius plot as shown later.
2. In order to understand the behavior of the rag layer, drops of rag layer samples A and B were spun in the respective brines in SDT.
3. The rag layer consists of W/O emulsion. To mimic the rag layer, synthetic emulsions were prepared using crude oils and different aqueous phases (deionized water, brine from normal operation, and brines from desalter upset incidences). An emulsion was prepared by mixing the crude oil and aqueous phase (1:1 v/v) by mild stirring at 500 rpm using a magnetic stirrer. The aqueous phase was incrementally added drop by drop into a beaker containing the oil while placed on the magnetic stirrer. The reason for choosing the 50% aqueous phase in the emulsion was because the rag layer is formed in the buffer zone where a very high concentration of water droplets exists. Hence, the water content of emulsion becomes very high in that region. To emulate the behavior of the rag layer, we used the highest brine loading that the oil could hold. We monitored water concentration in the emulsion using the Karl Fischer

Table 4. Properties of Crude Oils Used for Preparing Synthetic Mixed Crude Oil

crude oil	API	asphaltene (wt %)	TAN (mg KOH/g)	viscosity at 25 °C (cSt)	Ni (ppm)	V (ppm)	Na (ppm)	Ca (ppm)	salt (ptb)
heavy oil	20	10	<1	140	95	37	2.6	11.7	17
medium oil	30	3	<1	10	16.9	4.2	0.5	1.1	6
light oil	40	<1	<1	3	4.5	17.5	0.5	0.5	3

technique. At a 1:1 v/v loading of the aqueous phase, w/o emulsions were stable. Beyond this loading, the emulsion was unstable and rejected the excess aqueous phase. Another reason for using a high loading of brine was that the rate of spontaneous emulsification increases with an increase in the brine loading, which increases the sensitivity of our forecasting technique (this point is discussed in detail in Section 4). A drop of the emulsion was spun in the capillary of SDT. The continuous phase (brine) used in the spinning drop capillary was the same as the brine used while preparing the emulsion.

4. RESULTS AND DISCUSSION

4.1. Interfacial Tension of Feed Crude Oil against Brine. The rag layer is often believed to be a microemulsion of water in oil.¹⁵ If this is true, then the interfacial tension of the crude oil–brine system should become extremely low at the operating temperature of the desalter. To check this possibility, the interfacial tension of the sample of each crude oil from events A–C (listed in Table 1) was measured against the respective brines. Since the highest operating temperature of measurement is limited to 100 °C, whereas the desalter operates at 150 °C, the interfacial tension at the operating temperature of the desalter was extrapolated through Arrhenius plots. In Figure 4, we plotted the logarithm of interfacial

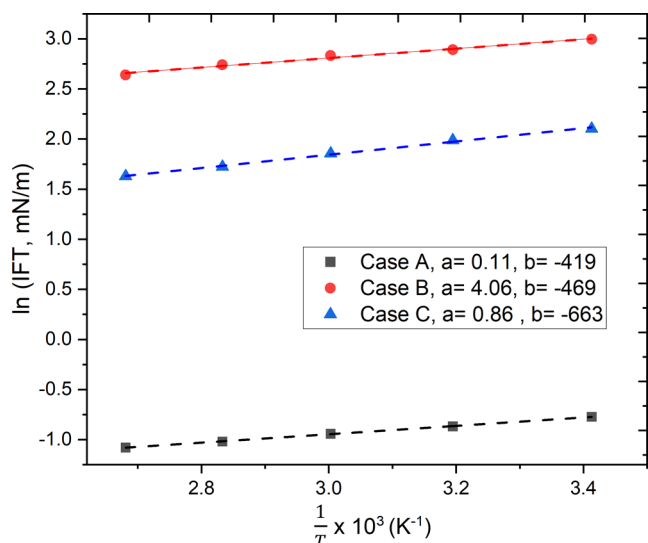


Figure 4. Interfacial tension of the feed crude oil against the respective brine for upset events, $\ln(IFT) = \ln(a) - b/T$.

tensions of the feed crude oil samples against the inverse of the absolute temperature. The coefficient of fit is excellent (>0.99) for all three cases; therefore, the plot can be extrapolated with confidence to 150 °C. Table 5 shows the estimated values of the IFT at 150 °C of the feed crude oil samples from the desalter upset incidences with the respective brines.

It is seen from Table 5 that the feed crude oil and brine pair exhibit low IFT values but are not low enough to classify the feed crude oil as a microemulsion. Moreover, the extent of the desalter upset reported for these instances does not correlate with the measured IFT. From this observation, we conclude that the measurement of the IFT of the feed crude oil against the corresponding brine from the desalter cannot be used as a technique to either detect or forecast the desalter upset.

Table 5. IFT of the Feed Crude Oils with the Respective Brine

case	dispersed phase	continuous phase	IFT (mN/m) at 150 °C (extrapolated)
A	feed crude A	brine A	0.3
B	feed crude B	brine B	12.3
C	feed crude C	brine C	4.1

4.2. Behavior of Rag Layer in Spinning Drop Tensiometer.

The rag layer appeared as a semisolid material to the naked eye. The flocculated plasticity was possibly attained due to the presence of a complex structure of water drops within the rag layer. Varadaraj and Brons¹⁵ characterized the bulk rheology of the rag layer and showed that it is viscoelastic with a higher loss modulus than the storage modulus. The semisolid appearance of the rag layer is consistent with this rheological behavior. In order to probe the interfacial behavior of this rag layer, experiments were conducted by using the spinning drop tensiometer. The capillary of the tensiometer was first filled with brine. A small portion of the rag layer was then stuck to the wall of the capillary by using a spatula. When the capillary was rotated at a sufficiently high speed, the major part of the rag layer disengaged from the wall of the capillary and formed a cylindrical drop on the capillary axis. Moreover, the residual rag layer sticking to the wall of the capillary disengaged slowly in the form of fine droplets, which rolled on the parent drop and formed a cluster at the tips of the drop. The behavior of the drop of the rag layer while spinning is depicted in Figure 5.

There were three important observations associated with the drop of the rag layer undergoing spinning. First, at a fixed speed, the rag layer drop kept on extending without attaining an equilibrium shape. Therefore, it was not possible to measure the IFT of the rag layer. Second, when the droplets of the residual rag layer disengaging from the capillary wall came in contact with the parent spinning rag layer drop, they did not merge with the parent drop but rather rolled on its surface, moved toward the ends of the drop, and formed chains at both ends of the drop. The rolling of these small droplets over the parent drop is depicted in the Supporting Information as a video. The extension of the drop formed by the chain of droplets is also shown in Figure 5a. The extended part of the parent drop is seen to have a diameter smaller than that of the parent drop. This diameter of the extended part of the parent drop is comparable to the size of the smaller droplets, which were detached from the residual rag layer stuck to the capillary wall. Third, when the speed of rotation was stepped down, the drop bent (see Figure 5b), and on a further decrease in the rotational speed, it underwent fragmentation into pieces (see Figure 5c).

Rolling of the emulsion drops on the surface of SD implies that a barrier against coalescence is formed on the surface of SD. We explain these observations as follows. Due to the centrifugal action of SD, the brine droplets present in the emulsion within SD are forced against its inner surface. A film of oil is, therefore, trapped between the drop attached to the inner surface of SD and the brine surrounding SD. The fraction of the total surface area of SD covered by the oil film is a function of the diameter of the droplets. The oil film trapped by larger diameter droplets occupies a smaller fraction of the total surface area of SD, as shown in Figure 6. The surface-active agents in the brine are adsorbed on this oil film to form a

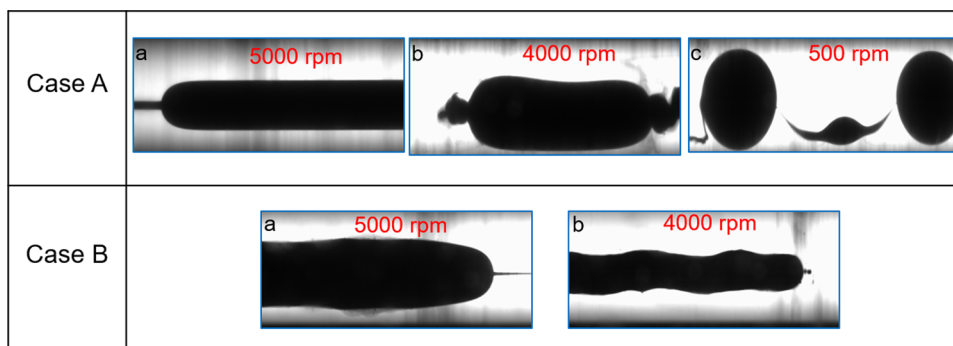


Figure 5. Images of the spinning drop for the rag layer of cases A and B against the respective brine: (a) capillary rotating at 5000 rpm at 20 °C, (b) when the rotational speed of the capillary is reduced to 4000 rpm, and (c) when the rotational speed of the capillary is reduced to 500 rpm.

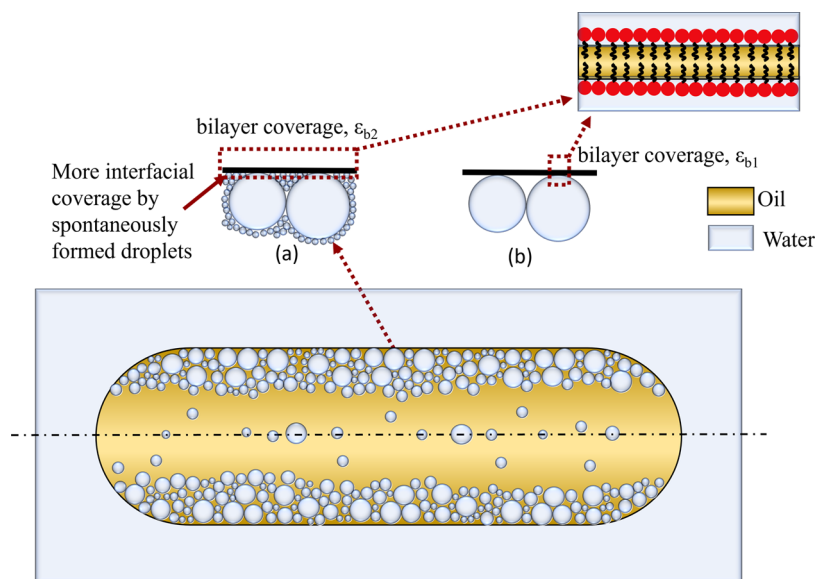


Figure 6. Schematic representation of the possible microstructures present in the parent drop while spinning, showing more bilayer coverage in the case of spontaneously formed microdroplets ϵ_{b2} in panel (a) is $> \epsilon_{b1}$ in panel (b).

bilayer. The headgroups of the surfactants are in the brine on both sides of the bilayer. The tails of these surfactants lie within the oil film. The bilayer so formed provides high stability to the oil film due to the lowering of surface energy on both sides of the film. It has been shown by Yang et al.³⁰ that the rupture time for the foam film, on which surfactants are adsorbed on both sides, is 1 order of magnitude higher than when no surfactants are present on its surface. This film also provides an adhesive force for the droplets to stick to the inner surface of SD. When the emulsion droplets are large, the contact area between them and SD is small, and hence, the strength of adhesion of a droplet with SD is smaller than the inertia of the droplet. Therefore, when SD undergoes axial contraction on the reduction of the spinning speed, the droplets easily detach from its surface and move into its core. In such cases, the SD does not appear to be rigid. When spontaneous emulsification happens, the original droplets degenerate into finer droplets. With the passage of time, these finer droplets can either grow or produce even finer water droplets through nucleation. With an increase in the propensity of spontaneous emulsification, the drop nucleation rate increases compared to the growth rate. As a result, progressively finer droplets are generated. Fine brine droplets pack well at the interface, as shown in Figure 6. As a result, the

area fraction of the SD surface occupied by the bilayer increases. The adhesive strength of these fine drops with the SD surface is also high. This bilayer film, flanked on one side by the densely packed brine droplets, acts as a rigid shell covering SD. This explains why the residual rag layer droplets arriving from the capillary wall do not merge with SD but roll over its surface. This also explains the buckling of the SD and distortion of its shape when the spinning speed is stepped down.

Another property of the emulsion drop when used as SD is the apparent interfacial tension registered by the drop. The surface area of SD is partly covered by the bilayer film and partly by the oil–brine interface. Hence, the interfacial tension γ measured by SD is given by

$$\gamma = (1 - \epsilon_b)\gamma_0 + \epsilon_b\gamma_b \quad (2)$$

In this equation, γ_0 is the interfacial tension of the crude oil–brine interface, γ_b is the interfacial tension of the bilayer, and ϵ_b is the fraction of the surface area of SD, which is covered by the bilayer. Since the surface free energy of the bilayer is lowered on both sides, it is expected to have a much lower interfacial tension. Hence, we expect $\gamma_b \ll \gamma_0$ and can approximate eq 2 by

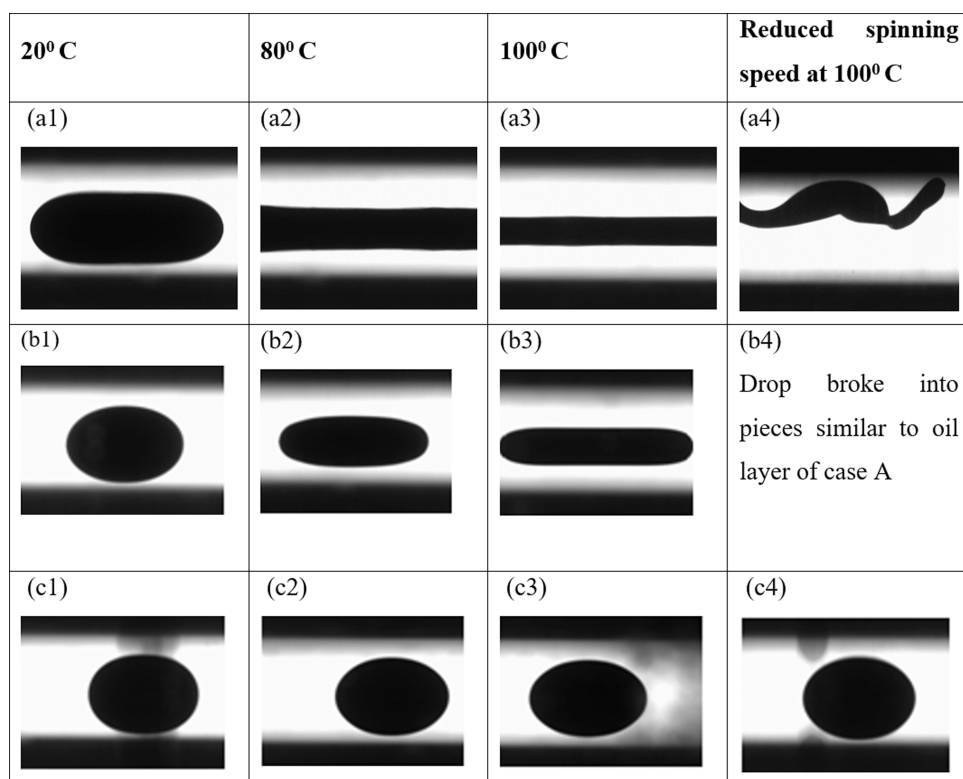


Figure 7. Spinning drop image of the emulsion prepared using synthetic crude oil and brine A (a1–a4), brine B (b1–b4), and deionized water (c1–c4).

$$\gamma = (1 - \epsilon_b)\gamma_0 \quad (3)$$

Equation 3 implies that the interfacial tension registered by the spinning drop decreases as the fraction of the area covered by the surfactant bilayer increases. As mentioned earlier, with an increase in the rate of spontaneous emulsification, fine drops are generated and form a bilayer film, which occupies a larger fraction of the surface of SD. Thus, the interfacial tension of the emulsion drop measured by the SD technique is a sensitive measure of spontaneous emulsification. This is evident from the fact that the rate of spontaneous emulsification is so high that the area fraction ϵ_b occupied by the bilayer film continuously increases with time during the spinning process itself, and hence, SD continuously extends with time, thereby registering a continuous decrease in interfacial tension.

The unique role played by the SD technique needs to be emphasized here. Spinning of the drop facilitates the formation of a bilayer film by forcing the brine droplets to attach to the inner surface of SD. No other known technique is capable of producing such a bilayer using conventional surfactants. Very low interfacial tension of the bilayer can therefore be exploited in order to increase the sensitivity of the technique. It is also important to note the role of the emulsion. First, the brine drops in the emulsion attach to the SD surface and facilitate the formation of a bilayer film. Second, since spontaneous emulsification originates at the oil–brine interface, its rate depends on the oil–water interfacial area. When the emulsion of brine in crude oil is used in SD, the emulsion droplets provide a large interfacial area for the nucleation of the water drops. Hence, the propensity for spontaneous emulsification is enormously enhanced with the emulsion drop. Since the oil–brine interfacial area in the emulsion depends on brine loading, the highest allowable brine loading should be used in order to

maximize the sensitivity of the technique. The role of emulsion in our technique is clear from the following experiment.

The rag layer of case A (which corresponded to the most severe desalter upset) was centrifuged to separate the brine from it. The resulting water-free crude oil drop suspended in the same brine was subjected to IFT measurement. While spinning, the drop did not show any of the phenomena exhibited by the rag layer. Also, the IFT of the centrifuged rag layer–brine interface was found to be nearly the same as that of the feed crude oil–brine interface. This establishes that the presence of small emulsified water droplets in the rag layer and their crowding at the interface of the emulsion drop with brine in the SDT are critical to the low apparent IFT and stretching of the rag layer drop in SDT.

4.3. Role of Brine in Rag Layer Generation. The nature of the brine plays an important role in spontaneous emulsification. It acts as a reservoir for osmogeneous species. A buildup of impurities occurs because the residence time of the brine stream in the desalter is much greater than that of the crude oil. Moreover, the mud present at the bottom of the reservoir also adsorbs the impurities from the brine and releases them at later times. In order to investigate the role of brine in spontaneous emulsification, a simulated rag layer was prepared by emulsifying crude oil with different brines. We call this emulsion a synthetic rag layer (SRL). The crude oil used for preparing SRL was a blend, in equal proportion by volume, of three crude oils with different API gravity received from three different oil reservoirs. The properties of these three crude oils are listed in Table 4 (see Section 3). The asphaltene content of the synthetic crude oil was about 5% w/w. Emulsions of this crude oil were prepared with various aqueous phases (deionized water, brine from upset events A and B, and brine from normal operation) using a magnetic stirrer under

mild stirring for 20 min. Loading of the aqueous phase in the emulsion was 50% v/v. The stability of the resulting SRLs was checked by measuring the water content in the emulsion (using the Karl Fischer technique) after allowing it to settle at 80 °C for 20 min. The emulsions were considered to be stable if the water loss was less than 5%. Figure 7 shows the behavior of the spinning drops of SRLs at different temperatures. Figure 7a–7c shows an emulsion drop formed by mixing synthetic crude oil and brine from events A, B, and deionized water, respectively.

Snapshots 7a1–a4 correspond to a drop of SRL prepared using brine A. The first three correspond to three different temperatures at a fixed spinning speed of 5000 rpm. In all three cases, the spinning drop shapes attained a steady state. The interfacial tension estimated from the drop shape is plotted against the temperature in Figure 8 (black squares). It is seen

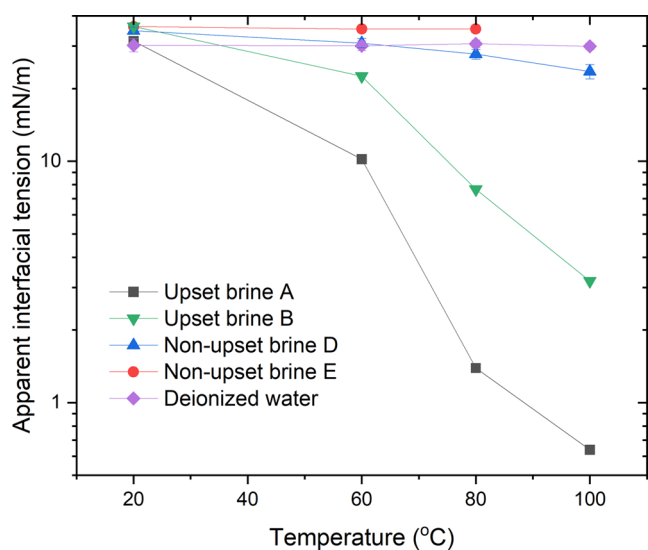


Figure 8. Variation of the apparent interfacial tension (IFT) of SRL with temperature measured in a spinning drop tensiometer at a spinning speed of 5000 rpm. The brine used as the continuous phase in the tensiometer (shown in the legends) is the same as that used in the preparation of SRL.

that the interfacial tension decreases by 2 orders of magnitude when the temperature is increased from 20 to 100 °C. When the spinning speed was stepped down to 4000 rpm from a steady value of 5000 rpm, distortion and bending of the drop were observed, as seen in snapshot a4.

Experimental observations for SRL drop spun in brine B at different temperatures at 5000 rpm are shown in parts b1–b3. The behavior of this drop is similar to the drop spun in brine A, albeit milder, as seen in Figure 8 (green inverted triangles), where the interfacial tension is seen to decrease only by 1 order of magnitude. Distortion and bending of the drop were also observed in this case. The behavior of the apparent interfacial tension of SRL prepared using DI water is shown by violet diamonds in Figure 8. The corresponding shapes of the drop are depicted in snapshots 7c1–c4. We see that the change in the interfacial tension with the temperature is insignificant.

This analysis clearly indicates that brine plays a crucial role in inducing spontaneous emulsification. This tendency arises from both the surface-active and osmogeneous species present in the brine. The literature indicates that asphaltenes and naphthenic acid present in crude oil are responsible for

spontaneous emulsification.^{17,18,31–33} To check the role of the crude oil in the stabilization of the rag layer, we aged the feed crude oil for a period of 2 months. The aged crude oil was unable to form a stable emulsion with any of the brines from the upset/normal incidences. On the other hand, the freshly received feed crude oil could readily form an emulsion with all brines. The inability of aged crude oil to form stable emulsions is most likely due to the deactivation of asphaltenes and other surface-active components. It should be noted that the feed crude oils used in this study were blends of crude oils from several different wells. The asphaltenes and resins present in these oils may not be compatible with each other. This may cause the precipitation of asphaltenes over time, impairing their ability to form a stable emulsion with brine. This implies that the presence of active species in the crude oil is also responsible for stabilizing the emulsion.

4.4. Comparison of the Rag Layer and Simulated Rag Layer (SRL). There are the following similarities between the behavior of the spinning drop of the rag layer and that of SRL prepared using brine from the upset events. Both show significantly low apparent interfacial tension, in contrast to the spinning drop of the crude oil alone or SRL prepared with deionized water. The second similarity is that the spinning drops of both the rag layer and the SRL (prepared with brines from upset events) undergo distortion and disintegration upon decreasing the spinning speed. The difference between SRL and the rag layer is that the deviations exhibited by the former are milder than those shown by the latter. A plausible reason for this observation is that the rate of spontaneous emulsification in the rag layer is much more rapid compared to that of SRL. Since the brine used to prepare the emulsions is the same in the two cases, the only reason for the mild response is that the crude oils used in preparing SRL do not have sufficient concentrations of surface-active impurities needed to mimic the rag layer quantitatively.

The difference in the behavior of SRL prepared with the brines from upset incidences and that with deionized water is also clear from the trends of the interfacial tension presented in Figure 8. For calculating interfacial tension using the Vonnegut formula, we have used the density of the drop phase as the volume-averaged density of the emulsion. However, we expect the number density of brine drops to be greater near the interface, as shown in Figure 6. Hence, the actual density difference is expected to be significantly lower than that used in calculating the apparent IFT. This would also mean that the actual IFT is much lower than that indicated in Figure 8. It is also seen from Figure 8 that the stretching tendency, reflected in the variation of the IFT with temperature, correlates with the extent of upset. When deionized water is used in forming the emulsion, the interfacial tension does not vary with temperature. SRL prepared using nonupset brines shows a much weaker dependence of IFT on temperature. On the other hand, when brines from the upset events are used, there is a sharp fall in IFT with temperature. The fall in interfacial tension is steeper for brine from severe upset than brine from less severe upset (Table 6). This reduction in interfacial tension results from the spontaneous emulsification caused by the brines from the desalter upset events. With an increase in temperature, the viscosity of the crude oil decreases. This facilitates spontaneous emulsification by reducing the capillary number associated with the drop oil interface. Thus, at a higher temperature, the interface is covered with a larger number of smaller drops, which lowers the apparent IFT. Now, the

Table 6. Correlation of the Extent of Upset and Experimental Parameters

case	extent of upset (%)	slope of $\ln(\text{IFT})$ v/s $1/T$	IFT at 100 °C
A	21.1	8702	0.6
B	10.7	6023	3.2
D	<0.03	935	23.5
E	<0.03	542	29.4
deionized water		91	29.7

question arises about how the brines from upset incidences differ from deionized water or other nonupset brines (D and E). The brine builds up impurities over time due to a number of reasons. First, the surface-active impurities present in the crude oil dissolve in the brine and accumulate over time. Therefore, the composition of brine strongly depends upon the type of crude oils with which it is in contact and the time duration of this contact. Second, the mud present at the bottom of the desalter can adsorb the surface-active impurities from brine and not only accumulate them by adsorption but also release them in a delayed manner, thereby acting as a reservoir of the impurities. Third, the recycled wash water can also bring impurities from various unit operations in the refinery through which it passes. Finally, the surfactants added in the oil fields for oil drilling could continue to remain in the crude oil produced in a refinery. It should be mentioned here that identifying the surface-active species that cause spontaneous emulsification is difficult to identify because they can be enormous and minute in amounts. Yet, their combination can have a collective synergistic effect that is very drastic.

5. FORECASTING OF THE IMPENDING UPSET OF ELECTRODESALTER

Based on the observation made in this study, we have devised the following test to forecast the impending upset of desalter. The steps involved in this test are listed below:

1. Collect a sample of the crude oil and the brine from the desalter.
2. Prepare an emulsion by mixing an equal volume of the crude oil and the brine. Use a magnetic stirrer and mild stirring. Mild stirring is purposely used in order not to induce emulsification under high shear.
3. Check the stability of the emulsion by allowing it to stand at 80 °C for 20 min. If the emulsion breaks to yield a separated layer of water, we conclude that the desalter is not susceptible to upset, and no further test is needed.
4. If the emulsion is stable, a drop of emulsion is injected into the spinning drop tensiometer, and the apparent interfacial tension of the drop is measured at 5000 rpm. The size of the drop should be such that at a temperature of 100 °C, its stretch should remain within the limit (i.e., the length of the drop should be about 10 mm from each end of the capillary).
5. The apparent interfacial tension is then plotted against temperature. The degree of variation of the interfacial tension with temperature is an indication of a stable desalter operation.
6. At the end of the test, the drop is spun at 100 °C and 5000 rpm. The speed of rotation of the capillary is then stepped down to 4000 rpm, and the shape of the drop is observed. No distortion of shape indicates that the desalter is operating normally.

7. The test is repeated at regular intervals of time. If the apparent interfacial tension shows a significant fall with temperature and if the steepness of the fall increases for consecutive samples, there is a strong possibility of an upset.
8. The same conclusion can be drawn if distortion of the spinning drop is observed on stepping down of the spinning speed and the extent of distortion increases for consecutive samples. Note that the steep fall of IFT and hysteresis in shape with the spinning speed are concomitant phenomena, and their extent is correlated with the degree of spontaneous emulsification. This test allows us to forecast the impending upset of the desalter.

6. CONCLUSIONS

In this work, an important problem associated with the operation of a desalter, i.e., desalter upset due to a rapid and uncontrollable buildup of the rag layer, is studied. The basic mechanism causing the generation of the rag layer in the desalter is spontaneous w/o emulsification at the oil–brine interface. The conditions needed for spontaneous emulsification are that the brine should have low salinity and the system should contain a critical concentration of osmogeneous species that can transport water from the brine phase into the oil phase. In the present work, we developed a technique based on SD that can detect the tendency toward spontaneous emulsification at an early stage. A drop of emulsion was prepared using the samples of crude oil and brine and mixed in equal volume to form a w/o emulsion. A drop of this emulsion is spun in the brine in the capillary of SDT to form a long cylindrical SD. Due to the centrifugal force generated during spinning, the brine droplets are forced against the SD surface and form a bilayer over the contact region. This bilayer has a very low interfacial tension. Spontaneous emulsification results in finer drops, which cover a greater fraction of the SD area by the bilayer. The bilayer-covered SD is more rigid and resists axial compression. Hence, stepping down the spinning speed results in buckling and distortion/disintegration of SD. Moreover, the bilayer has very low interfacial tension, and hence, the apparent interfacial tension measured by SDT decreases with an increase in the propensity for spontaneous emulsification. With an increase in temperature, the rate of transport of water from brine droplets in the emulsion to the oil phase in SD increases due to an increase in both the osmotic driving force and the diffusion coefficient of water. An increase in the rate of spontaneous emulsification with temperature is reflected in the temperature coefficient of the decrease in interfacial tension. We have shown that this coefficient is a sensitive measure of the tendency toward rag layer buildup and can be used to quantify the propensity to spontaneous emulsification. The trend in this coefficient, with time, can allow forecasting of the impending desalter upset and thereby allow the operator to take appropriate measures to prevent it.

We have also shown that brine separated in the desalter has a major role to play in the desalter upset. The buildup of both surface-active and osmogeneous impurities in the brine happens over time for a number of reasons. The impurities present in the crude oil may dissolve in brine and accumulate over time. Moreover, the mud present at the bottom of the desalter can adsorb the impurities from brine, accumulate them, and exhibit a slow release. Another source of impurities

could be the various uses the recycled wash water is subject to in a refinery, accumulating impurities in the process and bringing them back to the desalter. The exact identification of the components that cause spontaneous emulsification is difficult due to their synergistic effects. However, using this brine for conducting the SD test allows us to quantify its propensity to cause spontaneous emulsification without identifying either the species or their concentrations in the brine.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c08554>.

Rag layer undergoing spinning—rolling of small droplets over the parent drop (AVI)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Eow, J. S.; Ghadiri, M. Electrocoalesce-separators for the separation of aqueous drops from a flowing dielectric viscous liquid. *Sep. Purif. Technol.* **2002**, *29*, 63–77.
- (2) Czarnecki, J.; Moran, K.; Yang, X. On the “rag layer” and diluted bitumen froth dewatering. *Can. J. Chem. Eng.* **2007**, *85*, 748–755.
- (3) Xu, N.; Wang, W.; Han, P.; Lu, X. Effects of ultrasound on oily sludge deoiling. *J. Hazard. Mater.* **2009**, *171*, 914–917.
- (4) Schermer, W. E. M.; Melein, P. M. J.; van den Berg, F. G. A. Simple techniques for evaluation of crude oil compatibility. *Pet. Sci. Technol.* **2004**, *22*, 1045–1054.
- (5) Guzmán, R.; Rodríguez, S.; Torres-Mancera, P.; Ancheyta, J. Evaluation of asphaltene stability of a wide range of mexican crude oils. *Energy Fuels* **2021**, *35*, 408–418.

- (6) Wiehe, I. A.; Kennedy, R. J. The oil compatibility model and crude oil incompatibility. *Energy Fuels* **2000**, *14*, 56–59.
- (7) Liu, J.; Liu, S.; He, Y.; Zhong, L.; Hao, T.; Liu, Y.; Wang, P.; Gao, P.; Guo, Q. Experimental study of produced fluid emulsification during water/steam flooding for heavy oil recovery. *Energy Fuels* **2022**, *36*, 14838–14851.
- (8) Liu, J.; Zhong, L.; Lyu, C.; Liu, Y.; Zhang, S. W/o emulsions generated by heavy oil in porous medium and its effect on re-emulsification. *Fuel* **2022**, *310*, 122344.
- (9) Saadatmand, M.; Yarranton, H. W.; Moran, K. Rag layers in oil sand froths. *Ind. Eng. Chem. Res.* **2008**, *47*, 8828–8839.
- (10) Liu, J.; Liu, S.; Zhang, W.; Zhong, L.; Hao, Y.; Zhang, Y.; Cai, W.; Du, H. Influence of emulsification characteristics on the pressure dynamics during chemical flooding for oil recovery. *Energy Fuels* **2023**, *37*, 4308–4319.
- (11) Liu, J.; Zhong, L.; Hao, T.; Liu, Y.; Zhang, S. Pore-scale dynamic behavior and displacement mechanisms of surfactant flooding for heavy oil recovery. *J. Mol. Liq.* **2022**, *349*, No. 118207.
- (12) Liu, J.; Liu, S.; Zhong, L.; Yuan, S.; Wang, Q.; Wei, C. Study on the emulsification characteristics of heavy oil during chemical flooding. *Phys. Fluids* **2023**, *35*, No. 053330.
- (13) Liu, J.; Liu, S.; Zhong, L.; Wang, P.; Gao, P.; Guo, Q. Ultra-low interfacial tension anionic/cationic surfactants system with excellent emulsification ability for enhanced oil recovery. *J. Mol. Liq.* **2023**, *382*, No. 121989.
- (14) Liu, J.; Liu, S.; Zhong, L.; Li, Z.; Zhang, Y.; Du, H. Porous media flooding mechanism of nanoparticle-enhanced emulsification system. *Phys. Fluids* **2023**, *35*, No. 033304.
- (15) Varadaraj, R.; Brons, C. Molecular origins of crude oil interfacial activity part 3: characterization of the complex fluid rag layer formed at crude oil–water interfaces. *Energy Fuels* **2007**, *21*, 1617–1621.
- (16) Evdokimov, I. N.; Fesan, A. A.; Kronin, A. M.; Losev, A. P. Common features of “rag” layers in water-in-crude oil emulsions with different stability: possible presence of spontaneous emulsification. *J. Dispersion Sci. Technol.* **2016**, *37*, 1535–1543.
- (17) Bochner de Araujo, S.; Merola, M.; Vlassopoulos, D.; Fuller, G. G. Droplet coalescence and spontaneous emulsification in the presence of asphaltene adsorption. *Langmuir* **2017**, *33*, 10501–10510. doi:10.1021/acs.langmuir.7b02638. arXiv:https://doi.org/10.1021/acs.langmuir.7b02638, PMID: 28889742.
- (18) Rodríguez-Hakim, M.; Anand, S.; Tajuelo, J.; Yao, Z.; Kannan, A.; Fuller, G. G. Asphaltene-induced spontaneous emulsification: Effects of interfacial co-adsorption and viscoelasticity. *J. Rheol.* **2020**, *64*, 799–816.
- (19) Jiang, T.; Hirasaki, G. J.; Miller, C. A.; Moran, K. Using silicate and pH control for removal of the rag layer containing clay solids formed during demulsification. *Energy Fuels* **2008**, *22*, 4158–4164.
- (20) Sellman, E.; Mandewalkar, P. In *Highly Efficient Dehydration and Desalting of Crude Oil from Mature Fields in the Middle East*, Proceedings - SPE Annual Technical Conference and Exhibition, January, 2016.
- (21) Stark, J. L.; Asomaning, S. Synergies between asphaltene stabilizers and demulsifying agents giving improved demulsification of asphaltene-stabilized emulsions. *Energy Fuels* **2005**, *19*, 1342–1345.
- (22) Khan, M. K.; Cahyadi, H. S.; Kim, S.-M.; Kim, J. Efficient oil recovery from highly stable toxic oily sludge using supercritical water. *Fuel* **2019**, *235*, 460–472.
- (23) Balsamo, V.; Phan, J.; Nguyen, D. Interfacial films of diluted heavy oil–aqueous systems at elevated temperatures and pressures: Effect of reverse emulsion breakers. *Energy Fuels* **2015**, *29*, 2823–2832.
- (24) Adeyanju, O. A.; Oyekunle, L. O. Optimization of chemical demulsifications of water in crude oil emulsions. *Egypt. J. Pet.* **2019**, *28*, 349–353.
- (25) Hajivand, P.; Vaziri, A. Optimization of demulsifier formulation for separation of water from crude oil emulsions. *Braz. J. Chem. Eng.* **2015**, *32*, 107–118.

(26) Duboué, J.; Bourrel, M.; Carreras, E. S.; Klimenko, A.; Agenet, N.; Passade-Boupat, N.; Lequeux, F. Auto-emulsification of water at the crude oil/water interface: A mechanism driven by osmotic gradient. *Energy Fuels* **2019**, *33*, 7020–7027.

(27) Silva, P. S.; Zhdanov, S.; Starov, V. M.; Holdich, R. G. Spontaneous emulsification of water in oil at appreciable interfacial tensions. *Colloids Surf., A* **2017**, *521*, 141–146.

(28) Emadi, A.; Sohrabi, M. In *Visual Investigation of Oil Recovery by Low Salinity Water Injection: Formation of Water Micro-Dispersions and Wettability Alteration*, SPE Annual Technical Conference and Exhibition, SPE, 2013; p D021S030R004.

(29) Escobedo, J.; Mansoori, G. A. Viscometric Principles of Onsets of Colloidal Asphaltene Flocculation in Paraffinic Oils and Asphaltene Micellization in Aromatics. *SPE Prod. Facil.* **1997**, *12*, 116–122.

(30) Yang, S.; Kumar, S.; Dutcher, C. S. Instability and rupture of surfactant-laden bilayer thin liquid films. *Soft Matter* **2023**, *19*, 5737–5748.

(31) Bochner de Araujo, S.; Reyssat, M.; Monteux, C.; Fuller, G. G. Ablation of water drops suspended in asphaltene/Heptol solutions due to spontaneous emulsification. *Sci. Adv.* **2019**, *5*, No. eaax8227.

(32) Wu, T.; Firoozabadi, A. Surfactant-enhanced spontaneous emulsification near the crude oil–water interface. *Langmuir* **2021**, *37*, 4736–4743.

(33) Joonaki, E.; Buckman, J.; Burgass, R.; Tohidi, B. Water versus asphaltenes; liquid–liquid and solid–liquid molecular interactions unravel the mechanisms behind an improved oil recovery methodology. *Sci. Rep.* **2019**, *9*, No. 11369.