

Surfactants on oil/water interface studied by modified Scheludko-cell

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ABSTRACT

TLF dynamics is the cornerstone of emulsion stability. In this regard, we did a systematic study of TLF of n-dodecane as oil phase in surfactant solutions. A novel 3D-printed modified Scheludko-cell (MSC) has been employed due to its simplicity and the feasibility of gaining concurrent optical responses during the experiment. An increase in TLF conductivity by increasing surfactant concentration and by passing time for one surfactant concentration was concluded. Dynamic interfacial tension (IFT, mN/m) of O/W interface was measured experimentally and the adsorption time-scale was comparable to the study done by MSC.

INTRODUCTION

Interfacial properties of oil/water system plays an important role in designing environmentally sustainable bitumen recovery techniques, whether it is bitumen films in emulsions occurring in oil sands extractions techniques or bitumen droplets present in oil sands process-affected water (OSPW) (Razi et al., 2016). This is due to the occurrence of these stable emulsions that there is such an urgent need to find more environmentally sustainable techniques and methods to break such emulsions. Considering the type of emulsion which can be formed by two liquids, whether it is water in oil (W/O), oil in water (O/W) or oil in water in oil (O/W/O) multiple emulsions, the presence of surfactants is a necessity for emulsion stabilization (Tadros, 2009).

When it comes to emulsions in the oil and gas production and refinery, W/O and O/W emulsions play a significant role in this regard. These kinds of emulsions are very stable due to the presence of highly surface-active indigenous molecular structures which are mainly composed of saturates, asphaltenes, resins, aromatics, solids, clays, indigenous naphthenic acids and waxes (Kokal, 2005). The occurrence of these emulsions is not advantageous due to the problem they cause in oil transportation or catalytic poisoning

owing to their sticky natures. Therefore, there is always a need to find efficient and reliable methods and techniques to resolve these emulsions (Peng et al., 2012).

Steam Assisted Gravity Drainage (SAGD), a comparatively new technology in the category of Enhanced Oil Recovery (EOR) invented by Roger Butler in the 1970s, is utilized to produce bitumen and heavy crude oil. This technology which is a kind of steam stimulation process utilizes high pressure steam to decrease the bitumen froth viscosity and to cause the bitumen slurry to drain into the lower one of two wellbores. Afterwards, the slurry will be pumped out to reach the surface facilities (Council of Canadian Academies, 2015). SAGD offers a number of advantages in comparison with conventional surface mining extraction techniques and alternate thermal recovery methods including significantly greater per well production rates, greater reservoir recoveries, reduced water treating costs, and dramatic reductions in the steam/oil ratio (SOR) (Nguyen, Balsamo and Phan, 2014). In SAGD process, the extracted produced water (PW) is composed of water as the continuous phase, oil droplets which are dispersed in water, clay particles and dissolved organic matter (DOM). This reverse emulsion is generally very difficult to treat due to high total dissolved solids (TDS), total suspended solids (TSS) and high oil content, but it is very important to apply reverse emulsion breaking methods to treat these kinds of emulsions owing to the fact that there are limited numbers of disposal wells (Bosch et al., 2008). Investigating the factors affecting the stability of these O/W emulsions including the presence of endogenous surfactants, DOM, temperature, pH, PW salt content, shearing, mixing and solid contents provides the opportunity to understand the underlying interfacial phenomena in a fundamental level which leads to efficient demulsification. The necessity of breaking these reverse emulsions, by adding a group of ionic surfactants which can be a group of cationic polymers selected from different chemical families has been mentioned elsewhere (Bosch et al., 2008).

Razi et al., studied the effect of SAGD PW properties on oil/water transient interfacial tension. They monitored the interfacial activity of SAGD PW endogenous surfactants, humic acids (HAs), as well as the interaction dynamics of these surfactants with naphtha diluted Alberta oil sand bitumen (AOSB) present in a model SAGD PW, which pinpointed the effect of the dilution ratio of the naphtha-diluted AOSB and the pH of model SAGD PW on the dynamics of O/W interfacial tension (Razi et al., 2016).

In any emulsion system, rate of coalescence of dispersed phase droplets relates to the drainage of the film intervening them. Since the rate of film drainage, thinning and rupture is a kinetic process which depends on the surface properties of the medium, studying thin liquid films (TLF), which is the fundamental structural element of various dispersed systems widely spread in nature including foam and emulsions, is of paramount significance (Anklam, Saville and Prud'homme, 1999; Scheludko, 1967; Toshev, 2008). Razi et al., examined the effect of a different formulation of demulsifiers on the efficiency of chemical demulsification of heavy crude oil. They monitored the stability of these emulsions experimentally using bottle test method and also examined the effect of dynamic interfacial tension (IFT) during emulsion formation using a spinning drop tensiometer. They concluded that the TLF which is formed between water droplets and the oil phase can be analyzed to give a better understanding of the W/O emulsion separation mechanism at a molecular level (Razi et al., 2011).

TLFs hydrodynamics have been studied extensively by several researchers. Subramanian et al., used the interfacial dilational rheology to study the viscoelastic film formation at Oil/Water interface. According to them, this viscoelastic TLF is formed due to the reaction happening between tetrameric acids ARN and calcium ions and they aimed to understand the effects of naphthenic acids (NAs) and asphaltenes on this film. They measured remarkably high values of E' (130 mN/m) at low ARN concentration (10 μM), for the system under study. According to them, the values obtained are 5 to 10 times higher than the values which are obtainable in the case when no Ca^{2+} or other crude oil components such as NAs and asphaltenes are present. By monitoring the effect of presence of asphaltenes and NAs on the viscoelastic film formation, they concluded that the interfacial viscoelastic film is weakened in the presence of NAs or asphaltenes. These two components can inhibit the ARN/ Ca^{2+} film formation, according to Subramanian et al (Subramanian, Simon and Sjöblom, 2016).

In another study by Roberts et al., when DC electric fields are applied to TLFs, there is instability in interface and a series of pillars are formed. Using lubrication theory, they examined the application of AC electric fields to control the pillars size and shape. For perfect dielectric films, they monitored the effect of AC fields by considering an effective DC fields using linear stability analysis, whereas for leaky dielectric films, the Floquet theory was used to perform the linear stability analysis (Roberts and Kumar, 2009).

Bumajdad et al., studied the effect of D_2O content, surfactant concentration, and surfactant mixture composition on the electrical conductivity of D_2O /n-heptane micro-emulsions stabilized by cationic/nonionic surfactant mixtures. They found that micro-emulsion conductivity is independent of the concentration of cationic surfactant which was in agreement with the theoretical micro-emulsion conductivity models (Bumajdad and Eastoe, 2004). On the other hand, Rennell et al., performed the permittivity, loss factor and D.C. conductivity Measurements of TLFs of n-heptanol in both purified and non-purified states. They found clear evidence of interfacial polarization effects which can be fitted to a single mobile charge carrier model (Rennell and Anderson, 1975).

Swan et al. theoretically considered the electrical breakdown of liquid dielectrics (Swan, 1961). They proposed a theory which considers both the applied electric fields effects and positive ions' space-charge field which produces an increasing electron current at the cathode concluding the electrical breakdown of dielectric liquids can depend on the liquid or the cathode (Swan, 1961). Tchoukov et al., studied the TLF formation for the stability of petroleum emulsions. They measured the lifetime, thickness and thinning rates of different emulsions of water-in-diluted bitumen. According to them, the different film properties depend on the solvent-to-bitumen ratio (S/B) and solvent aromaticity. They found a change in the film properties at specific dilution ratio. They previously monitored the abrupt change in bulk emulsion properties at critical S/B. They observed rigid W/O interface and formation of small asphaltene aggregates at critical S/B and also formation of stable films and film thickness increase at dilution ratios above critical S/B. They concluded this may be due to the build-up of a multilayer at W/O interface.

TLFs stability measurements have been done using a micro-interferometric TLF technique (Tchoukov, Czarnecki and Dabros, 2010). Panchev et al., developed a method based on the micro-interferometric Thin Liquid Film-Pressure Balance Technique (TLF-PBT) to study W/O emulsion TLFs. They concluded that the rate of film drainage depended strongly on the bitumen to toluene dilution ratio with the most

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concentrated solution. They measured the critical rupture of TLF (with the diameter was being maintained at 200 μm) as a function of film thickness for two bitumen concentrations with the applied DC voltages of 25 mV/s (Panchev et al., 2008) which was in accordance with the research of Khristov et al. and Taylor (Khristov et al., 2000; Taylor, 2002). These studies show an urgent need for developing new and advanced technologies for TLF studies. Considering the fact that TLF dynamics is the cornerstone of emulsion stability, we did a systematic study of TLF of oil phase in surfactant solutions. A novel 3D-printed modified Scheludko-cell (MSC) has been employed due to its simplicity and also feasibility of gaining concurrent optical responses during experiment. Therefore, in the first section of this study, we present the formation of TLF of oil phase and its detection using DC voltage. In the second section of this work, we examine the effects of surfactants adsorption dynamics on TLF electrical behavior.

EXPERIMENTAL SECTION

Materials. Sodium dodecyl sulfate (SDS, chromatographically pure, Fisher Scientific, CAS 151-21-3), has been used as surfactant in water phase. Different aqueous surfactant concentrations has been prepared (0.02, 0.05, 0.1, 0.2 wt% of SDS). Water used in these experiments was milli-Q water (pH=5.73) obtained from lab-scale Millipore purification process. pH of the aqueous solutions was measured using a Mettler Toledo pH-meter. N-dodecane (Fisher Chemical, Laboratory grade, LOT 149004) has been used as oil phase. Supporting electrolyte was 0.2 M KCl (Fisher Scientific, Certified ACS). The modified Scheludko-cell (MSC) which has been designed using 3D CAD design software has been 3D-printed using Form2 3D-printer, using GPCL02 resin material as it is seen in Figure 1 (b). Copper wires (Malin Co., .0253 PHOS. Bronze, LOT#25611) have been used as electrodes inserted in the pre-fabricated place for electrodes in the cell.

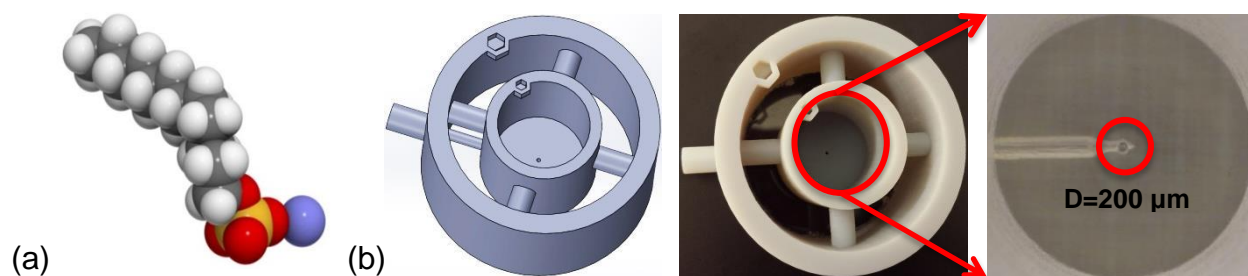


Figure 1. (a) sodium dodecyl sulfate (SDS) chemical structure as the water phase surfactant (b) Computer-aided design (CAD) model and 3D-printed modified Scheludko-cell (MSC) for study of W/O thin liquid films

Methods. The experimental setup used in the present work for electrical detection and visual observation of the formation of TLFs of oil phase is composed of the following parts. Hamilton micro-syringe (10000 μL , GASTIGHT#1010) has been used for the injection of the oil phase through the system. The electrical conductance of the system has been measured using a Princeton Applied Research Potentiostat/Galvanostat model 263A. CorrWare software has been used for data acquisition. The TLF formation

was visualized using a ZEISS Axiovert 40 CFL, inverted microscope. A Hitachi Kokusai Electric CCD camera model KP-M22AN was used for digital imaging of the films formed. The MSC is filled with the surfactant solution and using the Hamilton micro-syringe and syringe pump the oil phase is injected into the system. The electrodes are applied in the cell in such a manner that they have the same height inserted in the upper and lower surfactant aqueous phase. The electrical conductance of the system is monitored using the Princeton Applied Research Potentiostat/Galvanostat. Oil-phase TLF formation is then detected using the system resistance measurement. Using MSC depicted in Figure 1 (b), and using the experimental set up shown in Figure 2, we were able to generate the TLFs of oil phase (n-dodecane) in dispersed phase of SDS solution. To prepare the dispersed phase, we prepared different concentrations of SDS in Milli-Q water. Thin liquid films of n-dodecane (radius = 100 μm) were made in a 3D-printed modified Scheludko cell. A schematic drawing of the experimental setup is depicted in Figure 2.

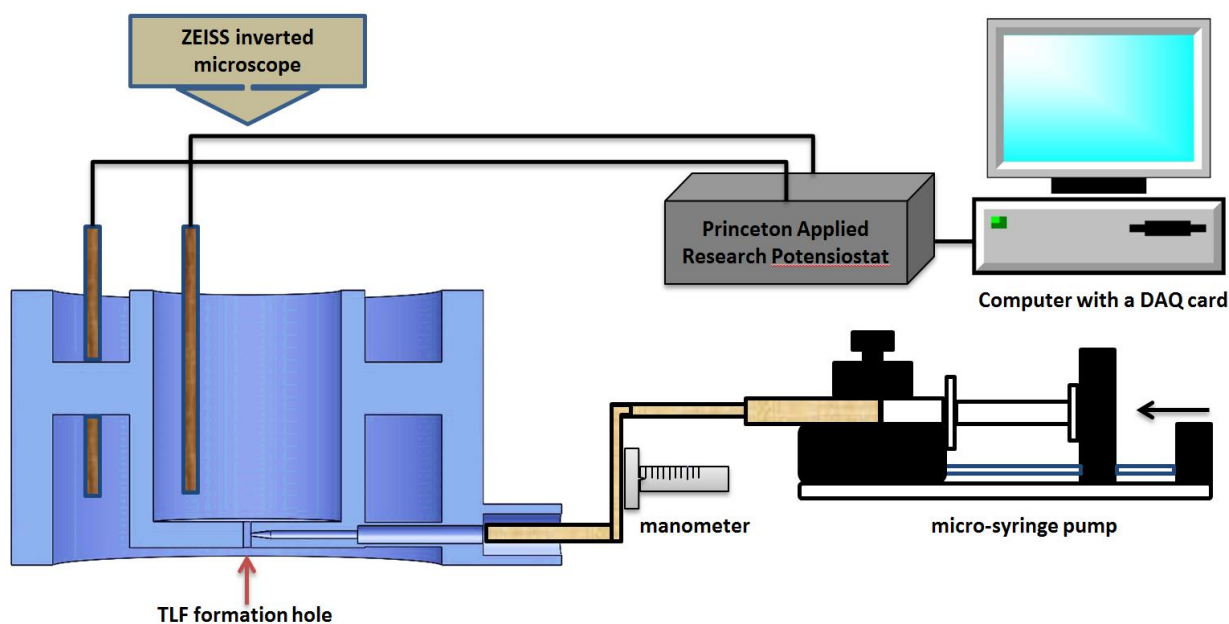


Figure 2. Simplified schematic representation of a Scheludko-cell for study of W/O thin liquid films of surfactant solution/n-dodecane

RESULTS AND DISCUSSION

We observed the generation of TLF, as it is shown in Figure 3. In Figure 3, we show the current vs voltage curve for the system composed of 0.1 wt% SDS in milli-Q water as aqueous phase and n-dodecane as oil phase (TLF phase, see Figure 3). We observed that the formation of TLF causes a decrease in the slope of current vs voltage curve for the system which is composed of upper and lower medium of SDS solutions and the TLF middle medium. Considering the change in current to μA (from 10^{-5} to 10^{-6} amp), the TLF formation is detected. The central finding expressed in Figure 3 is the variation of current vs voltage by formation of TLF. We hypothesize that this increase in resistance of the system is caused by the formation of another resistance in the system

which we considered as the TLF resistance. Treating the three layers of surfactant solution/n-dodecane/surfactant solution each as a resistor connected in series, the electrical behavior of the TLF is modelled in a circuit where they all are linked in series to the power supply. Such an electrical modelling treatment for O/W system has been mentioned elsewhere (Joos, Snaddon, 1985; Bailes, 1995). As n-dodecane can be considered as a leaky dielectric (LD) medium with a conductivity of 10^{-15} S/m for pure n-dodecane, there is possibility of the migration of charged species within the medium due to the imposed field (Piper and Thomas, 1954). This indicates its lack of perfection as insulator and demonstrates the presence of isolated electric charges within the body of the oil phase.

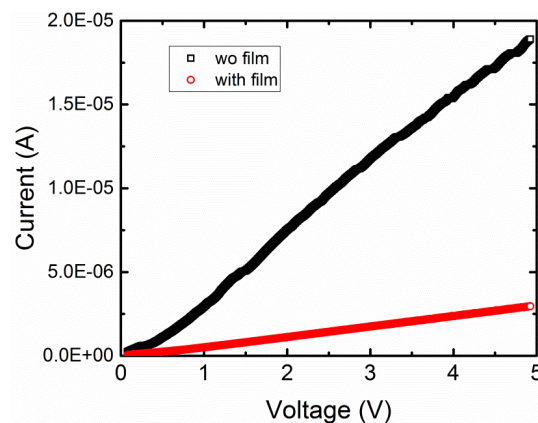


Figure 3. Current vs Voltage curve for the system composed of 0.1 wt% SDS in milli-Q water as aqueous phase and n-dodecane as oil phase (TLF phase). The black line and red line are before and after the formation of TLF, respectively.

In Figure 4, we show the effect of different concentration of surfactants on the resistance of the TLF. Surfactants have been added to the aqueous phase considering the HLB value of SDS Surfactants to be 40. As seen in this figure (see Figure 4), by changing surfactant concentrations, the abrupt change has happened in resistance of the system. We do consider the range of the experiment below 1.23 volts, as above this range the electrolysis of water will happen and In addition to electrolysis, there will also be loss of charge carriers through association and ion production by means of dissociation which is in agreement with the previous studies (Bailes, Lee and Parsons, 2000). The TLF conductance can be obtained using a modeling of the resistances present in the system using the following equations; Ohm's law must also be satisfied for the complete circuit. According to the Ohm's law, the current through any conductor is directly proportional to the voltage across the conductor at any constant physical conditions such as mechanical strain, pressure, temperature etc. As was mentioned earlier, we can express the modelling equations as the equations of a set of three resistors in the system; in which V , I , R , g are the applied voltage, current, resistance, and conductance, respectively.

$$V_{tot} = I_1R_1 + I_2R_2 + I_3R_3 \quad (1)$$

$$R_{equivalent} = R_1 + R_2 + R_3; \quad R_{equivalent} = \sum R_i \quad (2)$$

$$\frac{1}{g} = \sum \frac{1}{g_i} \quad (3)$$

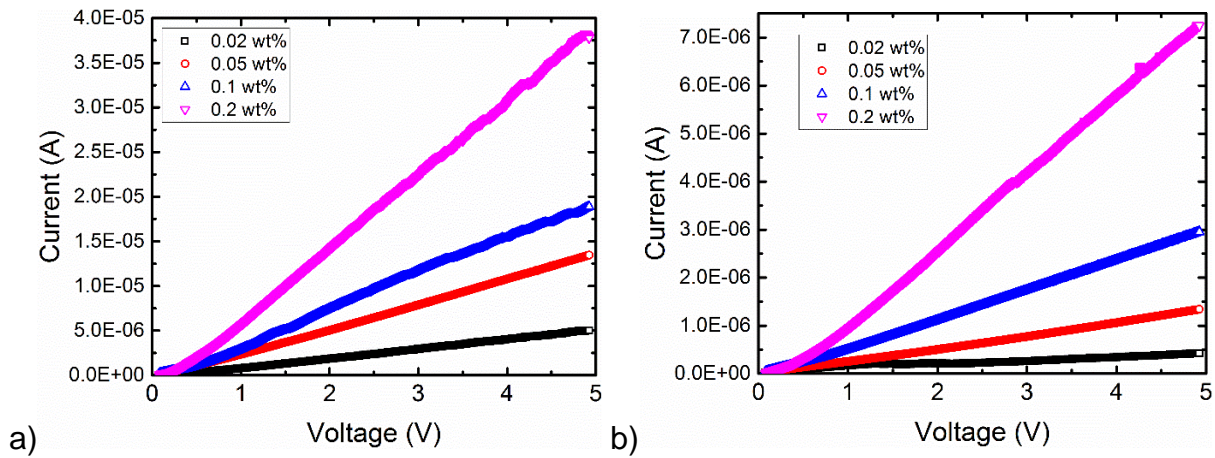


Figure 4. Current vs Voltage curve for the system composed of different SDS concentrations in milli-Q water as aqueous phase and n-dodecane as oil phase (TLF phase). a) Without formation of TLF. b) With formation of TLF of n-dodecane and reduction in the slope of the Current vs Voltage curve.

Figure 5 depicts TLF formation modelling of resistors in series and a schematically depicted formation of n-dodecane TLF. We hypothesize that, the surfactants adsorb at the oil-water interface in such a manner that the dodecyl sulfate anions are adsorbed towards water phase and the hydrophobic tails are arranged in the TLF phase which is consistent with the work reported by Kaisheva et al. (Kaisheva, Krasteva and Usui, 2000). Although Kaisheva et al. studied the stability and rupture of thin aqueous films formed between a hydrogen bubble and a mercury droplet in aqueous solutions of 5×10^{-6} or 10^{-3} M SDS in the presence of 0.05 M Na_2SO_4 , and concluded that at the negative electrode potential E and at the region of the potential of zero charge (PZC), dodecyl sulfate anions are adsorbed as a monolayer, in a way that their negatively charged “head” groups turned toward the surfactant solution and hydrophobic chains oriented toward mercury (Kaisheva, Krasteva and Usui, 2000).

In part (b) of this figure, effect of different surfactant concentration on TLF conductivity (S/m) has been shown. As it is seen in this figure, the conductivity of TLF has been increased by increasing the surfactant concentration. Observed increase in TLF conductivity at higher surfactant concentrations, can be due to the adsorption of surfactants at oil-water interface. The anionic “head group” of SDS moieties can act as a charge carrier at the oil-water interface thus increasing the conductivity of TLF. For a liquid such as n-dodecane which is a leaky-dielectric medium, there is a flow of a negligible yet finite free charge carriers present in the fluid, under the action of an applied electric field. In this regard, within a hydrocarbon liquid which is sandwiched

between two aqueous mediums to which there is an applied potential difference, the migration of negative ions towards the anode and positive ions towards the cathode will happen. As by passing time there will be more surfactants moieties adsorbed at O/W interface, the presence of more ions causes a higher electrochemical potential and charge carrier density at the interface thus higher electrochemical potential at O/W interface which causes the establishment of electrical field inside the TLF. This can be due to this fact that by adding surfactant concentration in the surfactant medium, there will be higher electrochemical potential at the O/W interface thus increasing the flow of the infinitesimal free charge present in the LD medium. The assumption of an infinitesimal free charge present in an LD fluid makes this model more dependable in explaining the phenomena of increasing the TLF conductivity by increasing the surfactant concentration. The number of free charges which accumulate at the interface can be estimated by a material balance which we intentionally do not show them here for the sake of brevity and can be found elsewhere (Joshi and Khandekar, 2015).

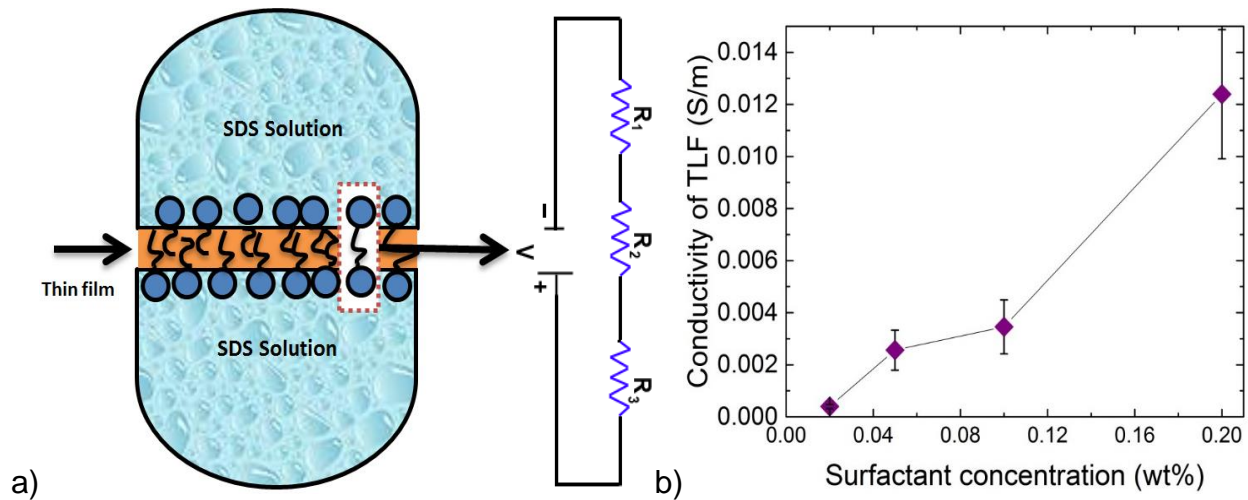


Figure 5. a) resistors in series modeling of the TLF formation and a schematic of formation of n-dodecane TLF. b) Effect of different surfactant concentration on TLF conductivity (S/m). The concentrations of surfactants are (0.02, 0.05, 0.1, 0.2 wt% of SDS in milli-Q water)

In Figure 6 (a) adsorption dynamics of SDS which is monitored using the dynamics of conductance of the system is shown in voltage range 0 to 1 (Volts). As seen in this figure, the conductivity of TLF has been increased by passing time. The observed dynamic in conductivity of the TLF for 0.1 wt% SDS in milli-Q water as water phase and n-dodecane as oil phase, can be related to the adsorption of SDS surfactants at oil-water interface. To justify the results observed for the adsorption of SDS at oil/water interface using the MSC used in these sets of experiments we did the pendant drop tensiometry analysis of the same oil-water interface using a KRÜSS pendant drop tensiometer. The results of these experiments are in accordance with the time-scale observed for SDS adsorption using the MSC used as seen in Figure 6 b) and Figure 7.

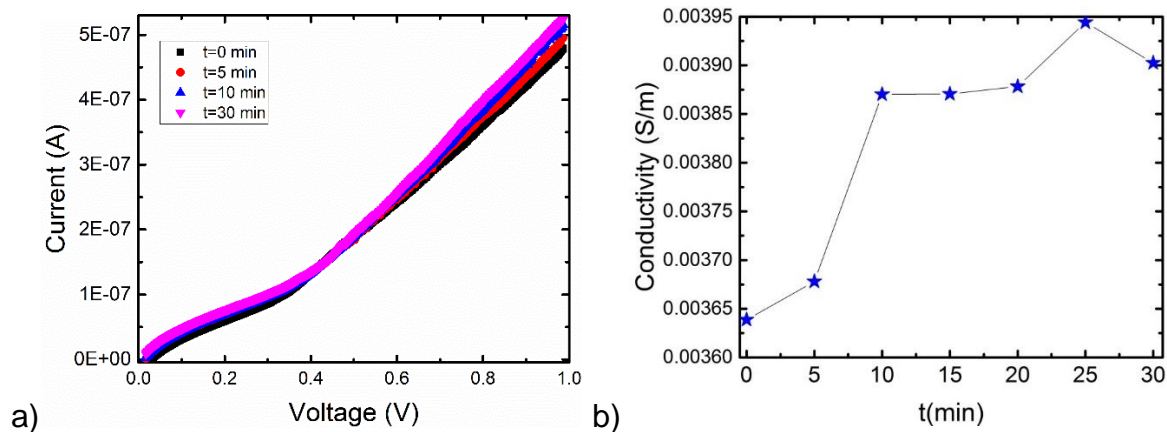


Figure 6. a) Adsorption dynamics of SDS surfactants at Oil-Water interface studied using our novel 3D-printed modified Scheludko-cell (MSC) b) Dynamics of TLF conductivity

In case the solution was susceptible to ion depletion, there was a chance of having conductivity to decline by time (Bailes, Lee and Parsons, 2000) but in our case Figure 6 (b), when an increasing supply of ions happens in the interface (for example adsorption of surfactant at interface) can cause an increase in the conductivity of TLF medium as was discussed earlier due to adsorption of SDS surfactants at O/W interface and the formation of electrochemical potential at the O/W interface which induces the electric field across the LD medium. By passing time, as more surfactant molecules are adsorbed at the interface and the concentration of SDS molecules is below its critical micelle concentration (CMC), there will be an increase in electrochemical potential at the O/W interface by passing time which results in more electrical field across the oil phase. The interfacial tension result which is depicted in Figure 7, shows reduction in interfacial tension of 0.1 wt% SDS in milli-Q water as water phase and n-dodecane as oil phase. The pendant drop tensiometry study was to confirm the experimental results obtained from MSC. In this part, we were able to confirm the adsorption time-scale for SDS surfactants using pendant drop tensiometry, but further experimental and theoretical analysis on the down-scaling of O/W interface length is needed for better understanding of adsorption of surfactants at different length-scales. One should consider the effect of the interfacial shear stresses that arise because of accumulation of the negligible but yet finite charge present in a LD medium interface. As these mediums have very low conductivities there is slow albeit limited charge relaxation time as has been pinpointed by other studies (Joshi and Khandekar, 2015).

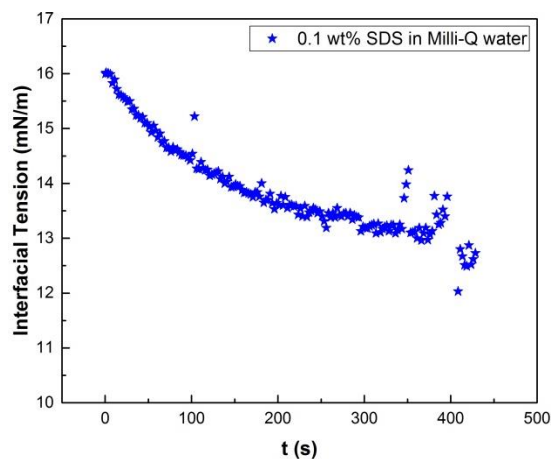


Figure 7. Dynamic interfacial tension (IFT, mN/m) of 0.1 wt% SDS solution as aqueous phase and n-dodecane as oil phase. The results are obtained using a KRÜSS pendant drop tensiometer

CONCLUSIONS

In this study, a novel 3D-printed modified Scheludko-cell (MSC) has been employed due to its simplicity and the feasibility of gaining concurrent optical responses during the experiment. An electrical modelling treatment for O/W interface has been done using resistors in series. Current vs voltage curve for the system composed of different SDS in milli-Q water as aqueous phase and n-dodecane as oil phase (TLF phase) has been obtained using the 3D-printed modified Scheludko-cell. In the first section of this study, the formation of TLF of oil phase and its effect on electrical conductivity of TLF has been studied. In the second section of this work, we examined the effects of surfactants adsorption dynamics on TLF electrical behavior. Effect of different surfactant concentration on TLF conductivity (S/m) has been monitored and it was concluded that by increasing surfactant concentration, the TLF conductivity (S/m) has been increased. Adsorption dynamics of SDS surfactants at Oil/Water interface has been studied using the 3D-printed modified Scheludko-cell. Dynamics of TLF conductivity has been monitored and it was concluded that the TLF conductivity was increasing for 0.1 wt% SDS concentration in water phase. Dynamic interfacial tension (IFT, mN/m) of 0.1 wt% SDS solution as aqueous phase and n-dodecane as oil phase was measured experimentally and the adsorption time-scale was comparable to the study done by 3D-printed modified Scheludko-cell. The results of this study can usher in a better quantification of interfacial film properties, thereby paving the way for a controllable O/W separation and thereby water treatment techniques.

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Author Contributions

M.R. and B.S. conceived the experiment. M.R., B.S. and M.S. designed the experiments. B.S. and M.R. conducted the experiments and collected data. M.R., B.S., M.S. and T.T. analyzed the data. M.S. and T.T. played an advisory role. All authors contributed to the writing of the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

SAGD, steam assisted gravity drainage; PW, produced water; DOMs, dissolved organic matters; HAs, humic acids; AOSB, Alberta oil sand bitumen; OSPW, oil sands process-affected water; EOR, Enhanced Oil Recovery; SOR, steam/oil ratio; TDS, Total Dissolved Solids; TSS, Total Suspended Solids; TLF, thin liquid film; BBD, boiler blow-down; NAs, naphthenic acids; SARA, Saturates aromatics resins and asphaltenes; TAN, total acid number; ASTM, American Society for Testing and Materials; CHNS, Carbon Hydrogen Nitrogen Sulfur; WLS, warm lime softening; IFT, interfacial tension; S/B, solvent-to-bitumen ratio; TLF-PBT, Thin Liquid Film-Pressure Balance Technique; leaky dielectric, LD; Hydrophilic-lipophilic balance, HLB

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