# Functional Molecules and the Stability of Water-in-Crude Oil Emulsions

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**Ⓢ** *Supporting Information*

**ABSTRACT:** In the production and transportation of crude oil, undesirable water-in-oil emulsions may form. Undesirable water-in-oil emulsions may also form in hydraulic fracking when acid is added to the injection water. We investigate the role of acid−base interactions in the stability of water-in-oil emulsions. Asphaltenes and resins, referred to as functional molecules, constitute the polar fractions of crude oil. They contain heteroatoms such as N, O, and S, which lead to acidic and basic functionalities in petroleum fluids and contribute to the stability of water-in-oil emulsions. We have quantified the acidity and the basicity of nine petroleum fluids (light, medium, heavy, and extra-heavy crude oils) by measuring their total acid number (TAN), total base number (TBN), and hydroxyl number (HN). Except in extra heavy oils where the TAN and TBN are close, all the other oils are basic (i.e., TBN > TAN). We observe that all the light crude oils form stable emulsions with deionized (DI) water, while medium, heavy, and extra-heavy oils do not. Addition of a strong acid (HCl, 4−37 wt %) to the aqueous phase enhances emulsion stability in light oils, induces the formation of water-in-oil emulsions in medium oils, and does not lead to emulsions in heavy and extra-heavy oils. Addition of a strong base (NaOH, 4−20 wt %) to the aqueous phase destabilizes emulsions in light oils, but leads to emulsions in a medium-density oil. There is no effect on heavy and extra heavy oils. The effect of salts on the stability of water-in-oil emulsions is also studied. At the salt concentrations studied (4−30 wt %), we observe that salts destabilize emulsion; multivalent salt solutions are more potent at weakening emulsions, compared with mono- and divalent salt solutions. These results are attributed to the preferential hydration of ions by water molecules, as compared to interactions of asphaltenes with water.

## 1. INTRODUCTION

Petroleum fluids are typically coproduced with brine of various salt concentrations. During extraction and transportation of crude, oil and water may mix to form emulsions.[1,2] Stable water-in-oil emulsions affect production efficiency and are undesirable due to high viscosity,[1,2] especially for flow in permeable media.[3] Emulsion formation can be addressed by an improved understanding of the structural and chemical constituents of crude oil that contribute to stable water-in-oil emulsions. The species in crude oil are generally classified as saturates, aromatics, resins, and apshaltenes (SARA fractionation). Asphaltenes are the most polar fraction of crude oil, followed by resins.[4] Asphaltenes are defined as the fraction of crude oil soluble in aromatics such as toluene and insoluble in aliphatics such as heptane.[5,6] They consist of a polyaromatic hydrocarbon core with aliphatic side chains. Asphaltenes contain heteroatoms such as N, S, and O on the periphery and metals such as Va, Ni, and Fe on porphyrin-like structures. Resins are defined as the polar fraction of deasphalted crude oil (called maltenes) that adsorb on a silica or alumina chromatography column on elution with a hydrocarbon solvent (such as pentane) and desorb by a polar solvent (such as toluene and acetone).[6] They contain more aliphatic side chains and less aromatic carbon compared to asphaltenes.[6] Resins also contain heteroatoms such as N, O, and S, but do not contain metals.[6]

Asphaltenes and resins exhibit acidic and basic functionalities due to heteroatoms. Strongly acidic groups, quantified by total acid number (TAN) include carboxylic acids (aliphatic, aromatic, and napthenic −COOH). Weakly acidic groups include hydroxyl (−OH) − quantified by hydroxyl number (HN), pyrrole (aromatic 5-membered =NH), and thiol (≡C-SH) functionalities.[4,7] Basicity is characterized by strong organic bases such as pyridines (aromatic 6-membered =N-) and quinolines (aromatic 6-membered bicyclic =N-), as well as by the salts of carboxylic acids and salts of heavy metals.[4,7] We refer to asphaltenes and resins as the functional molecules in petroleum fluids. Figure 1 schematically illustrates the various components of crude oil.

Water and oil form sparingly soluble mixtures. However, stable emulsions, especially water-in-oil, are often observed in the production of crude oil.[1,2,8−36] What determines stability of water-in-crude emulsions? It has been shown that interfacial molecules have high aromaticity, small alkyl tail length, and reduced branching, which indicate that functional molecules (mainly asphaltenes) are the most abundant fraction of the interfacial film.[1,2,8] Analysis of interfacial material indicates that the interface contains a higher abundance of N, O, and S functional groups than the bulk crude components.[9] Asphaltene adsorption at the oil−water interface depends on the interactions between asphaltenes and the other crude components, namely, resins and aromatics.[8,12−14] These interactions determine the state of the asphaltenes in the bulk, i.e., whether the asphaltenes are in a molecularly solvated state, or whether they are aggregates
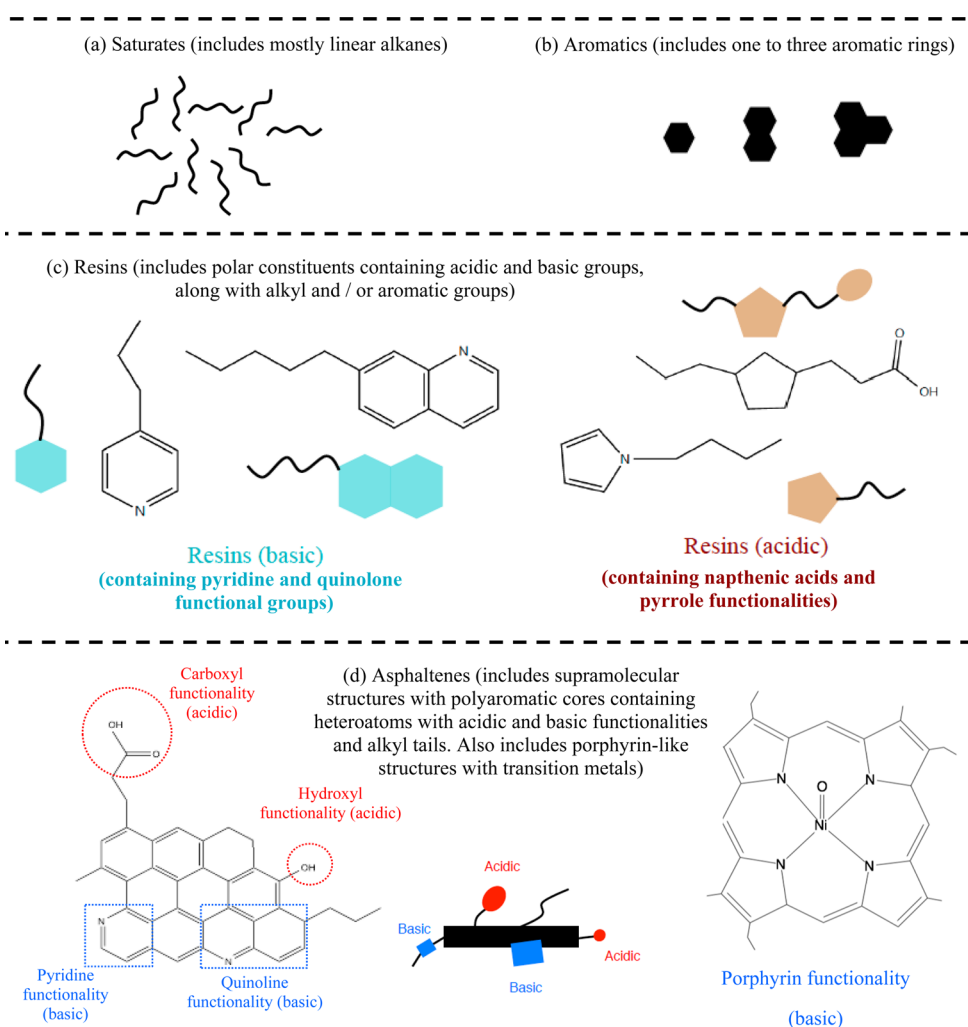
**Figure 1.** Schematic representation of the various components of petroleum fluids: (a) saturates, (b) aromatics, (c) resins, and (d) asphaltenes.

incipient to precipitation. If the resins or aromatics content of the oil is low, then the asphaltenes are "poorly" solubilized in the oil (exemplified by large aggregate size[15,31,33]) and have a higher propensity to adsorb onto the oil−water interface.[16] The adsorbed asphaltenes form a rigid elastic film around the water droplets preventing coalescence and leading to stable water-in-oil emulsions.[8,14,15] Resins alone do not stabilize emulsions.[15−18] However, the interactions between resins and asphaltenes could alter the solubility of the apshaltenes in the bulk and affect emulsion stability.[2,12,15]

Recent studies show that only a subfraction of asphaltenes, referred to as interfacially active asphaltenes, contribute to emulsion stability.[9,20−22,35] Advances in spectroscopy, such as instruments with higher resolution (i.e., electrospray ionization Fourier transform - ion cyclotron resonance mass spectroscopy, ESI FT-ICR MS), show that the interfacially active species consist of acidic and basic constituents of asphaltenes and include an abundance of N, O, and S compounds as compared to the bulk crude components.[9,30,31] The effect of acidic and basic constituents of functional molecules in stabilizing water-in-oil emulsions is not fully understood. Hemmingsen et al. show that removal of acidic components from crude oils, by extraction with aqueous solutions of different pH, increases emulsion stability.[10,11] Ese and Kilpatrick suggest that addition of napthenic acids to the aqueous phase enhances emulsion stability

of HepTol (1:1 v/v mixture of toluene and heptane) model oils.[37] Shi et al. discuss that emulsion stability is enhanced if the aqueous phase has a low pH.[38] Addition of base to the aqueous phase is shown to destabilize the emulsion.[39]

The effect of salt on the formation and stability of emulsions is not well understood and at times contradictory.[40−48] Some studies suggest that an increase in salt concentration may destabilize water-in-oil emulsions,[40−42] while other studies indicate that the effect of salt on emulsion stability is a function of salt concentration.[43−46] Rocha et al. suggest at low concentration (0.02 to 1 wt %) salts may enhance emulsion stability, and high salt concentration (1−15 wt %) does not impact emulsion stability.[43] Aman et al. observe that increasing salt concentration from 0 to 10 wt % increases emulsion stability,[44] while Perles et al. conclude that stability of brine-in-crude oil emulsions is enhanced up to a certain ionic strength of the salt (0.1−0.3 mol/L depending on the salt type) but further increase in salt concentration destabilizes the emulsion.[45] Moradi et al. report that water-in-oil emulsions are more stable at low salt concentration (<0.1 wt %) than higher salt concentration (>1 wt %).[46]

In this work, our goal is to investigate the effect of acid, base, and salts in the stability of water-in-oil emulsions (referred to as emulsions). We study emulsion stability in nine crude oils (light, medium, heavy, and extra-heavy oils) from three continents. The

acidity and basicity of the crude oils are determined by measuring the total acid number (TAN), total base number (TBN), and hydroxyl number (HN). These numbers are then correlated with the asphaltene and resin content of the crude. We observe that TAN has a weaker dependence on the amount of asphaltenes and resins in the crude compared to TBN and HN which exhibit a stronger dependence. Emulsion in water and brine (4−30 wt % sodium chloride NaCl, and 4−20 wt % calcium chloride CaCl$_2$ and two multicomponent salt solutions, seawater (SW) and formation water (FW) with compositions given in Table 1) is

**Table 1. Composition of Brines (wt %)**

| salt | brine − sea water | brine − formation water |
|---|---|---|
| NaCl | 2.84 | 8.87 |
| KCl | 0.30 | 0.95 |
| CaCl$_2$ | 0.70 | 2.19 |
| MgCl$_2$ | 0.35 | 1.10 |
| ionic strength[a] | 0.62 mol/L | 2.12 mol/L |

[a]Ionic strength is computed as

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2$$

where $c_i$ is the concentration of the species $i$ in mol/L and $z_i$ is its charge.

investigated. Emulsion stability on the addition of acid (hydrochloric acid, HCl 4−37 wt %) and base (sodium hydroxide, NaOH 4−20 wt %) to the aqueous phase is also examined. Our results show that all the light oils (TAN < 0.20 mg KOH/g oil) form stable water-in-oil emulsions (amount (i.e., volume) of emulsion varies with the oil). Medium, heavy, and extra-heavy crudes (with TAN > 0.20 mg KOH/g oil) do not form stable emulsions with water (nor brine). The addition of HCl (4 to 37 wt %) to the aqueous phase enhances emulsion stability of light oils, induces the formation of emulsion in medium oils, and does not lead to emulsions in heavy and extra-heavy oils. Addition of a base (from 4 to 20 wt %) to the aqueous phase, in general, weakens the emulsions formed in light oils and induces a small amount of emulsions in one of the medium oils. No emulsions are detected with heavy and extra-heavy crude oils. Salt destabilizes emulsions. Increasing the salt concentration (4−30 wt % for monovalent salt and 4−20 wt % for divalent salts) changes the emulsion in light oils from water-in-oil to "spongy" (or bicontinuous) phase to complete phase separation. No emulsion are detected with brine in medium, heavy, and extra-heavy oils.

## 2. MATERIALS AND METHODS

**2.1. Materials.** Nine different crude oils (sources shown in Table 2) are investigated in this work.

Toluene, ethanol, isopropanol, acetone, acetonitrile, anhydrous KOH, and glacial acetic acid are from Avantor Chemicals (solvents for resin extraction and potentiometric titration). *p*-Toluenesulfonyl isocyanate 98% purity, tetrabutylammonium hydroxide 1 M solution in methanol, and 0.1 M perchloric acid in glacial acetic acid (0.1 N) are from Sigma-Aldrich (solvents for potentiometric titration). Sodium chloride (NaCl), potassium chloride (KCl), calcium chloride (CaCl$_2$), magnesium chloride (MgCl$_2$), hydrochloric acid (HCl), and sodium hydroxide (NaOH) are from Sigma-Aldrich. Heptane and pentane (solvents for asphaltene and resin extraction) are from Fisher Scientific. Attapugulus clay (for resin extraction) is from Forcoven Products.

Deionized (DI) water is from a Millipore setup with a pH of around 5.5 (±0.5), measured by a pH indicator strip.

**2.2. Crude Oil Property Characterization Methods.** The oils are characterized by density, viscosity, asphaltene, and resin content (summarized in Table 2). The oils are also analyzed to determine the acidity (TAN), basicity (TBN), and hydroxyl number (HN). Measurements of all the properties are repeated multiple (2−9) times to confirm reproducibility of results (error bars ≤5%).

**2.3. Density.** Density of the oils are determined at 25 °C by using an Anton Paar densitometer. The density of highly viscous oils (viscosity >1 Pa·s) is determined by dilution in toluene and extrapolation to 0 wt % toluene. Once density is determined the API gravity is computed as follows:

$$\text{API gravity} = \frac{141.5}{\text{specific gravity}} - 131.5$$

**2.4. Viscosity.** Viscosity is determined at 25 °C by using the Anton-Paar MCR302 rheometer. Viscosity is measured over a range of shear rates ($10^{-2}$ to $10^2$ s$^{-1}$). For all the oils at low shear rates ($10^{-2}$ to $10^{-1}$ s$^{-1}$), the change in viscosity as a function of shear rate is less than 5%. For the heavy and extra-heavy oils, viscosity is reduced by about 50% only at shear rates greater than $10^0$ s$^{-1}$.[49] In this study, viscosity is determined as the average across the shear-rate range where the crudes show Newtonian behavior (i.e., between $10^{-2}$ and $10^{-1}$ s$^{-1}$). The cone and plate setup is used for the light and medium oils, while the parallel-plate setup is used for the heavy and extra-heavy oils. Further details on the methodology of viscosity measurements are given in our earlier paper.[49]

**2.5. Asphaltene Content.** The asphaltene content of the oils is measured according to the IP 143 standard. One gram of crude oil is mixed thoroughly with 40 mL of heptane (or pentane) and left to rest for about 24 h. The mixture is vacuum filtered with 200 nm cellulose-nitrate filters (Whatman), and the residue is left to dry overnight. The residue is collected and weighed to determine the amount of asphaltenes per gram of oil.

**2.6. Resin Content.** The resin content of the oils is determined in accordance with the ASTM D 2007 protocol.[50] Once the pentane-insoluble asphaltenes are filtered out, the deasphalted oil (eluted in pentane) is passed through a magnesium−aluminum-silicate (Attapugulus clay) column, where the resins are adsorbed. The column is desorbed by passing a 1:1 (v/v) mixture of toluene and acetone. The

**Table 2. Relevant data of the crude oils**

| ID | name | source | type | density, g/mL | API, degree | viscosity, Pa.s. | C$_7$ asphaltenes, wt % | C$_5$ asphaltenes, wt % | C$_5$ resins, wt % |
|---|---|---|---|---|---|---|---|---|---|
| L1 | Q1 | Middle East | light | 0.8690 | 31.3 | 0.0183 | 1.9 | 2.5 | 20.1 |
| L2 | BAB | Middle East | light | 0.8394 | 37.1 | 0.0055 | 1.0 | 1.4 | 11.4 |
| L3 | MN | Middle East | light | 0.8193 | 41.2 | 0.0043 | 1.5 | 1.8 | 11.7 |
| L4 | CV2 | North America | light | 0.8694 | 31.3 | 0.0158 | 2.2 | 3.1 | 15.9 |
| M1 | Q2 | Middle East | medium | 0.9068 | 24.5 | 0.1263 | 4.7 | 6.1 | 33.7 |
| M2 | CV1 | North America | medium | 0.9263 | 21.3 | 0.4490 | 4.0 | 8.0 | 36.8 |
| H1 | MXHO | North America | heavy | 0.978 | 13.2 | 60 | 22.9 | 26.8 | 20.1 |
| B1 | CAB | North America | extra-heavy | 1.000 | 10.0 | 240 | 14.1 | 23.5 | 59.7 |
| B2 | VEB | South America | extra-heavy | 1.001 | 9.9 | 560 | 13.8 | 17.2 | 46.2 |

**Figure 2.** Images of crude oil—water mixtures (1:1 by volume). Images are taken after ~24 h of sample preparation. Light, medium, heavy, and extra-heavy crude oils are designated as L, M, H, and B. Total acid number (TAN) is denoted in mg KOH/g oil. All the light oils form water-in-oil emulsions, but in varying quantities (L2 forms the least amount of water-in-oil emulsion, while L1 and L4 form the most amount of water-in-oil emulsion). No emulsion formation is observed in the medium, heavy, and extra-heavy oils.

desorbed mixture is evaporated and left to dry overnight. The residue is collected and weighed to determine the amount of resins per gram of oil.

**2.7. Potentiometric Titration.** The acidity, basicity, and hydroxyl number of the crude oils are measured using a potentiometric titrator unit (Metrohm 916 Ti-touch) combined with a glass electrode (MetrohmSolvotrode). The TAN is determined in accordance with ASTM D664,[51] the TBN in accordance with ASTM 2896,[52] and the HN in accordance with ASTM E 1899-08.[53] The titrating solvent in TAN measurements is 0.01 M KOH dissolved in isopropanol. The titrating solvent in TBN is 0.01 M perchloric acid in 0.1 N glacial acetic acid. The titrating solvent for HN is 0.1 M tetrabutylammonium hydroxide in 10% methanol and 90% isopropanol. While the samples are prepared for potentiometric titrations, the prescribed ASTM standards are slightly modified by adding 75−90 wt % toluene to ensure homogeneity of the oil−titrant mixture (the ratio of all other compounds is maintained as prescribed by the ASTM protocol).

**2.8. Emulsion Preparation and Characterization.** Oil is mixed with the aqueous phase in a 1:1 volume ratio (the volumetric ratio of aqueous phase to the organic phase is maintained constant in all the samples studied in this work). Acidity of the aqueous phase is varied by adding HCl to DI water from 4 to 37 wt % and basicity of aqueous phase is varied by adding NaOH to DI water (from 4 to 20 wt %). Effect of salt is tested by adding NaCl to DI water from 4 to 30 wt % and adding $CaCl_2$ to DI water (from 4 to 20 wt %). Effect of two brine solutions, sea water (SW), and formation water (FW), on emulsion stability is also investigated. The compositions of SW and FW are given in Table 1.

For the light and medium oils, the vials are manually agitated for about 30 s to ensure complete mixing. For heavy and extra-heavy crude oils, the oil−water mixture is agitated in an Analog Vortex mixer (with 4.9 mm orbit) from Fisher Scientific for about 30 s at 3000 rpm. All the samples are then equilibrated at room temperature (21 ± 0.5 °C), and images are taken after 24 h.

Emulsions are characterized based on visual observations. Starting from the top of the vial, if the liquid phase is completely black, then it is termed as almost pure oil. If the liquid phase is brown and can be easily distinguished from pure crude, then it is termed as water-in-oil emulsion. The external surface of this phase (observed visually) varies such that for some light oils, water droplets dispersed in oil are clearly seen, while for some other oils, the water droplets dispersed in oil phase are very small and not visually observed. If neither the oil droplets nor the water droplets form a continuous medium, then it is termed as the "spongy"

(or bicontinuous) phase. If the liquid phase is completely clear, then it is termed as almost pure water.

## 3. RESULTS

Emulsion formation in light, medium, heavy, and extra-heavy crude oils is studied in this work. Figure 2 indicates that all the light crude oils (L1, L2, L3, and L4) form varying quantities (i.e., volume) of stable water-in-oil emulsions. These emulsions are characterized by dispersed water droplets in a continuous oil phase (based on visual observations as explained in Section 2.8). The medium, heavy, and extra-heavy crude oils do not form emulsions with DI water.

Aqueous phase, with various concentrations of HCl (4−37 wt %) and NaOH (4−20 wt %), is mixed with the light, medium, heavy, and extra-heavy crude oils (1:1 by vol.) to examine emulsion stability. Compared to Figure 2, Figure 3a shows that addition of a strong acid to the aqueous phase enhances the formation of water-in-oil emulsion in the light crude oils (clearly observed in L2 oil) and induces small amounts of emulsion in the medium oils. Figure 3b shows that addition of a strong base to the aqueous phase, in general, either weakens or destabilizes emulsions in the light oils (clearly observed for L3 oil). Addition of NaOH to the aqueous phase of M1 medium oil does not lead to emulsions, but induces a small amount of emulsion in the M2 medium oil. Further discussion on characterization of these emulsions are presented in the Supporting Information. No emulsions are detected with the heavy and extra-heavy oils (images not shown).

The effect of salt is investigated next. Figure 4 shows the effect of brine (4−30 wt % NaCl, 4−20 wt % $CaCl_2$, and two multicomponent salt solutions SW and FW) on the stability of water-in-oil emulsions for the light crudes. Our observations reveal that at the concentrations studied in this work, salt destabilizes the emulsions. Mixture of mono- and divalent salt solutions are more potent at destabilizing the emulsion compared to single component brines. Increasing the salt concentration (and corresponding ionic strength) changes the

**Figure 3.** Images of crude oil−acid/base mixtures (1:1 by volume) for the light to medium oils. Images are taken after ~24 h of sample preparation. Aqueous phase consists of varying concentrations of (a) HCl and (b) NaOH (concentrations given in wt % and ionic strength in mol/L).

emulsion, from water-in-oil to "spongy" phase to complete phase separation. No emulsions are formed with brine in medium, heavy, and extra-heavy oils (images not shown). Additional information on the characterization of these emulsions can be found in the Supporting Information.

For all the oils studied in this work, emulsion stability with DI water and 8% NaCl brine were analyzed at different time intervals (0, 1, 3, and 24 h after sample preparation). The observations (shown for oil L2 in Supporting Information Figure S1) indicate the same trend as seen after 24 h of sample preparation. The primary focus of this paper is on the understanding of the role of

acid base interactions on emulsion stability and therefore kinetics of emulsion formation are not investigated.

In order to elucidate the effect of the functional molecules that stabilize emulsions, the acidity and basicity of the crude oils are measured via potentiometric titration. Sample titration plots are provided in Supporting Information (Figure S2). The TAN, TBN, and HN data of various crude oils are summarized in Table 3. To corroborate the results from potentiometric titration, Fourier transform infrared (FTIR) spectroscopy was also performed on crudes L2, L3, H1, B1, and B2 (details on FTIR spectroscopy are provided in Supporting Information, Figure

**Figure 4.** Images of crude oil−brine mixtures (1:1 by volume) for all the light oils. Images are taken after ∼24 h of sample preparation. Brine is characterized by various concentrations of NaCl, CaCl₂, and two multicomponent salt solutions SW and FW (concentrations indicated in wt % and ionic strength in mol/L).

**Table 3. Total Acid Number (TAN), Total Base Number (TBN), and Hydroxyl Number (HN) of Crude Oils**

| ID | Name | TAN | TBN | HN |
|----|------|-----|-----|-----|
| | | mg-KOH/g-oil or mg-KOH/g-asphaltene or mg-KOH/g-maltene | mg-equivalent KOH/g-oil or mg-equivalent/g-asphaltene or mg-equivalent/g-maltene | mg-equivalent KOH/g-oil or mg-KOH/g-asphaltene or mg-KOH/g-maltene |
| L1 | Q1 | 0.0165 | 1.00 | 0.94 |
| L2 | BAB | 0.056 | 0.71 | 0.89 |
| L3 | MN | 0.11 | 0.36 | 0.51 |
| L4 | CV2 | 0.184 | 1.14 | 2.2 |
| M1 | Q2 | 0.38 | 1.35 | 0.55 |
| M2 | CV1 | 0.21 | 5.6 | 2.8 |
| H1 | MXHO | 0.35 | 4.1 | 8.0 |
| B1 | CAB | 3.3 | 4.5 | 6.6 |
| B1-Asphaltenes | CAB-Asp | 4.03 | 10.41 | |
| B1-Maltenes | CAB-Maltenes | 5.6 | 4.0 | |
| B2 | VEB | 5.0 | 5.9 | 6.0 |
| B2-Asphaltenes | VEB-Asp | 7.8 | 14.34 | |
| B2-Maltenes | VEB-Maltenes | 7.5 | 5.6 | |

S3). Qualitative results from FTIR correlate with the trends observed from the TAN data.

The TAN, TBN, and HN are analyzed to investigate correlation with the amount of asphaltenes and resins in the crude. Table 3 indicates that the light to medium crude oils are basic (TBN is at least 3 times greater than TAN), heavy oil has low TAN, but high TBN and HN, and the extra-heavy oils are almost neutral (TAN and TBN are the same order of magnitude). HN of light oils indicates that L4 has the most amount of hydroxyl groups, while HN data for medium oils show

that M2 has a higher number of hydroxyl groups compared to M1. Table 3 also shows that the two extra-heavy oils studied in this work have equivalent HN, while heavy oil H1 has the highest HN among all the oils. Table 3 also indicates that oil L3 has the lowest TBN compared to all crudes. The same table also shows that oil M2 has a very high TBN compared to oil M1. The TAN and TBN values of the asphaltene and maltene ($C_5$-deasphalted oil) fraction of the extra-heavy oils are also determined. (TAN, TBN, and HN could not be determined for the asphaltenes and resins fraction of light to medium oils because of their low asphaltene content requiring large amounts of crudes for the TAN/TBN/HN analysis; similar analysis could not be performed for the asphaltene and maltene fraction of heavy oil due to the relative instability of the asphaltenes, which led to precipitation issues with the Solvotrode electrode). Data from Table 3 show that basicity in extra-heavy oils is mainly from the asphaltenes, while acidity is mainly from the maltenes. Figure 5 indicates that for light to medium crude oils, TBN and HN show a strong correlation with the amount of asphaltenes and resins in the crude, while TAN exhibits weak dependence (i.e., TAN is almost independent of the amount of functional molecules, while TBN and HN have a non-monotionic dependence of the amount of functional moelcules).
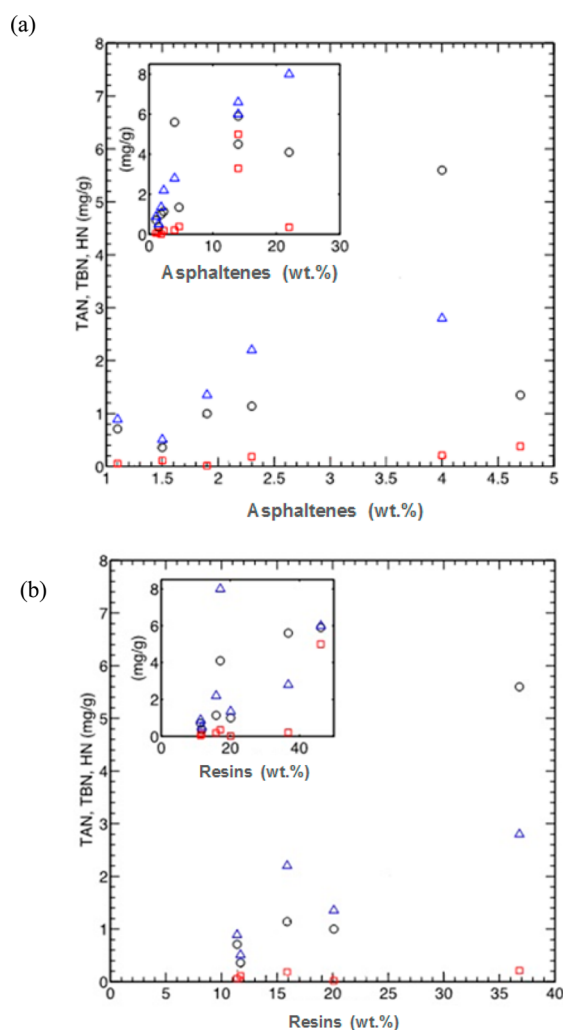


**Figure 5.** TAN (red open squares), TBN (O), and HN (blue open triangles) vs concentration of (a) asphaltenes and (b) resins in light and medium crude oils (insets show the data for all the nine oils).

## 4. DISCUSSION

Our results are the first-of-its-kind in correlating emulsion stability with TAN and TBN of nine different light, medium, heavy, to extra-heavy crude oils. We show the effect of the acidity and basicity of crude oils as well as the effect of the addition of acid, base, and salts to the aqueous phase in the stability of water-in-oil emulsions. The light and medium oils investigated are basic, while the extra-heavy oils are mostly neutral (TAN and TBN are the same order of magnitude). Heavy oil is characterized as almost neutral—although it has high TBN, this seems to be balanced with high HN (weakly acidic −OH functionality) and TAN (strongly acidic −COOH functionality). There is a stronger correlation between the amount of functional molecules and TBN (and HN) in light to medium crudes compared to TAN, which is weakly dependent on the amount of asphaltenes and resins.

All the light crude oils form stable emulsions with water (amount of emulsion depends on the oil), while the medium heavy and extra-heavy crude oils do not. For the light oils, addition of an acid to the aqueous phase enhances emulsion stability, while addition of a base to the aqueous phase weakens or destabilizes the emulsion. For the medium oils, addition of an acid to the aqueous phase induces a small amount of water-in-oil emulsion; addition of a base to the aqueous phase leads to a small amount of emulsion in M2 medium oil, while no emulsion is formed with M1 medium oil. The heavy and extra-heavy oils do not form emulsions with aqueous HCl and aqueous NaOH at room temperature and atmospheric pressure.

Brine has a strong influence on the emulsion stability of light oils. At the salt concentration studied (4−30 wt %), increasing the ionic strength destabilizes the emulsion and changes the emulsion from the water-in-oil phase to the "spongy" phase to complete phase separation in most cases. Multicomponent brine solutions are more potent at destabilizing emulsions compared to single component salts. We did not detect emulsions with brine in medium, heavy, and extra-heavy oils.

We observe that the acidic and basic properties of the crude oil as well as the acidity and basicity of the aqueous phase affects emulsion stability, but crude oils with a significant amount of asphaltenes and resins (such as H1, B1, B2) do not form emulsions with water. These results indicate, in agreement with the literature, that it is the molecular functionality rather than the amount of asphaltenes and resins that determines emulsion stability.[8−26] Most asphaltene deposition problems in flowlines occur when the asphaltene content of the crude oils is low, less than 2 wt %.[54] Addition of small amounts of water (0.05−3.5 wt %) to the crude oils possibly leads to the formation of hydrogen bonds between water and functional molecules, and lowers asphaltene depositon in flow lines.[54] It is the functional groups within the crude that have an impact on the bulk and interfacial properties of asphaltenes and resins, as opposed to the concentration of functional molecules.

Various authors have analyzed the water−oil interfacial film and report that it consists of asphaltenes and organic acids.[9,14,18,22,25,26,29,31,37] On the basis of our understanding that asphaltenes contain acidic components, we will not separate the interfacial constituents as asphaltenes and acids. The next question is what determines emulsion stability? This topic is extensively discussed, but a clear picture is yet to emerge.[2,20−22,32,35,38,41,55−57] On the basis of results from this study and our previous experience in characterizing asphaltene

aggregation behavior,[3,33,58−60] we propose the following picture to describe stability of water-in-oil emulsions.

Asphaltenes, driven by $\pi-\pi$ interactions among the polyaromatic cores, stack to form a nanoaggregate.[6,58−61] Organic acids, such as dodecylbenzenesulfonic acid (DBSA), solubilize asphaltenes by protonating the asphaltene molecule and pairing it with sulfonate ions, forming an ion−asphaltene complex.[62] We thus postulate that in addition to aromatic interactions, there exist acid−base interactions among asphaltenes (as shown in Figure 1d). Asphaltene molecules stack such that the acidic constituents align with the basic constituents to promote acid−base interactions. This model is illustrated in Figure 6.
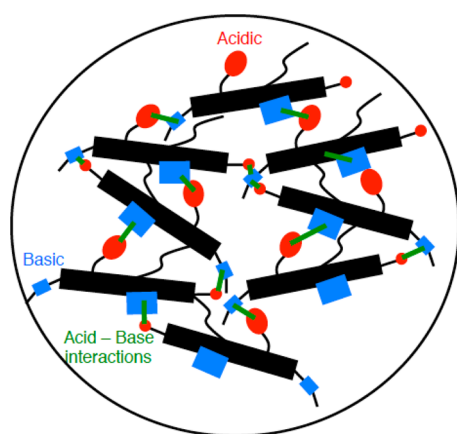


**Figure 6.** Schematic of asphaltene nanoaggreagte. Driven by $\pi-\pi$ interactions among polyaromatic cores (black), asphaltene molecules stack to form a nanoaggregate ($l \approx 4$ nm[41]). In addition to aromatic interactions, asphaltenes contain acidic (red ellipse) and basic (blue rectangle) functionalities exhibiting acid−base interactions (green lines).

In order to further understand the acid−base interactions within crude oil, let us revisit Figure 1. Acidic groups in functional molecules include the carboxyl, hydroxyl, or pyrolle groups. These groups can be considered electrophiles (exhibiting partial positive charge), such that they can (1) accept an electron pair (Lewis acid) or (2) donate a proton (Bronsted-Lowry acid). Basic functionalities in crude oils include pyridines or quinolines. These groups can be considered nucleophiles (exhibiting partial negative charge), such that they can (1) donate an electron pair (Lewis base) or (2) accept a proton (Bronsted-Lowry base). Acid−base interactions within crude oils could be such that the carboxyl acid functionality reacts with the pyiridinium base functionality to form pyridinium salt. If a strong acid or a strong base is added to the aqueous phase of an oil−water mixture, then the functional molecules will tend to interact with the added acid or base.

Asphaltene molecules and nanoaggregates are solubilized in the crude by resins and aromatics, dispersed in a medium of saturates and aromatics.[12,15,17,63] Hashmi and Firoozabadi have shown that resins can act cooperatively with added acid, such as DBSA, to solubilize asphaltenes within the crude mixture.[64] Therefore, we advance the above understanding and propose that the solubility of asphaltenes in the crude mixture is dependent on the acid−base interactions among the resins and asphaltenes, in addition to the amount of aromatics in the crude oil. The functional molecules would act in such a way that the acidic moieties of the resins would interact with the basic

moieties of the asphaltenes and vice versa. High solubilization of the asphaltenes within the crude occurs when the acidic and basic functionalities are balanced, and there is an abundance of resins and aromatics, as illustrated in Figure 7a. Low solubilization of
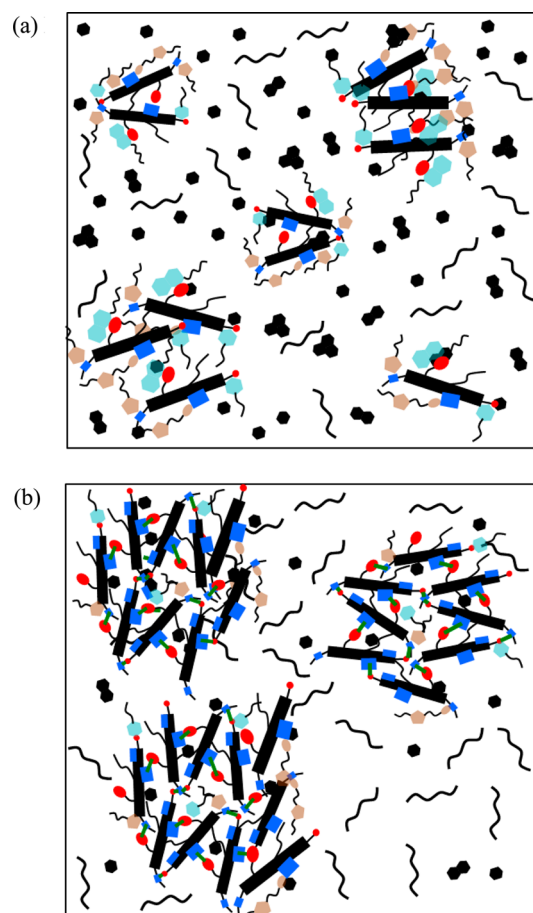


**Figure 7.** Illustration of (a) high solubilization of asphaltenes in crude (illustrated with smaller asphaltene aggregate size). All the acidic and basic moieties of asphaltenes are balanced and there is an abundance of resins and aromatics. (b) Low solubilization of asphaltenes in crude oil (illustrated with larger asphaltene aggregate size). All the acidic and basic moieties of asphaltenes are not balanced and there is a dearth of resins and aromatics.

asphaltenes within the crude is characterized by an imbalance of acidic and basic moieties among the functional molecules and a dearth of resins and aromatics, as shown in Figure 7b.

The light oils studied in this work form stable emulsions with water. They are basic (TBN greater substantially greater than TAN)—this leads to low solubilization of asphaltenes as the basic moieties of asphaltenes remain unbalanced. When such a crude oil is mixed with water, the asphaltenes seek the water−oil interface. Water can act as an acid or a base, and the acidic functionality of water would interact with the basic functionalities of asphaltenes and stabilize the interfacial film leading to stable water-in-oil emulsion. This film becomes stronger if the aqueous phase contains an acid, such as HCl. This mechanism also explains the emulsions observed in medium oils (where TBN is greater than TAN) in the aqueous HCl; the basic constituents in medium oils are stabilized with the acidic constituents in the aqueous phase leading to stable emulsions. The model is illustrated in Figure 8a. The proposed mechanism provides a
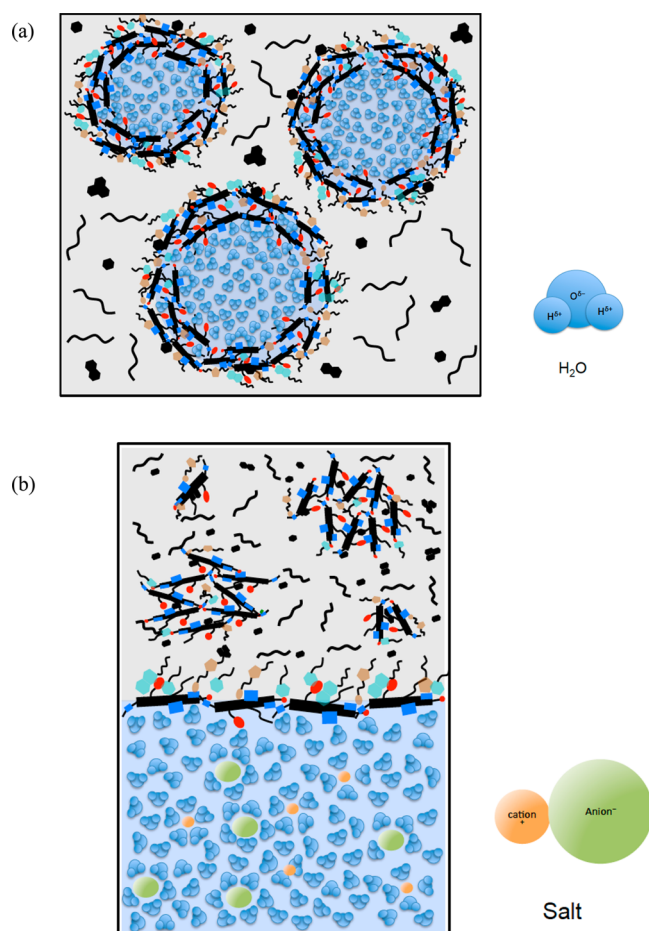
**Figure 8.** Schematic of (a) stable water-in-oil emulsion, where asphaltene molecules adsorb at the oil−water interface and form a rigid film. The acidic and basic constituents of asphaltenes are interacting with the water molecules or the resins. (b) Unstable brine-in-oil emulsion. The water molecules prefer to hydrate the ions rather than interact with the acidic and basic constituents of asphaltenes. This weakens the asphaltene film around the brine droplets and destabilizes the emulsion.

clearer picture for the results reported in ref 37 where the authors have increased acidity of the aqueous phase by adding napthenic acids and observed stable emulsions with HepTol (1:1 v/v heptane/toluene) under varying pH and soap/acid ratio. The illustrated mechanism also supports the results from ref 38, which show that aqueous solutions with low pH could enhance stability of water-in-oil emulsions.

The picture shown in Figure 8a is reversed if the aqueous phase contains a base. Since all the light crude oils are basic, addition of a base to the aqueous phase does not attract the asphaltenes to the interfacial layer and therefore destabilizes the emulsion. Results from heavy oils H1 may seem contradictory to the proposed mechanism (i.e., although heavy oil is quite basic, it does not form emulsions with water nor with aqueous HCl). The observation in H1 could possibly be explained by looking at heavy oil's HN, which is the highest of all the oils studied in this work. The weakly acidic −OH groups and strongly acidic −COOH groups could balance out the high TBN in H1, solubilizing asphaltenes in the bulk. As a result, asphaltenes do not move toward the water interface and do not lead to emulsions.

A key factor to note is that the effect of adding an acid (or base) to the aqueous phase could lead to different results than changing the acidic (or basic) properties of crude oil (as observed with model oils[8,17,19,20,37,38]). Question to address here is how does varying crude TAN and changing acidity of the aqueous phase affect emulsion stability? The answer to this question is not straightforward but also depends on the TBN of the crude. On the basis of observations in light and medium oils, where the TAN is much lower than TBN, addition of acid to aqueous phase enhances emulsion stability. For the heavy and extra-heavy oils, where the acidity (TAN and HN) seem comparable to basicity (TBN), addition of acid to the aqueous phase does not lead to emulsions. Therefore, the mechanism here is clear; i.e., if the acid−base moieties are not balanced in the crude, then the acidic components in the crude phase go toward the water or aqueous acid interface to form stable emulsions.

We also observe that medium oil M1 does not form emulsions with aqueous NaOH solution, while M2 forms a small amount of emulsion with aqueous NaOH (at 4% and 8%). The mechanism behind stable emulsions in M2 with aqueous NaOH is yet to be elucidated.

All the oils studied in this work are basic; the literature also reports that most crudes are basic, i.e., TBN > TAN.[63,65−67] In order to understand the reason why extra-heavy oils do not form emulsions, we investigate the acid−base properties of the functional molecules of extra-heavy oils. Given that the extra-heavy oils contain higher amounts of asphaltenes, resins, and higher TAN and TBN compared to light, medium, and heavy oils, we examine the TAN and TBN of their asphaltene fraction and resin fraction (i.e., $C_5$-deasphalted oil, also called maltenes). Results from Table 3 indicate that although the extra-heavy oils as a whole are almost neutral (i.e., TAN and TBN values are close to each other), basicity is from the asphaltenes and acidity is from the resins (as resins constitute the functional molecules of deasphalted oil). This result supports the view that basic moieties in asphaltenes are balanced by the acidic moieties of resins and vice versa. It also supports the results of Hashmi and Firoozabadi,[64] underscoring the role of resins in solubilizing asphaltenes. We deduce that the observations from extra-heavy oils corroborates the mechanism (exemplified in Figure 8a) behind stable emulsions observed in the light, medium, and heavy oils studied in this work.

Addition of salt changes the microenvironment. Results from our experimental studies and those from the literature indicate that salt concentration plays an important role in emulsion stability. Low salt concentrations in the aqueous phase (<0.1 wt %) have been shown to enhance water-in-oil emulsion stability.[43,45,46] We observe that increasing the salt concentration from about 4 wt % to about 30 wt % destabilizes the emulsions, in agreement with refs 40−42. We postulate that on the addition of salt, water molecules prefer to hydrate the salt ions rather than interact with the acidic and basic moieties of asphaltenes. The proposed model is illustrated in Figure 8b.

## 5. CONCLUSIONS

Stability of water-in-oil emulsions is related to the acidity and basicity of functional molecules in petroleum fluids (i.e., asphaltenes and resins). The light oils studied in this work form water-in-oil emulsions, while medium, heavy, and extra-heavy oils do not. Addition of a strong acid to the aqueous phase enhances emulsion stability in light oils, triggers emulsion formation in medium oils, and does not lead to formation of emulsions in heavy and extra-heavy oils. Addition of a strong base

to the aqueous phase destabilizes emulsions in light oils, forms emulsion in the medium-density oil which has a high TBN, does not lead to emulsions in another medium-density oil with low TBN, and no emulsions are formed in heavy oil and extra-heavy oils.

Results on emulsion stability are attributed to the acid−base interactions between the asphaltenes and the aqueous phase. If the asphaltenes are not well-solubilized in the bulk crude oil (i.e., the basicity of the asphaltenes (quantified by TBN) is not balanced by the acidity of the resins (quantified by TAN and HN) or vice versa), then the asphaltenes tend to accumulate at the water−oil interface forming stable water-in-oil emulsions. This result is exemplified by increase in emulsion stability when the aqueous phase is acidic and a decrease in emulsion stability when the aqueous phase is basic. Emulsion behavior in one of the medium oils with aqueous NaOH does not follow this trend and yet needs to be elucidated. We also observe that salt plays a key role in emulsion stability. Salts in the concentration range studied in this work (between 4−30 wt %) destabilize emulsions formed in light oils. Water molecules may hydrate the ions rather than interact with the acidic and basic moieties of the asphaltenes.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energy-fuels.7b01039.

> Additional information about Figures 3 and 4. Figure S1: Images of emulsion formation over time in L2 crude oil. Figure S2: Sample titration plot to determine properties of whole crude oil and asphaltene fractions. Figure S3: Fourier transform infrared (FTIR) spectra of L3 light oil, H1 heavy oil, and B2 extra-heavy oil (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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