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Interfacial sciences in unconventional petroleum production: From fundamentals to applications

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With ever increasing demand for energy to meet the needs of growth in population and improvement in living standards of developing countries, the abundant unconventional oil reserves (about 70% of total world oil), such as heavy oil, oil/tar sands and shale oil, are playing an increasingly important role in securing global energy supply. Compared with the conventional reverses unconventional oil reserves is characterized by extremely high viscosity and density, combined with complex chemistry. As a result, petroleum production from unconventional oil reserves is much more difficult and costly with more serious environmental impacts. As a key underpinning science, understanding the interfacial phenomena in unconventional petroleum production, such as oil liberation from host rocks, oil-water emulsions and demulsification, is critical for developing novel processes to improve oil production while reducing GHG emission and other environmental impacts at lower operating cost. In the past decade, significant efforts and advances have been made in applying the principles of interfacial sciences to better understand complex unconventional oil-systems, while many environmental and production challenges remain. In this critical review, the recent research findings and progress in the interfacial sciences related to unconventional petroleum production are critically reviewed. In particular, the chemistry of unconventional oils, liberation mechanisms of oil from host rocks and mechanisms of emulsion stability and destabilization in unconventional oil production systems are discussed in detail. This review also seeks to summarize the current state-of-the-art characterization techniques and brings forward the challenges and opportunities for future research in this important field of physical chemistry and petroleum. (481 references)

1. Introduction

Unconventional oils are the new-reality and emerging sources of petroleum fuels that differ significantly from conventional crudes. Even though lacking a strict definition, unconventional oils are characterized to be dense, extra viscous, chemically complex and of high carbon-to-hydrogen ratio.[1] They are often locked in highly heterogeneous, difficult-to-extract deposits and tightly bound to host rocks such as sands and clay minerals, as shown in **Fig. 1**.[2-4] Heavy oil, extra heavy oil, oil/tar sands bitumen, tight shale oil and

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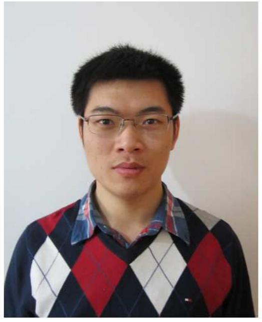

Lin He

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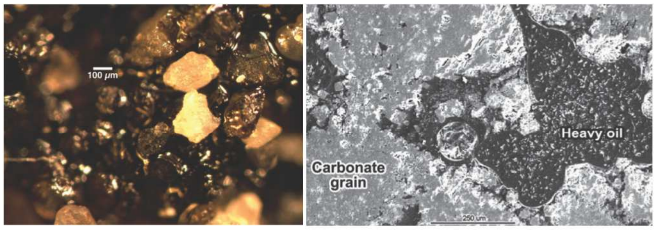
eventually the kerogen (an oil precursor) in oil shale are the typical forms of oils in these unconventional petroleum resources. Unconventional oil deposits, mostly located in North America, Eastern Europe and Latin America, are enormous with proven reserves of more than 6 trillion barrels of recoverable oil with current technologies, accounting for about 70% of total world oil reserves.[5, 6] In this review, the term "unconventional oils" refers to the heavy oil of high density and viscosity with bitumen of approximately 1050 kg/m^3 density and up to 10^3 Pa•s viscosity at a temperature of 15.7^{o}C as an example.[7] With a total of 1.7 trillion barrels of bitumen in place in Canadian oil sands alone, unconventional oils account for a major part of liquid fossil fuel resources and provide energy security for the unforeseeable future.[7]

The steady world-wide population increase, rapid improvement in living standards of developing countries and robust growth in new economies such as China and India have led to an ever increasing demand for petroleum fuels.[8] In contrast, the supply of conventional crudes has peaked and is depleting at an aggregate average of 4.5% annually.[9] In coping with this reality, our wisdom should be also unconventional: Oil is not running out, but different forms of oil need to be exploited. In fact, the high oil price over the past decade has stimulated the technological innovation of petroleum supplies, not a shift away from oil as the fuel, despite great effort on developing renewable energy resources driven by environmental concerns.[10] The forms of petroleum fuels have started to transform. Unconventional oils of reliable and abundant resources, if allowed to the market force, are undoubtedly anticipated to replace the loss of conventional crudes in the petroleum portfolios throughout the 21st century.

Despite sound economic incentives, the development of unconventional petroleum industries would be impractical without the application of new technologies developed based on modern science. Comparing with the recovery of conventional crude oils, recovery of unconventional petroleum fuels is more challenging. For these types of resources, chemical-integrated and/or thermo-intensive techniques are required. In general, there are two types of methods to extract these unconventional oils. The first is a non-thermal approach which primarily adds water, solvent and chemicals to allow for the separation of oils from host rocks. Typical examples of this type of non-thermal methods are water flooding, gas injection, alkaline flooding, carbon dioxide flooding, cyclic carbon dioxide stimulation, nitrogen flooding, polymer flooding, micelle-polymer flooding, microbial enhanced oil recovery, cold production, pressure pulse technology, solvent injection, hydraulic fracturing and surface mining. The second method is thermal production that is commonly achieved by injecting steam and heat into the deposits, allowing the flow of oil to the production wells where the oil is brought to the surface by gas lift or mechanical pumps. The thermal production method includes hot-fluid injection, steam injection, cyclic steam injection, steam drive, in situ combustion, forward combustion, reverse combustion, toe to heel air injection (THAI), inert gas injection and steam-assisted gravity drainage (SAGD), often coupled with horizontal well technology.[11-14]



(a) (b)

Fig. 1 (a) Reflected light view of an oil sand. Reproduced from Han *et al.*, 2006.[4] (b) SEM image of the Uvalde carbonate saturated with heavy oil. *Reproduced from Batzle et al., 2006.[3] Copyright 2006 Society of Exploration Geophysicists.*

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Regardless of the variations in operating parameters and stimulation methods of extracting unconventional oils, there involve at least two essential and fundamental sub-steps that are in common: Liberation of oil from reservoir solids or host rocks (see **Fig. 2 a**), and separation of oil and water (the origin of water can be connate water in the reservoirs and/or added water), shown in **Fig. 2 b**.[15, 16] To liberate the oil from solids, the oil needs to be displaced or recessed from solid surfaces. The degree and rate of oil displacement largely depend on interfacial properties of solid-oil-water systems, which are determined by physicochemical properties of oil, chemistry of water, and characteristics and wettability of host solids.[17-23] The separation of liberated oil and water, on the other hand, involves breaking the undesirable oil-in-water and/or water-in-oil emulsions that are inevitably generated during the liberation of unconventional oils from solids and transportation of produced oil-water mixtures. To effectively break these emulsions and achieve desired oil-water separation, it is critical to comprehend the underlying mechanisms that govern the formation and stability of oil-water emulsions. The stability of these emulsions is often attributed to the presence of indigenous interfacially-active components of unconventional oils, and their interactions with fine solids such as clays. When breaking down to the elemental sub-processes of unconventional oil production, understanding the physicochemical properties of various interfaces (such as solid-oil, solid-water and oil-water) and interactions among various phases is vital. Understanding these properties will ensure successful and economic recovery of unconventional oils with the lowest negative environmental impact (such as land disturbance, water consumption and contamination, air pollution and greenhouse gas emissions). Overcoming major challenges with unique solutions in oil production from unconventional oil resources, to a significant extent, relies on fundamental understanding of the associated interfacial sciences.

A number of extensive reviews on heavy oil recovery have been reported in the past.[14, 19, 24, 25] The focus of these reviews was mostly on technologies and methods for enhancing heavy oil recovery. There were a couple of overviews reported on stability of water-oil emulsions with the focus on crude oils.[26-29] At the same time, many advances including developing novel characterization techniques have been made in recent years that greatly enhanced our scientific understanding of interfacial sciences governing the oil production from unconventional petroleum resources. In particular, characterizing the alteration of reservoir rock wettability, probing the physicochemical properties of heavy oil-water interfacial films and determining the mechanisms of unconventional oil-water emulsion stabilization and demulsification have been improved dramatically. In this critical review, we aim to provide a comprehensive overview on current in-depth understanding of interfacial phenomena involved in oil production from unconventional petroleum resources. The review will focus on the underlying foundations governing liberation of unconventional oil from host rocks (solids) and separation of unconventional oil from water. The chemistry of unconventional petroleum components (mostly the heavy components such as asphaltenes), which are the major source in determining the interfacial behaviors of the systems, is first outlined as follows.

2. Chemistry of unconventional petroleum

Unconventional petroleum fuels are known to consist of many thousands of hydrocarbon molecules containing elevated levels of heteroatoms (*e.g.*, sulfur (S), nitrogen (N) and oxygen (O)) and heavy metals including nickel (Ni), iron (Fe), copper (Cu) and/or vanadium (V).[30-32] The heavy oil contains typically 80% to 88% carbon by weight. Chemically, the carbon over hydrogen (C/H) mass ratio is often used to characterize the quality of heavy oil, although low API number and high viscosity are two important characteristic features of heavy oil for practical purposes. In general, unconventional heavy oil is characterized by a high C/H mass ratio above 6.5 and sometimes even up to 11, implying a high aromaticity of hydrocarbon molecules in heavy oil.[32-34] Due to the extremely complex nature of heavy oil molecules, it is almost impossible to separate and determine molecular composition and structure of heavy oils by traditional chemical characterization techniques. In practice, SARA fractionation has been widely used to separate and characterize heavy oils.[35, 36] SARA fractionation separates heavy oil into four main chemical families named as saturates (S), aromatics (A), resins (R) and asphaltenes (A), based on the difference in polarity and solubility of these components. Saturates are light components of oil, consisting mainly of non-polar alkanes with linear or branched chains, and aliphatic cyclic paraffins.[5, 37] Aromatics are species with one or more aromatic rings linked with aliphatic chains. Heteroatoms, such as N, S and O, are normally embedded in aromatics.[32, 38] Aromatics have a similar molecular weight as saturates (450 to 550 g/mol) but feature a higher C/H mass ratio.[39, 40] Resins are operationally defined as the fraction of heavy oils that are soluble in heptane and pentane, but insoluble in liquid propane. Naphthenic acids are fractionated in the resins fraction. Asphaltenes are defined as the fraction soluble in aromatic solvents such as toluene but insoluble in alkanes. They are the least soluble and the heaviest fraction in heavy oil.

The SARA content in heavy oil from different reservoirs varies considerably. In general, the higher the content of asphaltenes and resins in the oil, the heavier and more viscous the heavy oil would be.[41-44] The resin and asphaltene fractions contain interfacially active materials such as naphthenic acids (NA) and interfacially active asphaltene (IAA) sub-fractions. These components play a central and often contradicting role in production and utilization of unconventional oils.[45-50] Recently, characterizing the chemistry of resins and asphaltenes as well as the interactions between these two fractions[51-57] has undergone a revitalization period, although many controversies and debates are yet to be resolved.

2.1 Resins

Despite the dependence on sample locations and separation methods, the petroleum resin fraction is known to consist of C, H, N, O and S, and features a narrow variation in carbon (85 ± 3%) and hydrogen (10.5 ± 1%) content. A similar percentage of nitrogen (0.5 ± 0.15%) and oxygen (1.0 ± 0.2%) is also found in resins. However, the sulfur content in resins varies significantly from 0.4% to 5.1% for different samples.[32, 58] In general, the molecular weight of resins varies little if at all. Using the vapor pressure osmometry (VPO) method, Peramanu *et al.*, for example, determined the average molecular weight of resins in bitumen from Athabasca and Cold Lake, Alberta, to be 947 and 825 g/mol, respectively.[59] Using a rheology method, Marques *et al.* determined molecular weight of resins to be 840 g/mol.[56] Woods *et al.* published a molecular weight of 700 g/mol for the resins using a gel permeation chromatography (GPC) method.[36] In contrast to strong self-associating nature of asphaltenes, resins do not show any significant tendency of self-association. Therefore, the measured molecular weight of resins can be safely assumed to be the actual molecular weight of a single resin molecule.

Despite the lack of well-defined molecular structures, resins are mainly polar, polynuclear molecules composed of aromatic rings, aliphatic side chains and few heteroatoms. A typical molecular structure of resins is shown in **Fig. 3 a**. It is claimed that resins contain a variety of water-loving functional groups, such as thiophene, benzothiophene, dibensothiophene, pyrrole N-H, ester, carbonyl, hydroxyl, carboxyl and sulfonic acids.[32, 41, 58, 60] Several natural surfactants including naphthenic and sulfonic acids (or corresponding salts) are important parts of the resin fraction although their content in the oil is less than 3 wt%. The molecular structures of these two types of natural surfactants are shown in **Fig. 4**.[61] Here, we provide a brief description on the chemistry of naphthenic acids that play an essential role in changing solid wettability, determining oil-water interfacial tension[62, 63] stability of oil-water emulsions,[64] causing corrosion[64] and toxicity of underground and fresh water.[65-67]

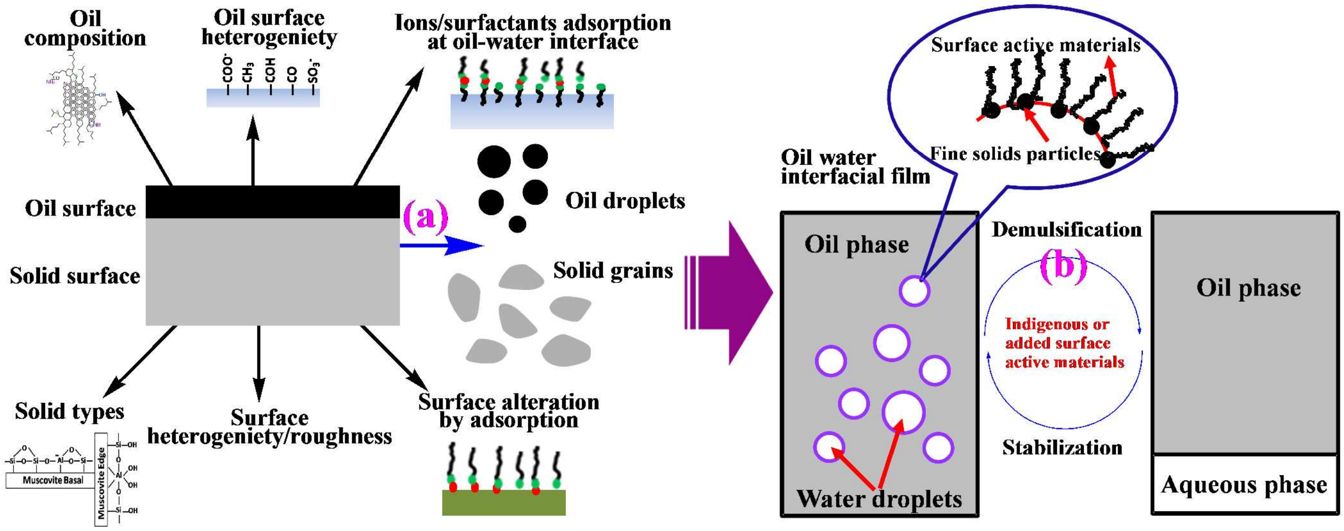


Fig. 2 Advances in interfacial sciences propel the development of unconventional petroleum fuels: (a) Liberation of unconventional oils from the surfaces of host solids/sands, which is mainly affected by parameters such as oil composition, oil surface heterogeneity, oil-water interfacial properties, solid surface characteristics and water chemistry; (b) separation of liberated unconventional petroleum from water, involving stabilization and destabilization of oil-water emulsions by chemicals or mineral particles.

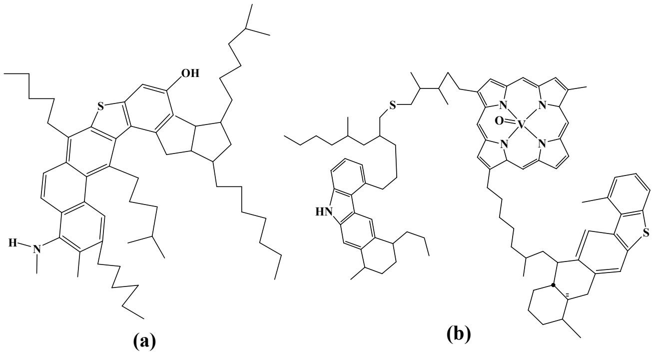


Fig. 3 Typical molecular structures of (a) resins; and (b) asphaltenes, showing aromatic and aliphatic rings connected by branches and containing hetero and heavy metal atoms. *Reproduced with permission from ref. 68 and ref. 69. Copyrights of 1996 American Chemical Society and 2004 American Chemical Society, respectively.*

2.2 Naphthenic acids (NAs)

Generally speaking, naphthenic acids are a group of indigenous surface active molecules, including mainly the alkyl-substituted cycloaliphatic carboxylic acids embedded with a small amount of acyclic aliphatic acids and a trace amount of hydroxy, aromatic, olefinic and dibasic acids.[70] NAs are often represented by a general formula of $C_nH_{2n+z}O_2$, where *n* denotes the carbon number and *z* indicates a homologous series. The value of *z* can vary from 0 to -2, -4, -6 and -8. Typical structures of NAs are shown in **Fig. 4 a.**

Considered as interfacially active materials, naphthenic acids (NAs) adsorb on solid surfaces usually by chemical bonding. In alkaline solutions, NAs are easily ionized and tend to accumulate at the unconventional petroleum-water interface as shown in **Eq. 1**.[61] NAs can also be considered as a sorbent of metal ions (*e.g.,* Ca^{2+}) and fine solids.[71] For the information on the occurrence, toxicity, biodegradation properties and corrosion impacts of NAs, readers are referred to existing references. [70, 72-75]

$$\sim\!\sim\!\sim COOH + NaOH \rightleftharpoons \sim\!\sim\!\sim COO^{-} + Na^{+} + H_2O \qquad \textbf{(Eq. 1)}$$

2.3 Asphaltenes

The chemical elements of asphaltenes are similar to those of resins but with relatively higher molecular weight, and embedded with a more significant trace amount of metals such as V, Ni, Fe and Cu. In the past, very little consensus was reached on the structure and chemical properties of asphaltene molecules.[53, 76, 77] Molecular weight values of asphaltenes, for example, were reported in wide ranges from less than 10^3 to 10^9 g/mol, depending on the methods of measurement. Using the VPO method, Akbarzadeh *et al.* determined the average molecular weight of single asphaltene molecules (C7-asphaltenes) from Athabasca oil sands bitumen to be 1400 to 2200 g/mol.[39] Using Monte Carlo simulation method, Sheremata *et al.* derived an average molecular weight of about 4000 g/mol for representative asphaltenes from Athabasca bitumen, and showed series of aromatic and aliphatic groups as building blocks of asphaltene molecules.[69] However, there still exists uncertainty whether the asphaltene molecules consist of one single polycyclic aromatic hydrocarbon (PAH) or many cross-linked PAHs, known as the island and archipelago model of asphaltenes, respectively. The asphaltenes were once reported as giant molecules containing small aromatic islands with some embedded metal atoms and linked by aliphatic chains.

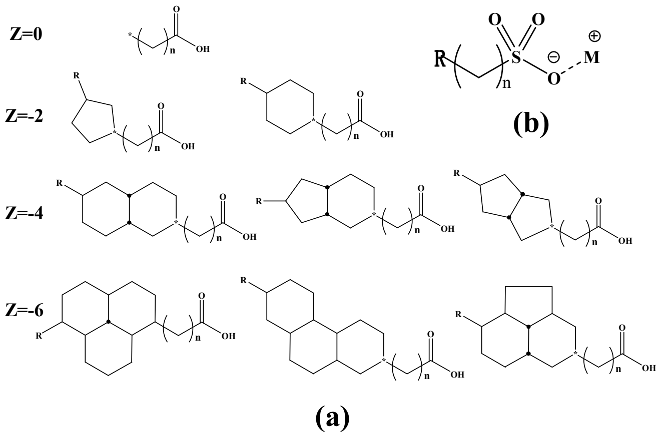


Fig. 4 Typical structures of natural surfactants: (a) Naphthenic acids with different carbon numbers and varying degree of condensation; (b) sulfonic acids or salts with M = H^+, Na^+, K^+, etc., and R represents the hydrocarbon tails. *Reproduced with permission from ref. 78. Copyright 1991 American Chemical Society.*

In the past decade, significant advances in asphaltene science have been achieved. Thanks to the advances in analytic techniques such as electrospray ionization, Fourier transform ion cyclotron resonance mass spectroscopy (ESI-FTICR-MS) and in particular the time-resolved fluorescence depolarization (TRFD) measurements, it is currently well established that the average molecular weight of asphaltene monomers is about 750 g/mol, and the molecular weight of asphaltene monomers can be as low as 400 g/mol and as high as 1000 g/mol, depending on the origin of petroleum oil.[46, 79, 80] It is now widely accepted that the asphaltene molecules contain one single, moderately large fused aromatic hydrocarbon ring with peripheral alkyl substituents. The typical asphaltene architecture is illustrated in **Fig. 3 b**. With the critical importance of asphaltene molecules in oil production and downstream conversion, other characterization techniques, such as IR, NMR, UV, LDI-MS, small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS), have also been used to probe the structure of asphaltene molecules.[81-86] In addition to studying real asphaltenes of poorly known molecular structure, a great deal of effort has been placed on the synthesis of different model molecules for asphaltenes.[87] For example, Akbarzadeh *et al.* applied the derivatives of pyrene and hexabenzocoronene as asphaltene model molecules to investigate their self-association properties.[88] Similar work has been conducted by Murray Gray *et al.* using pyrene derivatives of 2,2'-bipyridine.[89] In a different approach, Masliyah *et al.* focused on the molecular dynamic (MD) simulation using model asphaltene molecules.[90] Almost at the same time, Sjöblom *et al.* started a program on the synthesis of asphaltene model compounds that match typical molecular weight of real asphaltenes and include heteroatoms. The model compounds synthesized by Sjöblom *et al.* showed similar interfacial behavior such as pH and concentration dependence of interfacial tension. In addition, the MD simulation on the model compounds was possible, shedding the light on molecular mechanisms of emulsion stabilization by asphaltenes.[91] Relevant work on asphaltene model compounds has been summarized recently by Sjöblom *et al.*[87]

With their special molecular structure, asphaltenes are known for their inevitable self-aggregation, resulting in falsely large apparent molecular weight in some reported measurements.[53, 76, 77, 92] In 1967, Yen *et al.* suggested a model, known as the Yen model describing asphaltene molecules as being composed of individual sheets. Built on the investigation of different asphaltenes from different origins, the Yen model suggested the formation of large associated micelles by self-association of hundreds of asphaltene molecules.[92] Recently, the Yen model has been refined. The new model, known as Yen-Mullins model proposed an aggregation number of six asphaltene molecules to form a nanoaggregate with a single disordered PAH stack. The size of the nanoaggregate was estimated to be around 2 nm. The nanoaggregates could further aggregate to form a cluster containing approximately eight nanoaggregates.[46, 93] In a recent study, two complementary methods, ATR-FTIR spectroscopic imaging and NMR imaging, have been combined and applied to investigating the deposit properties of asphaltenes. The addition of heptane to the crude oil was shown to cause the most unstable asphaltenes to precipitate first. These asphaltenes mainly contained oxygen- and/or nitrogen- functional groups. Increasing the heptane addition to the oil caused subsequent precipitation and aggregation of asphaltenes containing predominantly aromatic species.[94] To simulate the precipitation of asphaltenes in solvent, Teklebrhan *et al.* investigated using MD simulation the aggregation of four synthetic perylene bisimide-based polyaromatic (PA) surfactants in toluene and heptane. It was shown from their results in **Fig. 5** that the aggregation of PA surfactants was enhanced with decreasing the aromaticity of the solvent due to the increased π–π stacking (T-stacking) between PA surfactant molecules. The authors also found that the presence of aliphatic functional groups in the PA surfactants would decrease the π–π interactions due to steric hindrance of the solvent.[95] The simulation results showed a general agreement with the trend of molecular aggregation determined using dynamic light scattering. Similar simulation results were reported by Jian *et al.*,[96] which agreed with the experimental results of Wang *et al.*[97]

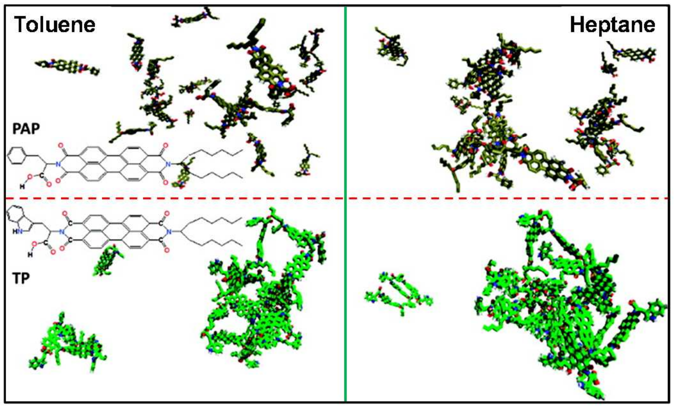


Fig. 5 Molecular configurations of different molecules (PAP represents N-(1-hexylheptyl)-N'-(2-phenylpropanoic acid)perylene-3,4,9,10-tetracarboxylicbisimide; TP is N-(1-hexylheptyl)-N'-(2-indol-3-yl-propanoic acid)-perylene-3,4,9,10-tetracarboxilicbisimide) in toluene (left) and heptane (right), respectively, showing an increased aggregation TP molecule than PAP, more so in heptane than in toluene. *Reproduced with permission from ref. 95. Copyright 2012 American Chemical Society.*

The above-stated strong self-aggregation would facilitate asphaltene molecules to form rigid films at the oil-water interface that stabilize oil-water emulsions.[98] More current studies argued that different sub-fractions of asphaltenes could possess different chemical compositions and exhibit distinct physicochemical properties such as interfacial activity and interfacial rheology.[99] In fact, only a small fraction of the total asphaltenes was found to be interfacially active and responsible for stabilization of oil-water emulsions. This topic will be revisited in more details in **Sections 3 and 4**.

2.4 Resin-asphaltene interactions

The stabilizing role of resins in asphaltene dispersion remains inconclusive. Earlier, resins had been considered to show a strong affinity to asphaltenes in petroleum due to their similar structures and compositions in terms of polarity and aromaticity. As a result, resins were thought to be responsible for stabilizing asphaltenes in unconventional oils as a colloidal micelle system.[100, 101] Until recently, the original concept of a resin-asphaltene micelle was claimed to be uncorroborated,[102] given that asphaltenes aggregate in toluene without the presence of resins. Using a centrifugation method, for example, Indo *et al.* demonstrated that bulk resins do not associate with asphaltenes in live black oil.[103] They found that asphaltene nanoaggregates contain approximately 15% heptane-soluble but pentane-insoluble surface-active materials. Pereira et al. reported that the role of resins in stabilizing asphaltenes from precipitation depends on the origin and intermolecular interactions of resins.[104] Yarranton *et al.* reported that the resins could be co-precipitated with asphaltenes.[53] Anisimov and coworkers showed that the onset of asphaltenes aggregation increases with increasing the addition of resins up to a resin to asphaltene mass ratio of 6.[57] However, Zhao and Shaw reported that asphaltenes did not associate preferentially with resins or other SAR fractions during the asphaltene precipitation.[105] Even in a later study, through direct-current (DC) conductivity measurement of charge carriers in the oil as a function of oil concentration in toluene, Mohammad et al. provided direct experimental evidence that resins are unlikely to coat asphaltene nanoaggregates over an oil concentration range from 10 to 10^3 ppm.[54]

The dominant interaction forces between resins and asphaltenes appear to be van der Waals forces, while hydrogen bonding and π-π interactions could make additional contributions.[37, 106] Using differential scanning calorimeter (DSC) and isothermal titration calorimetry (ITC) methods, the enthalpy of interactions between resins and asphaltenes was determined to be around 2 to 5 kJ/mol.[56, 107] However, based on the density functional theory (DFT) and compass-classical force field calculation, Alvarez-Ramirez et al. obtained relatively larger values of bonding energy between 12 to 14 kcal/mol for resin and asphaltene association. These values are comparable to 12 to 15 kcal/mol for asphaltene-asphaltene interactions, but much larger than 4 to 7.5 kcal/mol for resin-resin interactions.[108] These results suggest possible inclusions of resins in asphaltene aggregates.

3. Liberation of unconventional oils from host solids

As mentioned earlier, unconventional oils normally coexist tightly with host solids such as rocks, sands and clay minerals. Regardless of the extraction methods, an obvious requirement for effective recovery of unconventional oil from the corresponding unconventional oil reserves is the successful liberation (or separation) of unconventional oil from solids (**Fig. 2 a**), which is determined primarily by the interfacial properties of oil-solids, oil-water and water-solid interfaces. In this section, we discuss in great detail the tremendous development in studying the fundamentals of unconventional oil-solid separation in the aqueous phase, which is used as a flooding or processing medium. We will start with a brief summary on basic theory of wetting and contact angle, followed by descriptions on oil displacement and liberation dynamics, and oil-solid interactions. The effect of solid wettability, water chemistry and added chemicals on oil liberation and displacement from host rocks/sands in water will be also discussed.

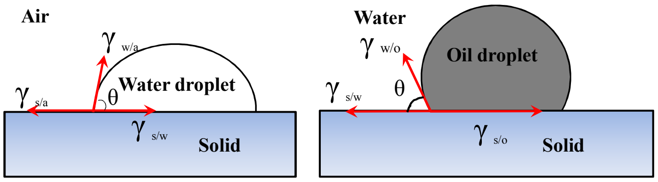
3.1. Wetting and contact angle

Wetting describes a phenomenon of one liquid displacing another immiscible fluid (air or liquid) on a solid surface. Studying wettability of a solid by liquid(s) is essential to understand science of unconventional oil liberation from solid surfaces in heterogeneous systems involving oil-water-solid three-phase contact. In such three phase systems, three interfacial energies (interfacial tensions) at phase boundaries control the extent to which a liquid wets the solid surface, known as wetting statics or wettability. The angle at the three-phase contact line is measured through the aqueous phase. For example, the contact angle shown in **Fig. 6** for (a) solid/water/air and (b) solid/oil/water systems is often used to characterize the wetting characteristics of solids (host rocks). The relation between the contact angle in an equilibrium configuration (*i.e.*, static or equilibrium contact angle) and the three interfacial tensions, in the simplest form, is described by the well-known Young's equation[109], given in **Eq. 2**: (a) for solid/water/air system, and (b) for solid/oil/water system.

$$\gamma_{s/a} - \gamma_{s/w} = \gamma_{w/a} \cdot \cos\theta \qquad \textbf{(Eq. 2-a)}$$

$$\gamma_{s/o} - \gamma_{s/w} = \gamma_{w/o} \cdot \cos\theta \qquad \textbf{(Eq. 2-b)}$$

where, γ and θ represent surface (or interfacial) tension and static contact angle, respectively, while subscripts *s, a, w* and *o* denote solid, gas, water and oil phases, respectively.



(a) (b)

Fig. 6 Schematics of wetting statics in the Young's equation for two systems: (a) solid/water/air system; and (b) solid/oil/water system. Contact angle is defined as the angle measured through the aqueous phase.

It is interesting to note that the contact angle is normally measured from the aqueous phase if water is involved. Solids with water contact angle close to zero are easily wetted by water and classified as hydrophilic (*i.e.*, water-wet). Otherwise, solids are considered hydrophobic (or oil-wet) if the water contact angle is larger than 90°. The solids of water contact angle around 90° are known to be bi-wettable, *i.e.*, they partition readily at the oil-water interface.

In addition to wetting statics, many processes are concerned about how fast the wetting of a substrate by liquid(s) takes place (also known as wetting dynamics). It is largely believed that the spontaneous wetting is driven by the imbalanced interfacial tensions, with the energy being dissipated at the vicinity of the moving three phase contact line and movement of the liquids. The question on which dissipation mechanism(s) dominates remains an open subject. Several theoretical models such as molecular kinetic theory (MKT), hydrodynamic (HD) model or a combination of these two models, have been used to understand the observed evolution of dynamic contact angles.[109-117] In the MKT, the energy dissipation is determined statistically by the frequency and length of individual molecular "jumps" (*i.e.*, attachments/detachments) that occur within the three-phase contact region, also known as contact line friction.[110-112] In the HD model, on the other hand, viscous dissipation in the bulk liquid(s) is considered as the main energy dissipation mechanism.[113, 114]

Relevant applications of wetting dynamics that go beyond the recovery of (unconventional) oils include mineral flotation, synthesis of nano- and bio-materials, surface fuctionalization, heterogeneous catalysis, ink jet-prinking and coating, detergency and soil decontamination, to name a few. Readers who are interested in the special subjects of wetting dynamics should consult the critical reviews by de Gennes,[109] Blake,[115] Bonn et al.,[116] and Ramiasa et al.[117]

3.2 Displacement/liberation dynamics of unconventional oils

3.2.1 Model solid surface

To simplify the complex situation, a flat glass surface was often used to simulate the silica sand found in the unconventional oil reservoirs. Heavy oil was displaced or liberated from the surface by water under different conditions. Using an induction timer, for example, Dai *et al.* investigated the bitumen-sand interaction in NaCl solutions (5 mM) through measuring the pickup time of sands by coker feed bitumen.[118] Increasing the solution pH (2 to 10) or temperature (22 to 60 °C) was found to facilitate bitumen liberation. They proposed that increasing pH of the solution made the surface charge of silica sand and bitumen more negative by ionization of the silanol groups and acidic groups of surfactants on the sand and bitumen, respectively, resulting in a stronger repulsive force between them. Increasing pH also increases wettability of silica surfaces by the increased hydrolysis and ionization of silanol groups. As a result, bitumen liberation becomes much easier as observed experimentally. Similarly, increasing the temperature also makes the surface charge of silica and bitumen more negative, enhancing bitumen liberation. Basu *et al.* investigated the heavy oil (bitumen) recession on a flat glass surface in aqueous solution by measuring the static and dynamic contact angles. They also found that increasing pH up to 11 favored bitumen liberation, resulting in a smaller equilibrium contact angle (about 10° at 40 °C and pH 11).[119] At the same temperature and pH, adding NaCl up to 8000 ppm into the aqueous solution increased the equilibrium contact angle up to 105°, suggesting poorer bitumen liberation. Adding a 150 ppm and 300 ppm MIBC-kerosene mixture into the solution of 8000 ppm NaCl restored the equilibrium contact angle to the case without NaCl addition, indicating an improved detachment of bitumen from the glass surface by surfactant-solvent addition.[120] The presence of calcium (even at low concentration of only 25 ppm) and montmorillonite clays in the aqueous phase was also found to increase the equilibrium contact angle of bitumen on the glass surface, leading to poorer bitumen liberation.[121] Wang and coworkers attributed improved bitumen recovery by short-chain amine (*e.g.*, n-propylamine, n-butylamine and n-pentylamine) addition to enhanced bitumen liberation by reducing the equilibrium contact angle as bitumen recessed from a flat glass surface.[122] Zeta potential measurement and XPS study confirmed the adsorption of n-butylamine on bitumen and fine solid surfaces, rendering bitumen more hydrophobic, and the solid more hydrophilic by removing the organic materials from the solid surface. Recently, Ren et al. carried out the bitumen liberation study by coating a thin layer of bitumen on the glass surface and investigating the effect of kerosene (up to 20% of bitumen) and fatty acid methyl ester (FAME) (up to 20% of bitumen) addition on bitumen liberation.[123] They proposed the viscosity reduction by the addition of kerosene and FAME as the mechanism of enhancing bitumen liberation. Recently, Lin *et al.* reported a micro-scale study of bitumen-water displacement dynamics on a spherical silica surface using the micropipette technique. It was showed that increasing the wettability of the solid surface was beneficial in decreasing the contact angle measured through water of an oil drop on the solid surface in the water, indicating an enhanced liberation of oil from the solid surface.[124]

3.2.2 Porous media

Much of unconventional petroleum is buried deep underground as porous reservoirs. Understanding heavy oil displacement in the porous medium would help develop strategies to enhance recovery and hence utilization of heavy oil. Studying oil displacement in a two-dimensional vuggy fractured porous cell to simulate the conditions of real unconventional petroleum production, Cruz-Hernandez *et al.* derived a model to describe the oil displacement in the cell.[125] Recently, Dehghan *et al.* developed a one-quarter five-spot glass micro model to study the displacement of an Iranian heavy oil in porous media.[126] In their study, n-heptane and four chemicals (*i.e.*, paraldehyde, t-butanol, methyl ethyl ketone (MEK), and ethylene glycol mono butyl ether (EGMBE)) were used as fluids to wash the heavy oil in the micro model. Their results showed that the efficiency of heavy oil displacement in the micro model depended strongly on the wettability of glass and the addition of solvents. Water-wet glass surface and the alcohol were found to be much more beneficial for the oil displacement. The geometrical properties of fractures (*e.g.*, fracture number, distribution, overlap, discontinuity, spacing, orientation) were also identified to play an important role in heavy oil displacement in the micro model.[127] The study using alkalis (sodium hydroxide and sodium carbonate) and surfactant mixtures (including sulfonic acid, nonylphenol 10-mole ethoxylted, triethanolamine, isobutanol and ammonium alkyl (C6-10) ether sulfate) showed a significant effect of salinity and oil-water interfacial tension on oil displacement.[128] When investigating the effect of salinity and pH on oil removal from kaolinite by water flushing, Fogden *et al.* obtained similar results.[129] Chen *et al.* reported a significantly enhanced heavy oil displacement in porous medium by reducing the oil-water interfacial tension to 10^{-4} mN/m with the addition of alkaline materials (*e.g.*, $NaCO_3$ (0.5%) and petroleum sulfonate (0.03%)) and surfactant (*e.g.*, alkyl polyglucoside (0.05%)).[130] Based on the results of self-emulsification experiments and microscopic visualization, they proposed the formation of water-in-oil emulsion with heavy oil at the displacement front and oil-in-water emulsion in the swept region as the mechanism of enhancing oil displacement with alkaline/surfactant flooding.

3.2.3 Studies using real oil sands

Inspired by previous model liberation work, Srinivasa *et al.*[131] and Harjai *et al.*[132] studied the bitumen liberation from real oil sands using an in situ, real time visualization device. They found that increasing the temperature, pH and/or adding diluents (*e.g.*, kerosene) could greatly enhance bitumen liberation from sand grains. However, weathering the ore or increasing the salt (*i.e.*, NaCl) concentration in the aqueous phase was observed to significantly retard the displacement of bitumen by water. A similar visualization device was used in a recent systematic study on the effect of solvent (diluent) addition on bitumen liberation.[133] This mechanistic study showed a significant improvement in bitumen liberation from real oil sand reservoir rock surfaces by reducing the viscosity of bitumen (< 10 Pa.s) and oil-water interfacial tension (< 1 mN/m). There also appeared to exist a linear correlation between oil liberation rate and interfacial tension/viscosity ratio.

The above-mentioned studies collectively reveal that the liberation/displacement processes of unconventional oils from host rock/sand surfaces are controlled by interfacial properties, as well as the chemistry (such as salinity and pH) of water, composition of oil, wettability of solids, oil-water interfacial tension, viscosity of oil and temperature of the system. The effect of these important parameters on heavy oil or bitumen liberation/displacement is reviewed next.

3.3 Solid wettability

3.3.1 Mineral solids associated with unconventional petroleum

The unconventional petroleum reservoir consists of host rocks or solid minerals saturated or impregnated with heavy oil. The solid minerals vary considerably in composition, mainly consisting of carbonate rocks (*e.g.*, calcite, dolomite, feldspar, magnesite, *etc.*), sands, clays and heavy minerals, etc., as shown in **Fig. 7**. The size of the solid minerals found in unconventional oil reservoirs ranges from less than 1 μm to several meters, and could in some cases be even a large plate as in the shale oil reservoirs. The composition and characteristics of the solids are complex and highly variable. Fine mineral solids could have a detrimental role in unconventional petroleum production, such as reducing oil recovery and quality of produced oil, leading to formation of rag layers by stabilizing oil-water emulsions, or causing corrosion to the refining equipment. For these reasons, investigation on mineral solids from unconventional petroleum reservoirs is becoming an increasingly important topic of academic and industrial research.

Kotlyar *et al.* isolated the solids from Utah tar sands using $Na_4P_2O_7$ solution and characterized them using the X-ray diffraction (XRD) method. The solids in Utah tar sands are mainly quartz (SiO_2), plagioclase ($Na[AlSi_3O_8](Na_2O\text{-}Al_2O_3\text{-}6SiO_2)\text{-}Ca[Al_2Si_2O_8](CaO\text{-}Al_2O_3\text{-}2SiO_2)$), microcline ($K[AlSi_3O_8]$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), chlorite ($(MgAlFe)_{12}[(SiAl)_8O_{20}](OH)_{16}$) and mica with a small amount of XRD amorphous components.[134] In their study, most of toluene insoluble organic substances on the solids from Utah tar sands were found to be associated with the XRD amorphous inorganic solids (possibly iron oxides and carbonates). The presence of these organic matter contaminated fine mineral solids was considered to be responsible for poor bitumen separation from solids. Later, these researchers identified the existence of nano size aluminosilicate clays in the recovered bitumen, which had a strong tendency to stay at the oil-water interface, resulting in a severe inclusion of water and salts in bitumen.[135, 136] Smith *et al.* reported the presence of polyvalent carbonates, clays and sulfates in Athabasca oil sands. These solids could consume the NaOH added for production of surfactants by reacting with the organic acidic components in bitumen and increasing solid wettability, both enhancing bitumen liberation from host solids.[137] Majid *et al.* developed a method using alkaline Tiron solution to separate the amorphous solids from Athabasca oil sands fine tailings. It was identified that the amorphous fine solids in the oil sands fine tailings consisted mainly of silica and a small amount of kaolinite, muscovite, corundum and calcite.[138] The results showed that about 50 wt% of the solids in the tailings fines were amorphous solids, such as amorphous silica, allophones, muscovite ($KAl_2[Si_3AlO_{10}](OH,F)_2$), and halloysites ($Al_4[Si_4O_{10}](OH)_8{\cdot}4H_2O$). Other mineral solids, such as rutile (TiO_2), anatase, brookite, ilmenite ($FeTiO_3$),[139] siderite, pyrite,[140] nanosized hematite, magnetite,[141, 142] chlorite,[143] illite, mixed layer illite–smectite, dolomite, siderite, K-feldspar, [144, 145] were also found in the Athabasca oil sands solids. Among these minerals, the titanium (Ti) and zirconium (Zr) containing minerals were found to be concentrated in the bitumen froth treatment tailings,[146] while the iron-bearing minerals had a higher affinity to heavy petroleum components such as asphaltenes.

The major minerals in heavy oil reservoirs are silicate minerals which have been studied extensively during the past decades.[147] The phyllosilicates (sheet silicates) are an important class of silicate minerals, including kaolinite, illite, montmorillonite, talc, muscovite, etc. These phyllosilicates consist of tetrahedral sheets (T: silicon-oxygen tetrahedron network) and octahedral sheets (O: six-fold coordination of aluminum with oxygen from the tetrahedral sheet and hydroxyl groups, while individual octahedral is linked laterally by sharing edges).[16, 147] Different stacking of T and O sheets leads to different types of clay minerals, such as trilayer (TOT) illite, montmorillonite, talc, muscovite, and bilayer (TO) kaolinite.[147] The physiochemical properties of these platy minerals determine their fate in unconventional petroleum production. More importantly, these platy phyllosilicate clay minerals exhibit anisotropic surface properties,[148, 149] leading to highly variable interfacial interactions between heavy oil and various (basal plane and edge) surfaces of clay minerals.

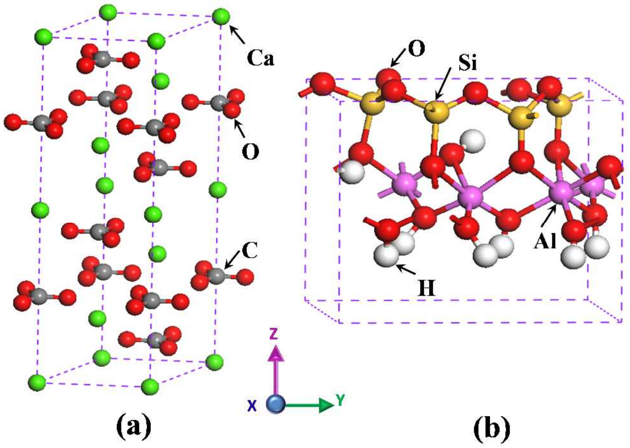


Fig. 7 Typical crystal structures of mineral solids: (a) calcite (carbonate rocks), and (b) kaolinite (aluminum silicate rocks) found in unconventional petroleum reservoirs. *Reproduced with permission from ref. 150 and ref. 151. Copyrights of 2014 American Chemical Society.*

Although extensive research has been conducted to investigate the minerals in heavy oil reservoirs, there exists little information on the roughness and heterogeneity of mineral surface. In fact, there are still many unknown minerals embedded in unconventional petroleum reservoirs and their roles in petroleum production remain to be explored.

3.3.2 Characterization of solids wettability

As mentioned earlier, the solids can be classified as hydrophilic (water-wet) and hydrophobic (oil-wet). In practice, the wettability of solids is influenced by many factors such as crystal structure, surface roughness, surface heterogeneity, particle size, temperature, pressure, and more importantly the interactions of the solids with (or contamination by) petroleum components.[109, 117, 152, 153] Due to the complex nature of solids in unconventional oil reservoirs, characterizing the wettability of solids could be challenging.[154] One of the widely-accepted methods for evaluating wettability of solids is contact angle measurement.[109, 117, 155-157] This method is the simplest but usually requires a well-defined smooth, flat surface. Unfortunately, this method is not suitable for characterizing the wettability of particulate fine solids as found in unconventional petroleum reservoirs, as the solids there are often rough, porous and of irregular shapes. Anderson summarized other methods of wettability measurements, including quantitative Amott and the U.S. Bureau of Mines (USBM) methods, and semi-quantitative methods such as imbibition, film flotation, relative permeability, capillary pressure, displacement capillary pressure and permeability-saturation curve.[156] The reservoir log method, such as nuclear magnetic relaxation and dye adsorption, are often used for measuring the wettability of solid mixtures.[156] There are some indirect methods of solid wettability measurement, including heat of immersion and inverse gas chromatography.[158-161] Among these methods, imbibition is the most commonly used method for measuring the wettability of porous reservoir rocks. However, the results of imbibition measurement are highly dependent on the relative permeability and pore structure of solids, viscosity of liquid, oil-water interfacial tension and initial saturation of the core. This method is insensitive to the solids of moderate wettability.

Recently, Alipour Tabrizy *et al.* reported a novel method to characterize the wettability of solids by measuring the enthalpy of adsorption using thermal gravimetric analysis.[162] Based on the isothermal adsorption of water vapour on the mineral surfaces, a new wettability index (WI) was proposed by measuring the capacity of remaining mineral surface area (defined as the ratio of the adsorbed monolayer of water vapour on the modified surface to that of unmodified surface). This method measures the wettability at a microscopic level of solid surfaces. However, the general applicability of this method to the solids in petroleum reservoirs remains to be determined due to the lack of comprehensive and creditable database information.

With the above methods, the wettability of solids in unconventional petroleum reservoirs can be measured. The wettability of solids is generally recognized to be determined by the composition of reservoirs and to vary significantly with the sample preparation conditions. Applying imbibition method to six different reservoir rocks (limestone or sandstone), for example, Bobek *et al.* demonstrated the ore dependency of solid wettability, even though all the rocks being investigated were water-wet. The authors reported that the wettability of reservoir rocks was influenced by the adsorbed materials.[163] Similar phenomena were found for Athabasca oil sands solids.[154] The accuracy of the measurement was found to be influenced by the particle size and the methods used, referring to sample preparation or wettability measurement methods.[154, 164]

3.3.3 Alteration of solid wettability

Solid wettability is one of the key factors in controlling the liberation of unconventional petroleum. Generally speaking, solid minerals in many unconventional oil reservoirs are intrinsically water-wet. The adsorption of asphaltenes or other organic components in the petroleum has a profound effect on altering the wettability of solid surfaces to be oil-wet.[165] As a result, the efficiency of unconventional oil liberation from oil-wet solids would be reduced significantly, resulting in poor recovery and product quality of unconventional oil. In addressing these problems, functional chemicals, salts, alkalis and surfactants have been added to improve the recovery of unconventional petroleum by modifying the wettability of reservoir solids. An overview on these chemical modifiers of solid wettability and their underlying working mechanisms are given below.

Asphaltene modifiers. Among the components of unconventional petroleum, asphaltenes are considered as a major component that could alter the hydrophilic character of solids to be hydrophobic.[166] It is clear that asphaltene molecules contain both surface-active polar groups and non-polar hydrocarbon framework. The polar groups have a strong affinity to reservoir rock surfaces through chemical and hydrogen bonds, leaving the non-polar framework facing the surface to trigger the hydrophobic character.[124] Using mica and silica as solid substrates, Kumar et al. found that the asphaltenes could easily adsorb on these solid surfaces, making them to be hydrophobic.[165] The extent of asphaltene modification of the solids wettability was found to be largely dependent on asphaltene concentration in the oil.[167, 168] Asphaltenes were also found to adsorb on the carbonate rock and clay mineral surfaces. Using a model surface coating of the kaolinite on a glass surface, Fogden *et al.* demonstrated the alteration of the kaolinite surface to become hydrophobic by adsorption or deposition of asphaltenes in the pores between the platelets of kaolinite clays.[129, 169] Alipour *et al.* reported a strong role of asphaltenes and/or stearic acids in modifying the wettability of humidified calcite surfaces to become more oil-wet.[162]

The ability of asphaltenes to modify solid wettability was attributed to the interactions between asphaltene polar groups and solid surfaces. Wang et al. reported adsorption of asphaltenes on hydrophilic solid surfaces such as silica or alumina through polar-polar interactions.[170] Based on IR spectroscopic analysis, Qi et al. concluded that polar interactions were the main mechanism of asphaltene adsorption on quartz surfaces.[168]

Surfactant modifiers. Surfactants are commonly used to change the hydrophobic character of (asphaltene-contaminated) solids to be hydrophilic in unconventional petroleum production. Based on the charge characteristics of polar (hydrophilic) groups, there are three main types of surfactants: cationic, anionic and nonionic. The cationic surfactants primarily include amines of pH-dependent ionization such as octenidine dihydrochloride, and permanently-charged ammonium chemicals such as cetrimonium bromide and benzalkonium chloride, shown in **Fig. 8 a**. Cationic surfactants that contain $R–N^+(CH_3)_3$ groups are able to adsorb on the chalk cores irreversibly, leading to modification of solid surface wettability.[171] During imbibition tests with brine, Xie *et al.* observed an additional oil recovery of 5 to 15 % accounting for original oil in place (OOIP) from three different dolomitic reservoir cores (*i.e.*, Cottonwood Creek, Dagger Draw and Lustre fields) by applying a commercial cationic surfactant, known as cocoalkyltrimethyl ammonium chloride ($R_2N(CH_3)_3Cl$, where R = cocoalkyl with a chain of 12 to 16 carbons).[172] The enhancement in oil recovery by surfactant was attributed to wettability alteration of the rocks from oil-wet to water-wet. Four ammonium (*i.e.*, n-Decyl trimethylammonium bromide, n-Dodecyl trimethylammonium bromide, coconub oil alkyl (C_{12}-C_{14}) trimethylammonium chloride, and trimethyl tallowalkyl (C_{16}-C_{18}) ammonium chloride) and two phosphonium (*i.e.*, n-Decyl triphenylphosphonium bromide and n- Dodecyl triphenylphosphonium bromide) cationic surfactants were tested by imbibition method for improving oil recovery from naphthenic acid treated calcite powders.[173] The efficiency of the surfactants on enhancing oil recovery was found to be dependent on the molecular structure and molecular weight of the surfactants. The phosphonium cationic surfactants performed better at 52 to 62% oil recovery than the ammonium surfactants at 40 to 48% oil recovery. N, N-dimethyldodecylamine (NN-DMDA) has been shown to modify the wettability of quartz, kaolinite and calcite by its adsorption on the solid surfaces, resulting in a more hydrophobic surface and hence reduced oil recovery.[162, 174] Recently, cetyl trimethylammonium bromide (CTAB) was successfully used to alter the wettability of bitumen-treated glass surface under alkaline conditions, but was shown to be less effective than anionic surfactants (*e.g.*, sodium methylnaphthalene sulfonate (SMNS) and sodium dodecyl sulfate (SDS)).[175] For the same type of surfactants, the ability of altering the wettability by surfactants is found to be dependent on molecular structure. For example, a Gemini type of cationic surfactant named alkanediyl-α,ω-bis(dimethylalky1ammonium bromide) showed a stronger ability than CTAB to adsorb on the mineral surfaces to alter their wettability.[176, 177]

Anionic surfactants are more commonly used to increase the wettability of reservoir rocks for enhancing petroleum recovery. This kind of surfactant includes sulfates ($-OSO_3^-$), sulfonates ($-SO_3^-$), phosphate esters ($-P(OR)(OR')(OR'')O^-$) or carboxylates ($-COO^-$), *etc.* as anionic functional groups connected to a long hydrocarbon chain/ring tail, as shown in **Fig. 8 b**. By conducting spontaneous imbibition tests at 40 °C, Standnes *et al.* investigated the ability of this type of anionic surfactants to increase the wettability of oil-aged chalk surfaces.[171] The sulfonates were shown to perform more efficiently than carboxylates, followed by phosphates and sulfates. In the study conducted by Seethepalli *et al.*, sulphonates such as alkyl aryl ethoxylated sulphlnated phenol, alkyl aryl sulphonate and alkyl aryl ethoxylated sulphonate, and propoxylated sulfates with different numbers of PO (propylene oxide) groups were used as wettability modifiers of carbonate surfaces (lithographic limestone, marble, dolomite and calcite).[178] Compared with dodecyltrimethylammonium bromide (DTAB), these anionic surfactants were shown to perform better in increasing the wettability of these solid surfaces to be intermediate water-wet when a Texas crude oil was used as the test oil. Together with the sodium carbonate, some other sulfate anionic surfactants containing different numbers of PO groups were also found to be effective in changing the wettability of calcite. The effectiveness however was found to be influenced by the aging time, temperature and the formulation of surfactant.[179] Adsorption tests showed an active role of naphthenic acids (carboxylate surfactants, C7 to C12) and fatty acids in changing an originally strong water-wet calcite surface to be intermediate water-wet in n-decane.[173, 180] The extent of wettability alteration was shown to be affected by the molecular weight of the surfactant. Other anionic surfactants, such as sodium dodecyl sulfate (SDS),[173] sodium lauryl ether sulfates,[181] polyether sulfonate, alkyldiphenyloxide disulfonate,[182] alkyl propoxy ethoxy sulfates, alkyl ethoxy sulfonates, sulfates[183, 184] stearic acid (SA: $CH_3(CH_2)_{16}COOH$),[162] sodium methylnaphthalene sulfonate (SMNS),[175] C_{13}-$(EO)_{27}$-sulfate, and 15−18 internal olefin sulfonate,[185] were frequently reported to be able to alter the wettability of calcite, sands and clays. Interestingly, Giraldo *et al.* reported an enhanced role of anionic surfactants in modifying the wettability of solids in the presence of nanoparticles.[186] Details on the anionic surfactants studied previously are summarized in **Table 1**.

Also applied in laboratory investigation and industry practices are non-ionic surfactants, including the long chain alcohols, esters, ethers, *etc*. Over the last decade, some non-ionic surfactants have been tested as the process aids for improving petroleum recovery from unconventional petroleum reservoirs. Poly-oxyethylene alcohol ($(C_9$-$C_{11})(OCH_2CH_2O)_nH$) is one of the non-ionic surfactants, which has been found to be more effective than cocoalkyltrimethyl ammonium chloride in enhancing oil recovery from the dolomitic-type of reservoirs.[172] Similarly, alcohols, such as ethoxylated C11-C15 secondary alcohol, nonylphenoxypoly (ethyleneoxy) ethanol, C12-C15 linear primary alcohol ethoxylate, are proven to be adsorbed on the naphthenic acids-treated calcite surfaces, leading to an increase in wettability of solids by removing the originally adsorbed naphthenic acids.[173] Gupta *et al.* pointed out that the addition of secondary alcohol ethoxylates or nonyl phenol ethoxylate could alter the oil treated calcite surface from highly oil-wet (with contact angle greater than 165° at 25 °C) to weakly oil-wet (with contact angle around 115° at 25 °C) or even water-wet (with contact angle lower than 80° at 70 °C).[182]

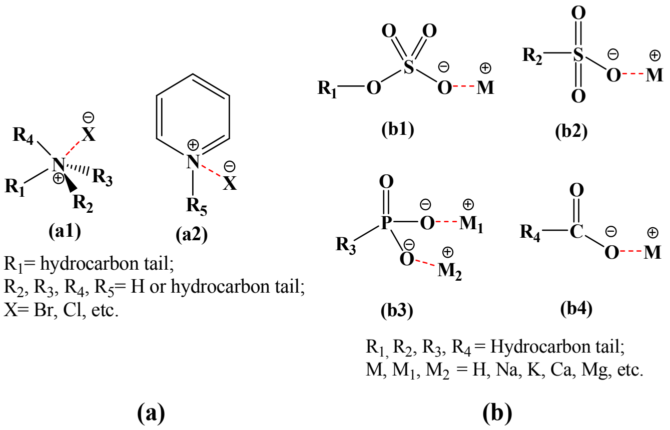


Fig. 8 Typical structures of surfactants involved in petroleum industry: (a) cationic surfactants, referring to the amines (a1) and ammoniums (a2); and (b) anionic surfactants, including organic sulfates (b1), sulfonates (b2), phosphates (b3) and carboxylates (b4).

Recently, an environmentally-friendly polymer, ethyl cellulose (EC) has been intensively investigated as solid surface modifier by Xu's group.[170, 124] In their study, the originally hydrophilic silica and alumina surfaces were first treated by asphaltenes- or bitumen-in-toluene solutions, followed by immersing in EC-in-toluene solutions. The characterization using quartz crystal microbalance with dissipation (QCM-D), atomic force microscope (AFM) imaging and contact angle measurement showed an irreversible adsorption of asphaltenes on the silica and alumina surfaces, resulting in an intermediate water-wet surface of water contact angle around 88°. When the treated solid surfaces were immersed in the EC-in-toluene solutions, the pre-adsorbed asphaltenes were found to be displaced by EC, making the solid surface less hydrophobic with a water contact angle around 20°, a value similar to EC treated silica surfaces without asphaltenes or bitumen.[170] Lin *et al.* observed a similar trend when investigating bitumen-water displacement from oil-contaminated and EC-treated micro-scale glass surfaces.[124] Other non-ionic surfactants, such as ethoxylated nonylphenol-4 mol (NON-EO4: $C_{15}H_{23}(OCH_2CH_2)_4OH$), lauryl alcohol-7 mol (LA7: $C_{12}H_{25}(OCH_2CH_2)_7OH$), tween 80 ($C_{64}H_{124}O_{26}$) and span 80 ($C_{24}H_{44}O_6$) were used together with nanoparticles to alter the wettability of reservoir rock surfaces.[187] Some recent studies on wettability alteration by surfactants are summarized in **Table 1**.

Here is a quick summary on how solid wettability is altered by surfactants. In general, the reservoir rocks can be divided into two categories: carbonate type and silicate type. Although dependent on the pH of the solution, the carbonate rocks (**Fig. 7 a**) are in general positively charged while the silicate minerals (**Fig. 7 b**) are always negatively charged when placed in water. When the solids are contaminated by the petroleum components, such as asphaltenes and/or carboxylic acids, the solid surfaces change from water-wet to intermediate water-wet or even oil-wet due to adsorption of the petroleum materials.

When cationic surfactants are added into the aqueous solution to modify a silicate surface (*i.e.*, quartz, glass), the added surfactants could desorb the adsorbed (**Fig. 9 a**) petroleum carboxylates from or co-adsorb with the carboxylate on the solid surfaces by forming ion pairs, resulting in wettability alteration.[188, 189] When carbonate rock surfaces are involved, such as chalk, calcite, *etc.*, the ion-pair formation (**Fig. 9 b**) between the cationic surfactants and adsorbed negatively charged carboxylates (**Fig. 9 a**) from the oil reduces interactions between petroleum carboxylates and solid surfaces, increasing the wettability of solids.[171, 173] The solubilisation of the formed ion pairs in the oil phase would improve the efficiency of the surfactants as a result of emulsion formation as shown in **Fig. 10**.[130]

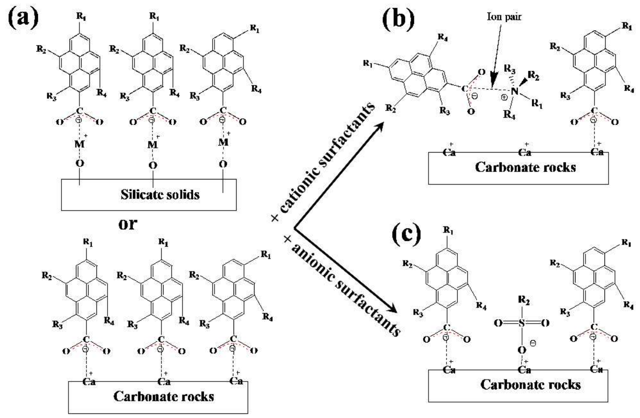


Fig. 9 Formation of ion pairs between added surfactants and adsorbed petroleum components, and/or adsorption of surfactants on the solid surfaces in place of petroleum substances: (a) adsorption of petroleum components on solids surfaces; (b) replacement/liberation of adsorbed petroleum components by cationic surfactants due to ion pair formation; (c) replacement/co-adsorption of anionic surfactants with petroleum substances on solid surfaces. M represents the metal ions such as Na^+, Ca^{2+}, Mg^{2+}; R_1, R_2, R_3 and R_4 denote the hydrocarbon branches or heteroatom groups, such as –N-, -S-, -OH.

In addition, Standnes *et al.* also found that the adsorption of surfactants was influenced by many other factors, such as solubility, hydrophobic character, critical micelle concentration (CMC), oil-water interfacial tension and steric effects of the surfactant near N-atoms.[171] Liu *et al.* reported that the cationic surfactant, such as CTAB, was ineffective in removing the adsorbed bituminous materials from glass surfaces.[175] These inconsistent findings suggest the need for further investigation on the mechanisms of altering the wettability of petroleum reservoir rocks by cationic surfactants.

Anionic surfactants often perform well in an alkaline environment but influence the solid surfaces in a similar way as cationic counterparts. Although negatively charged carboxylates are sometimes not easily desorbed by anionic surfactants,[171] the reduction in interfacial tension could help to enhance oil displacement. As shown in **Fig. 9 c**, when a strong anionic surfactant such as SDS is used, it can also desorb the adsorbed carboxylic materials, and even adsorb on the solid surface instead, resulting in a change in solid wettability.[173] Gupta *et al.* observed that anionic surfactants could desorb naphthenic acids from a calcite surface, altering the surface to be less hydrophobic.[184] For a negatively charged solid surface, anionic surfactants dissolve into the oil phase and desorb the anionic molecules from the surface by forming ion pairs.[165] Liu *et al.* found that the addition of sodium carbonate into the solution could enhance the role of anionic surfactant in altering the solid surface wettability through a synergistic effect.[175] Non-ionic surfactants work through similar mechanisms by stronger (both van der Waals and polar) interactions with the solid surface than the petroleum components.[170]

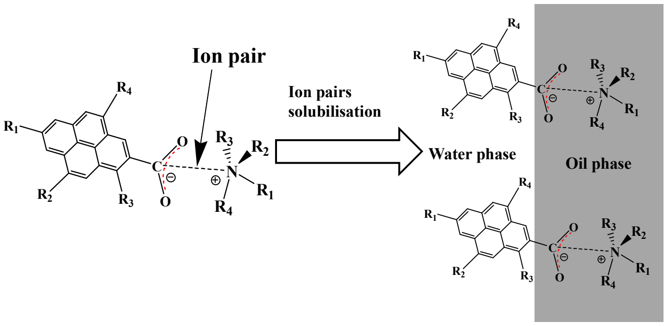


Fig. 10 Solubilization of ion pairs formed by added surfactants and adsorbed petroleum components in oil phase.

Table 1 Surfactants used for wettability alteration

Surfactants	Water system	$C_{surfactant}$	Solids	Oil	T/°C	Impact or Contact angle*	Ref.
Cationic surfactants							
n-C_{12}–$N(CH_3)_3Br$	brine	1.0 wt.%	chalk[a]	C.H.	50	12	171
n-C_{12}–$N(CH_3)_3Br$	brine	0.1 wt.%	chalk[a]	C.H.	50	28	171
n-C_{16}–$N(CH_3)_3Br$	brine	1.0 wt.%	chalk[a]	C.H.	50	27	171
n-Ph-$(EO)_2$-$N(CH_3)_2(CH_2$-Ph)Cl	brine	0.2 wt.%	chalk[a]	C.H.	50	21	171
(n-(C_8-C_{18})-$N(CH_3)_2(CH_2$-Ph)Cl	brine	0.5 wt.%	chalk[a]	C.H.	50	26	171
n-C_{10}–$N(CH_3)_3Br$	brine	2.5 wt.%	chalk[a]	C.H.	50	31	171
n-C_8–$N(CH_3)_3Br$	brine	4.0 wt.%	chalk[a]	C.H.	50	57	171
$R_2N(CH_3)_3Cl$	brine	<2620 ppm	dolomite	crude oil	>55	+	172
$CH_3(CH_2)_9N(CH_3)_3Br$	water	14.3 mM	calcite	NAs[e]	25	++	173
$CH_3(CH_2)_{11}N(CH_3)_3Br$	water	13 mM	calcite	NAs	25	+++	173
$CH_3(CH_2)_9P(C_6H_5)_3Br$	water	7.8 mM	calcite	NAs	25	+++	173
$CH_3(CH_2)_{11}P(C_6H_5)_3Br$	water	14.4 mM	calcite	NAs	25	+++	173
Dodecyl trimethyl ammonium bromide	brine	0.05 wt.%	silicon and mica	oil fractions	25	78[c]/129[d]	165
Anionic surfactants							

n-$C_8O_2CCH_2$)(n-C_8O_2C)CH–SO_3Na	brine	0.5 wt.%	chalk[a]	C.H.	50	55	171
n-(C_{12}-C_{15})-$(PO)_4$-$(EO)_2$–SO_3Na	brine	1.0 wt.%	chalk[a]	C.H.	50	44	171
n-C_9-Ph-$(EO)_x$-PO_3Na	brine	0.5 wt.%	chalk[a]	C.H.	50	75	171
(n-C_8-$(EO)_8$-OCH_2-COONa	brine	0.5 wt.%	chalk[a]	C.H.	50	48	171
n-C_{12}–OSO_3 Na	brine	0.1 wt.%	chalk[a]	C.H.	50	39	171
n-C_8-$(EO)_3$–OSO_3 Na	brine	0.5 wt.%	chalk[a]	C.H.	50	49	171
n-(C_{12}-C_{15})-$(EO)_{15}$–OSO_3 Na	brine	0.5 wt.%	chalk[a]	C.H.	50	63	171
Sodium dodecyl 3 EO sulfate	NaCl	0.05 wt.%	calcite	crude oil	80	~180	179
C_{12-15}-$(PO)_4$- $(EO)_2$-OSO_3Na	brine	1.0 wt.%	chalk cores	n-heptane	25		190
Stearic acid ($CH_3(CH_2)_{16}COOH$)	water	10 mM	calcite	n-decane	25/50/80	160/131/90	180
($C_8H_{17}CH=CH(CH_2)_7COOH$) Oleic acid	water	10 mM	calcite	n-decane	25/50/80	103/85/54	180
$C_6H_5CH=CH(CH_2)_{17}COOH$	water	10 mM	calcite	n-decane	25/50/80	135/NA/110	180
C_6H_{11} $(CH_2)_{17}COOH$	water	10 mM	calcite	n-decane	25/50/80	96/NA/67	180
SDS ($CH_3(CH_2)_{11}OSO_3Na$)	water	13.9 mM	calcite	NAs	25	+	173
Propoxylated sufateds-8PO	brine	0.05wt%	silicon and mica	oil fractions	25	48[c]/99[d]	165
Alkyldiphenyloxide disulfonate	$NaCO_3$[b]	0.05 wt%	limestone	Texas oil	25/50/70/90	155/137/128/110	182
Polyether sulfonate	$NaCO_3$[b]	0.3 wt%	limestone	Texas oil	25/50/70/90	129/121/90/80	182
C_{12}-C_{15} ethylene oxide sulfonate (7EO)	$NaCO_3$[b]	0.1 wt%	limestone	Texas oil	25/50/70/90	NA/NA/100/85	182
C_{12}-C_{13} propoxy sulfonate (7EO)	$NaCO_3$[b]	0.05 wt%	limestone	Texas oil	25/50/70/90	135/130/85/65	182
Alkyldiphenyloxide disulphonate	$NaCO_3$[b]	0.05 wt%	limestone	Texas oil	25/50/70/90	69/56/50/40	182
+C14 T-isofol propoxy sulphate (8PO)	$NaCO_3$[b]	0.1wt%	limestone	Texas oil	25/50/70/90	126/120/90/75	182
$C_6H_{11}COOH$	water		calcite		25	-	173
$CH_3(CH_2)_4C_6H_{10}COOH$	water		calcite		25	--	173
Asphaltenes/bitumen	oil		silica / alumina		21	---	170
Non-ionic surfactants							
$(C_9\sim C_{11})(OCH_2CH_2O)_nH$	brine	750~1050 ppm	dolomite	crude oil	>55	+	172
(C_mH_{2m+1}) $(C_nH_{2n+1})CH(OCH_2CH_2)_7OH$, m+n=10~14	water	7.77 mM	calcite	NAs	25	++	173
(C_mH_{2m+1}) $(C_nH_{2n+1})CH(OCH_2CH_2)_{40}OH$, m+n=10~14	water	2 mM	calcite	NAs	25	+/-	173
$C_9H_{19}C_6H_4(OCH_2CH_2)_6OH$	water	8.26 mM	calcite	NAs	25	+++	173
$C_nH_{2n+1}(OCH_2CH_2)_7OH$	water	7.77 mM	calcite	NAs	25	+	173
Secondary alcohol ethoxylates	$NaCO_3$[b]	0.1wt%	limestone	Texas oil	25/50/70/90	145/71/40/18	182
Nonyl phenol ethoxylate	$NaCO_3$[b]	0.1wt%	limestone	Texas oil	25/50/70/90	118/109/85/76	182

*contact angle is in degree. C.H. denotes the oil mixture composed by crude oil: n-heptane at 60:40 by volume. [a] chalk aged by crude oil. [b] $NaCO_3$ solution. [c] receding contact angle; [d] advancing contact angle; [e] Naphthenic acids; NA: no data. +++: increase wettability a lot (strongly); ++: moderately increase; +: slightly increase; -: slightly decrease wettability; --: moderately decrease; ---: strongly decrease.

Inorganic ion modifiers. Inorganic substances such as salts and alkalis can also exert a significant impact on altering the wettability of mineral solids. In fact, brine is often used in unconventional petroleum production for water flooding. Changing the salinity of the brine has been considered as an easy and convenient method to impact the petroleum recovery due to its ability to change the wettability of the reservoir rocks and alter oil-water interfacial properties. With an oil-treated glass surface, Al-Aulaqi *et al.* found a significant increase in advancing contact angle from 20° to 138° by increasing NaCl concentration from 0 to 3 M under the ambient conditions, indicating a change of the glass surface from strongly water-wet to oil-wet.[167] In a separate study, Gupta *et al.* made similar observations.[184] However, they found that Mg^{2+} ions could increase the hydrophobicity of carbonate rocks (*i.e.*, calcite and chalk) only in the presence of SO_4^{2-}, while Ca^{2+} ions are able to increase the hydrophobicity of calcite by themselves, which could be enhanced by the presence of SO_4^{2-}. The ability of divalent ions in increasing the hydrophobicity of oil-aged calcite surface was attributed to desorption of cyclohexanepentanoic acids by the occupation of the ions. Zhang *et al.* proposed a mechanism of SO_4^{2-} in altering the wettability of carbonate reservoir rocks as follows: initially the SO_4^{2-} ions adsorbed on the solid surface, making the positively charged solid surface less positively charged or even reversed to be negatively charged. This change in the surface charge reduced the adhesion force between the solid surface and negatively charged carboxylic molecules, resulting in the desorption of the carboxylic molecules.[191]

Testing the effect of Mg^{2+}, SO_4^{2-} on the wettability alteration of calcilte, quartz and kaolinite surfaces aged by stearic acid, N,N-dimethyldodecylamine or asphaltens, Tabrizy *et al.* observed that both Mg^{2+} and SO_4^{2-} ions could make the treated calcite surface more hydrophilic, while a marginal effect of SO_4^{2-} ions was observed on silicate minerals (quartz and kaolinite). Mg^{2+} ions were found to make the N,N-dimethyldodecylamine treated silicate surfaces more hydrophilic, but the asphaltene-treated silicate surfaces more hydrophobic.[174] The ion exchange/precipitation was proposed to be the reason for increasing the wettability by reducing the interaction/adsorption of polar components of heavy oil on the calcite surface, while the bridging between the hydrated Mg^{2+} ions and asphaltenes was the reason for increasing the hydrophobicity of the asphaltene treated silicate surface. A similar phenomenon was observed by Qi *et al.*[168] Based on the zeta potential measurements and characterization by IR spectroscopy, they proposed the compression of the electrical double layer of quartz by divalent cations (*e.g.*, Ca^{2+}, Mg^{2+}) as the reason for such change. The compression of the electrical double layer facilitates the adsorption of asphaltenes on quartz. The divalent cations also provide a binding bridge between natural surfactants and solids, leading to a strong affinity of oil to solids and difficulties in oil liberation.[131]

In practice, low salinity processes are often applied to the recovery of unconventional petroleum. Lager *et al.* observed a negligible effect of mineral oil on solids wettability when low salinity water was used, due to the absence of polar compounds in the mineral oil to strongly interact with the clay minerals. Based on such findings they proposed a binding mechanism of indigenous surface active molecules in oil with mineral solids in low salinity water, as shown in **Fig. 11**. They attributed the enhanced oil recovery by low salinity water flooding to the cation exchange between the mineral surface and the invading brine.[188] Later, Nasralla *et al.* reported a similar phenomenon that the low salinity was effective in increasing the wettability of oil-contaminated mica sheets. Their results showed that lower salinity of water was beneficial to reduce the contact angle of the oil-contaminated mica, leading to a more water-wet surface. Zeta potential measurements further indicated that the wettability alteration of the minerals by the low salinity water flooding was attributed to the changes in electrokinetics of solids.[192]

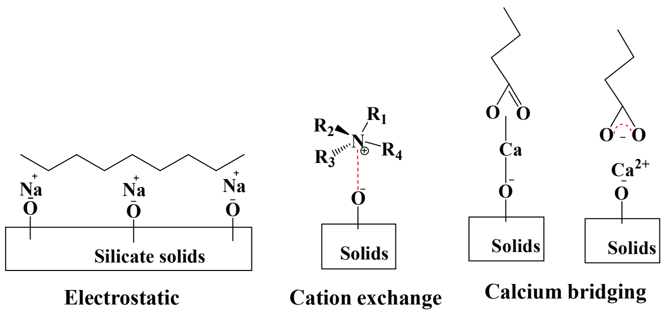


Fig. 11 Representation of the diverse adhesion mechanism occurring between clay surface and crude oil. *Modified from Lager et al. 2008.*[188] *Copyright 2008 SPWLA.*

Effect of temperature. From a thermodynamic point of view, temperature is an important factor influencing the physical-chemical processes, likely including the alteration of solid wettability. However, different phenomena have been observed on the wettability alteration of solids by changing the temperature. Al-Aulaqi *et al.* reported a decrease in wettability of crude oil contaminated glass surface with increasing the temperature, while there is no significant change for the glass surfaces contaminated by refined oils.[167] Testing the mica sheets aged by crude oil, Nasralla *et al.* observed an increase in contact angle of rocks when increasing the temperature or pressure.[192] However, there was a significant decrease in contact angle of MgCa2S brines (containing 13 mM Mg^{2+}, 45 mM Ca^{2+} and 50 mM SO_4^{2-}) from about 150^{o} to 86^{o} on an oil-contaminated calcite when the temperature was increased to 70 ^{o}C.[184] The beneficial effect of higher temperature on increasing the wettability of oil-contaminated calcite was attributed to the increase in cation exchange between the bulk solution and the solid surface. To study the effect of temperature on wettability of reservoir rocks, Kim *et al.* also conducted their tests at elevated temperature up to 170 °C and observed a significant increase in wettability of rocks with increasing temperature.[193] From their observations, the rock was found to be dissolved at 170°C due to the increased solubility of dolomite. The above controversies may be due to the variations in composition of the system, and further investigations on this aspect remain a necessity.

Nanofluid modifiers. Recently, a new class of nanoparticle-based materials was found to be effective in altering the wettability of petroleum reservoir rocks. For example, Karimi *et al.* formulated a nanofluid consisting of 0.05 g/ml nanosize ZrO_2 particles and 5 wt% non-ionic surfactants in water of pH 2-3. Treating a carbonate plate aged in a crude oil for 200 hrs with such nanofluid, the contact angle of *n*-heptane on the carbonate plate in water was decreased from 150° to 30°, indicating significant modification of a strongly oil-wet carbonate surface to highly water-wet.[187] Later, anatase and amorphous TiO_2 nanoparticles were found to exhibit a stronger ability to modify the wettability of oil-wet core plug surfaces at particle concentrations as low as 0.01 wt%.[21] Aluminum nanoparticles[186] and silica nanoparticles,[194] were also reported to change the wettability (from oil-wet to water-wet) of reservoir rocks. For a given system, the extent of increasing the wettability of reservoir rocks was found to be highly dependent on the concentration of nanoparticles in the nanofluid.[186]

The ability of nanoparticles to increase the wettability of reservoir rocks is believed to stem from the adsorption/deposition of hydrophilic nanoparticles, and the corresponding change in roughness, on the rock surfaces. Karimi *et al.* proposed the formation of nanostructures by adsorbed hydrophilic nanoparticles on oil-wet rock surfaces, converting the originally-smooth oil film to rough composite surfaces. Such nanostructure of composite surfaces with hydrophilic protrusions is known to exhibit super-hydrophilic character, converting the original oil-wet rock surfaces to water-wet, facilitating the liberation of oil from rocks and increasing oil recovery.[187] Ehtesabi *et al.* proposed an alternative mechanism of rock wettability alteration by nanofluids, involving -OH groups being produced as a result of the occupancy of oxygen vacancies on the nanoparticles by water molecules that triggered the surface to be hydrophilic.[21]

3.4 Oil-solid interactions

The interactions (or forces) between oil molecules and solid surfaces have been considered as one of the important factors that control the liberation dynamics of unconventional oil from reservoir solids. For a reservoir of strong oil-rock attractions, the separation of oil from the rock would be difficult. Experimentally, zeta potential and direct force measurements are often used to characterize the interactions between the oil and rock surfaces. Theoretically, the well-known DLVO (Derjaguin-Landau-Verwey-Overbeek) and extended DLVO theories[195] are applied to interpreting the colloidal interactions between particles or/and oil droplets in an aqueous medium.

3.4.1 Forces between oil droplets and solids in aqueous solutions

Silica sands, carbonate rocks and clay minerals are three main classes of mineral solids in unconventional oil reservoirs. In the past two decades, the interactions between quartz/silica sands and bitumen have been studied extensively.[118, 196-198] In general, the interactions between silica sands and bitumen are highly dependent on the water chemistry (*e.g.*, pH, divalent cation concentration, and ionic strength) and temperature. Dai *et al.* observed an easier detachment of silica particles from the bitumen surface at pH above 6 than at pH below 6, suggesting a stronger adhesion between silica and bitumen in lower pH aqueous solutions.[118] This observation was confirmed by AFM force measurements which showed an adhesive force between silica sands and bitumen in 1 mM KCl solutions of pH less than 8.2.[197] Increasing the concentration of ions, such as Na^+ and Ca^{2+}, reduces repulsive forces. Increasing concentration of ions can even reverse the repulsive forces to become attractive between bitumen and silica in alkaline solution, as a result of compressing the electric double layers around silica and bitumen surfaces or specific adsorption on these surfaces.[197] A strong coagulation of bitumen with silica in an alkaline aqueous solution was observed with Ca^{2+} addition, which agreed with the results of above force measurements and was attributed to the specific adsorption of calcium ions on silica, acting as a bridge between the silica particles and bitumen droplets in aqueous solution.[196] When investigating the interactions between bitumen and silica or clay surfaces, Long *et al.*[199] and Zhao *et al.*[71] obtained similar results. The surfactants such as sodium dodecyl sulfate (SDS) were found to reduce the adhesion force between silica and bitumen, which explains the role of surfactants in enhancing the bitumen liberation from sand surfaces.[71] It was found that the adhesion forces between bitumen and silica decreased as divalent cations (*e.g.*, Ca^{2+}) were added in combination with ionic surfactants. An increase in solid hydrophobicity as a result of reservoir (oil sand) weathering led to a stronger adhesion between bitumen and solid surfaces, resulting in a much lower recovery of bitumen.[200-202] Similar observations on the interactions between altered solid surfaces and oil were reported elsewhere.[165]

The interactions of bitumen with clays are similar to, but more strongly adhesive than those with silica sands.[203, 204] Xu *et al.* found that the adhesion forces in 1mM KCl solutions of pH 8 are 0.3 mN/m and 3~9 mN/m for bitumen-silica and bitumen-clays, respectively.[197] Different clays were shown to have different affinity to bitumen. The adhesion forces between bitumen and montmorillonite are much stronger than that between bitumen and kaolinite, especially in the presence of calcium ions in aqueous solutions.[197] The stronger adhesion forces led to a severe slime coating of montmorillonite clays on bitumen and hence reduced recovery of bitumen from oil sands by flotation.[197, 205] Interestingly, Kumar *et al.* reported that the chemistry of petroleum also impacted the oil-rock interactions.[165] The polar components in the petroleum show a stronger affinity to rock surfaces, making them more oil-wet.

Increasing temperature has been reported to be beneficial for bitumen liberation from solids and hence for bitumen recovery. This finding was supported scientifically by reduced adhesion between solids and bitumen with increasing temperature, measured using the AFM probe technique.[200]

It is evident that the intermolecular interactions between oil and solids play a critical role in petroleum production, which are strongly influenced by oil composition, type of solids, pH, ion concentration, temperature, *etc*. However, the effect of surface heterogeneity and anisotropy of solids on the interactions between the solids and bitumen remains to be explored.[206] The interactions of carbonate rocks and heavy petroleum under reservoir conditions need to be studied to fill the gap.

3.4.2 Forces between asphaltenes and solid

From the molecular point of view, it is the polar components in the petroleum that play an important role in modifying the wettability of solid surfaces due to their strong binding forces with and hence adsorption on the solids. Such strong bindings of polar organic molecules make the solids more oil-wet and hence hinder the liberation of petroleum from them. With the AFM probe technique, Abraham *et al.* reported an enhanced repulsion between asphaltene-coated silica surfaces and silica sphere by increasing the pH of aqueous solutions, suggesting the presence of pH-dependent ionizable/polarizable groups on the asphaltene surface.[207] In a number of recent studies, the interactions between asphaltenes and solids (*e.g.*, quartz and silica) in crude oil are considered as polar interactions to explain the results of force measurements and determination of functional groups.[168, 170]

Once the solid surfaces are altered by the adsorption of organic polar compounds of oil, especially the asphaltenes, the strong interactions between the asphaltenes and the oil become the controlling factor, which makes the liberation of oil more difficult. During the past decade, the interactions between asphaltenes in different systems have been studied extensively by AFM and SFA (surface force apparatus).[97, 208, 209] In 1mM KCl aqueous solution of pH 5.7, the interactions between asphaltenes are weakly repulsive or even attractive, which is very different from the observed strong repulsion between asphaltenes and silica surfaces under the same conditions.[208] Increasing the pH or temperature, or decreasing (monovalent or divalent) electrolyte concentrations imparts strong repulsive forces between asphaltene surfaces. Wang *et al.* carried out a similar measurement in organic solvents (mixture of toluene and heptane at different volume ratios, known as heptol).[97] They observed a long-range steric repulsion between asphaltene surfaces in toluene, which could be weakened or even reversed to be attractive with increasing the volume ratio of poor solvent (heptane) in heptol. The steric repulsion and attraction in toluene and heptane could be described by Alexander-de Gennes' polymer scaling theory and van der Waals forces, respectively.[209] They proposed that the asphaltenes in toluene were able to swell, while the branches were collapsed in the heptane, as shown schematically in **Fig. 12**.

3.5 Viscosity of unconventional oil

Viscosity of oil is another important factor influencing the liberation of oil from reservoir rock surfaces.[133] Due to the high concentration of heavy polar molecules such as asphaltenes, unconventional oil is characterized to be highly viscous as shown in **Table 2** and does not flow freely under gravity at room temperature. The asphaltene molecules in unconventional oil interact strongly with the host rock surface and among themselves in oil to make the flow of the oil extremely difficult if not impossible.[210, 211] Therefore, one of the effective ways of liberating the oil from the rock solids is to reduce such intermolecular interactions by increasing the temperature or adding chemicals, such as solvents, neutral gases, and asphaltene dispersants, to lower the viscosity of the oil.

3.5.1 Thermal treatment

Thermal method for viscosity reduction can be divided into low temperature heating or high temperature cracking. Low temperature heating mainly weakens intermolecular forces by increasing thermal energy of molecules without chemical reactions. A well-established empirical formula given below is often used to link the viscosity with temperature:[212]

$$\mu = Ae^{b/T} \qquad \textbf{(Eq. 3)}$$

where, μ is the viscosity, T is the absolute temperature, and A and b are empirical constants. Later, this basic relationship has been further developed for different heavy oil systems with the results shown in **Fig. 13 a**.[210, 211, 213-216] However, the physical significance of constants A and b in the context of structure and concentration of dominant heavy molecules that dictate intermolecular interactions remains to be established.

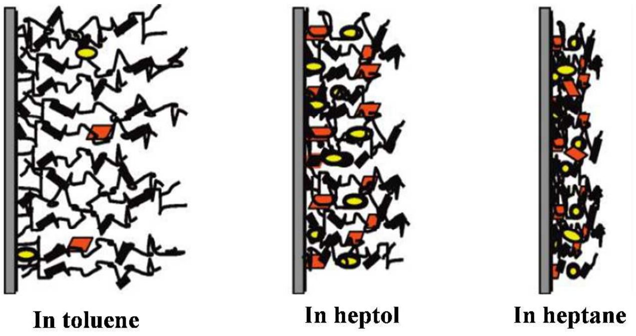


Fig. 12 Schematic representation of conformational transition of asphaltene layers in heptol of different volume ratios of heptane (black, orange and yellow symbols represent the fused aromatic ring sheet or consolidated part of asphaltenes), showing swollen structures and collapsed aggregates in good solvent (toluene) and poor solvent (heptane) of asphaltenes, respectively. *Reproduced with permission from ref. 97. Copyright 2009 American Chemical Society.*

Recently, nano-particles have been used in an attempt to reduce the viscosity of unconventional oil. It is hypothesized that the nano-particles dispersed in the heavy oil are able to effectively crack unconventional oil molecules, producing lighter petroleum fractions. For example, the nano-nickel catalysts synthesized in methylcyclohexane-water-n-octanol-AEO9 micro-emulsion, were proven to reduce the viscosity of Liaohe extra-heavy petroleum.[217] At temperatures as low as 50 °C, a sharp reduction in viscosity from 139.8 Pa•s to 2.4 Pa•s was observed for the sample oil due to the aquathermolysis as a result of hydrogen transfer from methylcyclohexane to the extra-heavy components of unconventional oil. Chen *et al.* reported a similar observation in reducing the viscosity of an extra heavy oil (about 800 Pa•s) by nano-keggin-$K_3PMo_{12}O_{40}$.[218] Injection into the underground heavy petroleum of ultradispersed trimetallic particles containing Mo, Ni and W (wolframium) has been shown to enhance the production of heavy petroleum. The dispersed particles in this case acted as catalysts, leading to effective cracking of the heavy fractions of petroleum into smaller and lighter molecules.[219, 220] Shokrlu *et al.* found that the Athabasca bitumen could be transformed to lower-viscosity petroleum even at ambient temperature when mixed with nano-iron (oxides), nano-nickel or nano-copper (oxide) particles.[221] They proposed that the viscosity reduction was mainly attributed to the following chemical reactions:

$$\mathrm{R-COOH+Heat \rightarrow R-H+CO_2} \qquad \textbf{(Eq. 4-a)}$$

$$\mathrm{4Fe(s) + 3O_2 + xH_2O(l) \rightarrow 2Fe_2O_3.xH_2O(s) + Heat} \qquad \textbf{(Eq. 4-b)}$$

The presence of carboxylic acids was shown to facilitate the reaction of **Eq. 4-b**. The heat being released from the reaction of **Eq**. **4-b** is provided to initiate the reaction as shown in **Eq. 4-a**. The removal of oxygen from the organics reduces the viscosity of the oil even at room temperature as observed in their study. The removal of sulfur (S) from the organics also contributes to viscosity reduction of the oil.[221] Interestingly, there was an optimal dosage of nanoparticles to achieve a maximum reduction in oil viscosity.

3.5.2 Chemical addition

One of the evident limitations of the thermal methods described above is either high energy input or usage of heavy metals. The addition of chemicals such as hydrocarbon solvents or neutral gases of CO_2, N_2 and CH_4 could also decrease the viscosity of heavy petroleum dramatically at ambient temperature without input of thermal energy.

Liquid solvents. Toluene, heptane, pentane, naphtha, kerosene and diesel are the common organic solvents for reducing viscosity of heavy petroleum.[131-133, 216] As shown in **Fig. 13 b**, the extent of the viscosity reduction by solvent addition depends on the solubility of solvents in petroleum and properties of the solvents.[124, 216, 224, 225] Essentially, the small solvent molecules are able to penetrate between heavy petroleum molecules and swell their branches, leading to a more fluid state and hence lower viscosity of the oil. In contrast, if the heavy components such as asphaltenes are concentrated in petroleum, more small molecules would be attached to or solvated around the asphaltenes, leaving less room for the molecules to move, which could potentially increase the viscosity of unconventional oil.[45, 226-228]

Gaseous solvents. In the recent decades, a group of gas molecules such as C_2H_6, CH_4, CO, CO_2 and N_2 have been used to reduce the viscosity of unconventional oil or bitumen.[216] The extent of the viscosity reduction of unconventional oil by these gases is determined by their diffusion rate into the oil. The diffusion coefficient of these gases into the bitumen is reported to be in the order of 10^{-10} m^2/s at room temperature and 4 MPa pressure.[24, 229, 230] Increasing the temperature or pressure is found to be beneficial to some extent for improving diffusion of gases into unconventional oil and hence for reducing the viscosity of unconventional oil.

3.6 Oil-water interfacial tension

Interfacial tension (IFT) is defined as the amount of work required to bring the molecules from the bulk phases to the contact boundary of unit area. It is described by the following Gibbs free energy equation:[231]

$$\gamma = \frac{dG}{dA}\Big|_{T,P} \qquad \textbf{(Eq. 5)}$$

where, γ is the interfacial/surface tension; G denotes the Gibbs free energy; A stands for the area; T is the absolute temperature; and P represents the pressure. Based on this definition, the IFT can be measured by many different methods, such as pendant drop, spinning drop, or sessile drop.[232-234] For fluids of matching densities, Moran *et al.* developed a novel micropipette technique to measure the bitumen-water IFT.[235-237] The IFT is often related to the surface excess of surface active species due to their adsorption at the oil-water or water-air interfaces. The Gibbs equation given below is often used to determine the excess concentration (Γ) of surface active species at an oil-water interface:

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln C}\Big|_P \qquad \textbf{(Eq. 6)}$$

where, R is the universal gas constant; and C is the bulk concentration of surface-active species. This equation correlates the IFT with surface excess and surface-active species concentration, making the investigation of molecular interfacial activities more convenient.

Table 2 Viscosities of some typical unconventional petroleum in the world

Location	Viscosity (mPa•s)	API gravity (°)	Ref.
Canadian oil sands bitumen (Athabasca)	Up to 10^6	<10	38
Indonesia heavy oil (Duri field)	330	~20	1
Alaska heavy oil (West Sak field)	20~90	17~21	1
Alaska heavy oil (Ugnu field)	$200\sim10^4$	8~12	1
Venesula heavy oil (Faja del Orinoco)	1000~5000	8.5~10	222
Utah heavy oil	>106	8~14	1
Chinese heavy oil (Lian Hua)	403~5650 (at 50 °C)		223
India heavy oil (Bikaner-Naguar basin)	$10^4 \sim 1.6\times10^4$		1

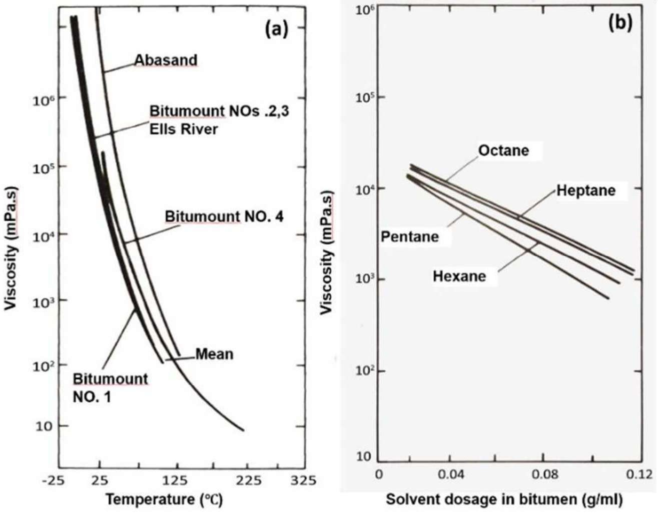


Fig. 13 Viscosity of bitumen from various sources as a function of (a) temperature and (b) dosage of aliphatic solvents, showing a more significant reduction of bitumen viscosity with increasing temperature than adding low molecular weight aliphatic solvent. *Reproduced from Seyer et al. 1989.[216] Alberta Oil Sands Technology and Research Authority 1989.*

It has been well-established that the recovery of unconventional oil is strongly dependent on the oil-water interfacial tension. The lower the oil-water interfacial tension, the higher the oil recovery would be, as a result of spontaneous emulsification of heavy oil in flooding water.[238-240] A recent study showed a clear benefit of decreasing the oil-water interfacial tension to enhance the liberation of heavy oil from its host rocks.[133]

Clearly, the oil-water interfacial tension plays a critical role in determining the liberation or displacement of unconventional oil. It is shown in **Fig. 6 b** and **Eq. 2-b** that the smaller the contact angle, the more complete the oil displacement. If the solid surfaces are kept constant as often the case in a given oil reservoir, the reduction in oil-water interfacial tension is one of the effective ways of decreasing the contact angle and hence increasing the liberation of oil from sand grains. In general, the unconventional oil-water interfacial tension is influenced by various factors, including the salinity and pH of the aqueous phase, the acid/base number, asphaltenes content, type of heteroatoms[241] the viscosity[124] of the oil, and the temperature and pressure. The presence of fine solids is also known to affect the oil-water interfacial tension.[242] The effect of temperature and pressure on the unconventional oil-water interfacial tension is shown to be significant but not well understood until now. Although increasing the temperature or decreasing the pressure is known to decrease the oil-water interfacial tension,[231, 243-245] some researchers reported a negligible dependence of oil-water interfacial tensions on the pressure and temperature, but highly dependent on the aerobic/anaerobic conditions.[246, 247] Moeini *et al.* observed a linear decrease in the oil-water IFT with increasing the temperature, but a slight increase in the IFT with increasing the pressure. The observed controversies stem mainly from the complex composition of the unconventional oil.

It is demonstrated that the oil-water IFT is also controlled by the synergic action of the acid/base number of the unconventional oil and the pH of the aqueous phase. The acid/base content of unconventional oil is often characterized by the total acid/base number. The organic acid in unconventional oil, for example, could be highly ionized in the alkaline aqueous solution. The ionized carboxylates accumulate at the oil-water interfaces or even get transferred into the bulk aqueous phase, resulting in a significant reduction in the oil-water interfacial tension. The higher the acid/base number of an oil, the lower the oil-water interfacial tension at a higher (for high acid number) or lower (for high base number) aqueous pH.[248-250] The effect of surfactants and salinity of the water on the oil-water interfacial tension is discussed in the following section.

3.6.1 Effect of surfactants

At a given external condition, surfactants play an important role in controlling oil-water interfacial tensions.[61-63] In unconventional oil production, the surfactants could come from oil or be added externally.

Natural surfactants. Naphthenic acids, sulfonate acids, asphaltenes and resins have been demonstrated to be the main sources of natural surfactants. The acid groups of these natural surfactants dissociate at the oil-water interface as follows:

$$\mathrm{Rt\,the(oil)} \overset{\mathrm{interface}}{\Longleftrightarrow} \mathrm{Rinterf(aq.)} \overset{\mathrm{OH^-}}{\Longleftrightarrow} \mathrm{Rq.OO^-} + \mathrm{H_2O} \qquad \textbf{(Eq. 7)}$$

Increasing pH of the aqueous phase favors the dissociation reaction of **Eq. 7**, enhancing transport of the naphthenic acids from the bulk oil to the oil-water interface and into the bulk aqueous phase, which decreases the oil-water interfacial tension with increasing pH of aqueous phase as shown in **Fig. 14**.[251]

Despite their limitations of directly reducing oil-water interfacial tension, asphaltenes are known to self-associate at the oil-water interface, which results in formation of stable oil-in-water (O/W) or water-in-oil (W/O) emulsions, depending on the water content, water chemistry and composition of oil. The mechanisms of asphaltenes in reducing oil-water interfacial tension, however, are not well understood. After testing 41 oil samples, Buckley *et al.* reported a general trend of reducing interfacial tension with increasing the asphaltene content in the oil.[241] In a recent study, Bai *et al.* reported a more significant role of asphaltenes than resins in reducing the oil-water interfacial tension.[248] Due to undefined composition and molecular structure of the asphaltenes and resins, a great deal of effort has been devoted to the fractionation of asphaltenes for the purpose of identifying signatures of molecules, which are responsible for their interfacial activity and molecular association at the oil-water interfaces. For example, Neuville *et al.* observed a slower diffusion of the endogenous surfactants from asphaltenes than from deasphalted oil to the oil-water interface. However, the endogenous surfactants from asphaltenes could displace the surfactants of deasphalted oil from the oil-water interface, forming a much more viscous interfacial layer of limited compressibility.[252] Recently, Yang *et al.* showed that only a small fraction (less than 2%) of pentane-precipitated asphaltenes was responsible for interfacial activity and hence formation of elastic interfacial films.[99] Although they showed slightly higher molecular weight and higher oxygen content of interfacially active asphaltenes than remaining 98% asphaltenes, the exact structure of these interfacially active asphaltene molecules remains to be determined. Nevertheless, it is well established that changing the pH, temperature and/or salinity of the oil-water system can stimulate the activity of the natural surfactants to facilitate the production of unconventional oils.[61, 241]

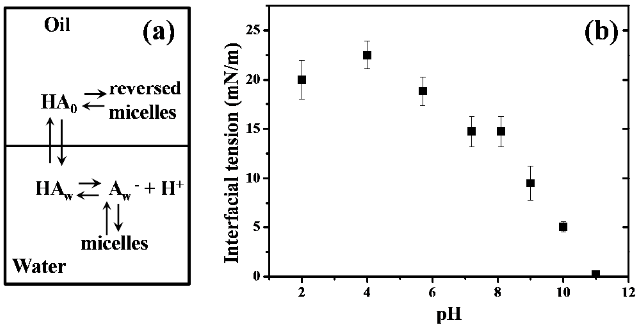


Fig. 14 (a) Equilibria in water-oil-naphthenic acid systems with HA_0 and HA_w representing undissociated surfactant in the oil and water phase, respectively; and A_w^-, the dissociated acid ion in the water phase: high pH (low hydroxyl ion, H^+) leads to formation of micelles in aqueous phase and low pH, reverse micelles in oil phase. Adapted from Havre *et al*, 2003.[251] Copyright 2003 by Marcel Dekker, Inc. (b) oil-water interfacial tension as a function of pH of the solution. *Reproduced with permission from ref. 236. Copyright 2000 Elsevier Science B.V.*

Externally added surfactants. In practice, the role of natural surfactants in reducing the oil-water interfacial tension for enhancing petroleum production is often limited. To improve oil recovery, synthetic surfactants are frequently used in unconventional oil production. Trabelsi *et al.* tested sodium dodecyl benzene sulfonate (SDBS), Triton X405 and sodium dodecyl sulfonic acid (SDS) on the enhancement of heavy oil recovery.[253] A sharp reduction in oil-water interfacial tension to as low as 4×10^{-4} mN/m was observed when 0.05 wt% of SDBS was added to the aqueous phase at pH 11. The effective reduction in the oil-water interfacial tension was attributed to the synergistic effect of the endogenous surfactants and the externally added surfactants. When investigating two acidic surfactants of hexanoic acid ($C_5H_{11}COOH$, HAA) and 3-cyclopentylpropionic acid ($C_5H_9CH_2CH_2COOH$, CPPA) with sodium naphthenates (SNs), Angle *et al.* found that the efficiency of the surfactants on reducing the oil-water interfacial tension was highly dependent on the surfactant concentration.[254] For instance, near the critical micelle concentration (CMC), the SNs could adsorb or partition efficiently at the oil-water interface, leading to a sharp reduction in interfacial tension from 30 mN/m to 3 mN/m at the concentration of 0.0517 mol/kg oil in toluene. They proposed a more efficient binding of SN molecules than the other two surfactants formed at the bitumen-water interface. Pei *et al.* synthesized several anionic and non-ionic palmitoyl diglycol amide (PDGA) type surfactants and used them to reduce the oil-water interfacial tension.[255] Their results showed that the non-ionic derivatives of palmitoyl monoethanol amide ethoxylates (PMEA-EO_n, $n = 2, 3, 4$) were more efficient in reducing the oil-water interfacial tension to as low as 10^{-3} mN/m than the anionic counterpart such as palmitoyl diglycol amide sulfate (PDGAS) and palmitoyl diglycol amide carbonate (PDGAC). For the non-ionic PDGA derivatives at a lower concentration (0.05 to 0.1 wt%), more time was found to be needed for the derivatives to diffuse to the oil-water interface and to reach equilibrium state. Increasing the EO number in the molecules was found to delay the equilibria. These results seem to suggest that the reduction of the IFT by surfactant addition is highly dependent on the size and structure of surfactant molecules as reported by others.[255-257]

In addition to the traditional surfactants, some specialty chemicals such as ionic liquids (*i.e.*, 1-dodecyl-3-methylimidazolium chloride) have been recently reported to act as surfactants in reducing the oil-water interfacial tension.[258, 259] Different from the conventional surfactants, the surface active ionic liquids (IL) are able to reduce the oil-water interfacial tension below 1 mN/m even at a high salt concentration up to 10^5 ppm NaCl in the aqueous phase. Hezave *et al.* suggested that screening charges of cationic IL surfactant at the oil-water interface (by increasing the salinity of the aqueous phase) enhanced the movement of more and more surfactant molecules to the interface, leading to a more substantial reduction in the oil-water interfacial tension.

Although it is well accepted that the reduction in the oil-water interfacial tension by surfactants is primarily due to the dissociation of the natural surface active molecules and/or adsorption of added surface active molecules at the oil-water interface, there exists a competition between different types of surface active molecules to occupy the limited space at the oil-water interface.[260] Further qualitative and quantitative investigations are needed to understand the working mechanisms of reducing the oil-water interfacial tensions by surface active materials in complex petroleum systems.

3.6.2 Effect of inorganic ions

Naturally, the inorganic ions such as Na^+, K^+, Ca^{2+} and Mg^{2+} are present in the aqueous phase of unconventional petroleum systems.[245] During the past decade, some studies have shown that the oil-water interfacial tension increased with increasing the salinity of the aqueous phase,[245, 261, 262] while the others reported the opposite trend.[245] These results, although obtained mostly from pure oil-water systems, show the complex effect of the aqueous salinity on oil-water interfacial properties of unconventional oil systems. Considering the crude oil/heavy oil being comprised of millions of molecular species such as asphaltenes and resins of largely unknown molecular structures, observing such complex or even controversial oil-water interfacial properties of unconventional oil systems is not unexpected.[241] When studying the effect of salinity on oil-water interfacial properties using real oil systems, some researchers observed only a marginal effect of NaCl concentration on the heavy oil-water IFT.[248] However, Vijapurapu *et al.* and Moeini *et al.* observed an optimal salinity concentration of 4.5 g/L and 35000 ppm, respectively, at which the oil-water IFT reached the minimum value of around 12 mN/m.[231, 263] Xu *et al.* reported little effect of the salinity on the dynamic IFT, but a significant increase in the oil-water IFT when the brine was diluted.[243] When studying the effect of salinity on Athabasca bitumen-water IFT, Isaacs *et al.* observed a dramatic decrease in the bitumen-water IFT to less than 0.01 mN/m with increasing salt concentration up to 15 g/L in the aqueous phase containing a commercial petroleum sulfonate surfactant (TRS 10-80) at 50 °C.[264]

Moeini *et al.* investigated the mechanisms of salinity in reducing the heavy oil-water IFT by NaCl and $CaCl_2$ over a concentration range from 0 to 200,000 ppm, and observed an optimal salinity concentration of 30,000 and 40,000 ppm to achieve a minimum IFT value of about 12 mN/m for $CaCl_2$ and NaCl, respectively as shown in **Fig. 15**.[231] To explain these results, they proposed that the salt ions are likely hydrated by the water molecules, forming a hydrogen bonded cage structure. The hydrogen bonding among the water molecules is inevitably disrupted when the water molecules are in contact with the oil-water interface, resulting in the salt ions being depleted from the interface. The negative surface excess of salt ions leads to an increase in the oil-water IFT. The asphaltenes, on the other hand, possess a large hydrocarbon skeleton containing different heteroatoms that drive the asphaltene molecules to accumulate at the oil-water interface.[251] Since the asphaltenes and ionic surfactants contain ionizable groups, their accumulation at the oil-water interface makes the oil-water IFT highly dependent on the interactions between the salt and the ionized surfactants. At low salt concentration, the asphaltenes are anticipated to transfer from the bulk oil to the oil-water interface, where the salt effect is overwhelmed by the presence (adsorption) of asphaltenes at the interface. In this case, the interactions between the surface active, polar asphaltenes and cations increase the solubility of asphaltenes in both the aqueous and oleic phases, thus reducing the IFT with increasing the salt concentration as shown in **Eq. 6**. The continued increase in the salinity of the aqueous phase beyond the optimum value reduces the solubility of surface active unconventional oil components in the aqueous phase, a phenomenon known as the salting-out effect.[265] Under this condition, the water molecules are no longer to keep polarities and charges of both asphaltenes and ions, forming separated layers of asphaltenes and ions in organic and aqueous phases, respectively.[266] As a result, the oil-water IFT increases with further increasing the salinity of the aqueous phase. Similar mechanisms operate in oil-water systems containing externally added ionic surfactants. In these systems, the ionic surfactants would be expelled to the oil-water interface by increasing the salinity of the aqueous phase, reducing the oil-water IFT.[267, 268] Gupta *et al.* observed an increase in oil-water IFT with increasing the salinity beyond the optimal concentration,[184] as reported in the above-mentioned natural surfactant systems.

The unconventional oil-water IFT is also influenced by the valence of the cations. Ralston *et al.* and Johansson *et al.* proposed the negative adsorption of these divalent cations at the oil-water interface as the most plausible reason for the observed increase in the oil-water IFT.[269-270] Due to their strong potency of hydration, these divalent cations tend to stay in the bulk aqueous phase and show a strong attraction to the water molecules from the interface to the bulk aqueous phase, which increases the oil-water IFT. The higher the valence of the cations, the stronger the attraction to the water molecules. Therefore, the addition (presence) of higher valence cations leads to a much higher increase in the oil-water IFT.[269-271]

Negative ions are also able to alter the oil-water interfacial tensions. When investigating the effect of inorganic anions (*i.e.*, Cl^-, Br^-, F^-, I^-, and ClO_4^-,), Santos *et al.* observed strong adsorption of I^- and ClO_4^- anions at the oil-water interface, leading to a significant reduction in the oil-water IFT. However, the presence of Cl^-, Br^-, F^-, ClO_3^-, NO_3^-, *etc.* in the aqueous solution was found to increase the oil-water interfacial tension.[272] They proposed that, as chaotropic anions by losing their hydration sheath, I^- and ClO_4^- would adsorb at the oil-water interface due to dispersion interactions. In contrast, Cl^-, Br^-, F^-, ClO_3^-, NO_3^-, *etc*., as kosmotropic anions, would be repelled from the interface because of their strong hydration in aqueous solutions, resulting in an increase in the oil-water interfacial tension.[272, 273] The adsorption of inorganic anions was found to be well fitted with the Jones–Dole viscosity B-coefficient.[273] These findings were also observed in a further study by Rankin *et al.*,[274] who investigated the interactions of Na^+, F^-, and I^- anions with hydrophobic groups using Raman spectroscopy and multivariate curve deconvolution. They also observed that I^- ions were able to enter the hydrophobic hydration shell, while Na^+ and F^- were strongly expelled from the first hydration shells of the hydrophobic (methyl) groups.

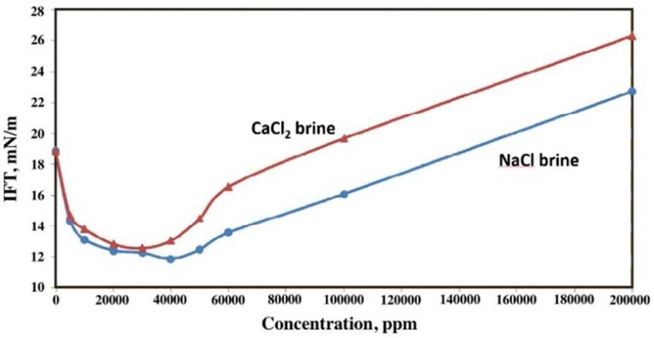


Fig. 15 Interfacial tension between crude oil and brine as a function of NaCl and $CaCl_2$ concentration, showing more significant effect of divalent calcium ions than monovalent sodium ions. *Reproduced with permission from ref. 231. Copyright 2014 Elsevier B.V.*

Since the surface excess concentration is one of the most effective approaches to characterize the interfacial properties, numerous adsorption models have been proposed to describe the surface excess/adsorption profiles at the oil-water or air-water interfaces, including the Langmuir adsorption model, Frumkin adsorption model, Davies adsorption model,[275] Frumkin-Davies adsorption model,[276] Gibbs-Langmuir or Szyszkowski non-ionic surfactant adsorption model, Borwankar and Wasan ionic surfactant adsorption model,[277] and Kalinin and Radke counterion binding model.[278]

3.7 Role of caustic in unconventional oil production

As stated above, the liberation of unconventional oil from the reservoir rock surfaces or porous medium is mainly controlled by physicochemical properties of the system, including the wettability of mineral surfaces and oil-water interfacial intensions. For water flooding, the oil reservoirs (both oil and rocks) are made in contact with flooding water. Changing water chemistry will modify both oil-water and water-solid interfacial properties. A common method to enhance oil production from unconventional oil reservoirs is by caustic injection.[18, 279-283] The addition of caustics (*e.g.*, NaOH, Na_2CO_3 and $NH_3{\cdot}H_2O$) into the flooding water provides hydroxyl groups (OH^-) which ionizes the weakly acidic natural surfactants of the oil. Such a reaction increases the surface activity and transfers the natural surfactants to the oil-water interface and then into the aqueous phase, resulting in a significant reduction in the IFT as shown in **Fig. 14** and **Eq. 7**.[283] The reduction in the oil-water IFT provides a stronger driving force for heavy oil liberation from the solid surfaces as shown in **Fig. 6 b.** The extent of the IFT reduction depends on the amount of caustic added. In general, there is an optimal dosage of the caustic to achieve a minimum IFT. Jennings *et al.* reported a minimum oil-water interfacial tension of 0.01 mN/m at 0.1 wt% NaOH concentration.[279] The addition of Na_2CO_3 was also found to be effective in reducing the oil-water IFT, while the presence of Ca^{2+} in the aqueous solution was found to be detrimental to reducing the IFT.[278] In a recent study, ammonium hydroxide (NH_4OH) was reported to act as a caustic and enhance bitumen liberation from oil sands.[283] The combination of caustics and surfactants was found to be much more effective in reducing the IFT and hence improving oil recovery from unconventional oil reservoirs.[18, 130, 278, 281, 282] Caustic addition is also known to increase the wettability of reservoir rocks by ionizing the solid surface hydroxyl groups, further enhancing liberation of heavy oil from the host mineral surfaces.[283, 284]

4. Oil and water separation

During oil production from unconventional oil resources, oil-water emulsions are inevitably generated. Although emulsifying oil enhances oil liberation, these petroleum emulsions are often detrimental to downstream oil-water separation, even leading to overall low oil recovery and poor oil quality.[26] Understanding how the surface active species stabilize the oil-water emulsions is essential for the control of emulsions and subsequent demulsification. Knowledge on molecular mechanisms of emulsion stabilization will also shed light on design and synthesis of specialty chemical emulsifiers and demulsifiers.

In this section, the properties of W/O and O/W emulsions in unconventional oil production will be summarized first, followed by a critical review on the principles and applications of advanced characterization techniques for studying oil-water interfacial films. After an overview on oil-water emulsions and physicochemical properties of interfacial films, the advances in understanding stabilization mechanisms of petroleum emulsions by asphaltenes, natural surfactants, fine solids and/or added chemicals will be reviewed, followed by a thorough review on chemical demulsification mechanisms, such as the flocculation and coalescence of oil droplets in water or water droplets in oil for effective oil-water separation.

4.1 W/O and O/W emulsions

As shown in **Fig. 16 a**, emulsions could form in different types: water-in-oil (W/O), oil-in-water (O/W) and multiple emulsions such as (water-in-oil)-in-water (W/O/W) or (oil-in-water)-in-oil (O/W/O) emulsions.[26, 285] During oil production by water-flooding and transportation of produced fluid, the most common emulsions are O/W, while the W/O type of emulsions are frequently encountered in crude oil transportation, bitumen froth treatments and oil desalting prior to oil refining.[27, 285] The general properties of oil-water emulsions, such as drop size distribution and viscosity, are described elsewhere.[26, 286] Theoretically, the emulsions are thermodynamically unstable, as a result of excess energy of interfaces. However, the emulsions can be kinetically stable for a long period of time, from several hours to several months or even longer, due to the presence of stabilizing molecules and/or particles at the oil-water interfaces. According to the source and properties, the emulsion stabilizers can be classified as indigenous surface-active components of oil (*e.g.*, asphaltenes, resins, and natural surfactants), mineral particles and externally added surfactants, typically shown in **Figs. 16 b and c**. These stabilizers accumulate at the oil-water interfaces, forming rigid and/or gel-like films which protect the droplets and prevent them from coalescence. A typical structure of a stable oil-water interfacial film is shown in **Fig. 16 b.** In this review, we focus on recent advances in understanding stabilization mechanisms of oil-water emulsions and their demulsification.

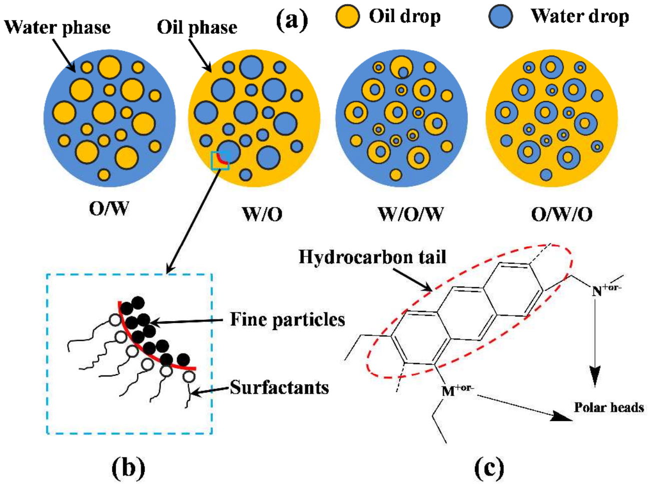


Fig. 16 (a) Different types of emulsions found in heavy oil production and transport with schematic representation of perceived structure of surface active asphaltenes and their role in stabilizing water droplets in diluted-bitumen. Reproduced with permission from ref. 285. Copyright 2010 Elsevier B.V. (b) Formation of rigid film at oil-water interface; and (c) surface activity of asphaltene molecules. *Reproduced with permission from ref. 27. Copyright 2013 American Chemical Society.*

4.2. Advanced emulsion characterization techniques

In essence, the stability of the oil-water emulsions is determined by physicochemical properties of films formed at the oil-water interfaces. Understanding the properties of the oil-water interfacial films, such as interfacial tension, surface pressure-area isotherm, crumpling ratio, film thickness, film rheology (storage modulus, G', and loss modulus G''), and film compositions, is essential to control the stability of oil-water emulsions or to achieve effective demulsification. Unsderstanding the properties of oil-water interfacial films also provides fundamental insights on the design and synthesis of specialty chemical emulsifiers and demulsifiers. In the past years, some advanced characterization techniques, such as interfacial Langmuir trough (or Langmuir–Blodgett (LB) trough), interfacial shear rheometry (ISR), Brewster angle microscopy (BAM), micropipette, atomic force microscope (AFM), surface force apparatus (SFA), thin liquid film balance (TFB), along with specialty devices such as integrated thin film drainage apparatus (ITFDA), have been either adapted or developed to characterize the oil-water interfacial films and emulsion stability. The principles and applications of these advanced characterization techniques are reviewed critically as follows.

4.2.1 Langmuir-Blodgett trough

The Langmuir trough,[287, 288] has been extensively used to investigate the physical properties of amphiphilic molecules, at air-water or oil-water interfaces. A simplified schematic of Langmuir trough is shown in **Fig. 17 a**. In a typical Langmuir trough experiment, the amphiphilic molecules at the air-water or oil-water interface are compressed or expanded by changing the interfacial area in a well-controlled manner, while monitoring the surface and interfacial tension using a Wilhelmy plate. The surface or interfacial pressure (Π) defined as the difference between the surface or interfacial tensions of the interface in the absence and presence of the interfacially active molecules. This interfacial pressure is typically used to quantify the properties of amphiphilic molecules at the interfaces.[289, 290]

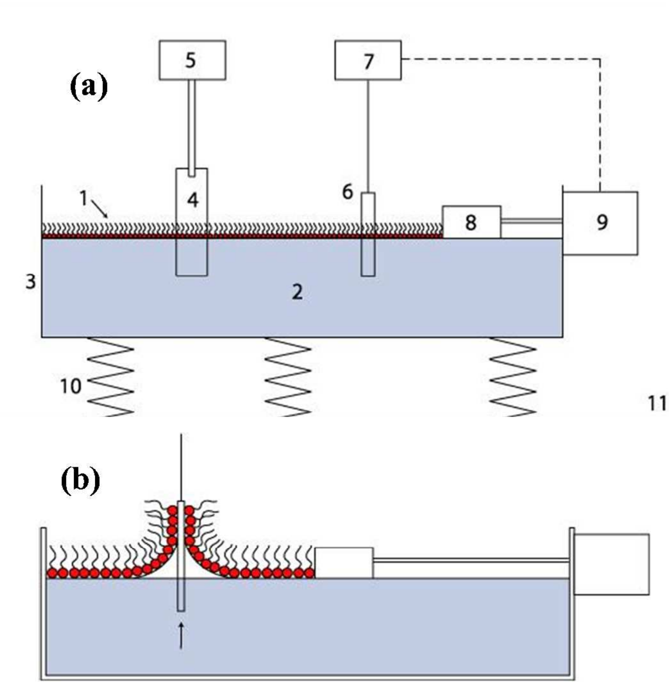


Fig. 17 (a) A schematic diagram of a Langmuir trough with an interfacial film transfer mechanism: 1. Amphiphile monolayer, 2. Liquid subphase, 3. Langmuir Trough, 4. Solid substrate, 5. Dipping mechanism, 6. Wilhelmy Plate, 7. Electrobalance, 8. Barrier, 9. Barrier displacement mechanism, and 10. Vibration reduction system; and (b) Transfer of interfacial molecules onto a substrate after film compression, with the hydrophilic substrate moving upperward to allow the polar head groups adhering to the surface. *Adapted from Wikipedia, the free encyclopedia.*

In addition to studying interfacial properties of biofilms or quantum dots at the air-water surface,[260, 290-293] the Langmuir trough has also been widely used in studying oil-water interfacial films, especially the films formed by heavy oil components such as asphaltenes.[97, 260, 289, 290, 294-298] The microscopic morphology of the interfacial films can be investigated in situ using a Brewster angle microscope (BAM), while the rheology of the interfacial film can be studied using an interfacial shear rheolometer.[299]

To determine the molecular association at the interface, the molecules at the interface are often transferred to a molecularly smooth solid substrate such as cleaved mica basal planes or silicon wafers. The molecules can, for example, be transferred using the Langmuir-Blodgett deposition technique as shown in **Fig. 17 b**. Under the proper transfer conditions of interfacial molecules to the substrate, the molecular arrangement at the air-water or oil-water interface can be effectively preserved. The sample can then be used for high resolution molecular imaging using the AFM; for wettability and electric charge determination using drop shape analyser and stream potential device, respectively; for chemical composition analysis using x-ray photoelectron spectroscopy and surface ionization mass spectroscopy; and for spectroscopic characterization by FTIR and/or spectroscopic ellipsometry.[300]

4.2.2 Interfacial shear rheometer

The rheological properties (*i.e.*, the elastic and viscous moduli) of molecular films at the air-water or oil-water interfaces are known to play an important role in emulsion stabilization and demulsification. For this reason, studying interfacial rheology has been a subject of strong research interests for many years.[301, 302] The accurate measurement on the responses of the interfacial films to the forces shearing the films at different thermodynamic (*i.e.*, temperature and surface pressure, *etc.*) and dynamic (shear rate at different deformations) conditions can provide valuable information complement as to that obtained with surface pressure-area isotherms.[303] Knowing the flow behavior of air-water or oil-water interfacial films helps to understand the molecular interactions, such as hydrogen bonding, physical entanglements, covalent cross-linking, at the oil-water interfaces. Considering the critical importance of interfacial rheology, interfacial shear rheometry (ISR) was developed for the measurement of rheological properties of air-water or oil-water interfaces. In the ISR as schematically shown in **Fig. 18 a,** a pair of concentric Helmholtz coils are mounted at a given separation distance around a Langmuir trough. A magnetic rod (needle) is placed on the top of the sub-phase or at the oil-water interface in the middle of the trough. The needle is driven by the magnetic field created by the Helmholtz coils and its movement is recorded by an overhead digital camera. The recorded movement of the needle is synchronized with the applied magnetic field to determine the phase angle shift of the needle movement, from which the rheological properties of the film is obtained.[303, 304] The ISR has been used to study various types of interfacial films, such as the eicosanol film at the air-water interface,[303, 304] and protein or protein/surfactant films[302] and asphaltenes films[299, 305, 306] at oil-water interfaces.

Recently, the double-wall ring (DWR) geometry as shown in **Fig. 18 b** has been used in a TA commercial rheometer to measure the evolution of elastic and viscous moduli of asphaltene films at solvent-water interfaces.[299, 307] Studies using DWR revealed the aging of asphaltenes adsorbed at the oil-water interface to build up an eleatic interfacial films responsible for stabilization of water-in-oil emulsions.[299]

4.2.3 Brewster angle microscopy

Brewster angle microscopy (BAM), invented in the 1990s, is a useful tool to image the morphology of interfacial films in situ at the air-water and oil-water interface.[308-310] The p-polarized light is known to possess a special property that no light is reflected when the incidence angle of the light equals the Brewster angle of the surface or interface. Brewster angle microscopy (BAM) as shown in **Fig. 19** was invented based on this property of the p-polarized light.[311-313] The quasi 2-dimensional interfacial films formed by surface-active molecules often possess different phases which may exert different tilt azimuth, orientation or rotational degrees of freedom. These features can be characterized from the reflected light using the BAM, produing an image of characteristic morphological properties of the films. Typically a domain of sizes ranging from 20 to 200 μm could be visulized by a commercial BAM which is often installed on a Langmuir trough for investigation of interfacial films.[311] Recent progress on the applications of BAM to study the molecular film at the air-water interface is given in a recent review by Vollhardt.[309] With proper modification, the BAM can also be applied to study interfacial films formed by different kinds of surface-active materials, such as alkanols (octadecanol and 1,1,2,2-tetrahydroperfluorododecanol) at the hexane/water interface,[308] protein films at the oil-water interface,[314] and graphite oxide at oil-water interfaces.[315] BAM has also been used to study the interfacial films formed by bitumen or asphaltenes in petroleum.[316, 317]

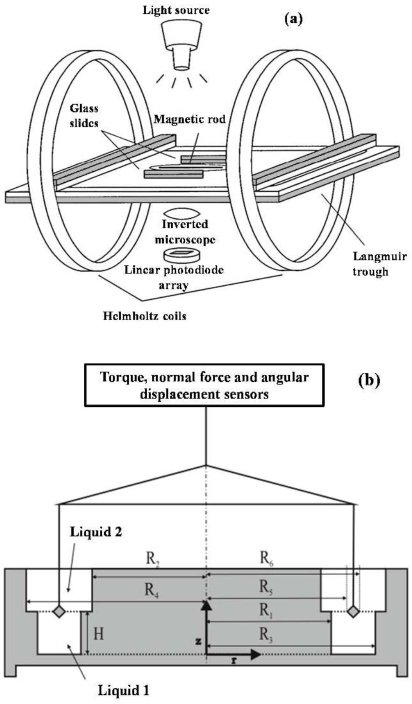


Fig. 18 Schematic overview of (a) interfacial shear rheometer, and (b) cross section of the double wall ring (DWR) shear rheometer. *Reproduced with permission from ref. 303 and ref. 307. Copyrights of 1999 American Chemical Society and Springer-Verlag 2009, respectively.*

4.2.4 Micropipette

The micropipette is a new technique designed to quantify the micron scale interactions between individual solid particles, liquid droplets and air bubbles in-situ. This technique was initially developed in the field of biophysics to study biological cell adhesion,[318] and then introduced by Yeung *et al.*[98, 319-320] to study the stability of unconventional oil-water emulsions, as well as being adopted to study the wetting and dewetting behaviors of micro-droplets on solid surfaces.[124] The micropipette can be fabricated as a straightforward suction pipette as shown in **Fig. 20** (inset in the red dashed rectangle),[98] or shaped into a periscope-like cantilever, with two right angle bends for force measurement. The latter is also called micro-cantilever.[235, 236] The end of small pipette tip can be open and of smooth cylindrical geometry,[98, 235] or of closed spherical shape[124] depending on the research application (see **Fig. 20**). The diameter of the pipette is typically of several microns.

Despite the variations in configuration of micropipette, the procedures of conducting micropipette experiments are similar. In studies of emulsion stability, for example, individual droplets (typically 10 μm in diameter) are grabbed from an emulsion by two micropipettes. The micropipettes are mounted on hydraulic manipulators that ensure the smooth, three-dimensional movement of the pipette tips over a macro scale range. With these capabilities, two emulsion droplets grabbed by the micropipettes could be precisely brought in contact with each other. The state of droplet interactions such as attachment (flocculation) or coalescence is monitored using an inverted optical microscope. The microscope is equipped with a high resolution digital CCD camera which is connected to a computer. Video sequences of the entire droplet contact process are analyzed to gain insight on droplet coalescence.[98]

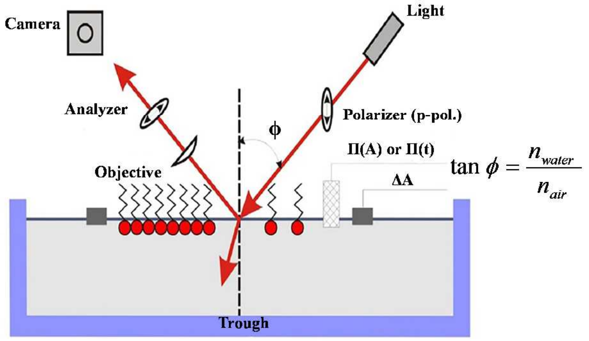


Fig. 19 Schematic drawing of a Brewster angle microscopy together with the Langmuir trough, illustrating its working principles. ϕ is the incident angle of the light, n_{water} and n_{air} denote the reflective index of water and air, respectively. *Reproduced with permission from ref. 309. Copyright 2014 Elsevier Ltd.*

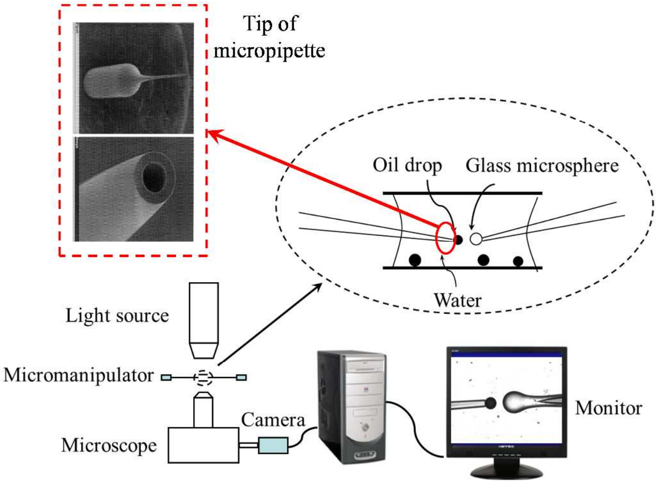


Fig. 20 Schematics of micropipette experimental setup: An individual emulsified oil droplet in water inside the sample cell is captured by the micropipette on left; the micropipette on the right, with a closed and rounded tip, functions as a spherical glass particle. The inset of the figure in the red dashed rectangle is scanning electron micrographs of a micropipette: (Upper) overview of the pipette with the bottom (thicker) section being 1 mm in diameter; (lower) close-up view of the pipette tip with the inside diameter being about 7 μm. *Reproduced with permission from ref. 98 and ref. 124. Copyrights of 2000 Elsevier Science B.V. and 2014 American Chemical Society respectively.*

Due to the micro sizes of the droplets that can be studied by the micropipette technique, the gravity effect of system can be eliminated, allowing interfacial tensions of similar density fluids to be determined by shape recovery methods.[235-237] In addition to determination of liquid-liquid interfacial tensions, the micropipette technique has been used to study surfactants partition,[98] heterogeneity of surface charges,[319] steric emulsion layers,[323] film adsorption, dilatational rheology and plasticity of unconventional oils,[320, 321] viscosity of extra viscous materials,[324] flocculation and coalescence of emulsion droplets,[98, 319, 325] adhesion and cohesion, particle-particle interactions, [326] wetting/dewetting and contact angle of microsphere particles.[124]

4.2.5 Atomic force microscopy

The Atomic force microscope (AFM), originally developed from the scanning tunneling microscope (STM), is a powerful tool for the direct mapping of atomic scale surface topography and determination of intermolecular forces.[327-329] Since being invented, the AFM has been widely used to gain scientific insights in nanotechnology, materials engineering, life sciences, microbiology, colloidal sciences, mineral processing and environmental science and technology. A general schematic diagram of AFM is shown in **Fig. 21**. Due to its critical importance in modern research, the principle of the AFM has been reviewed extensively.[327-330] Here, only a brief introduction of the AFM is provided.

A basic AFM consists of a piezoelectric transducer, a cantilever with a probing tip, a laser beam system and a photodiode for detecting the deflection of the cantilever, and a high speed controller. In a typical AFM imaging experiment, the sharp tip on the AFM cantilever approaches the sample surfaces and scans over the surface in the x and y directions.[16] The surface topographic features in direct or soft contact with the AFM tip cause the cantilever to deflect. By focusing a laser beam on the other side of the AFM cantilever at the tip location, the cantilever deflections are precisely detected by a photodiode as a digital signal as the tip scans across the surface. After calibration of cantilever deflection, a topographic map of surface can be accurately constructed at sub-nanometer spatial resolution.

With recent advances, AFM is capable of imaging the topography of hard and soft surfaces, mapping phase shift (phase imaging) and magnetic domains, measuring the friction forces, determining interactions of single molecules with solid surfaces, *etc*. In a recent study, for example, AFM was used to measure the local surface potentials (or equivalently, surface charges) at the bitumen-water interface.[206] One of the most striking features of AFM is its nanoscale imaging or measurement performed in liquids where interfacial phenomena can be studied in situ in real time with applied external forces as such electrochemical potential or magnetic field. The AFM has been now extended to study interaction forces between deformable surfaces such as the emulsion droplets encountered in petroleum emulsions.[331-338] The AFM technique has been widely used for morphological characterization of bituminous materials and even their microscopic mechanical properties.[339-342] Loeber *et al.* firstly reported rippled microstructures on the surface of a thin-film bitumen and described the microstructure as "bee-structures".[339] Later, much effort was made to reveal the chemical origins of bee-structures using AFM with different sample preparation methods, such as heat-cast method, solution-cast method or their combination.[343-349] With the advanced AFM techniques (*e.g.*, contact mode, dynamic mode, tapping mode, peak force Tapping^{TM} mode, lateral force microscopy mode), the microstructures (*e.g.,* bee-structures, percolating network structures) on bitumen surfaces have been observed. The effect of film thickness, sample preparation methods, thermal history, chemical composition, etc. on bitumen microstructures have also been intensively investigated accordingly by AFM.[340, 342, 345] The technique has also been used to measure interaction forces between asphaltenes immobilized on solid surfaces in nonaqueous solutions, revealing a critical role of solvent aromaticity in controlling interactions from steric repulsive to attractive long range forces.[97]

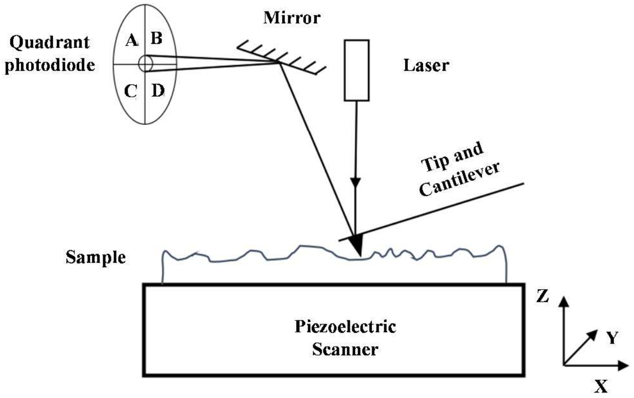


Fig. 21 Working principle of an atomic force microscopy (AFM). *Reproduced with permission from ref. 342. Copyright 2015 Elsevier B.V.*

4.2.6. Surface force apparatus

The surface force apparatus (SFA) was developed by Israelachvili *et al.* to measure interaction forces between surfaces in air or liquids, such as van der Waals (including Casimir) and electrostatic forces.[350] The working principle of SFA is schematically illustrated in **Fig. 22**. Briefly, two molecularly smooth, micron thick mica sheets are coated with a thin layer of silver films and glued with silver layer facing down onto two cylindrical silica discs. One of the silica discs is mounted on a piezo tube for nanometer resolution displacement, while the other is fixed at the free end of a double cantilever spring. The surfaces are arranged in a cross cylinder configuration in the measurement cell. During a typical force measurement, the surfaces are brought to each other by micrometer (lower surface) and piezo tube (upper surface) for coarse and fine displacement, respectively. The silver layers on the back sides of the mica surfaces form a multi-reflection interferometer when a white light passes through the two surfaces. Measuring the position and shape of Fringes of Equal Chromatic Order (FECO) using a grating spectrometer allows the distance between the two surfaces and local geometry of the surfaces to be measured to a sub-nanometer and sub-micron resolution, respectively. From the displacement of surface and the actual distance between the two surfaces, the deflection of the cantilever spring can be measured accurately. With the known spring constant, the interaction forces between the two surfaces as a function of measured separation distance can be calculated using Hooke's law. More details on the working principles of SFA are given by Israelachvili *et al.*[350] The SFA has been widely used to measure forces in air and liquids between different surfaces or films, such as cellulose surfaces, chitosan-coated surfaces, cellulose- and chitosan-coated surfaces,[351] surfactants (hexadecyltrimethylammonium salicylate) films,[352] and asphaltene surfaces.[209, 353] Taking the advantage of subnanometer resolution of SFA distance measurement, for example, Nataranja *et al*. determined adsorption kinetics and interactions forces of asphaltene-in toluene solutions on mica surfaces, revealling a continous build up of asphaltene molecules on mica surfaces and steric repulsion between adsorbed asphaltenes from toluene solutions.[209,353]

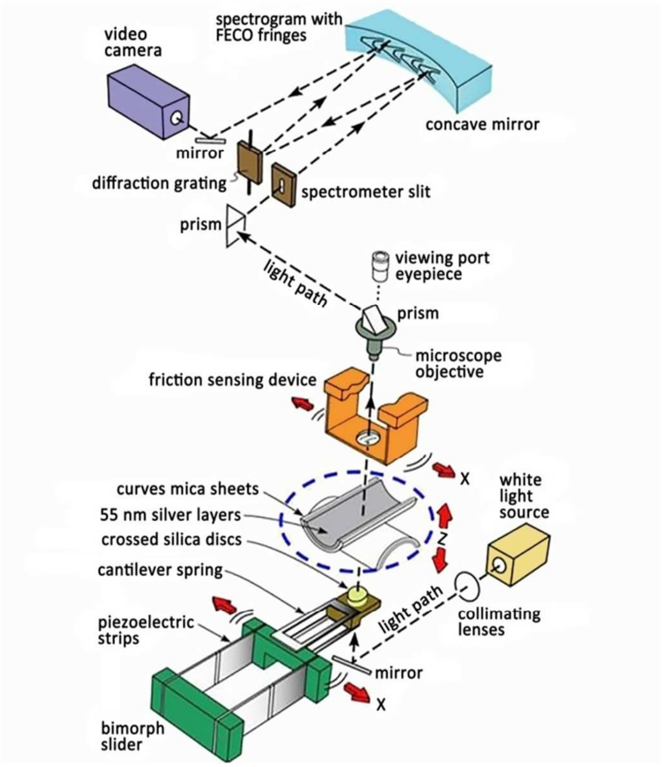


Fig. 22 Experimental setup of a surface force apparaus (SFA). *Reproduced from Dr. Hongbo Zeng's presentation*[354] *at Petrophase conference, June 2010.*

4.2.7 Thin film balance

In separating water from oil in petroleum emulsions, the drainage of intervening liquid is a key step, which is controlled by the properties of thin liquid films and the forces resisting the film drainage, known as the disjoining pressure. The disjoining pressure is defined as the excess pressure acting normal to the film interface. This pressure, produced as a result of molecular interactions between the interfacial layers across a thin liquid film, is a function of the film thickness.[355] The disjoining pressure could be negative (conjoining) or positive (disjoining), which facilitates or retards the drainage of the intervening liquid film, respectively. When two emulsion droplets come to contact with each other, the successful coalescence of the droplets requires complete drainage of the intervening liquid films, which depends on the balance of the disjoining pressure, capillary force and hydrodynamic force. The disjoining pressure between two liquid droplets can be measured by the thin film balance (TFB) developed originally by Scheludko *et al.* to study foam films. A history of TFB has been provided by Claesson *et al.* in 1996,[356] followed by a new period of development and applications in petroleum industry.[357, 358]

In principle, the balancing of the imposed capillary pressure with the film disjoining pressure coupled with film thickness measurement by interferometer laid the foundation of the TFB technique as shown in **Fig. 23**.[358] For the water-in-oil emulsion systems, a biconcave oil drop is formed in the hole of a porous plate holder which is immersed in the other immiscible continuous phase (water in this case). After a given period of equilibrium time, some of the oil is withdrawn to impose hydrodynamic forces of the intervening thin liquid oil film to form. Due to the curvature of the oil-water interface, a capillary pressure arises at the edge of the parallel oil film. The flat interfaces, which bound the film, begin to interact through surface forces, such as van der Waals force, electrostatic force, steric force, hydrophobic forces and/or others. The forces collectively act as the disjoining pressure, and are balanced by the capillary pressure of the curved interfaces. The disjoining pressure is a function of the intervening liquid film thickness. The intervening liquid will form a stable film of a given thickness which is determined by balancing the disjoining pressure at this thickness with the capillary pressure. If the capillary pressure is greater than the maximum disjoining pressure, the film will be unstable and rupture, which causes the coalescence of the emulsion droplets. Equipped with other accessories, the TFB technique could be used to measure the film thickness of different compositions, including asphaltenes, maltenes, surfactants, demulsifiers and even solid particles encountered in petroleum emulsions.[357, 358] With TFB, Tchoukov *et al*. determined differences in stabilizing intervening toluene films containing bitumen, asphaltenes or maltenes between two water droplets.[377] Their study showed continuous buildup of asphaltene films at the toluene-water interface that eventually led to the formation of supermolecular aggregates and extended three dimensional network. Such a network behaved as a soft gel with yield stress and prevented further thinning of the film before it could reach the critical thickness for film rupture. This characteristics of the film was considered as a major contributor to stabilizing water-in-petroleum emulsions.

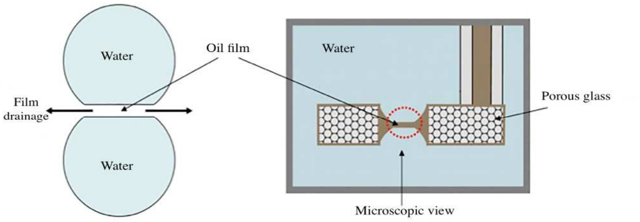


Fig. 23 Concept of thin liquid film-pressure balance technique. The thin liquid oil film formed between two water droplets is recreated in a specially designed measuring cell. *Reproduced with permission from ref. 358. Copyright 2000 Elsevier Science.*

4.2.8 Integrated thin film drainage apparatus (ITFDA)

Recently, a custom-built integrated thin film drainage apparatus (ITFDA) shown in **Fig. 24 a** was developed by Wang *et al.*,[359] taking combined advantages of an induction timer[360] and a measurement and analysis of surface interactions and forces (MASIF) device.[361] The development of ITFDA represents a significant advance as it allows direct and simultaneous measurement of both the time-dependent interaction forces and interfacial deformation between bubbles, droplets and particles under a wide range of hydrodynamic conditions. In particular, the measurement of the ITFDA covers an intermediate Reynolds (Re) number region ($0.01 \ll Re \ll 100$) that is common in unconventional oil recovery applications but beyond the measurement range of other devices such as the AFM, TFB and SFA.

The schematics in **Fig. 24 a** outline the main features of the ITFDA and the details of its design principles have been described elsewhere.[360] Briefly, a bimorph cantilever (shown in **Fig. 24 b**) and a high-frequency speaker are used as the force sensor and the drive for a precise and controllable displacement, respectively. Usually, a droplet (or bubble) is generated at one end of the capillary tube controlled by a micro-syringe. The movement of the droplet (or bubble) to approach or retract from a lower surface is driven by the speaker using a waveform voltage generated by an external amplifier which is connected to a computer. The lower droplets or bubbles are positioned on a solid surface which is clamped at the free end of a bimorph beam. The deflection of the bimorph beam as a result of forces applied to the oil droplets generates a proportional charge (or voltage) which is determined by a high impedance charge amplifier connected align to the computer for real time measurement. Two CCD cameras placed perpendicular to each other are installed in the front and side of the sample chamber to control the size of the droplets and initial gap between the droplets and to measure the droplet deformation under the applied external hydrodynamic forces.

In addition to accurate determination of dynamic and static receding and advancing contact angles with the above-mentioned features, the ITFDA was successfully applied to measuring the film drainage time and dynamic resistance force of water droplet coalescence in nontransparent heavy oils under controlled external forces.[359, 362, 363] Recently, the ITFDA was extended to quantify the droplet coalescence time of two water droplets aged in asphaltene solutions.[299] The measured increase in coalescence time with aging time of the droplets correlated well with the rheological properties of the interfacial asphaltene films measured using the DWR interfacial rheometer under the equivalent surface area to volume ratio of the two techniques.[299]

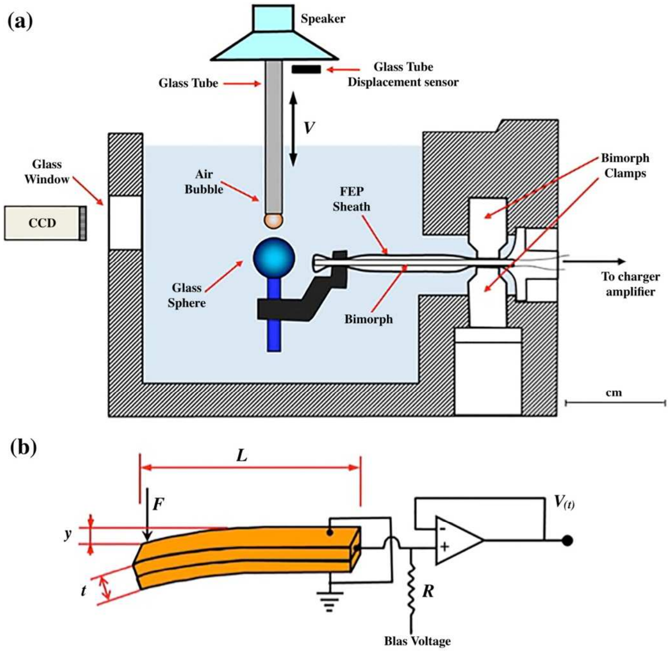


Fig. 24 Schematic view of the integrated thin film drainage apparatus (ITFDA): (a) instrument configuration; and (b) description of a piezoelectric bimorph and a high input impedance charge amplifier used to measure the charge generated on the bimorph cantilever under an external force. *Reproduced with permission from ref. 359 and ref. 361. Copyrights of 2013 American Chemical Society and 1992 American Chemical Society.*

4.3 Petroleum emulsions

4.3.1. Stabilization of emulsions

As stated earlier, emulsions are thermodynamically unstable systems because of the additional energy associated with oil-water interfaces that drives coalescence of dispersed droplets, which reduces the interfacial areas and hence the system energy. However, most of the oil-water emulsions in the petroleum industry are kinetically stable for a sufficiently long period of time. Generally speaking, the kinetic stability of oil-water emulsions is attributed mainly to the formation of protective interfacial films at the oil-water interfaces. The interfacial films stabilize the oil-water emulsions through three main mechanisms: (i) steric stabilization by the films formed by asphaltenes, wax and/or solid particles; (ii) depletion stabilization due to the excluded-volume effect of high concentration solutes; and (iii) structural stabilization arisen from the long-range colloidal structure formed inside the intervening liquid films in the presence of a sufficient volume fraction of colloidal particles such as asphaltene precipitates.[364, 365] Understanding the properties of the interfacial films is essential to control the stability of oil-water emulsions and the desired demulsification for effective oil-water separation.

From the molecular point of view, the films are formed by three types of materials. The most common components are the heaviest fractions of petroleum such as asphaltenes and resins. As stated in **Section 2**, these molecules contain heteroatoms or polar groups which impart surface activity to these molecules and drive them to accumulate at the oil-water interface. The second group of molecules are natural or externally added surfactants which readily adsorb at the oil-water interface to reduce the interfacial energy. The mineral solids, such as fine sands and clay minerals contaminated by heavy organic matters of unconventional oil and hence bi-wettable, are the third type of stabilizers of petroleum oil-water emulsions. Although inorganic mineral solids are naturally water-wet, their surface wettability is often altered to be bi-wettable or even oil-wet by the adsorption of heavy petroleum components such as asphaltenes and resins. In addition to these three main types of petroleum emulsion stabilizers, the stability of the emulsions is also influenced by the size and size distribution of emulsion droplets, temperature, mechanical state, pH and salinity of the aqueous phase, *etc*.[286]

There are a number of early reviews on petroleum emulsions.[26, 286, 366-368] However, during the past decade or so, several major advances related to understanding the stability of petroleum oil-water emulsions have been reported, such as identifying the key components and structure of indigenous stabilizers, interfacial association and physicochemical properties of interfacial films formed from these indigenous interfacial stabilizers, role of solvent quality and water chemistry, and the stabilizing mechanisms of solid-stabilized oil-water emulsions. In the following sections, these advances in understanding the stabilization of oil-water petroleum emulsions will be reviewed and discussed.

4.3.2. Role of asphaltenes and resins in stabilizing petroleum emulsions

The heavy fractions of petroleum, such as asphaltenes and resins, are blamed for stabilizing the oil-water emulsions because of their surface-active properties.[51, 369-371] The role of resins in stablizing the oil-water emulsions remains a subject of debate. A number of studies has shown that resins alone could not stabilize oil-water emulsions,[372] while others reported the contributions of resins to stabilizing petroleum emulsions. The effect of resins on stabilizing petroleum emulsions could be overshadowed by applying centrifugation to the emulsions.[373] Despite controversal findings on the role of resins in stabilizing petroleum emulsions, there is one common finding that the adsorption behavior of resins and asphaltenes at the oil-water interface is drastically different. Resins can adsorb at the oil-water interface quickly to reduce interfacial tension significantly, while asphaltenes adsorb slowly at the oil-water interface without a significant impact on interfacial tension. The adsorption of resins at the oil-water interface is often reversable, in contrast to asphaltenes which show irreversable adsorption with continuous buildup of increasingly more rigid films at the oil-water interface. The rapid adsorption of resins paves the way for the subsequent asphaltene adsorption over a long period of time at the oil-water interface, which prevents the coalescence of the droplets.[371, 373] The formation of rigid asphaltene films as shown in **Fig. 25**,[320] hinders the coalescence of the emulsion droplets, resulting in a kinetically stable oil-water emulsion. However, the presence of resins in the asphaltenes films is shown to decrease the rigidity and dilatational elasticity of the films.[374]

In addition to the composition of oil (solvency), the ability of asphalenes in stabilzing water-oil petroleum emulsions is also highly linked to the physical properties and chemical structures of asphaltene molecules, such as molecular weight, aromaticity, number and lenghth of side branch chains.[51, 375] Kilpatrick summarized the work up to 2009 on the role of solvency and chemical structure of asphaltenes in stablizing the oil-water emulsions.[368] A concluding remark in his review is that only a part of the asphaltenes is responsible for stabilizing the oil-water emulsions. Some recent studies further confirmed that only 2% of asphaltens in bitumen were responsible for stabilizing petroleum oil-water emulsions.[370, 376] On studying the stability of oil-water emulsions prepared by asphaltenes after gradual removal of a subfraction of asphaltenes accumulated at the oil-water interface, Yang *et al.* also concluded that although these interfacially active asphaltene fractions accounted for less than 2% of the whole asphaltenes, they played the major role in stabilizing oil-water emulsions by their adsorption at the oil-water interface and formation of a thick and rigid interfacial film which aged and became much thicker with time.[99]

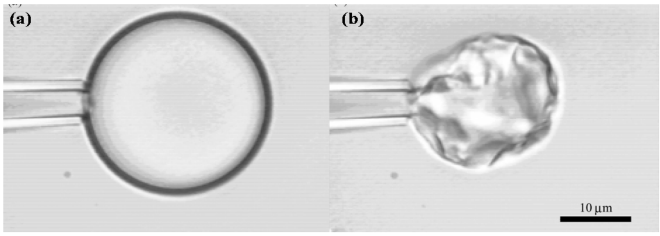


Fig. 25 (a) Micrograph of a water droplet being generated in 0.1 wt% of bitumen-in-toluene solutions using a micropipette; (b) significant crumpling is observed as the droplet is deflated, revealing a rigid film at the oil-water interface that is attributed to the adsorption of natural surfactants at the oil–water interface. *Reproduced with permission from ref. 320. Copyright 1999 the Royal Society.*

Due to the importance of the interfacial films in emulsion stablitiy, the interfacial properties of asphaltene films have been studied intensively during the past decades. In summary, SFA and TFB measurements have shown a slow diffusion of asphaltene molecules to the interfaces to form a dense, irreversable interfacial films of thickness easily in the order of 8 to 20 nm that could grow with time.[368] Tchoukov *et al.* for example measured the size of asphaltene aggregates at the oil-water interface up to 300 nm by aging the oil-water interface for 2.5 h.[377] Using SFA, Nataranja *et al.* measured an increase in thickness of the asphaltene films adsorbed on mica from 1.0 wt% toluene solutions to 100 nm after 1.5 h.[353] The interfacial rheology measurement revealed the transition of the interfacial film from viscous to elastic type with time. This change coincided with a significant increase in life time of intervening liquid films determined by TFB and coalescence time measured by ITFDA,[50, 299] corresponding to more stable W/O petroleum emulsions observed in the field and laboratory experiments.[50, 368] As shown in **Fig. 26**, the observed transition from unstable to stable films as observed in film lift time and emulsion stability measurements corresponded well with the transition of the interfacial film from viscous to elastic (*i.e.*, change from G'<G'' to G'>G'', where G' and G" are the storage and loss modulus, respectively), indicating a critical role of rheological properties of the interfacial film in controlling the stability of W/O petroleum emulsions.[299]

The aromaticity of the oil phase was found to impact the formation and properties of the asphaltene films at the oil-water interface.[378] Asphaltenes precipitate more readily at the oil-water interface from the oil phase (heptol) of higher aliphatic content than from aromatic solvent (toluene). With the TFB, Tchoukov *et al.* measured the thickness of the asphaltene films to be 40 to 90 nm, which is much thicker than those (about 10 nm) stabilized by bitumen or maltenes (deasphalted bitumen).[377] From a molecular point of view, the intermolecular interactions between asphaltene molecules are mainly through π−π stacking, acid−base interactions, hydrogen bonding, metal coordination complexation and electrostatic and van der Waals forces.[379] These binding forces are confirmed by direct force measurements using AFM and SFA, which also show strong dependence of dominant forces between the asphaltene films on the solvent/oil type. In a good solvent such as toluene, the interactions between the asphaltene films are dominated by steric repulsive forces, while in poor solvents such as heptane, the forces become attractive as a result of van der Waals forces and/or π−π stacking.[97, 209]

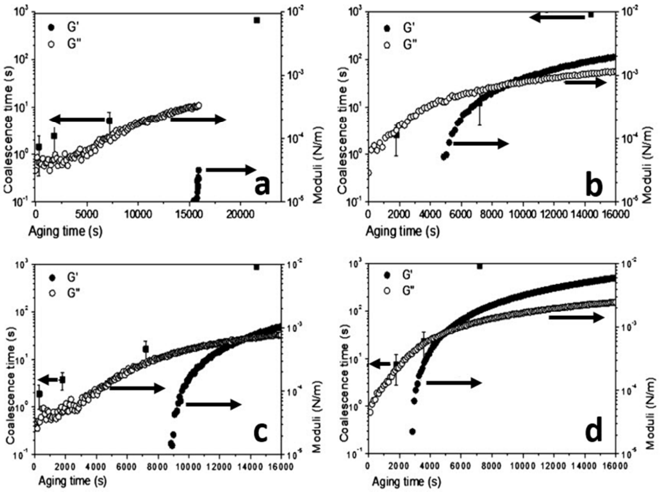


Fig. 26 Direct comparisons of interfacial viscoelastic properties and drop−drop coalescence time as a function of aging time: (a) 0.1 g/L asphaltene in toluene, (b) 0.1 g/L asphaltene in heptol 1:1 (where 1:1 indicates heptane to toluene mass ratio of 1:1 in the heptane-toluene mixture), (c) 0.4 g/L asphaltene in toluene, and (d) 0.4 g/L asphaltene in heptol 1:1, illustrating stabilization of emulsion droplets by elastic propertity of the interfacial film formed after prolonged aging time, and critical role of solvent quality. *Reproduced with permission from ref. 299. Copyright 2014 American Chemical Society.*

Recent advances on asphaltene adsorption and association at the oil-water interfaces using molecular dynamic (MD) simulation confirm that intermolecular π−π (face-to-face) interactions are primary forces for asphaltene aggregates accumulating at the oil-water interface, leading to the stability of the oil-water emulsions.[380-382] Interestingly, when simulating the behaviors of uncharged polyaromatics (PAs) at the oil-water interface, Teklebrhan *et al.* found that the principal plane of the uncharged PA molecules was perpendicular to the oil−water interface. Increasing the polarity of the PA terminal moieties was found to enhance the accumulation of PAs at the oil-water interface. However, the interfacial activity of PAs at the oil-water interface would be reduced by increasing the aromaticity of the PAs due to the strengthened $\pi-\pi$ interactions and molecular aggregation in the bulk oil phase.[380] If the polyaromatics (*e.g.*, asphaltenes) are ionized by deprotonation, they would be much easier to transfer to the oil-water interface instead of staying in the bulk oil phase.[382] In a most recent study by MD simulation, Liu *et al.*[381] reported similar results as those reported by Teklebrhan *et al.*[380] With statistical analysis, they proposed that the asphaltene molecules accumulated at the oil-water interface as stacked nano aggregates and were oriented perpendicular to the interface. These asphaltenes nano aggregates would further combine to form a protective film by "fencing" with each other at the oil-water interface as shown in **Fig. 27**.[381] Other simulation studies with experimental investigations using model compounds on interfacial properties of asphaltenes in the context of stabilizing oil-water emulsions have been summarized elsewhere.[87]

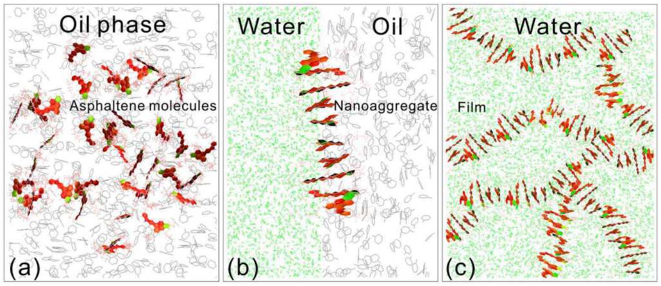


Fig. 27 A schematic view of the asphaltene protecting film formed at the oil-water interface as predicted from MD simulations: (a) at the beginning of MD simulation, the asphaltene molecules are randomly distributed in the solvent; (b) a few asphaltene molecules assembled to form nano-aggregate with the molecular PAHs planes face-to-face stacked at the oil-water interface; and (c) the fence-like asphaltene aggregates pinned perpendicularly on the water surface and knitted together to form a protecting film. *Reproduced with permission from ref. 381. Copyright 2015 American Chemical Society.*

The stability of W/O emulsions is also highly influenced by the adsorption kinetics of surface active agents at the oil-water interfaces. Fast adsorption favors formation of more stable emulsions of smaller droplet sizes. The adsorption kinetics of asphaltenes at the oil-water interface have been investigated intensively by Rane *et al.*[383, 384] and Natarajan *et al.*[353] Asphaltene molecules were reported to adsorb onto the oil-water interfaces as monomers, resulting in a reduction in interfacial tension. The adsorption was found to be diffusion-controlled initially, followed by a non-diffusion-controlled stage of slower rate.[383] Diffusion of asphaltenes to the interfaces was found to be positively correlated to their concentration in the oil phase and inversely proportional to the viscosity of the oil. Rane *et al.* reported that the asphaltenes appeared as monomers in the oil phase at low concentration (< 80 ppm), while they were in the form of aggregates when the concentration was above 80 ppm.[383] Further study showed a sharp reduction in adsorption rate when the asphaltene coverage at the interface reached 35 to 40%, in contrast to the initial diffusion-controlled adsorption. Above such surface coverage, the rate of surface pressure increase was found to be less related to the oil viscosity, but dependent on both asphaltene mass concentration and surface pressure itself. In addition, random sequential adsorption (RSA) theory was found to be suitable for describing the long-term asymptotic adsorption behavior of asphaltenes.[384] Natarajan *et al.* reported similar diffusion controlled behavior when investigating the adsorption kinetics of asphaltenes from asphaltene-in toluene solutions onto mica surfaces using SFA. They found that the asphaltenes adsorbed onto the mica surface as monomers at low concentrations, which was diffusion-controlled and dependent on the asphaltene concentation. The diffusion coefficient on the order of 10^{-10} m^2/s as calculated from the film growth data was shown to be in excellent agreement with the values measured using the NMR technique on bulk solutions.[353] Unfortunately, the diffusion coefficients of asphaltenes from bulk solutions to the oil-water interface under different conditions are rarely reported until now.

The role of asphaltenes in stabilizing oil-water emulsions has also been found to be highly dependent on the chemistry of the aqueous phase, such as pH, salinity and composition of electrolytes. The presence of monovalent or multivalent cations can increase the stability of oil-water emulsions due to enhanced formation and accumulation of surface active materials at the oil-water interface.[385, 386] Changing the pH of the aqueous phase to more basic or more acidic was found to enhance the ionization of asphaltenes, producing more surface active materials and hence resulting in higher interfacial activity.[386, 387] Other acidic/basic substances are present in the system and are known to compete with asphaltenes for the oil-water interface.[387] This subject is reviewed in the following sections.

4.3.3. Role of surfactants in stabilizing W/O petroleum emulsions

Another mechanism of stabilizing oil-water emulsions is by the surfactants which could be from the petroleum itself or added intentionally. As given in **Section 2**, unconventional (heavy) oil often contains endogenous surfactants, mainly naphthenic acids with a small amount of linear alkanoic acids, tetra-acids, sulfonic acids and asphaltenic acids, *etc.*[61, 73, 386, 388] In food processing and other emulsion systems, both natural and synthetic surfactants are used as emulsifiers, including commercial nonionic surfactants,[389] bioemulsifiers,[390] polymers,[391] and CO_2-responsive switchable surfactants.[392]

Natural surfactants. Naphthenic acids are weak-acid type of natural surfactants often contained in unconventional (heavy) oil. Due to their amphiphilic nature, naphthenic acids adsorb at the oil-water interfaces and reduce the oil-water interfacial tension. At the oil-water interface, the naphthenic acids ionize by reacting with the hydroxyl groups, as shown in **Fig. 14** and **Eq. 7**, further increasing their surface activity.[283, 393] The accumulation of naphthenic acids at the oil-water interface plays an important role in stabilizing the oil-water emulsions, enhanced by increasing naphthenic acid concentrations.[394] Early studies on stabilization of oil-water emulsions by naphthenic acids are summarized by Kilpatrick in a comprehensive review.[368] The most recent studies have been focused on the interactions between natural surfactants and the asphaltenes at the oil-water interfaces. Gao *et al.* for example reported that the removal of the indigenous naphthenic acids could increase the ability of asphaltenes in stabilizing the water-in-diluted bitumen emulsions. Their tests using the micropipette technique and Langmuir trough showed that the presence of naphthenic acids lowered the bitumen-water interfacial tension considerably to 3 mN/m and reduced the rigidity of the asphaltene or bitumen films formed at the oil-water interface, which resulted in an increased probability of water droplet coalescence. Their results suggested that the naphthenic acids were able to replace the asphaltene molecules at the interface and break the association among the asphaltene molecules.[64] Neuville *et al.* investigated the adsorption of two indigenous surfactants at the oil-water interface and reported that one of the surfactants adsorbed to the interface faster than the other.[252] The slow adsorbing surfactant was able to replace the fast adsorbing surfactant from the oil-water interface at a longer adsorption time. The adsorption of the fast adsorbing surfactant at the oil-water interface was found to be diffusion-controlled for the surfactant molecules in the bulk-phase.

Externally added surfactants. When producing the oil from unconventional petroleum resources, surfactants are often added into the flooding fluid as stated in **Section 3**. These surfactants play a critical role in emulsifying the oil and stabilizing O/W emulsions.[395] In some cases, the surfactants are added to enhance the ability of asphaltenes to stabilize oil-water emulsions, while in the other cases the surfactants are added to destabilize oil-water emulsions as desired for the downstream oil-water separation processes.[389]

Although naphthenic acid is known to adsorb reversibly at the oil-water interface, Gonzalez observed that together with asphaltenes, sodium naphthenates and linear and/or branched dodecylbenzene sulfonic acids were able to adsorb at the oil-water interface irreversibly. This adsorption led to an increased interfacial pressure (π) and compressibility of the interfacial film. Kang *et al.* extracted sulfonate type of surfactants from petroleum and used them as co-surfactants with a polymer (partly hydrolyzed polyacrylamide, HPAM) in stabilizing oil-water emulsions.[391] They found that the HPAM contributed significantly to the stability of water-in-oil emulsions which were co-stabilized by surfactants. They attributed the enhanced stability of emulsions to the formation of the rigid network at the oil-water interface. A mechanistic study showed that the petroleum sulfonate played an important role in reducing the interfacial tension, while their presence had a negligible influence on the interfacial shear rheology (*e.g.*, storage modulus G' and loss modulus G''). Although little reduction in the interfacial tension was observed, the adsorption of polymer at the oil-water interface strengthened the storage modulus G' of the films. The surface elasticity was found to be further enhanced by increasing the polymer concentration.[391]

The role of non-ionic surfactants in stabilizing oil-water emulsions could be very different, depending on their molecular structures. Sanatkaran *et al.* found an synergistic effect of 10 wt% non-ionic Spans (oil soluble) and/or Tweens (water soluble) with 90 wt% basic poly(isobutylene) succinic anhydride derivative surfactant (PIBSA-Mea) in stabilzing concentrated water-in-oil (synthetic oil) emulsions. In their study, the stabilizing role of the co-surfactants was found to be highly dependent on the chemistry of hydrophilic head groups and the molecular structure of hydrophobic tails such as hydrocarbon chain lenghth, number of branches and presence of double bonds. The hydrophobic tails of Spans impart a strong influence on stablizing oil-water emulsions, in contrast to a marginal effect from the hydrophilic Tweens.[396] However, when the non-ionic surfactants were present together with asphaltenes, different stabilizing effects were observed. Gonzalez reported that both AOT (Aerosol OT) and NEO (nonylphenol ethoxylate) as co-surfactants were able to destabilize the heavy oil-water emulsions stabilized by asphaltenes films. The destablization was especially apparent when the concentration of NEO and AOT surfactants was increased to 100 ppm and 500 ppm, respectively, at which the asphaltene films were completely expelled from the oil-water interfaces reversibly.[389] These results indicate favorable competition of added surfactant with the asphaltenes for limited oil-water interfaces.

The more favorable adsorption of added surfactant than asphaltenes at the oil-water interface is linked to the well-defined structure of surfactant molecules. In general, surfactant molecules contain a hydrophilic head(s) and hydrophobic tail(s). When diffusing to the oil-water interface, the hydrophilic head digs into the aqueous phase, while the hydrophobic tail protrudes into the oil phase. The accumulation of the surfactants at the oil-water interface reduces the interfacial energy and interfacial tension gradient, resulting in a much more stable emulsion system. A recent study with vibrational sum frequency scattering measurements showed that anionic and cationic surfactants adopted considerably different structures at oil-water interfaces. While no detectable dodecylsulfate (DS^-) ions were found in the oil phase, a measureable amount of dodecyltrimethylammonium (DTA^+) ions appeared in the oil phase. Using Raman solvation shell spectroscopy and second harmonic scattering (SHS), Schen *et al.* observed significant differences between the interfacial water structures and the hydration-shells.[397] They proposed that the specific interactions with water played a key role in driving the anionic head group toward the water phase and the cationic head group toward the oil phase. This finding helps to understand the stabilization and demulsification mechanisms of oil-water emulsions, which provides scientific insights on designing specialty chemicals for controlling the stability of oil-water emulsions.

Recently, some novel surfactants have been reported to be effective in stabilizing the oil-water emulsions. Four bioemulsifiers, extracted from indigenous strains of Bacillus licheniformis (ACO1 and ACO4) and Rhodococcus ergthropolis (1072 and 91-B), are used as co-surfactant with Tween 80 (a chemical emulsifier) to emulsify the heavy oil. Although the molecular mechanisms of enhanced emulsification remain to be established, a viscosity reduction of the heavy oil has been observed as a result of emulsion formation when surfactants are added into the system.[390] The swichable surfactants are another important type of novel emulsifiers for controlling the stability of oil-water emulsions.[392, 398] As reported, the acetamidines containing a long hydrophobic hydrocarbon chain could serve as switchable surfactants responsive to CO_2 addition. As shown in **Fig. 28,** the reaction of acetamidines with CO_2 produces surface active amidinium bicarbonate surfactants which emulsify and stabilize oil-water emulsions for oil production. The removal of CO_2 from the emulsion system reverses reaction to convert surface active amidinium bicarbonate to non-surface active acetamidines, destabilizing the formed emulsions to enhance oil-water separation. Furthermore, both of these steps could be accomplished at ambient pressures. Jessop's group synthesized several swichable surfactants of different tail lengths, HLB values and pKa. Applying these switchable surfactants to stabilizing the oil-water emulsions, they found that N'-hexadecyl-N,N-dimethylacetamidinium bicarbonate was effective in stabilizing the light crude oil-in-water emulsions while it worked poorly on stabilizing heavy oil-water emulsions.[398] However, working with CO_2, long chain acetamidines containing ethylene oxide units ($R\text{-}CH_2OCH_2\text{-}R$) were able to stabilize a water-in-heavy oil emulsion.[392] Interestingly, they also found that the endigenous surfactants in the heavy oil can be activated by deprotonation with bases to stabilize the oil-in-water emulsions, and then deactivated by purging the emulsion with CO_2 to break the emulsion.

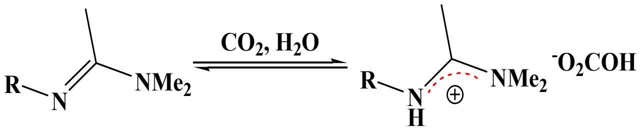


Fig. 28 Working principle of CO_2-switchable surfactants: addition of CO_2 converts non-surface active acetamidines to surface active amidinium bicarbonate surfactants, while removal of CO_2 would reverse the conversion. *Adapted from Liu et al., 2006.[398] Copyright 2006 by the American Association for the Advancement of Science.*

In addition to the effect of molecular structure of hydrocarbon tails, the performance of these swichable surfactants also depends on the properties of their head groups. In a more recent study, Jessop *et al*. synthesized another two types of CO_2-triggered switchable surfactants (*i.e.*, aryl amidine and tertiary amine) of similar basicity and investigated their ability in stabilizing oil-water emulsions. They found that the amidinium and ammonium bicarbonates could stabilize emulsions of high volume fraction of dispersed phase with emulsion droplet sizes ranging from 80 to 470 nm. The droplet sizes were further reduced by adding a cosurfactant, using a different initiator or increasing the pressure of CO_2.[399] The effect of head groups on their function as swichable surfactants was further investigated instensively. They reported that the switchable head group affected the basicity, solubility, heat of protonation, rate and extent of switching, and ability of the surfactant to reversibly stabilize and demulsify oil–water emulsions.[400] There is of special interest in using CO_2-triggered swichable surfactants to stabilize and then distabilize the oil-water emulsions for heavy oil production and materials synthesis.[401-403] However, many issues, such as the fate of the surfactants,[399] need to be addressed through extensive research to make this type of novel switchable surfactants commercially acceptable and widely used.

4.3.4. Emulsions stabilized by mineral solids

Fine solids with appropriate surface wettability are well known to stabilize O/W or W/O emulsions. These emulsions are known as Pickering emulsions which retain the properties of traditional emulsions stabilized by surfactants.[404] For unconventional petroleum production, such as oil extraction from oil/tar sands, oil shale and heavy petroleum reservoirs, the presence of fine solids including asphaltene aggregates/precipitates,[369] wax particles,[405] silica,[406, 407] clay minerals,[408, 409] and fine carbonate rocks, in the produced fluids is a common phenomenon. These solids often stabilize oil-water emulsions as shown in **Fig. 29**,[410] forming a gel-like layer, known as rag layers in oil-water separation vessels that upset oil-water separation processes.[411] The difficulties in removing stable emulsions with associated fine solids give fine solids a chance to be carried to downstream processes, where they cause severe damage to the equipment. The roles of mineral solid in stabilizing oil-water emulsions are reviewed in the following section.

Solid properties for stabilizing emulsions. It is well recognized that not all solid particles can stabilize oil-water emulsions. The successful formation of solid-stabilized emulsions requires solid particles to be sufficiently small and of desired wettability. In general, the particles of sizes ranging from nano-meters to microns are ideal for stabilizing oil-water emulsions. Nano-size particles can stabilize the droplets as small as a few micron in diameter, while micron size particles stabilize droplets with a few millimeters.[404, 412] The shape (aspect ratio) of the particles also plays an important role in stabilizing oil-water emulsions. For a given condition, non-spherical particles tend to form a much more stable emulsion than spherical particles due to stronger interface-mediated capillary interactions.[413] However, the most important factor influencing the stability of particle-stabilized emulsions is the wettability of particles. From a thermodynamic point of view, only bi-wettable particles can stabilize the oil-water emulsions as shown in **Fig. 30**.[367] Completely hydrophobic or hydrophilic particles are ineffective in emulsifying and stabilizing the emulsions as they are repelled from the interface into either the oil or aqueous phase, respectively.[414, 415] Solids of contact angles close to 90° are the most effective in stabilizing oil-in-water emulsions, with particles of contact angle greater and smaller than 90° stabilizing W/O and O/W emulsions, respectively.[412, 416] Increasing the particle concentration is known to be beneficial to stabilizing oil-water emulsions as a result of higher particle surface coverage.[408, 413] Extensive review on particle stabilized petroleum emulsions can be found elsewhere.[367, 404, 416, 417]

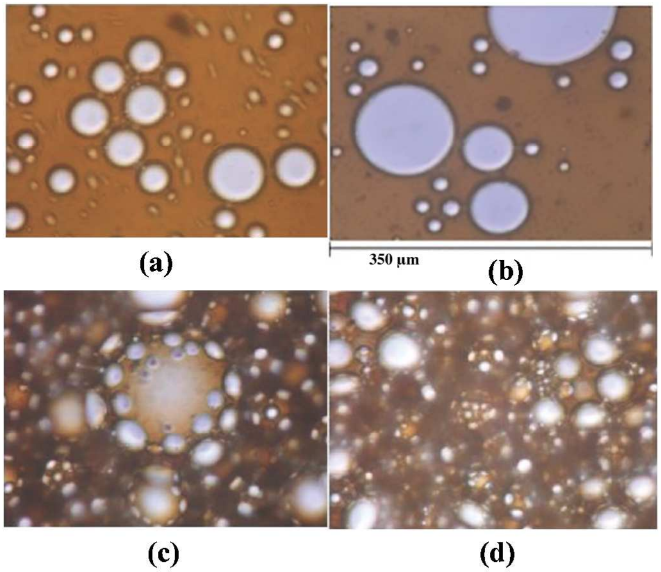


Fig. 29 Photographs of emulsions produced for systems consisting of (a) 10 wt% heptol 4:1, 15 wt% bitumen and 75 wt% SW (saline water); (b) 12.5 wt% heptol 4:1, 12.5 wt% bitumen and 75 wt% SW; (c) 10 wt% heptol 1:1, 15 wt% bitumen and 75 wt% SW; and (d) 12.5 wt% Heptol 1:1, 12.5 wt% bitumen and 75 wt% SW, showing an increased emulsion stability of smaller sizes of water droplets in emulsions of higher concentration of heptane. *Reproduced with permission from ref. 410. Copyright 2009 American Chemical Society.*

Solids as petroleum emulsion stabilizers. In an unconventional petroleum reservoir or during the production of oil from unconventional oil reservoirs, the intrinsically hydrophilic mineral solids such as calcite, kaolinite, silica/quartz, montmorillonite, illite, sandstone and chlorite could be inevitably modified by the adsorption of surface active petroleum components to become biwettable or even oil-wet. As a result, these solid particles have a strong affinity to the oil-water interface, forming a rigid protective layer to prevent the coalescence of emulsified droplets.

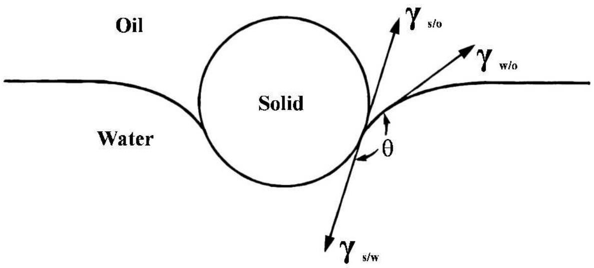


Fig. 30 Definition of three-phase contact angle (θ) when a solid particle is deposited at an oil-water interface. *Reproduced with permission from ref. 367. Copyright 1988 Marcel Dekker, Inc.*

Bensebaa *et al.* determined the adsorption of humic and asphaltic materials on the surfaces of clays with less than 200 nm in size, and found incomplete and patchy coverage of the surfaces. The adsorption of such polar petroleum components altered the wettability of the solid surface to be more hydrophobic, which makes the hydrophobic patches on solid particles to contact the oil phase at the oil-water interface as shown in **Fig. 31**.[408] These contaminated solid particles were found to be able to stabilize the water-in-bitumen emulsions.[418] Increasing the adsorption of petroleum materials on the solid surface makes the solid more oil-wet, resulting in a much more stable accumulation of the solids at the oil-water interface. The alteration of the solid wettability by the polar petroleum components was found to be solid type-dependent. Comparing the effect of different solids on stabilizing the emulsions when asphaltenes and resins were involved, Sullivan *et al.* found that montmorillonite and $Ca(OH)_2$ particles were better stabilizers due to their stronger interactions with asphaltenes than kaolin and Fe_2O_3 particles.[408]

With the help of advanced characterization techniques, such as near-infrared (NIR) spectroscopy and the QCM-D, the adsorption of asphaltenes, resins and other polar components of unconventional oils on the solid surfaces has been analyzed qualitatively and quantitatively. The adsorption of asphaltenes on the sand surface was found to be stronger and less reversible than resins.[406, 419, 420]

Extensive study of asphaltene adsorption on minerals solids such as kaolinite, calcite, dolomite, quartz, montmorillonite, feldspar, smectite, magnesite, hematite, illite, sandstone and thuringite revealed that the adsorption capacity of asphaltenes on these mineral solids is closely related to the cation exchange capacity of the solids.[421-428] In essence, the adsorption of asphaltenes or other polar petroleum components on the mineral surfaces is attributed to the existence of polar sites on the mineral surface, such as octahedral Al-OH, tetrahedral Si-OH and Ca-OH groups as shown in **Fig. 7**.[429, 430] In addition to the molecular size of asphaltenes, the size of mineral particles and porosity of the rocks are also important factors influencing asphaltene adsorption on solid surfaces. Major findings of asphaltene adsorption on different solid surfaces were summarized in a comprehensive review elsewhere.[49] However, little has been reported on the quantitative relation between the wettability of solids and their ability to stabilize oil-water petroleum emulsions. The reasons why reservoir solids are selectively contaminated by petroleum components remain to be revealed. In particular, little is known on the role of solid surface heterogeneity and anisotropy in adsorption of petroleum polar components and other surfactants on mineral surfaces, although such selective adsorption could potentially lead to the formation of so-called Janus particles.[431] These particles are of special ability in stabilizing oil-water emulsions as a result of liquid pining at the boundaries of wettability transitions.

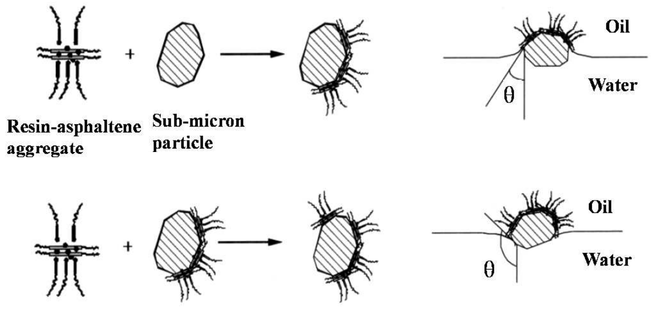


Fig. 31 Adsorption of resin/asphaltene aggregates on a hydrophilic particle, forming a Janusz-like particle. (Upper) at low surface coverage, the particle is preferentially wetted by the aqueous phase (θ < 90°) and favors formation of O/W emulsions. (Lower) as more aggregates adsorb, the particle becomes preferentially wetted by the oil phase (θ > 90°), favoring the formation of W/O emulsions. *Reproduced with permission from ref. 408. Copyright 2002 American Chemical Society.*

Due to wettability alteration, the mineral solids not only stabilize the oil-water emulsions, but also cause the formation of a thick, viscous layer (called “rag layer”) between the oil and aqueous phases in a separation vessel, which prevents further oil-water separation and hence causes damage to the operation.[432] Recent studies on rag layers revealed that asphaltenes and naphthenic acids were the main surface active materials which stabilized the water droplets with associated solids in crude oils.[433, 434] Iron-containing minerals such as siderite and pyrite were found to be enriched in the rag layers.[411] It was strongly suggested that the stability of gel-like rag layers depended on the type of mineral solids, aromaticity of the oil, and temperature.[410, 435, 436]

In addition to the petroleum surface-active components, the minerals solids also work together with externally added surfactants to stabilize oil-water emulsions. Using silica nanoparticles and cationic surfactants (*e.g.*, hexadecyltrimethylammonium bromide, CTAB) to stabilize oil (n-dodecane)-water emulsions, Binks *et al.* reported a synergistic role of the silica nanoparticles with CTAB in stabilizing the emulsions. Although both the nanoparticles and surfactants alone can stabilize the emulsions at low pH, the efficiency of nanoparticles was weakened while the surfactants worked much more effectively in stabilizing the emulsions with increasing the pH of the aqueous phase.[407] Using silica nanoparticles and palmitic acids to stabilize water-in-hexane emulsions,[437] Santini *et al.* reported that the nanoparticles and surfactants (palmitic acids) would form complexes, accumulating at the oil-water interfaces. These particles at the oil-water interface provide a steric hindrance to prevent the water droplets from coalescence. Their further investigation showed that the formation of the complexes was only achieved after the formation of a surfactant layer on the nanoparticle surfaces first. The properties of the complexes were found to be dependent on the surfactant concentration and the volume ratio of the phases. A recent study showed that the ability of the hydrophilic silica particles to stabilize emulsions was determined by the type of surfactants presented in the system and their concentrations. A competitive adsorption/deposition between the nanoparticles and surfactants at the oil-water interface might occur, which was controlled by the surfactant concentration and types of emulsions (O/W type or W/O type).[438]

The interfacial properties of oil-water emulsions stabilized by solids have been studied extensively and the major findings were reviewed critically elsewhere.[415, 439] Two recent comprehensive volumes on this subject are highly recommended as further reading materials.[416, 417]

4.4. Demulsification of heavy oil emulsions

In contrast to emulsification, demulsifying oil-water emulsions is highly desirable for oil-water separation. Separation of an oil-water emulsion into corresponding water and oil phases typically involves two steps: flocculation and coalescence. During the flocculation stage (aggregation, agglomeration, or coagulation), the emulsion droplets come close to each other driven by hydrodynamic forces and form aggregates or flocs under the colloidal forces and bridging force of polymers. In this stage, the droplets retain their original features or identity. Upon the contact of the droplets with each other, the intervening liquid films between the emulsion droplets start to thin. The coalescence of the droplets occurs when the unstable or meta-stable liquid films rupture, forming a larger droplet. Due to the difference in density, the coalesced water droplets settle down to the bottom of the container by gravitation, while the oil phase moves in the opposite direction to the top. Either of these two steps can be the rate-determining step in emulsion breaking.

There are many different ways to break emulsions by for example thermal,[440] mechanical, electrical and/or chemical means as the driving force.[26] In this critical review, we focus on chemical demulsification, in which the chemical demulsifiers play a key role. During the past decades, thousands of demulsifiers have been invented for breaking oil-water emulsions. However, the significant advances on understanding the mechanisms of chemical demulsification were made only very recently. A number of hypotheses and theories were proposed to explain the observed chemical demulsification. Practically, the basic requirements for a chemical to be a demulsifier for breaking W/O petroleum emulsions are: i) solubility in oil phase as they are delivered through the oil phase; ii) interfacial activity to adsorb in competition with emulsifying species at the oil-water interfaces; iii) ability to break original stabilizing interfacial films; iv) inability to form stable interfacial films upon its occupancy at the oil-water interface; and v) nontoxic and readily available at an affordable cost for large scale usage. In the following section, working mechanisms of chemical demulsifiers developed recently for breaking water-in-oil (petroleum) emulsions will be discussed. The effect of water chemistry such as salinity and pH on chemical demulsification is also discussed, followed by a brief review on enhanced demulsification by external electric and magnetic field and by microwave radiation.

4.4.1. Demulsification by polymers

The presence of demulsifiers at the oil-water interface can reduce the mechanical properties and rigidity of interfacial films formed by petroleum components (*e.g.*, asphaltenes). The efficiency of demulsification by chemical demulsifiers is often related to the molecular size, structure and hydrophobic/hydrophilic balance of demulsifiers. Using a Langmuir trough, Zhang *et al.* investigated the effect of a chemical demulsifier (mixture of oxyalkylated alkylphenol formaldehyde resin of 3000 Da average MW) on the properties of asphaltene films at air-water and oil-water interfaces. They observed a significant reduction in the surface pressure and the rigidity of the asphaltene films as a result of demulsifier adsorption and insertion into the asphaltene films, destabilizing or breaking the original asphaltene films. Increasing demulsifier concentration in the oil phase was found to enhance the weakening of the interfacial asphaltene films. [290]

Surface active polymers were found to be of particular interest in demulsifying petroleum W/O emulsions. The presence of multiple surface active sites ensures high probability of the polymer demulsifier molecules attaching to the oil-water interface as in the case of crabs and displace the original stabilizing interfacial films. Ethylene oxide (EO)-propylene oxide (PO) copolymers (shown in the inset of **Fig. 32 b**) and their derivatives are an important type of polymeric demulsifiers used widely due to their controllable amphiphilic properties with hydrophilic groups (EO) and hydrophobic ends (PO).[441-449] Zaki *et al.* synthesized a series of EO-PO copolymers with variable EO/PO ratios (denotes hydrophilic-lipophilic balance: HLB value) and molecular weights. These polymer demulsifiers were used to break synthetic water-in-benzene emulsions stabilized by asphaltenes. From their experimental results, Zaki *et al*. concluded that high HLB values and molecular weights of the demulsifiers were beneficial to the demulsification. They speculated that the synthesized demulsifiers with high HLB values possessed a higher ability to adsorb at the oil-water interface due to simultaneous attaching of multiple hydrophilic groups to the aqueous phase. Increasing the molecule weight is anticipated to increase the number of water-loving sites and excluded volume of the polymeric molecules adsorbed in the films, resulting in a higher exclusion for asphaltenes from the interface, however, excessive large molecular weight may not be effective due to lower molecular diffusion to the oil-water interface.[442] The efficiency of the demulsifiers was also found to be dependent on the salinity and pH of the water phase.[443] With modification of EO/PO by substitution of the functional groups, Peña *et al.* conducted demulsification tests of brine-in-crude oil emulsions by six EO + PO alkylphenolformaldehyde resins (about 3500 Da) and five cross-linked polyurethanes (12,000 to 20,000 Da).[444] The presence of phenolic resins was found to promote the coalescence of the emulsion droplets with good performance being observed for resins of intermediate hydrophilicity. Although polyurethanes were shown to flocculate the droplets, they showed little effect on coalescence of the emulsified water droplets. In their study, increasing the MW of the demulsifiers was shown to be beneficial for breaking emulsions, and co-addition of two different types of demulsifiers led to a synergistic effect on demulsification of the emulsions. To account for their results, two demulsification mechanisms were proposed: the resins adsorbed on the droplet surfaces were able to reduce the interfacial tension, which led to a fast coalescence of the emulsion droplets; while the polyurethanes were able to act as bridges for the flocculation and sedimentation of the droplets.

In other studies, the molecular weight and EO/PO ratio of EO/PO copolymer demulsifiers were shown to have a significant effect on demulsification efficiency of oil-water emulsions.[448, 449] Furthermore, a shorter hydrophobic chain was found to be beneficial as it ensured the contact of the demulsifiers with the water phase.[447] Other derivatives of EO/PO, such as polyoxyalkylated diethylene triamine EO/PO (DETA(PO)$_m$-(EO)$_n$),[450] PEO–PDMS–PEO block copolymers, PPO–PDMS–PPO block copolymer,[445] PDMS/PEO/PPO,[447] DAOE/DAOP,[451] α, ω-diamino-polyoxyethylene-polyoxypropylene polyoxyethylene (PEO$_y$–PO$_x$–PEO$_y$),[452] α,ω-diamines of polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) triblock copolymer,[446] were also shown to be good candidates for demulsifying the oil-water emulsions under different conditions.

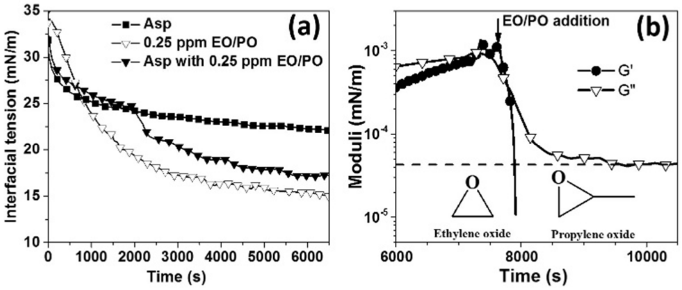


Fig. 32 Effect of EO/PO copolymer demulsifier on dynamic interfacial tension (a) and rheology (b) of asphaltene-in toluene-water interfaces. Molecular structures of monomer EO (C_2H_4O) and PO (C_3H_6O) are shown in the inset of (b). *Reproduced with permission from ref. 453. Copyright 2014 American Chemical Society.*

It is proposed that the EO/PO polymers demulsify oil-water emulsions through the adsorption at the oil-water interface, competing for the surfaces occupied by the films formed by the petroleum components. Using a triblock copolymer consisting of dimethyl-siloxanes (PDMS) linked with poly EO-PO as the demulsifiers, Le Follotec *et al.* studied the effect of adding demulsifiers on the physical properties of asphaltene films at air-water and oil-water interfaces using the AFM and Langmuir trough techniques.[447] When the demulsifiers were introduced in their experiments, the interfacial tension was observed to decrease, along with a significant modification of interfacial asphaltene film properties. Recently, Pensini *et al.* conducted a systematic study on the mechanisms of demulsifying asphaltene-stabilized water-in-toluene emulsions by EO/PO based polymeric demulsifiers. As shown in **Fig 32 a**, addition of 0.25 ppm EO/PO demulsifier reduced the asphaltene-containing toluene-water interfacial tension substantially, but could not reach the same level as 0.25 ppm EO/PO demulsifier in toluene-water interfacial tension, suggesting at most a partial replacement of asphaltenes by EO/PO demulsifiers from the interface. With assistance of Langmuir trough, Brewster angle microscopy and AFM, the asphaltene films at the toluene-water interface were found to be softened due to the penetration of demulsifiers, resulting in reduced viscoelastic moduli and modified interfacial mobility and morphology of the asphaltene films.[453] Interestingly, after establishing an elastic interfacial film of asphaltenes at the oil-water interface, the addition of 2.3 ppm EO/PO reverted the film to be viscous as shown in **Fig 32 b**, corresponding to an unstable interfacial film. Based on the results of bottle tests and droplet coalescence measurements by micropipette, they established an optimal EO/PO polymeric demulsifier dosage of 2.3 ppm dosage. Increasing the demulsifier concentration above this optimal dosage was observed to be detrimental to demulsification as a result of steric repulsion between the water droplets, produced by the intrinsic stabilizing capacity of the demulsifier at the oil-water interfaces.

Recent studies focused on biodegradable natural polymers, such as ethyle cellulose (EC) as shown in the inset of **Fig. 33.** Similar phenomena have been observed with EC as with EO/PO demulsifiers to remove the water from W/O emulsions. As shown in **Fig. 33**, increasing EC concentration in naphtha-diluted bitumen could reduce significantly the interfacial tension, although it is less effective than the case of naphtha without bitumen, due to the competitive nature in adsorption at the oil-water interface.[454] The results in **Fig. 33** also show incomplete dispel of asphaltenes from the oil-water interface, as the interfacial tension of naphtha-diluted bitumen-water interfacial tension remains slightly higher than that of naphtha-water interface even at 500 ppm EC concentration.

Recently, Hou *et al.* reported Langmuir isotherms of bitumen- or asphaltene-containing toluene-water interfaces in the absence and presence of EC.[260] Although interfacial bitumen films behave similarly to asphaltene films with high rigidity or small compressibility as shown in **Fig. 34**, the addition of EC makes the film much softer and very much similar to the films of EC alone formed at the toluene-water interface. These results clearly indicate the ability of EC to adsorb and penetrate the bitumen/asphaltene films originally formed at the oil-water interface, a conclusion that could also be derived from the interfacial tension measurement. These findings agree with the results of AFM measurements given by Feng, *et al.* in **Fig. 35**. It is clear from **Fig. 35** that the bitumen interfacial film is homogeneous, consisting of fully packed asphaltene molecular aggregates, while the fully packed film becomes "broken" upon EC addition, leaving large area of the interface occupied by EC molecules. [454] The ability of EC to displace petroleum surface-active components from the oil-water interface was further confirmed by the study with QCM-D in Wang *et al.*'s work.[170] With advanced computing techniques, such as MD simulation, Liu *et al.* simulated the demulsification process of asphaltene stabilized water-in-oil (toluene) emulsions by EC. Their simulation results also suggested penetration of demulsifier EC molecules dissolved in the toluene into the asphaltene protective film, partially replacing the adsorbed asphaltene molecules. As a result, the surface of the water droplets becomes only partially covered by the protective film, resulting in ease coalescence by the contact of asphaltene-free areas on the droplets, as shown in **Fig. 36**.[381]

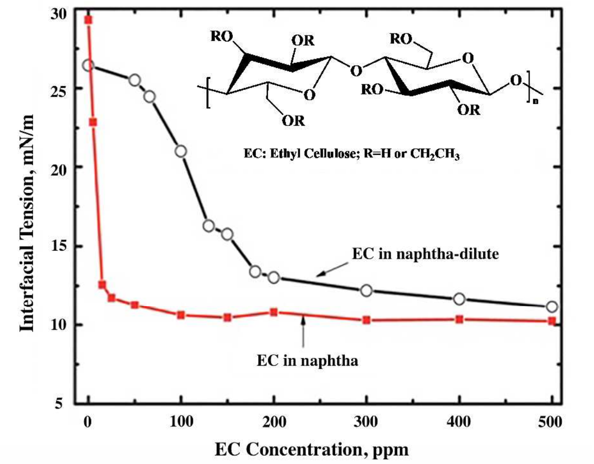


Fig. 33 Naphtha-water and naphtha-diluted bitumen-water interfacial tension as a function of EC concentration in naphtha or naphtha-diluted bitumen: EC reduced naphtha-water interfacial tension significantly, although at higher EC concentrations in the presence of asphaltenes contained in bitumen due to competitive adsorption at the oil-water interface. Inset in the figure: the basic molecular structure of ethyl cellulose (EC). *Reproduced with permission from ref. 454. Copyright 2010 American Chemical Society.*

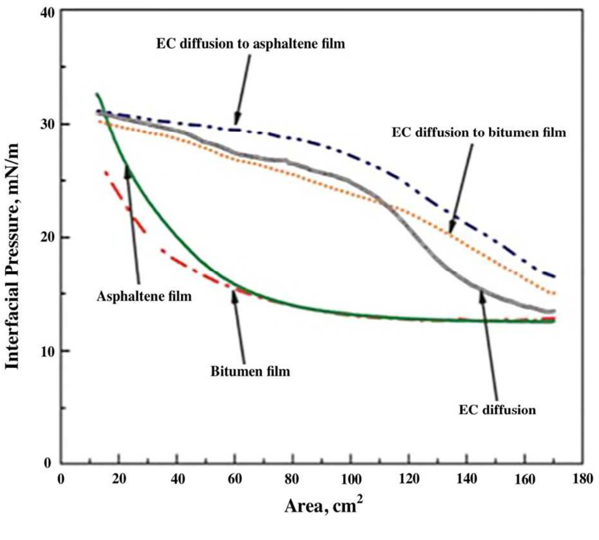


Fig. 34 Pressure−area isotherms of bitumen/asphaltene interfacial films formed by spreading 200 μL of 1 mg/mL bitumen or 20 μL of 1 mg/mL asphaltene to the interface and by diffusing 20 μL of 1 mg/mL EC through the toluene top phase to the interface where a film was already formed by 200 μL of 1 mg/mL bitumen or 20 μL of 1 mg/mL asphaltene. The asphaltene content of 200 μL of 1 mg/mL bitumen is the same as that of 20 μL of 1 mg/mL asphaltene. Interfacial bitumen films behave similarly to asphaltene films which become much softer in the presence of EC and behave almost the

same as EC films, in particular at the compressed interfacial areas less than 100 cm^2. *Reproduced with permission from ref. 260. Copyright 2012 American Chemical Society.*

The study by Feng *et al.* showed that the efficiency of dewatering by EC addition could be enhanced by increasing EC dosages. As shown in **Fig. 37** more than 90% water removal was achieved at about 130 ppm EC addition.[455] The micropipette experiments in their study showed the flocculation of two individual emulsified water droplets at 35 ppm concentration of EC dosage, as shown in row B of **Fig. 38**. At higher EC concentration above 130 ppm for example, the emulsified water droplets coalesced upon contact with each other as shown in row C of **Fig. 38**. In contrast to stable water droplets emulsified in naphtha-diluted bitumen as shown in row A of **Fig. 38**, water droplets emulsified in EC-in naphtha solutions were unstable, shown in row D of **Fig. 38** by spontaneous coalescence of the droplets upon contact with each other. Based on their further study using the LB trough and AFM imaging, they proposed that EC molecules were able to adsorb into the bitumen/asphaltene films at the oil-water interface and displace them from the interface, resulting in a reduced interfacial tension and thickness of the films. The demulsification process of water in diluted bitumen emulsions by EC is accomplished by flocculation of the emulsified water droplets, followed by their coalescence, as schematically illustrated in the right column of **Fig. 38**.[260, 454]

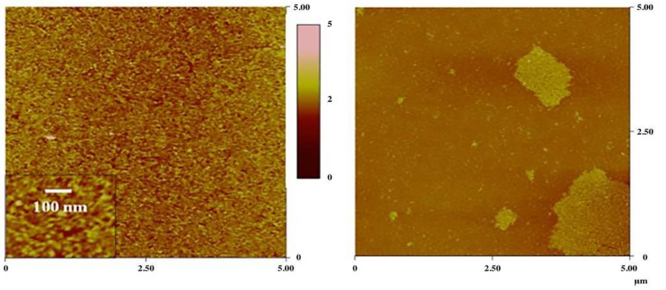


Fig. 35 AFM images of interfacial films for: (a) bitumen LB interfacial film; (b) bitumen/EC LB interfacial film. Both of the films are transferred from the naphtha-water interface at 2 mN/m interfacial pressure. The film in (b) was prepared by spreading a mixture of 20 µL of 1 mg/mL bitumen and 20 µL of 1 mg/mL EC at the interface. *Reproduced with permission from ref. 454. Copyright 2010 American Chemical Society.*

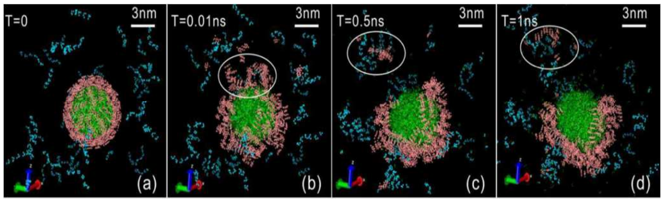


Fig. 36 Snapshots of the demulsification steps by EC in molecular dynamics simulation: (a) the EC molecules are dissolved in the toluene and diffuse to the oil-water interface; (b) the EC molecules penetrate into the asphaltenes film at the oil-water interface; (c) the penetrated EC molecules gradually pull out the fencelike structure of asphaltenes, a process similar to peeling off an orange; (d) asphaltene protective film was broken, which led to the exposure of water droplet surface. (The water, EC and asphaltene molecules are represented in green, light blue and pink, respectively with the toluene molecules being hidden). *Reproduced with permission from ref. 381. Copyright 2015 American Chemical Society.*

Recently, other chemical demulsifiers have been applied to breaking oil-water emulsions. Using Langmuir trough and Brewster angle microscopy (BAM), for example, Fan *et al.* investigated the effect of non-ionic surfactants, *e.g.,* polyoxyethylene nonylphenols ($C_9H_{19}C_6H_4(OC_2H_4)_nOH$, where n=5, 10.5-12, and 40 for CO-520, CO-720 and CO-890, respectively), on physical properties of asphaltene films at air-water and oil-water interfaces. They observed that the surfactants diffused faster to the air-water and oil-water interfaces than asphaltenes to form a film which acted as emulsion inhibitors.[317] Using their synthesized alternating hydrophilic-lipophilic copolymers (HaLCs), Yan *et al.* reported a complete demulsification at room temperature in less than 10 min.[456] Aburto *et al.* observed a high demulsification efficiency using a synthetic ionic surface-active choline carboxylates together with microwave irradiation.[457] Rhamnolipid was also found to be able to destabilize the oil-water emulsions.[458] Non-ionic surfactants (*e.g.*, polyoxyethylene nonylphenols),[317, 459] acid-alkaline additives,[460] and derivatives of 1,3,5-triethanolhexahydro-1,3,5-triazine[461] can play, to some extent, an important role in demulsifying the oil-water emulsions. Even solids, such as artificial zeolite, natural zeolite, diatomite, bentonite and natural soil,[462] or the nano-titania particles modified by demulsifiers (*e.g.*, cethyltrimethyl ammonium bromide(CTAB), sodium dodecyl sulfate (SDS))[463] are reported to be effective in breaking water-in-oil emulsions.

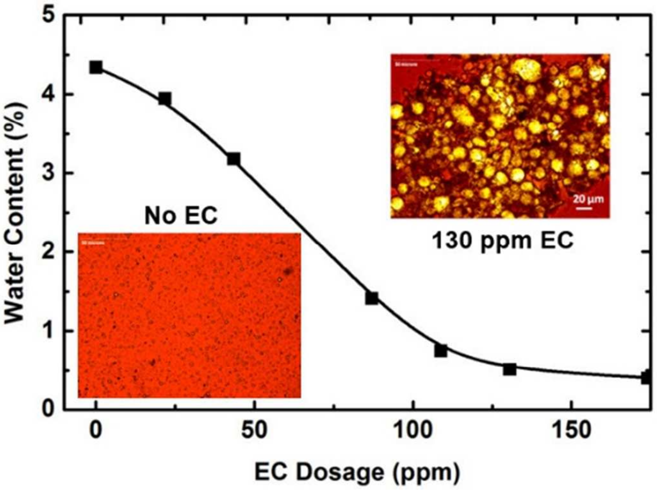


Fig. 37 Water removal percentage from 5 wt% water in naphtha-diluted bitumen emulsions as a function of EC dosage added into the system by gravity settling at 80 °C for 1 h. The inset: micrographs of emulsions destabilized by 130 ppm EC. The emulsions for imaging were taken from the bottom of the test tubes. *Reproduced with permission from ref. 455. Copyright 2009 American Chemical Society.*

Intrinsically, successful demulsification is attributed to the balance of interactions across the films between two contacting droplets. For W/O emulsions, interactions occur through the oil film between two water droplets, while in O/W emulsions, the oil droplets interact across an aqueous film. Liu *et al.* investigated the interactions between asphaltene films deposited on silica surfaces in aqueous solutions by the AFM. In this case, the long-range forces and hydrophobic forces were detected between the asphaltene films. The hydrophobic forces were also found to be pH dependent. A decreased force barrier was found when decreasing the pH or increasing the temperature or salinity of water. However, the adhesion forces were observed to be affected by only the pH and temperature.[208] In non-aqueous systems (*e.g.*, toluene), the temperature had a smaller effect on the interactions between asphaltene films. Although the DLVO forces were detected in aqueous solutions, the interactions between asphaltene surfaces in toluene were found to originate from steric forces and interdigitating of dangling asphaltene branches. They also observed the influence of the asphaltene deposition/adsorption method on the interactions due to different orientation and compactness of the films on the solid surfaces.[464] When changing the oil phase by adding a poor solvent, such as heptane, the steric repulsive forces between asphaltene films became increasingly weaker and even reversed to become weak attractive forces which can be described by van der Waals forces.[97] Similar results are observed by Natarajan *et al.* using surface force apparatus (SFA).[209] However, little force data are reported involving demulsifiers mixed in the films.

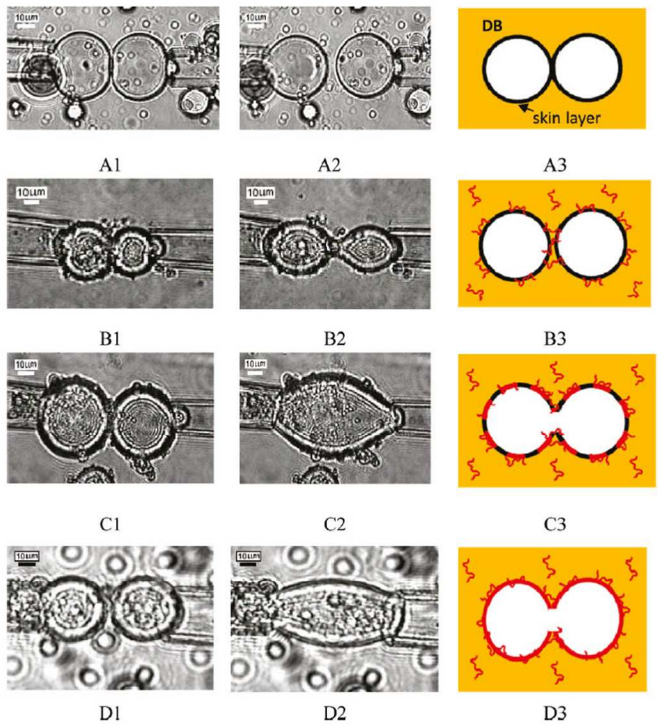


Fig. 38 Interactions of water droplets visualized by the micropipette technique. Water droplets were present in 0.1 wt% naphtha-diluted bitumen emulsion (A1, A2, B1, B2, C1, and C2) or in naphtha (D1 and D2). (A1) Water droplets were brought into contact with each other in the diluted bitumen without EC addition; (A2) water droplets were detached from each other, appearing no significant change in shape and size in the emulsion containing no EC; (B1) water droplets were brought into contact with each other in the diluted bitumen with 35 ppm EC addition; (B2) detaching of water droplets from each other after generating significant deformation (stretching) of flocculated droplets in the presence of 35 ppm EC; (C1) approaching and contacting of water droplets in the emulsion with 130 ppm EC addition; (C2) water droplets coalesced into one large droplet in the emulsion with 130 ppm EC addition; (D1) water droplets were brought into contact with each other in naphtha with 35 ppm EC addition; and (D2) water droplets coalesced into one large droplet in naphtha with 35 ppm EC addition. A3, B3, C3, and D3 are schematic representations of A1, B1, C1, and D1, respectively. *Reproduced with permission from ref. 454. Copyright 2010 American Chemical Society.*

4.4.2 Demulsification by ionic liquids

With "green" properties such as low vapor pressure, thermal stability, and nonflammability, ionic liquids have been recently applied as demulsifiers to demulsification of oil-water emulsions.[465-467] The efficiency of the demulsification by ionic liquid depends on the type of the ionic liquids, oil composition and temperature. After testing 10 different ionic liquids (*e.g.*, *N-alkyltriethylamonium bromide, triethylhexylammonium bromide, triethyldodecylammonium bromide, triethyloctadecylammonium bromide, 1-methyl-3-tetradecylimidazolium bromide, 1-methyl-3-octadecylimidazolium bromide, 1-tetradecylpyridonium bromide, 1-octadecylpiridonium bromide, tripentylmethylamminium chloride, trihexylmethylamminium chloride, trioctylmethylammonium chloride*), Guzmán-Lucero *et al.* observed that all the ionic liquids tested were efficient in demulsifying emulsions formed from medium oils. However, the demulsification of emulsions formed from heavy oil or extra heavy oil was relatively poor when the same ionic liquids were used. In their work, the longer chain ionic liquids were found to be more effective.[465] Similar phenomena were observed by Lemos *et al.*[466] and Silva *et al.*[467] Although both studies suggested that the reduction of oil-water interfacial tensions was responsible for demulsification of oil-water emulsions by ionic liquids, there still lacks the fundamental evidence on demulsification mechanisms of ionic liquids.

4.4.3 Demulsification by interfacially active magnetic particles

Based on the success in demulsification of W/O petroleum emulsions by EC, Peng *et al.* synthesized a magnetic demulsifiers by grafting the bromoesterified EC on the surfaces of Fe_3O_4 nanoparticles as shown in **Fig. 39**, forming interfacially-active magnetic nanoparticles, known as M-EC.[468] M-EC shows a strong affinity to the oil-water interface and hence adsorbs effectively on the emulsified water droplet surfaces. The magnetic property of M-EC allows a rapid separation of the magnetically tagged water droplets from emulsions by an external magnetic field. In a bench study, the M-EC was found to be much more rapid and effective in separating water from W/O emulsions than normal EC or M-EC without external magnetic field, as shown in **Fig. 40**.[469] Water titration analysis on emulsion samples extracted from different heights of the test tube showed the production of larger volume of clean oil and smaller volume waste by 1.5 wt% M-EC than by 130 ppm EC. The micrographs of optical microscope in **Fig. 41** show an enhanced coalescence of emulsified water droplets by M-EC under an external magnetic field than by chemical demulsifier EC alone. In further recycling tests, the M-EC was found to remain effective in demulsifying water in diluted bitumen emulsions after up to 10 times reuse by magnetic separation and solvent washing.[469] Interestingly, this novel concept of magnetic nanoparticle-based demulsifiers has been further developed for the synthesis of other novel demulsifiers, such as magnetic Poly (methylmethacrylate-acrylic acid-divinylbenzene) iron oxide (P(MMA-AA-DVB)/Fe_3O_4) Janus particles,[470] nanostructured magnetic amphiphilic composites,[471] and single-layer oleic acid-coated magnetite (Fe_3O_4@OA) nanoparticles.[472]

4.4.4. Electric field enhanced demulsification

In addition to the above chemical demulsification methods, another efficient chemical demulsification process is the electrochemical demulsification.[28, 473, 474] In this process, the separation of water from oil or oil from water is driven by an electric field, which involves several sub-steps similar to the above demulsification process. Under the electrical driving force, the surface charged emulsion droplets move to approach each other or contact with the electrodes. In an external electric field, the droplets also undergo inhomogeneous polarization and droplet deformations, resulting in the enhanced thinning and rupture of intervening liquid films. Many factors, such as electric field type and strength, oil properties and water chemistry affect the film thinning and coalescence process. A detailed discussion on these parameters is reviewed elsewhere.[28] Recently the coalescence of water droplets in the oil phase under an alternating electric field has been intensively studied by Mousavi *et al.*[474] In their study three different droplet contact patterns were observed: complete coalescence, partial coalescence and rebound without coalescence. Their results showed that the droplets coalescence patterns were highly dependent on the waveform types. Unfortunately, detailed mechanisms on the variation of surface properties under the electric fields have not been studied in great detail. Considering the competitiveness of cost, the electrochemical demulsification should be further studied in order to further improve the process.

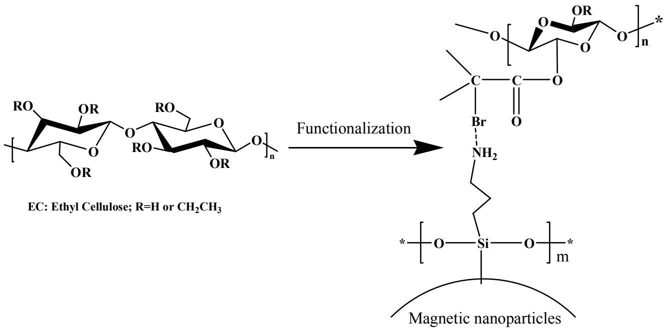


Fig. 39 Anchor of modified ethyl cellulose on magnetic nanoparticles to produce interfacially active and recyclable magnetic demulsifiers *Reproduced with permission from ref. 468. Copyright 2012 John Wiley & Sons*.

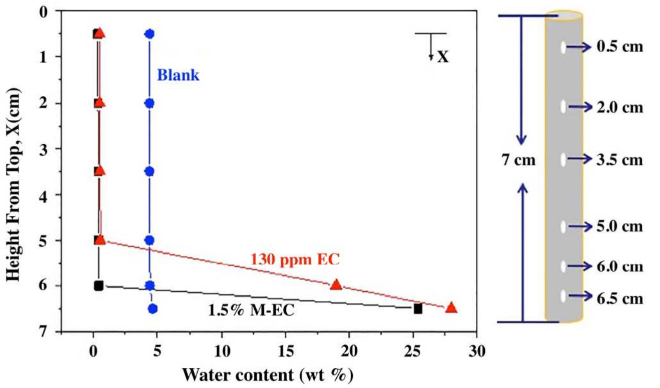


Fig. 40 Water content at different depths of water-in diluted bitumen emulsions treated with 1.5 wt % M-EC or 130 ppm EC after settling on a hand magnet for 1 h at 80 °C, showing concentration of water droplets in smaller volume emulsions at bottom when treated by M-EC than by EC. *Reproduced with permission from ref. 469. Copyright 2012 American Chemical Society*.

4.4.5. Microwave radiation enhanced demulsification

Breaking oil-water emulsions by demulsifiers can be enhanced by microwave irradiation.[440, 457, 475-477] The mechanisms of microwave irradiation for demulsification are complex and remain unclear. However, a common consensus on the enhanced demulsification by the microwave irradiation is the localized heating effect on emulsions. The local temperature rise is able to modify the surface properties of emulsion droplets, resulting in easier coalescence of the emulsion droplets.[476] More interestingly, the heating of emulsions by microwave irradiation was found to be beneficial to enhancing demulsification of petroleum emulsions by ionic liquids. Silva *et al.* proposed that the microwave irradiation provided the opportunity for rapid rise of temperature and quick viscosity reduction along with surface charge modification, which improved the emulsion droplet coalescence. [465-467]

4.4.6 Demulsification for solids stabilized emulsions

As stated above, the presence of fine solids in petroleum-water interface makes breaking the emulsions much more difficult. Since the solids adsorbed at the oil-water interfaces are altered by petroleum components to be partially water-wet or even oil-wet, the effective chemical methods to destabilize the solid-stabilized emulsions should be based on the wettability alteration of the solids or bridging of the emulsion droplets for enhancing sedimentation or creaming.[414]

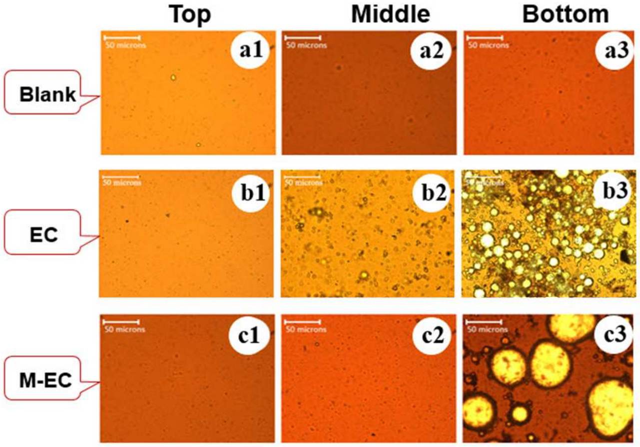


Fig. 41 Micrographs obtained at the same magnification of diluted bitumen emulsions at different depths without (a1, a2, and a3) and with 130 ppm EC (b1, b2, and b3) or 1.5 wt % M-EC (c1, c2, and c3) addition after settling on a hand magnet for 1 h at 80 °C, showing enhanced coalescence of emulsified water droplets by M-EC with an external magnetic force than by EC only. *Reproduced with permission from ref. 469. Copyright 2012 American Chemical Society.*

Yan *et al.* reported that adding fresh oil was beneficial to break clay particle stabilized oil-in-water emulsions due to the reduced surface coverage.[478] Later, changing the pH of the aqueous phase to be alkaline or adding some sodium silicate was also found to be effective to alter the mineral solid wettability to be more hydrophilic, leading to stronger repulsive forces between minerals and petroleum components. As a result, removal of minerals from the interfaces was achieved, improving the demulsification of mineral solid-stabilized emulsions.[479] Similar to demulsification of O/W emulsions, dilution of the oil phase was found to be practicable to break the water-in-oil emulsions. Jiang *et al.* reported that increasing the naphtha/bitumen ratio of the diluted bitumen from 0.7 to 4 was able to destabilize the water-in-diluted bitumen emulsions. They proposed that the dilution of the oil phase allowed a faster solids sedimentation velocity due to the increased difference in density and viscosity between particles and oil. The addition of sodium *m*-silicate was found to increase the wettability of clay minerals, leading to an increased removal of water.[480, 481] When demulsifying the water-in-oil emulsions, Feng *et al.* observed the effective demulsification of solid stabilized water-in-diluted bitumen emulsions by biodegradable EC when the fine solids content in the emulsion was low. However, a poor efficiency of the demulsification by EC was observed when the mineral solids content was increased up to 30 wt%.[455] The addition of demulsifiers, *e.g.*, series of polyoxyethylene (EO)/polyoxy-propylene (PO) alkylphenol formaldehyde resin was also observed to enhance the efficiency of water removal.[481] In a separate study using sodium naphthenate and cationic or amphoteric surfactants such as alkyl quaternary ammonium bromide, betaine and amine oxide as wettability alteration agents, Jiang *et al.* confirmed the ability of modifying emulsion stability by changing the wettability of mineral solids.[189] Comprehensive reviews on recent advances in particle-stabilized emulsions and demulsification can be found elsewhere.[404-405]

5. Knowledge gaps and conclusions

As an alternative energy resource with huge reservoirs, the unconventional petroleum (oil) is attracting increased attention from people around the world. However, the production of these unconventional petroleum is an integrated and extremely complex process due to their relatively high viscosity, density and the co-existence of different types of host rocks or mineral solids (*e.g.*, calcite, sands, kaolinite, illite, montmorillonite.). Therefore, a general process for producing the unconventional oils by water flooding consists of two main steps: oil liberation from the host rocks and separation of the oil and water. In this process, many interfacially scientific aspects are involved through changing physicochemical conditions, *e.g.*, wettability alteration of reservoir rock surfaces, reduction of unconventional petroleum viscosity, modification of the oil-water interfacial tension, stabilization and destabilization of oil-water emulsions, oil-water films characterization. In this review, the above-stated aspects have been discussed comprehensively, as well as the corresponding mechanisms for wettability alteration, interfacial tension modification, viscosity reduction, oil-water emulsion stability and demulsification by chemicals. In addition to our review on recent advances in this field, it would be even useful to provide a framework for research prospects which would guide the future research direction in laboratories and industries focused on producing unconventional petroleum. It would also be of great interest to widespread interdisciplinary researchers (chemists, physicists and material scientists) who are working on interfaces, surfaces, colloids and energy.

Naturally, the reservoir rocks are inevitably modified from water-wet to bi-wettalbe or even to oil-wet by the adsorption/deposition of polar components of petroleum (*e.g.*, asphaltenes, resins, naphthenic acids or other natural surface active substances) through chemical or physical binding. Contamination of the host rocks causes separation (liberation or detachment) of unconventional oil from to become more difficult. Therefore, alteration of the wettability of host reservoir rocks is considered to be one of the most efficient ways to enhance the liberation/displacement of heavy oil from the rocks by water. During the past decades, a large number of man-made chemicals with proper formulation have been applied to alter the wettability of oil-contaminated solids. The efficiency of the alteration is found to be dependent on the chemical composition, molecular structures and molecular size or molecular weight. Although a large number of experimental studies on adsorption have shown that the more the petroleum components are adsorbed, the more oil-wet the solid surfaces become. A quantitative relationship between amount of petroleum components adsorbed and the extent of wettability alteration remains largely to be established because of the complexity of petroleum chemistry, types and heterogeneity of reservoir rocks and variations in locations. The binding mechanisms of different components of unconventional oils with rock surfaces under the reservoir water chemistry and flooding water chemistry environment in the context of wettability alteration of rocks need to be further investigated. A major challenge to make progress is to develop a viable method to collect and preserve the representative solid samples from reservoirs for advanced characterization.

Reducing the oil-water interfacial tension (IFT) is another effective way to enhance the liberation of unconventional petroleum from the host rock. The addition of functional surfactants, salts and alkaline chemicals has been shown to reduce the oil-water interfacial tension by increasing the accumulation of interfacially active materials at the oil-water interface. The reduced IFT helps form oil-water emulsions and hence facilitate the liberation of unconventional oil from rock surfaces. However, there remains debate on the mechanisms of reducing the oil-water IFT by the surfactants, ions and natural surface active materials. The effective reduction of unconventional oil viscosity is another area of importance for making significant progress in improving oil liberation from host rocks under optimal energy utilization conditions.

Ionic liquids (ILs) have been intensively reported recently in modifying the properties of solid surfaces and oil-water interfaces simultaneously. However, the working mechanisms of ILs in reducing oil-water interfacial tension and altering the wettability of rock surfaces under unconventional oil production environment remains an open area for research. Such questions as how the ILs diffuse to the solid surfaces and displace the originally adsorbed heavy oil contaminants remain to be answered. Another novel application of chemicals in unconventional petroleum production is the use of nano-particles to modify surface wettability, or to use as reactive sorbents in reducing the viscosity of unconventional petroleum. The research on these new chemicals not only sheds the lights on the future unconventional petroleum production, but also provides opportunity for academics and industrial researchers to make breakthrough contributions to better utilize our limited liquid fossil fuel resources.

Natural components of petroleum such as naphthenic acids, resins and asphaltenes are well known for stabilizing the oil-water emulsions by forming rigid and stable films at the oil-water interface. Much effort has been made in understanding molecular mechanisms on how these various components stabilize oil-water emulsions. Different advanced characterization techniques are invented and applied to characterizing the oil-water emulsion films successfully. However, there are still needs for intensive fundamental research and practical innovation. For example, the chemical structure and molecular association of interfacially active asphaltene subfractions at the oil-water interfaces remain largely unknown. In addition, the interactions between the natural materials and some added chemicals in the interfacial films are still needed to be established to design next generation of demulsifiers of petroleum emulsions. Understanding the diffusion dynamics of these surface active chemicals to the interfaces, which plays an important role in forming stable emulsions or controlling the demulsification operation, is still in its infancy.

Chemical demulsification has been considered to be an effective process option for breaking oil-water emulsions. Many kinds of chemicals, such as EC, EO/PO and their derivatives, ionic liquids, switchable-CO_2 demulsifiers, *etc.*, have been successfully applied to breaking the emulsions by displacing the asphaltene molecules or other natural petroleum components at the oil-water interface. The critical role of the bridging effect in breaking emulsion needs to be quantified to optimize the design of "greener" polymer demulsifiers.

Particle stabilized unconventional petroleum-water emulsions are commonly encountered in unconventional petroleum production and often cause damages (*e.g.*, forming rag layers, leading to corrosion to the facilities) to downstream processes due to the presence of solids and high concentration of inorganic ions trapped in water. The adsorption and deposition of petroleum components on the reservoir solids enhance the ability of these solids to stabilize the oil-water emulsions. Increasing the particle concentration or reducing the particle size is beneficial to the stabilization. However, quantifying interactions between these particles at the oil-water interface under unconventional oil production environment is rarely seen due to the complexity of the systems and limitations in characterization techniques. Although the demulsification of this solid-stabilized petroleum emulsion is of great importance, more effective advanced technologies are urgently needed. The advances in this area remain slow, especially for the oil sands processing and shale gas fracturing processes.

One should not underestimate the importance and corresponding molecular mechanisms of operating parameters, *e.g.*, temperature, pressure, magnetic field, electric field, microwave irradiation. in determining the properties of oil-water, oil-solid and water-solid interfaces. In resolving controversial phenomena observed and reported by different researchers, it would be of great value to understand the impact of these parameters on enhancement of physical and/or chemical interactions by studying dynamic molecular interactions, droplet coalescence, *etc.*

Last but not least, future research should emphasize the rational design of highly functional chemicals, such as efficient surfactants, switchable and multiple functional chemical demulsifiers, in combination with process integration to not only improve the oil recovery from these vast unconventional petroleum resources but also reduce the cost and environmental impact (such as of GHG emission and water contamination).

Acknowledgements

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Abbreviations

GHG	Greenhouse gases
THAI	Toe to heel air injection
SAGD	Steam-assisted gravity drainage
SEM	Scanning electron microscope
SARA	Saturates, Aromatics, Resins and Asphaltenes
API	American Petroleum Institute
NA(s)	Naphthenic acid(s)
IAA	Interfacially active asphaltene
VPO	Vapor pressure osmometry
GPC	Gel permeation chromatography
PAH(s)	Polycyclic aromatic hydrocarbon(s)
ESI-FTICR-MS	Electrospray ionization, Fourier transform ion cyclotron resonance mass spectroscopy
TRFD	Time-resolved fluorescence depolarization
IR	Infrared Rediation
NIR	Near-Infrared Rediation
NMR	Nuclear magnetic resonance
UV	Ultra violet
LDI-MS	Laser desorption ionization mass spectrometry
SAXS	Small-angle X-ray scattering
SANS	Small-angle neutron scattering
ATR-FTIR	Attenuated total reflectance-Fourier transform infrared spectroscopy
MD	Molecular dynamic
PA	Polyaromatic
TP	N-(1-hexylheptyl)-N'-(2-indol-3-yl-propanoic acid)-perylene-3,4,9,10-tetracarboxilicbisimide
PAP	N-(1-hexylheptyl)-N'-(2-phenylpropanoic acid)perylene-3,4,9,10-tetracarboxylicbisimide
DC	Direct-current
DSC	Differential scanning calorimeter
ITC	Isothermal titration calorimetry
DFT	the density functional theory
MKT	Molecular kinetic theory
HD	Hydrodynamic
XPS	X-ray photoelectron spectroscopy
FAME	Fatty acid methyl ester
MEK	Methyl ethyl ketone
EGMBE	Ethylene glycol mono butyl ether
WI	Wettability index
OOIP	Original oil in place
NN-DMDA	N, N-dimethyldodecylamine
CTAB	Cetyl trimethylammonium bromide
SMNS	Sodium methylnaphthalene sulfonate
SDS	Sodium dodecyl sulfate
SDBS	Sodium dodecyl benzene sulfonate
PO	Propylene oxide
DTAB	Dodecyltrimethylammonium bromide
EO	Ethylene oxide
EC	Ethyl cellulose
QCM-D	Quartz crystal microbalance with dissipation
AFM	Atomic force microscope
CMC	Critical micelle concentration
DLVO	Derjaguin-Landau-Verwey-Overbeek
IFT	Interfacial tension
HAA	Hexanoic acid
CPPA	3-cyclopentylpropionic acid
SNs	Sodium naphthenates
PDGA	Palmitoyl diglycol amide
PDGAS	Palmitoyl diglycol amide sulfate
PDGAC	Palmitoyl diglycol amide carbonate
IL	Ionic liquids
W/O	Water-in-oil
O/W	Oil-in-water
W/O/W	(water-in-oil)-in-water
O/W/O	(oil-in-water)-in-oil
ISR	Interfacial shear rheometry
BAM	Brewster angle microscopy
LB	Langmuir–Blodgett

SFA	Surface force apparatus
TFB	Thin liquid film balance
ITFDA	Integrated thin film drainage apparatus
DWR	Double wall ring
CCD	Charge coupled device
STM	Scanning tunneling microscope
FECO	Fringes of Equal Chromatic Order
MASIF	Measurement and analysis of surface interactions and forces
Re	Reynolds number
RSA	Random sequential adsorption
HPAM	Hydrolyzed polyacrylamide
NEO	Nonylphenol ethoxylate
DS	Dodecylsulfate
DTA	Dodecyltrimethylammonium
SHS	Second harmonic scattering
HLB	Hydrophile-Lipophile Balance
MW	Molecular weight
HaLCs	Hydrophilic-lipophilic copolymers
M-EC	Magnetic nanoparticles anchoring with ethyl cellulose
P(MMA-AADVB)/Fe_3O_4	Magnetic Poly (methylmethacrylate-acrylic acid-divinylbenzene) iron oxide

Terminology

Petroleum	A dark oil consisting mainly of hydrocarbons
Bitumen	A sticky, black and highly viscous liquid or semi-solid form of petroleum.
Asphaltene	The *n*-heptane-insoluble, toluene-soluble component of a carbonaceous material such as crude oil, bitumen, or coal.
Wettability	The ability of a solid surface to reduce the surface tension of a liquid in contact with it such that it spreads over the surface and wets it
Viscosity	a measure of the resistance of a fluid to gradual deformation by shear stress or tensile stress
Interfacial tension	The force that holds the surface of a particular phase together
Surfactant	The compounds that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid
Contact angle	The angle, generally measured through the liquid, where a liquid/vapor interface or liquid/liquid interface meets a solid surface
Emulsion	A mixture of two or more liquids that are normally immiscible (unmixable or unblendable).
Demulsification	A process of prevention or breaking of liquid-liquid emulsions by chemical, mechanical or electrical demulsifiers
Rag layer	A mixture of dispersed oil, water, and solids, which is often formed at the oil-water interfaces when producing the petroleum, especially the unconventional oil.
Ionic liquid	A salt in the liquid state

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