Emulsification requiring very little input energy can be induced at an oil–water interface that is initially in a state of equilibrium. The process involves destabilization, through contraction, of local interfacial regions. For emulsification to occur, it is necessary for the interfacial structure to have no resistance to surface shearing. Such a mechanism of emulsification may have important implications for the approach to solving emulsion problems in the petroleum industry.

**Key Words:** spontaneous emulsification; crude oil; fluid interfaces; rigid interfaces; budding.

### 1. INTRODUCTION

Interfacial instability is most prevalently observed in situations where two immiscible and *unequilibrated* liquids are brought into contact (1–3). Such instability often results in very easy—even spontaneous—emulsification of one phase into the other and finds applications in, for example, preparation of pesticide or herbicide oil-in-water emulsions. A basic requirement for such mechanisms of emulsification is that transport processes at the interface must induce local disturbances that intensify and eventually lead to the creation of small emulsion droplets. The destabilizing mechanism can be hydrodynamic—as in the case of interfacial turbulence resulting from the Marangoni effect (4, 5), and may also involve chemical reactions on the interfacial plane (6, 7). Where hydrodynamic destabilization is not appreciable, it has been suggested that the emulsion droplets are formed (e.g., through nucleation) within local regions of supersaturation near the interface; these supersaturated regions, in turn, result from mass diffusion across the interface (8). Regardless of the underlying mechanism, it is noted that the above-mentioned instabilities invariably involve systems that are initially well away from thermodynamic equilibrium. The resulting emulsification processes, which require little or no input energy, are often quite dramatic and can be observed without the aid of microscopy (4).

We report here evidence for another means of destabilization that applies to a special class of interfacial structures (discussed in Section 4); the system can be brought out of equilibrium through rapid\(^1\) reduction in the interfacial area, resulting in production of small droplets that appear as *buds* detaching from the interface. The importance of our finding is that we begin with a two-phase system that initially is in a state of equilibrium. Indeed, such an idea of interfacial destabilization was first conceived by Langmuir half a century ago when he worked with absorbed layers of protein molecules (Ref. (1), Chap. 5). No emulsification was reportedly observed for that system; instead, the interface crumpled upon area compression. A possible explanation for Langmuir’s observation is discussed in Section 4.

\(^{1}\) i.e., much faster than the desorption and diffusion processes that can restore the system back to a state of equilibrium.

### 2. TECHNOLOGICAL RELEVANCE

The removal of emulsified water from crude oil has been a continual challenge to the petroleum industry worldwide. In the production of synthetic crude oil from mined oil sands (e.g., at Syncrude Canada Ltd., Ref. (9)), water-in-oil emulsions are of particular concern because of the chloride salts that can be solubilized in the aqueous phase. After various stages of water removal during oil sands processing—which involve centrifuges, gravity settlers, and the addition of demulsifying agents—the intermediate product, known as diluted bitumen, may still contain up to 2% emulsified water; the majority of the droplets have sizes in the 1 to 3 \(\mu\)m range. When transported to downstream (refinery) operations, the chloride salts in the water droplets can be deposited onto the machineries and, over extended periods, create serious corrosion problems.

In a related study (10), it had been shown that a remarkably similar emulsion of water (~2% water, with droplet sizes in the 1 to 3 \(\mu\)m range) can be created when diluted bitumen is brought into contact with water under the lowest possible shear—the shear is only introduced to disperse water droplets that apparently form spontaneously (or at least very easily) in the oil phase. A different mechanism, other than the conventional view of emulsification by destructive hydrodynamic stresses, is therefore needed to explain such a phenomenon and may indeed hold the key to understanding the problem of water emulsions that plagues the petroleum industry.

### 3. EXPERIMENTAL

The hydrocarbon (continuous) phase is composed of bitumen—a heavy form of crude oil with API gravity of 10.5 at 16°C—that is extracted from Canada’s Athabasca deposit. The particular sample used for this study is *coker feed* bitumen supplied by Syncrude Canada Ltd. To attain workable viscosities, bitumen is diluted in a solvent that is a 1:1 mixture, by volume, of \(n\)-heptane and toluene (both HPLC grade with no further purification). Such a mixture, which will be called *heptol* from here on, is chosen to simulate the aromatic/aliphatic content of the solvent used in commercial oil sands processing (9). In this study, bitumen content will be expressed as a volume percentage. Distilled and deionized water is used for the aqueous phase.

Using micropipet techniques (11), the surface area of individual emulsion droplets can be controlled on the micrometer scale. The procedure involves first immersing a water-filled glass pipet into diluted bitumen; the inner diameter of the pipet tip is typically several micrometers. With the use of a micropyringe, a droplet can be created by expelling a small amount of water from the pipet tip. Care is taken to prevent the droplet from *pinching off*; as such, the droplet remains connected to the aqueous reservoir that occupies the pipet interior. By controlling the flow of water at the pipet orifice, the droplet volume—and hence its interfacial area—can be varied (see Figs. 1 and 2).

### 4. RESULTS AND DISCUSSION

Crude oil contains many surface active components that accumulate at the oil–water interface to form adsorbed layers. The presence of such a layer is clearly revealed in Fig. 1. As shown, deflating a large water drop in heptol-diluted bitumen, at bitumen concentrations below 1%, results in the surface of the droplet crumpling like a paper bag (11). By contrast, at higher bitumen
concentrations (i.e., above ~1% bitumen), the shape of the deflating droplet remains spherical (Fig. 2a) as it shrinks. As the interfacial area continues to decrease, the overall shape of the droplet continues to remain spherical, but small surface protrusions resembling goose bumps begin to appear on the droplet surface (Fig. 2b). These surface imperfections become more prominent on further area reduction, resulting in formation of micrometer-sized water droplets that eventually detach from the original mother drop (Fig. 2c). Note that such a process is irreversible—in a sense that the small water droplets, once detached, cannot be incorporated back into the mother drop. Furthermore, it is noted that after several minutes of the deflation experiment, the initially clear oil phase becomes polluted with small (roughly 1 μm) water droplets that are clearly visible in the background in Fig. 2. This is in contrast with the situation in Fig. 1, where no budding is observed at the droplet surface and the surrounding hydrocarbon remains free of small water droplets.

The behaviors in Figs. 1 and 2 point to very different material properties of the interfaces. From the standpoint of surface mechanics, such behaviors are determined by the interface’s resistance to shear (11). [Following Scriven (12), shear is defined as the change in interfacial shape at constant area.] Thus, a droplet whose surface possesses shear resistance has mechanical properties similar to those of a paper bag and will crumple upon area compression (Fig. 1). Such interfaces are not likely to undergo budding (Fig. 2) as the process requires extensive shearing in regions local to the surface protrusions. Indeed, in the study of model biological membranes, similar budding phenomena are observed only in systems that have zero resistance to shearing (13, 14). A detailed account of the mechanics of interfacial crumpling and budding will be the subject of a subsequent study (15). Finally, we speculate that Langmuir’s observation of the protein film under area contraction—the display of crumpling and the absence of spontaneous emulsification (Chap. 5 in Ref. (1))—is similar to the behavior of the crude oil–water interface shown in Fig. 1.

5. CONCLUSIONS

A water emulsion can be created in crude oil even under very low shear—by orders of magnitude lower than what is required to tear large water drops into micrometer-sized emulsion droplets. In this communication, a possible mechanism for the associated emulsification process is proposed: by bringing the interfacial structure out of equilibrium through rapid area contraction, as in our droplet deflation experiments (cf. Fig. 2), micrometer-sized water droplets can be created at the contracting interfacial surface. It is important to note that, for oil–water mixtures on length scales of centimeters or larger, the level of shear required to compress local regions of the interface can be extremely low. As a result, emulsion droplets are formed almost spontaneously via the mechanism depicted in Fig. 2. Such a phenomenon has profound implications on the petroleum industry: it suggests that the avoidance of high shear, to the contrary of common belief, is not likely to prevent the formation of water-in-oil emulsions. The same or a similar mechanism may also be relevant to other industrial and biological systems.

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2 On the 10-μm scale, the interfacial tension must be ~10⁻⁴ mN/m or lower before any deviation from the spherical shape (due either to gravity or thermal excitations) can be observed.
REFERENCES


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