Full Length Article

The roles of contact time and contact pressure on the coalescence of water droplets suspended in concentrated bitumen solutions

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ABSTRACT

The coalescence of water drops in diluted bitumen solutions has been previously studied via micropipette experiments in which water drops are brought to contact, and the onset of drop coalescence is evaluated as a function of bitumen dilution, type of solvent, etc. Due to the opacity of concentrated bitumen solutions, most of these studies have been conducted in highly diluted systems. Under those conditions (typically solvent/bitumen or S/B mass ratios greater than 4), asphaltenes tend to form skins at the oil/water interface that prevent coalescence altogether. In 'naphthenic' froth treatment (NFT) process, however, S/B ratios of 0.5–2 are often used. To study S/B ratios relevant to NFT operations, we developed a Hele-Shaw version of the micropipette aspiration experiment, in which drops held on micropipettes are sandwiched to disks by two hydrophobically-treated plates spaced less than a few hundred microns apart. The resulting thin layer of bitumen is optically transparent in brightfield microscopy, allowing us to execute micropipette contacting experiments at industrially relevant bitumen dilutions. Another departure from almost all the literature in the past is that we have measured the time, t_c, required to observe coalescence from the moment two disk-shaped drops are contacted under an imposed contact pressure, P. t_c was observed to decrease when P, pH or bitumen dilution was increased. Deasphalting bitumen also led to a significant decrease in t_c, while increasing the aging time of the interface from 15 to 60 min dramatically increased t_c. The coalescence time was found to obey an exponential relationship with P, and was explained to be a result of an activated process related to the formation of a bridge of water across the thin film of bitumen in the contact zone between the drops. The t_c−P correlations measured in this work provide the foundation for designing coalescers that coarsen the drop size distribution in water-in-bitumen emulsions under given conditions of bitumen concentration and water pH.

1. Introduction

The Clark Hot Water Extraction (CHWE) process [6] has been extensively employed in the oil sands industry to liberate bitumen from excavated deposits. The froth obtained at the end of the extraction stage has a typical composition of 60% bitumen, 30% water, and 10% solids by weight [29,30], and needs to be treated further to obtain a product fit for upgraders and downstream reactors. Two froth treatment processes, paraffinic and naphthenic, are commonly used by the industry to remove majority of water and solids from froth and produce a diluted bitumen (dilbit) product. The paraffinic froth treatment process uses a paraffinic solvent such as pentane to produce a dilbit product that can be sent directly to the refineries. The naphthenic froth treatment process utilizes naphtha as a solvent to produce a naphtha-diluted froth, which is subsequently passed through a series of separation processes comprised of inclined plate settlers and centrifuges to obtain the dilbit

product. This product is subsequently sent to the upgrading section for pre-refinery processes [9]. Dilbit obtained from the naphthenic froth treatment process typically contains about 2–5 wt% water [29,37]. Research [37] has shown that this water is actually present in the form of small drops (typically less than 10 microns), which are difficult to eliminate using conventional unit operations such as inclined settling and centrifugation. The residual water is highly undesirable in upgrading operations. Process water is recycled during the bitumen extraction process, which results in the accumulation of chloride, sulfate and bicarbonate salts of sodium and calcium in the water [9]. When dilbit with the salt-containing process water is sent to the hydrotreating section for further processing, the salts in process water can be converted to acids, thereby corroding equipment and causing downtime [9]. The salts can also act as a poison to the catalysts used in downstream reactors [31,34]. The oil sands industry spends millions of dollars each year on the maintenance of pipelines and reactor catalysts.

Nomenclature		t_b	bridge formation drainage time (s)
		E_a	activation energy (J)
P	contact pressure (N/m^2)	k_b	Boltzmann constant (J K^{-1})
γ	interfacial tension (N/m)	T	temperature (K)
R	drop radius (m)	h	film thickness (m)
t_c	coalescence time (s)	μ	viscosity (Pa s)
t_h	hydrodynamic drainage time (s)	b	channel half-depth (m)
t_{nh}	non-hydrodynamic drainage time (s)	F	contact force (N)

Removal of water from dilbit is, therefore, a necessity to prolong the life time of the downstream operations.

Over the years, the most common approach to remove the fine water droplets from bitumen has been to induce their coalescence with themselves and/or bigger water droplets, thereby increasing their sizes and enabling their facile removal using the conventional methods. A key factor required to bring about coalescence at a reasonable rate is an adequately high efficiency of a collision to lead to a coalescence event [5,25]. To investigate the efficiency of coalescence of water drops in dilbit, researchers have employed two types of studies in the last two decades: bench-scale studies and drop-scale investigations. In the bench-scale studies, the relationship between the stability of water-in-bitumen emulsions and such various parameters as the type of interfacially-active species in bitumen (e.g. asphaltenes and naphthenic acids), solvent aromaticity, degree of dilution, and process water chemistry, are studied by rag layer (or washing) experiments [22,39]. On the other hand, in the drop-scale studies, the micromechanical/micropipette technique [16,55] and the thin liquid film-pressure balance technique (TLF-PBT) [10,13,47,48] are employed to examine the film drainage process at the drop and thin film scales. Using these techniques, researchers have disinterred many interesting trends related to the stability of the emulsified water is greatly controlled by asphaltenes [16,33,52,53]. Among all naturally occurring interfacially-active species in bitumen, asphaltenes are known to be the largest molecules, and this leads to slower adsorption of asphaltenes at the interface [16,45]. Furthermore, after creating an asphaltene monolayer at the interface, asphaltenes can stack up at the interface due to intermolecular interactions such as the pi-pi, dipolar and charge-transfer interactions [32], which results in the 'ageing' of the interface [48]. This effect becomes significantly stronger at higher bitumen, and hence, higher asphaltene, concentrations. Once asphaltenes are removed from bitumen, the stability of water droplets against coalescence diminishes drastically. Additionally, increasing the aromaticity of the solvent reduces the interfacial activity of asphaltenes, which decreases the stability of the water-in-bitumen emulsion. Moreover, raising the pH enhances the coalescence of water droplets in bitumen [31,23,2]. A possible explanation for this effect is that higher pH drives more ionization of surfactants at the interface, leading to greater accumulation of charges at the interfacial film. This disrupts the interfacial skin covering the water droplets, thereby aiding the coalescence process [31,35,2].

Although TLF-PBT and micromechanical techniques have been extensively used to study coalescence at the microscale for the water-in-bitumen system, there still remain several gaps in the literature. Over the operating range of bitumen concentrations (33–67% by weight), bitumen is inaccessible by brightfield microscopy due to its opacity beyond optical depths of a few hundred microns [41]. This has restricted most previous drop-scale studies to very dilute bitumen solutions (typically < 10 wt%). However, it is well known that the properties of the water-bitumen interface depend strongly on the bitumen concentration [11]. For instance, there exists a critical dilution [11,47] above which an asphaltenic skin is formed at the water-bitumen interface, thereby rendering the interface rigid [47,55]. For dilute bitumen solutions [20,40,45,51], once the interface is allowed to age for a time governed by the concentration of asphaltenes and the type of

solvent, its rheology is dominated by elastic contributions, and the increased stiffness of the interface inhibits coalescence. On the other hand, below this critical dilution, the water-bitumen interface, even after aging, is relatively more flexible due to higher interfacial concentration of naphthenic acids [47], and flexible interfaces are more likely to coalesce than stiff ones [1]. This critical solvent to bitumen ratio, which depends on a diluent type, is ∼ 4 for naphtha [11]. Since the characteristics of the interface are markedly different below and above the critical dilutions, it appears unreasonable to extrapolate the results and trends obtained using very dilute bitumen solutions to higher bitumen concentrations.

These lacunae in the literature motivated us to study the coalescence process over the industrially relevant bitumen concentration range of 33 wt% to 67 wt% on an in–house, microfluidic, micropipette-based platform. This setup adopts a Hele-Shaw configuration with disk-shaped drops to overcome the challenge of opacity mentioned previously. The main focus of this study is to determine the contact pressure (the applied force pushing the drops against each other per unit area of contact), bitumen solution properties, aging time and water chemistry that can lead to coalescence of water drops in bitumen. The characteristic feature that distinguishes our experiments from prior experiments in the literature is that we have measured the coalescence time as a function of applied pressure for the bitumen-water system. This information is critical for the prediction of coalescence rates in emulsions subjected to mixing. There have been efforts in the direction of measuring coalescence times recently [20], but these studies have been again been limited to very low concentrations of asphaltenes.

This manuscript is set up as follows. Section 2 describes the materials and protocols employed in the experiments. Section 3 presents the experimental results, while Section 4 discusses these results in the light of prior data while providing insights into the nature of the results. We conclude in Section 5 with a summary of our findings.

2. Materials and methods

2.1. Materials

Coker-feed bitumen (viscosity and density of approximately 11135 mPa s and 991 kg/m^3, respectively at $T = 320$ K and $P = 1$ MPa [19]) containing 20.2 wt% saturates, 30.0 wt% aromatics, 29.5 wt% resins and 20.3 wt% nC5-insoluble asphaltenes (from SARA analysis), and ≈ 0.87 wt% acids (standard ASTM 177/96) [41], which was donated by Syncrude Canada Ltd, was used in our experiments. A mixture of heptane and toluene (Caledon Laboratories) was employed as the organic solvent. For the aqueous phase, 25 mM NaCl (BioShop Canada Inc.), 15 mM NaHCO$_3$ (Sigma Aldrich), 2 mM Na$_2$SO$_4$ (Sigma Aldrich), 0.3 mM MgCl$_2$ (BioShop Canada Inc.), 0.3 mM CaCl$_2$ (BioShop Canada Inc.) and 500 ppm of sodium naphthenates (Tokyo Chemical Industry) were added to milli-Q water in order to simulate industrial process water [41]. The pH of the aqueous phase was rendered basic using a 10 M NaOH solution, and measured using an Oakton pH meter.

2.2. Bitumen solution formulation

Following prior protocols [41], the oil phase was prepared fresh