# Effect of solvent addition on bitumen–air bubble attachment in process water

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HIGHLIGHTS

- Minimum induction time of bitumen–bubble attachment at 10 wt% solvent dilution.
- Bubble coalescence time sensitive to concentration of surfactants released in water.
- Increased migration of surfactants to bitumen–water interface due to solvent addition.
- Reduced bitumen–bubble attachment by surfactants at bitumen–/air–water interface.

GRAPHICAL ABSTRACT
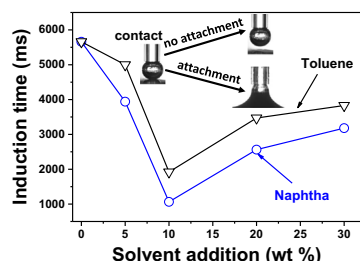
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ABSTRACT

Bitumen–air bubble attachment is an essential element for bitumen recovery from oil sands by flotation. Effect of solvent addition to bitumen on bitumen–air bubble attachment in an industrial process water was investigated by determining the minimum time required to achieve the bitumen–air bubble attachment, known as induction time. Proper addition of solvent to bitumen significantly reduced the induction time of bitumen–air bubble attachment, more so for naphtha than for toluene and reaching optimal at 10 wt% solvent added to bitumen. The measurement of bubble coalescence time and total organic carbon content in the resulting process water revealed a critical role in bitumen–air bubble attachment of air bubble interfacial properties controlled primarily by surfactants in the process water and water chemistry. Increasing the solvent addition to bitumen led to an increased migration of natural surfactants to the bitumen–water interface. At a given solvent dosage, more surfactants adsorbed at toluene–diluted bitumen–water interface than at naphtha–diluted bitumen–water interface. Interestingly, zeta potentials of diluted bitumen droplets in the process water exhibited a maximum at about 10 wt% of solvent addition to bitumen for both toluene and naphtha. At an identical dosage of solvent, toluene–diluted bitumen in the tailings water possesses a more negative zeta potential than naphtha–diluted bitumen. Finally, a possible adsorption mechanism of ions and surfactants accumulating at the diluted bitumen–water interface under the impact of solvent addition is proposed.

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1. Introduction

Increasing attention has been given to the production of oils from unconventional resources such as heavy oil, shale oil and oil (tar) sands, due to the enormity of these reserves that offer an alternative to satisfy the global energy needs (Chilingar and Yen, 2011; Demaison, 1977; Hertz et al., 1980; Regtop et al., 1982). Canadian oil sands are an important part of these unconventional resources, from which molasses-like extra heavy oil – also known as bitumen with an API gravity < 10 can be produced (Bedair, 2013; Burrowes et al., 2010; Hall et al., 2012; Li et al., 2012). Currently, mining-extraction method, as in mining and mineral processing, is widely used in the oil sands industry to recover bitumen at greater than 90% recovery (Masliyah et al., 2004; Sepulveda and Miller, 1978). In this method, several sub-processes such as lump reduction of oil sands ores, bitumen recession and liberation from sand grains, aeration of liberated bitumen and flotation of aerated bitumen are involved (Masliyah et al., 2004; Masliyah and Gray, 2011). Due to similar density of bitumen to water, the bitumen aeration, a process of bitumen droplets attaching to air bubbles is essential to enrich the bitumen on top of the slurry as froth by flotation (Cymerman et al., 2005; Masliyah et al., 2004; Schramm, 1989). To achieve a desirable bitumen recovery, successful attachment of bitumen droplets to air bubbles is therefore a clear must.

The efficiency of bitumen–bubble attachment in an aqueous electrolyte is often characterized by the minimum time needed for the thinning of intervening water film to a critical thickness and spontaneous rupture to form a stable two-phase attachment of air bubble to bitumen, known as induction time (Gu et al., 2003). The apparatus to measure such time is referred to as Induction Timer. It is largely accepted that the thinning and rupture of aqueous films to achieve the attachment of bitumen to the air bubbles are influenced by many operational parameters such as temperature, pH, electrolyte type and concentration, and bitumen droplet-air bubble approach velocity (Dai et al., 1999; Gu et al., 2003; Hewitt et al., 1995; Nguyen et al., 1997; Ralston et al., 2002; Van, 1993). Gu et al. (2003) reported that the bitumen–air bubble attachment could be improved significantly by increasing the operating temperature or reducing the size of air bubbles and the concentration of divalent cations such as calcium and magnesium ions in solution, as indicated by shorter induction time. Moreover, the addition of small amount of kerosene to bitumen was shown to enhance the efficiency of bitumen–air bubble attachment even at lower temperatures of 35 °C (Harjai et al., 2012).

To conserve the required thermal energy and hence reduce greenhouse gas emissions, great effort has been made to develop low-temperature technologies of bitumen extraction from mined oil sands. For instance, Hupka et al. investigated the effect of kerosene and MIBC (methyl isobutyl carbinol) addition on bitumen recovery from oil-wetted Utah tar sands, showing a significant reduction in the extraction temperature to about 50 °C (Hupka and Miller, 1991; Hupka et al., 2004; Hupka et al., 1987). Harjai et al. (2012) reported that the soaking of kerosene to the Athabasca oil sands could significantly enhance the recovery of bitumen at ambient temperatures (25 °C), obtaining a comparable recovery rate with that at 50 °C without kerosene addition. These studies demonstrated that bitumen could be competently recovered from oil/tar sands at a lower temperature with the assistance of a process aid. Recently, the working mechanisms of enhancing bitumen liberation – another essential step of bitumen extraction from oil sands via the addition of process aids including toluene, naphtha have been derived to guide design and selection of process aids (He et al., 2014; Lin et al., 2014). To our best knowledge, there exists little information in open literature on the role of adding process aids in bitumen–air bubble interaction and attachment in water.

Therefore, the aims of the current study are to (i) determine the optimal dosage of solvent, if there is any, for effective bitumen–bubble attachment (i.e., minimum induction time) in aqueous solutions; (ii) study the effect of solvent type and dosage on the interfacial properties of bubble and bitumen in aqueous solutions; and (iii) determine the mechanisms of improving bitumen–bubble attachment by solvent addition through correlating the amount of the natural surfactants adsorbed on diluted bitumen–water interface to the induction time of bitumen–air bubble attachment.

2. Materials and methods

2.1. Materials

Coker-feed bitumen provided by Syncrude Canada was used in this study. Toluene and naphtha were purchased from Fisher Scientific and used as solvents. The viscosity of toluene- or naphtha–diluted bitumen and interfacial tensions of the corresponding diluted bitumen–water interface as a function of solvent dosage to bitumen were given in our previous study (Lin et al., 2014). It was shown that both the viscosity of diluted bitumen and the diluted bitumen–water interfacial tension decreased with increasing the solvent dosage in bitumen.

To ensure that our study bears direct relevance to industrial applications, the industrial recycling process water supplied from Syncrude was used as the aqueous solution. The industrial process water contained approximately 22 ppm K^+, 484 ppm Na^+, 17 ppm Mg^{2+}, 41 ppm Ca^{2+}, 602–724 ppm Cl^-, 128 ppm SO_4^{2-}, $556-659$ ppm HCO_3^-, 7 ppm NO_3^- and 50–70 ppm natural surfactants (mainly carboxylic acids). The pH of the process water was maintained at 8.0. The dynamic surface tensions of the water in the presence of bitumen with variable solvent addition were measured using a Kruss K-12 process tensiometer at 20 ± 0.5 °C and the values at 120 min were taken as equilibrium surface tensions, shown in Fig. 1. In a few control tests, the simulated process water whose ionic concentrations and pH were adjusted to the same values as those in the process water but contained no surfactants was used as the aqueous phase.

2.2. Induction time of bitumen–air bubble attachment

A custom-built induction time device, namely Induction Timer, was used to determine the effect of solvent addition on the induction time required for the solvent-diluted bitumen–air bubble attachment (Fig. 2a). Details on the experimental setup and operating procedures of induction time measurement were reported earlier by Gu et al. (2003). In this study, the solvent–diluted bitumen samples were prepared by adding a predetermined amount of solvent from 5 to 30 wt% of bitumen into "coker feed" bitumen and soaking for at least 24h to ensure uniform distribution of the solvent in bitumen. In the induction time measurement, bitumen or solvent–diluted bitumen was placed in a shallow cylindrical shaped socket made on a smooth Teflon disks (ϕ12.5 × 8.5 mm). Bitumen or diluted bitumen surfaces were relaxed at room temperature to form a mirror-like smooth surface. For each measurement, two such samples were placed in a cubic glass cell (20 mm × 20 mm × 20 mm) filled with testing aqueous solutions and equilibrated for 15 min. A fresh bubble of 1.5 mm diameter was then generated on one end of a glass capillary tube using a micro syringe connected to the other end of the glass capillary tube. The size of the bubble was precisely controlled using a real time digital camera mounted side way. The glass capillary tube was attached to the diaphragm of a speaker connected to a charge amplifier interfaced to a computer that controls the extent and rate of the bubble displacement. The initial