



# The role of naphthenates and kaolinite in toluene and toluene–bitumen emulsions



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## HIGHLIGHTS

- Naphthenates aid in the adsorption of kaolinite at toluene–water interfaces.
- Naphthenates + kaolinite stabilize toluene–water emulsions.
- Bitumen suppresses the interfacial activity of naphthenate-coated kaolinite.
- Bitumen promotes the separation of toluene–kaolinite–naphthenate emulsions.
- Bitumen-coated kaolinite stabilize toluene–bitumen–naphthenate emulsions.

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## ABSTRACT

The study of toluene emulsions is relevant to understand the behavior, and the separation of solvent-diluted bitumen emulsions. Previous studies of similar systems have revealed that the presence of naphthenates, particles – specifically kaolinite- and asphaltenes can play an important role in the formation and stability of solvent-diluted bitumen emulsions. The objective of this work was to elucidate the relative importance of these factors. It was determined that in bitumen-free systems the presence of sodium naphthenates facilitates the entrapment of kaolinite in the emulsion and its segregation at the oil–water interface, which contributes to stabilize the emulsions. However, bitumen components (asphaltenes, resins, and other components) were shown to be more interfacially active than naphthenate-adsorbed kaolinite, resulting in the rejection of kaolinite from the emulsion. In naphthenate-adsorbed kaolinite emulsions, the presence of bitumen components is the dominant factor in determining the level of particles and water entrapped in the emulsion. Bitumen-coated kaolinite emulsions behaved in the same way as bitumen-free systems, suggesting that as long as the particle is pre-adsorbed with the dominant surface active species, particles can contribute to stabilize emulsions.

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## 1. Introduction

During the process of recovering bitumen from surface mined oil sands, the formation of stable intermediate emulsion layers, commonly known as rag layers, in various separation units has a negative impact on the fraction of oil extracted and the quality of the extracted oil [1–3]. During the bitumen extraction process, the oil sand grains are first sent to a digester unit. Here, the bitumen detaches from the sand and attaches to air bubbles. This slurry composed of aerated bitumen, water, and solids is then sent to a separation vessel. It is in this vessel that the bitumen froth rises to the top. The froth from the primary settling unit is

composed of 60% bitumen, 30% water, and 10% sands [4,5]. This froth is subsequently diluted using naphtha and heated to promote the separation of the emulsion. Finally, this mixture is sent to inclined plate settlers and centrifuges where the majority of the remaining water and solids are removed from the oil. The diluted bitumen contains 2–3% water and 0.4% solids [1]. This water is in the form of emulsified droplets that are stable and therefore resistant to coalescence [6]. This water and the solvent are removed in a diluent recovery unit (DRU).

The salts within the water and the solids that remain with the bitumen subsequently causes corrosion related problems in downstream unit operations and fouling in unexpected regions of the upgrading facility [7–12]. Therefore it is critical that water in oil emulsions found in rag layers are prevented, and that water is removed from the oil well before the upgrading steps. To do this,

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it is essential to understand the combined effect of the factors that contribute to the formation and stability of bitumen emulsions.

Rag layers form in separators, in between the top bitumen layer and the bottom aqueous phase. This layer contains bitumen, solids, and water [13]. It has been found that bitumen-associated fine solids exhibit biwettable behavior and can contribute to rag layer formation [2,8,10,14]. These solids tend to accumulate at the oil–water interface and aid in emulsion stability [2,8,10,15,16]. In addition, oil-retained solids act as a barrier between droplets further hindering coalescence [1,13]. Of the solids present, clays are said to be key contributors to the formation and stability of rag layers [2,10,13,16]. Within this clay fraction it is believed that kaolinite is the main contributor to the stability of rag layers as it preferentially adsorbs to oil [17]. Studies show that asphaltenes preferentially adsorb to kaolinite versus illite [18,19]. However, the role of kaolinite on the stabilization of bitumen emulsions, is not completely clear since a previous study by Gu et al. [20] revealed that the addition of kaolinite to water in bitumen–toluene emulsions can produce emulsion inversion (to oil in water) and destabilization. Another important aspect on the issue of emulsion stability controlled by particles is the size of the particles involved. Sztukowski and Yarranton [21] determined that sub-micron particles contribute to forming stable bitumen emulsions. Hannisdal et al. [22] reached similar conclusions.

In addition to solids, naphthenic acids also play a role in emulsion stability. Sodium naphthenates are produced during the alkaline recovery of bitumen. These naphthenates are composed of alkyl-substituted cycloaliphatic carboxylic acids and are among the most important class of naturally occurring surfactants [23–25]. Sodium naphthenates can substantially reduce the oil–water interfacial tension [23–28]. The hydrophilic nature of sodium naphthenates gives them the ability to stabilize oil in water emulsions [27]. Studies on the interfacial material found in naphtha-diluted bitumen show that naphthenates adsorb at the oil–water interface and help stabilize O/W emulsions at high naphthenate concentrations [27,29].

Bitumen components, and more specifically asphaltenes, have been considered the leading factors that contribute to the stability of bitumen emulsions, mainly through the formation of asphaltene “skins” at the oil–water interface [4,6]. Yan et al. [2] compared the role of bitumen components on emulsion stability, particularly asphaltenes, asphaltene–solids, resins and aromatic components, and determined that asphaltenes, and asphaltene-derived solids of about 2  $\mu\text{m}$  were the ones responsible for the stabilization of the emulsion. Kiran et al. [27] determined that asphaltenes tend to dominate the formation of W/O emulsions found in rag layers, but that in emulsions produced with sodium naphthenates (at concentrations higher than its critical micelle concentration), these surfactants invert the emulsion to an O/W emulsion.

Most of the literature fails to appreciate the multiplicity of effects, particularly the combined relative roles of naphthenates, particles, and bitumen components, and in some cases the findings seem to be inconsistent. For example, despite the fact that several references argue that the presence of solids in bitumen aggravate the emulsification of water and particles in bitumen [1,2,10,15,16], the work of Gu et al. [20] shows that the addition of kaolinite to toluene-diluted bitumen produces an inversion of the water in bitumen emulsion (to O/W), along with a partial destabilizing effect.

The purpose of this paper is to clarify the gaps and address some of the inconsistencies in the understanding of the relative role of naphthenates, kaolinite and bitumen on the formation of stable emulsions. To this end, the first part of this work concentrates on understanding the interaction of naphthenates and kaolinite through adsorption isotherms and kaolinite dispersion studies. The second part builds up complexity by introducing the solvent,

toluene, into the system to understand the way that naphthenates and kaolinite affect the formation of emulsions in the presence of the solvent. Finally, bitumen is introduced into the system to evaluate the fate of these emulsions in the presence of bitumen components.

The partition of kaolinite into the resulting emulsions was reported as an oil-retained particle fraction. Side-by-side comparisons between naphthenate emulsions with toluene in the presence and absence of kaolinite were used to evaluate the role of kaolinite–solvent interactions. Polarized light and fluorescence microscopy techniques were used to assess the mechanisms by which kaolinite can affect the formation and stability of these naphthenate–kaolinite–solvent emulsions. The interfacial activity of solvent–naphthenate solution, solvent–kaolinite–naphthenate solution, and (solvent + bitumen) – kaolinite–naphthenate solutions were also evaluated to understand the degree to which each of the components evaluated affects the properties of the oil–water interface. Finally, the relationship between kaolinite retention and water retention in the different emulsions was also considered, and discussed.

Overall, the results support the idea that naphthenates adsorption leads to the formation of organic coatings on kaolinite, and that, in the absence of bitumen, these particles tend to be retained in emulsions that can be best described as water-continuous emulsions. However, in the presence of bitumen, asphaltenes and bitumen-coated particles are responsible for the formation of stable emulsions.

## 2. Experimental

### 2.1. Materials

For this study kaolinite (Fluka) with 99% particles < 45  $\mu\text{m}$  and mean particle size of 2.1  $\mu\text{m}$  were used to represent the clay fraction of oil sand particles. A 99% purity toluene (Caledon Laboratories) was used as the organic solvent. Simulated process water (simply referred to as the aqueous phase) was prepared with the following composition: 25 mM NaCl, 15 mM NaHCO<sub>3</sub>, 2 mM Na<sub>2</sub>SO<sub>4</sub>, 0.3 mM CaCl<sub>2</sub>, 0.3 mM MgCl<sub>2</sub> [27]. Naphthenic acid sodium salts (across organics) were used at various concentrations. Coker feed bitumen (15 wt% asphaltenes [27]) was obtained from Syncrude Canada Ltd.

### 2.2. Methods

#### 2.2.1. Emulsification

1.5 g of kaolinite, 25 mL of solvent (toluene) containing the oil-soluble dye Nile red, and 25 mL of process water (containing naphthenates) were introduced into a 120 mL glass vial with an outer diameter of 48 mm. These samples were then mixed at 2000 rpm for 5 min using a Eurostar mixer (IKA). Upon mixing, each sample was transferred into a 60 mL syringe and allowed to settle for 24 h. After 24 h the settled particles and aqueous phase were collected and separated from the free oil and emulsion layer. Each phase was further centrifuged and dried in order to determine the mass fraction of solids in each phase. Based on this method of analysis an average error of 4.64% was obtained in the kaolinite mass balance closure of 41 samples. Phase heights were measured before mixing and after settling in order to determine the water losses to the emulsion layer.

#### 2.2.2. Adsorption isotherm for sodium naphthenates on kaolinite

For this study, 3% w/w kaolinite solids were added to process water containing 0.05, 0.5, 1, 2, and 3 g/100 mL sodium naphthenates in 25 mL flat bottom vials. Each sample was then mixed for

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