University of Alberta

Role of Biodegradable Ethyl Cellulose in Bitumen Production

by

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Abstract

Recently, a commercially available biodegradable polymer, ethyl cellulose (EC) has been found to be effective in destabilizing water-in-diluted bitumen emulsions. In this study, the role of hydroxyl content and molecular weight of ECs and the effect of mixing and operating temperature in demulsifiation process were studied. In addition, the behavior of EC at the water-oil interface and changes in surface properties of the protective interfacial films with EC addition were investigated. Finally, the role of EC in bitumen extraction was explored.

In this communication, Langmuir trough isotherms demonstrated the ability of EC to soften, weaken and finally displace the interfacial film with progressive increase in EC addition. EC of an intermediate molecular weight operating bitumen-froth cleaning at high temperature was found to be most effective. Furthermore, the bitumen froth quality was improved greatly by the addition of EC-in-toluene solutions during a flotation process without scarifying bitumen recovery.

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List of Symbols

η	intrinsic viscosity
π	interfacial pressure
γ_0	interfacial tension in the absence of interfacially active materials
γ	interfacial tension in the presence of interfacially active materials
C^s	compressibility of interfacial film
A	area of Langmuir trough
B/S	mass ratio of bitumen to solids in the froth
B/W	mass ratio of bitumen to water in the froth

List of Acronyms

SAGD	Steam-assisted gravity drainage
CSS	Cyclic steam simulation
EC	Ethyl cellulose
AFM	Atomic force microscope
FTIR	Fourier transforms infrared spectroscopy
LB	Langmuir-Blodgett
QCM-D	Quart crystal microbalance with dissipation
PMIRAS	Polarization modulation infrared reflection absorption spectroscopy
PEM	Photoelastic modulator
HLB	Hydrophile-lipophile balance
RSN	Relative solubility number
FBRM	Focused beam reflectance measurements
SDS	Sodium dodecyl sulfate
DMSO	Dimethyl sulfoxide
TBAF	Tetra-n-butylammonium fluoride
$TBAF\cdot 3H_2O$	Tetrabutyl ammonium fluoride trihydrate
DHS	Degrees of hydroxyl substitution
Al-PAM	$Al(OH)_3$-polyacrylamide
HPAM	Hydrolyzed polyacrylamide

Chapter 1

Introduction and Objectives

1.1 The Importance of Unconventional Oil

With the remarkable improvement of people's living standard, a large amount of energy is consumed. Historically, the majority of energy came from conventional oils. As the resources of conventional oil are rapidly declining, the future availability of such resources becomes a serious concern [1-3]. For this reason, finding a replacement energy source has become an urgent issue. In fact, only 30% of the current world oil reserves are conventional oils, and remaining resources are unconventional oils in the forms of heavy oil, extra heavy oil or bitumen from oil sands [4]. Therefore, processing of unconventional oils has become extremely important to meet the world's energy demand.

1.2 Oil Sands

1.2.1 Oil Sands Processing

There are 1.7 trillion barrels of bitumen contained in the oil sands deposits in Alberta, Canada [5]. Based on the depth of oil sands deposits, two types of bitumen recovery technologies have been employed by oil sands industry, namely surface (open pit) mining and in-situ recovery. Surface mining normally deals with oil sands less than 75 meters below the surface. In-situ recovery such as steam-assisted gravity drainage (SAGD) or cyclic steam simulation (CSS) is applied to recovery of bitumen from oil sands deposits at a depth more than 100 meters from the surface.

1.2.1.1 Surface Mining

The scheme in Figure 1-1 shows a surface mining bitumen production process. The hot water extraction method was introduced by Clark [7, 8] and has been used in oil sands industry for surface mining operations since its invention. This method is successful because of the presence of a thin water film (c.a. 10 nm) sandwiched between sand grains and bitumen, which is stabilized by electrostatic forces arising from the electrical double layers at the water-oil and water-sand grain interfaces [9-11]. Figure 1-2 [10] illustrates the structure of mineable oil sands.

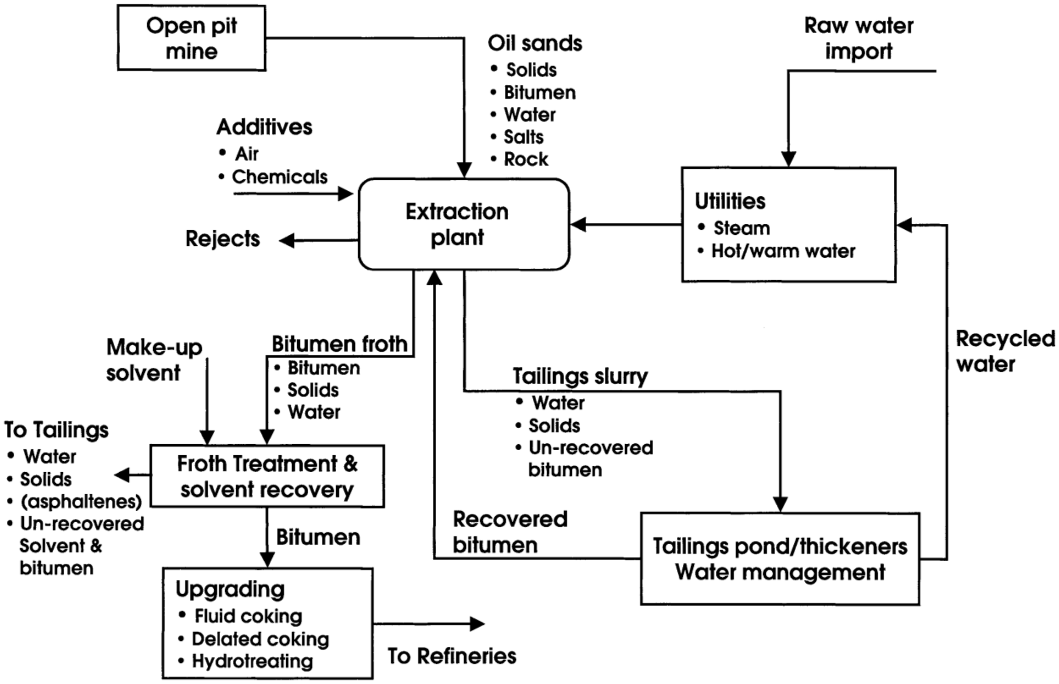

Figure 1-1. Generalized scheme of mineable oil sands processing [6].

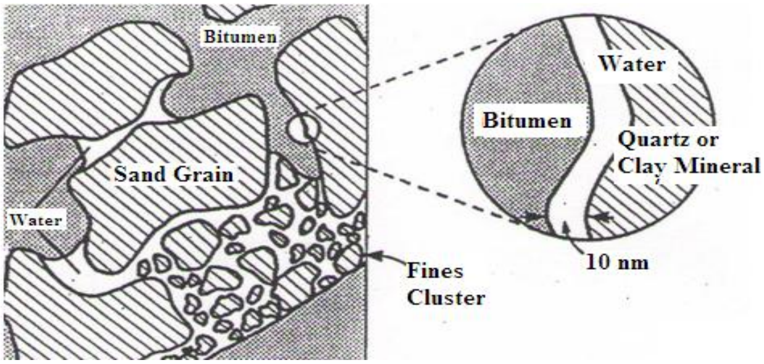

Figure 1-2. The structure of Athabasca oil sand [10].

In surface mining operation, oil sands ore from the shallow deposit is mined with shovels. After crushed, hot water and additives are added to the ore to make oil sands slurry. The slurry is sent through hydrotransport pipeline to the separation vessels where bitumen is extracted. The extraction is usually carried out at 40 ~ 50 ^{o}C in an alkaline (around pH 8.5) environment, which promotes release of bitumen from sand grains. During extraction, air is introduced into the slurry to aerate the liberated bitumen droplets. The aerated bitumen droplets float to the top of the slurry and form a bitumen-rich froth layer in the gravity separation vessel. The remaining water and solids with a limited amount of bitumen are further processed by secondary bitumen recovery and tailing treatment process. The separated water in the thickener or tailings pond is recycled to the extraction plant. The bitumen froth is collected and heated in a deaerator to remove the air in it. The de-aerated bitumen froth typically contains approximately 60 wt% bitumen, 30 wt% water and 10 wt% solids. The bitumen froth needs to be treated to remove the water and solids before upgrading.

1.2.1.2 Steam-Assisted Gravity Drainage (SAGD)

To recover bitumen from deeper oil sands deposits, in-situ bitumen recovery has to be used. A widely employed in-situ operation is SAGD. In this operation, two parallel horizontal wells are drilled from the surface and stay near the base of the oil sands formation. Steam is injected into the upper horizontal well. Bitumen is heated by the steam, and it drains under the gravity to the lower production well from which it is transported to the ground surface. Similar to the surface mining production, the water and solids in the produced fluid need to be removed before the bitumen is sent to upgrading.

1.2.2 Bitumen Froth Treatment

To obtain clean bitumen, water and solids in bitumen froth have to be removed. Use of solvent to dilute bitumen froth can facilitate separation of water and solids from bitumen. In oil sands industry, two froth treatments are used: paraffin-based froth treatment in which paraffinic solvents are used as diluent and naphtha-based froth treatment in which naphtha is used as diluent [6].

In paraffin-based froth treatment, paraffinic solvents, e.g., pentane and hexane, are used as diluent. The diluent to bitumen ratio must be sufficiently high to induce asphaltene precipitation for water and solids limitation. Typically, the diluent to bitumen ratio is 2:1 by volume in a paraffinic froth treatment process [12]. The froth treatment temperature is lower than that used in naphtha-based froth treatment.

Since solubility of asphaltenes (components of bitumen) is low in paraffinic solvents, they will precipitate out and form large aggregates with water and solids, settling out quickly under gravity. Although this process produces cleaner diluted bitumen product (water < 100 ppm, solids < 800 ppm), there are some challenges for this process. For example, asphaltene aggregates may reduce the fluidity of the underflow generated from the froth treatment, creating difficulty for pumping. Another issue associated with this process is high solvent loss to tailings [13]. Therefore, chemical aids such as asphaltene dispersants, defoamers and solvent recovery aids have to be employed in the paraffin-based froth treatment process [14, 15].

In naphtha-based froth treatment, a diluent to bitumen ratio of about 0.7 is employed [16]. The froth treatment is performed at 80 ^{o}C. The naphtha-based froth treatment process yields 98% of bitumen recovery. However, there are two major challenges associated with this process: breaking water-in-oil emulsions and removing bi-wettable fine solids from the diluted bitumen product. Although they are small in quantity (2 wt% water, 0.5 wt% solids) [17], chloride ions contained in the residual water cause corrosion of the downstream upgrading equipment, and fine solids lead to reactor plugging and catalyst poisoning [18]. Efficient demulsification of water-in-diluted bitumen emulsion and demineralization are required for this type of froth treatment process. Therefore, an in-depth understanding of the characteristics of bitumen, emulsified water droplets and fine solids is necessary to design better processes and create more benefits.

1.2.3 Bitumen

Bitumen is an extremely complex substance containing a very large number of different hydrocarbon components. It is most frequently described according to the solubility class and adsorption characteristics of molecules, and this classification plays a significant role in the froth treatment process of bitumen production [19]. Bitumen can be fractionated into saturates, aromatic, resins and asphaltenes (SARA) in terms of their solubility class [20]. The soluble fraction of bitumen in paraffinic solvent is called maltene or deasphaltene-bitumen. Maltenes can be further separated into saturates, aromatics and resins according to their adsorption characteristics. Asphaltenes are the fractions of bitumen that insoluble in paraffinic solvents, heptanes and pentane, for instance, but soluble in toluene. In addition, the amount and composition of asphaltene precipitates depend strongly on the origin of oil samples, solvent to bitumen ratio, alkane type and methods used for asphaltenes extraction [26]. An alkane with a low molecular weight can precipitate more asphaltenes than a similar solvent of a higher molecular weight. In this work, asphaltenes were extracted from bitumen using a 40:1 heptane to bitumen volume ratio at room temperature.

1.2.3.1 Asphaltene

The properties and stability of a crude oil have been found to be dependent to a great extent on the behavior of asphaltenes [21]. Extensive research has been focused on the structure and chemical properties of asphaltenes [22-25] as asphaltenes contain a wide range of molecular chemistries.

Generally speaking, asphaltenes are poly-aromatic hydrocarbons bearing a small amount of transition metals. Asphaltenes contain fused aromatic rings with aliphatic side chains and substituted polar heteroatom functional groups [22, 27, 28]. Asphaltenes aggregate in crude oils even at a concentration as low as 0.1%. It is believed that the aggregation of asphaltenes is due to overlapping of π orbital of fused aromatic rings and/or hydrogen bonding among polar groups [29]. The size of the aggregates depends mainly on the molecular weight of asphaltenes, which varies from a few hundred Daltons to more than a few thousands Daltons [30, 31].

In general, asphaltene molecules contain both hydrophilic and hydrophobic structures. Due to the amphiphilic nature of asphaltenes, they tend to accumulate at water-oil and solid-oil interfaces. Asphaltenes adsorb irreversibly at water-oil interface, and the large cross-linked asphaltene clusters at the interface form steric barriers between water droplets, preventing water droplets from coalescence [32-37]. The water droplets and solids with an asphaltene-coated exterior can stably disperse in organic media that is a good solvent for asphaltenes. Therefore, asphaltenes are believed to be the major contributor in stabilizing water-in-diluted-bitumen emulsions.

1.2.3.2 Resin

Resins are the fraction of maltenes that are insoluble in propane [38]. Similar to asphaltenes, resins also have polar and aromatic structures. However, resins are believed to have negligible effect in stabilize water-in-oil emulsions [36]. In fact, resins can enhance solubility of asphaltenes in crude oil by solvating the polar and aromatic portions of asphaltene molecules [29]. Spiecker et al. [39] evaluated the effect of resins addition on asphaltene aggregation and emulsion stability. They found that at a resin to asphaltene ratio of 1:1 by mass, asphaltene aggregates became smaller in size and the toluene concentration at which asphaltenes began to precipitate in heptol was reduced by 10%. Thus, the presence of resins can destabilize the emulsions via asphaltene salvation or partially replacement of asphaltenes from the interface [38].

1.3 Emulsions in Crude Oil and Bitumen

A colloidal system in which at least one type of liquid exhibits negligible miscibility and is finely dispersed as droplets in another liquid is called emulsion [41]. In crude oil and bitumen production, crude oil and bitumen can be dispersed in water to form oil-in-water (o/w) emulsions or water is dispersed in crude oil and bitumen to form water-in-oil (w/o) emulsions. Both emulsions are undesirable and need to be resolved [41]. Emulsions formed in the oil industry are predominately w/o emulsions in which water droplets are dispersed in the continuous oil phase. The emulsified water droplets are usually small in size and suspended in the continuous oil phase. They barely coalesce or settle under gravity.

1.3.1 Emulsion Stability

Great effort has been given to the studies of the water-in-crude oil or water-in-diluted bitumen emulsions. Usually, four mechanisms are proposed to explain the absence of water droplets coalescence [29]: (1) electrical double layer repulsion, (2) steric repulsion, (3) Gibbs-Marangoni effect, and (4) formation of rigid and cross-linked network at water-oil interface.

A stable emulsion usually is a result of the presence of emulsifying agents in the system. Without emulsifying agents, the electrical double layer and/or steric repulsion originated from charge carriers cannot make emulsions stable as there is very little charge on the dispersed water droplets in organic solvents [42]. In emulsions, an electric double layer may form around dispersed water droplets. However, this electric double layer repulsion is weak due to the low dielectric constant of oil. The steric stabilization occurs usually for water droplets with nonionic polymers adsorbed on their surface [29]. According to the Marangoni-Gibbs effect, a diffusion flux is generated due to surface tension gradient to oppose the drainage of the continuous phase between the two water droplets as they approach each other. However, Marangoni-Gibbs effects do not play a significant role in stabilizing w/o emulsions. Emulsifying agents are surface active materials (surfactants) with amphiphilic nature: one part with an affinity to the oil phase, and the other part with an affinity to the water phase. The most favorable orientation for these molecules is to stay at water-oil interface where they form a protective interfacial film around the water droplets. The interfacial film stabilizes emulsions by preventing water droplets from coalescing. Water-in-diluted bitumen emulsions are stabilized by asphaltenes, which are surfactants naturally present in bitumen, and solids such as wax crystals and clay particles [40, 41, 43].

The properties of asphaltenes have been studied extensively. Mclean et al. [29] suggested that the formation of interfacial film is a result of surface adsorption of asphaltene molecules that is probably driven by hydration of polar functional groups in the aromatic core of asphaltenes. Strausz et al. [44] found that the Athabasca asphaltenes contain hydrophilic functional groups such as hydroxyl and carboxyl, and hydrophobic alkyl side chains. The amphiphilic nature of asphaltenes enables them to adsorb at the water-oil interface with the hydrophilic head groups immersing in the water phase while the alkyl side chains partitioning in the oil phase. Techniques, such as micropipette [45], Langmuir trough [31, 46, 47] and atomic force microscope (AFM) [48, 49] have been applied to understand the mechanisms of asphaltenes in stabilizing w/o emulsions. The micropipette technique is used to directly measure the interfacial tension of emulsified water droplets, which are several microns in size. The decrease of interfacial tension of a water droplet dispersed in an oil phase is attributed to the adsorption of surface active materials at the water-oil interface. Song et al. [50] measured the interfacial tension of water droplets in three different oils (asphaltene, maltene, and bitumen-in-toluene/n-heptane (1:4 by volume) solutions). They found that the interfacial tension of water droplets in the asphaltene solution was lower than that in bitumen solution, and the interfacial tension of water droplets in bitumen solution is lower than that in maltene solution, provided that all three solutions had an equivalent content of bitumen. A lower interfacial tension of water droplets indicates the presence of more surface active materials at the interface. A bitumen solution contains both asphaltenes and maltenes. An intermediate interfacial tension of water-in-diluted bitumen solution suggests the competitive adsorption between asphaltens and malthenes at the interface, and that asphaltene molecules were more surface-active than maltenes. The Langmuir trough technique characterizes the properties of the interfacial film formed at water-oil interface. By applying the Langmuir trough technique, Solovyev et al. [20] found that asphaltene thin films were rigid and hard to wash away from the interface by adding fresh toluene. Negligible changes were observed in the interfacial isotherms upon washing of the interfacial asphaltene thin film with toluene. Zhang et al. [31]

compared the isotherms of asphaltene interfacial films at 20 °C and 50 °C, and observed a negligible difference between the two isotherms. The authors also obtained identical isotherms at pH 3.3, 5.8 and 11.2 of the water subphase. These results indicate an irreversible adsorption of asphaltenes at the interface and illustrated the difficulty to break the protective asphaltene layer surrounding the emulsified water droplets in diluted bitumen. Using a silica surface to represent a hydrophilic surface, i.e., a water droplet or a solid surface, AFM is able to measure the interaction forces of asphaltene films against the hydrophilic surface， or between asphaltene films in various media. Also, AFM allows imaging the topography of the asphaltene films. From AFM images, it was known that asphaltenes at the water-oil interface is in the form of a closely packed-rigid film [46, 51]. Wang et al. [52] measured the forces between two asphaltene LB films in toluene. They found that the force profiles for approaching and retraction overlapped, indicating no adhesion between the two asphaltene-coated surfaces in toluene.

1.3.2 Solids Stabilized Emulsions

Solid-stabilized emulsions are commonly encountered in oilfield operations. The emulsions stabilized by fine solids are called Pickering emulsions [55]. Solids stabilize the emulsion through steric interactions or possibly via depletion mechanisms [43, 53, 54]. These solid particles are much smaller than the size of water droplets, and have a strong affinity to the water-oil interface. The fine solids are typically clays with an asphaltene-coated exterior layer. The asphaltene-coated layer changes the surface wettability of clays from water-wet (hydrophilic) to somewhat oil-wet (hydrophobic), which makes clay surface biwettable. These types of fine solids accumulate at water-oil interface and stabilize emulsions. The presence of solids also increases the strength of an interfacial film formed by asphaltenes. Zaki et al. [6] reported that an emulsion with a 1:1 clay to asphaltene ratio by weight had higher stability.

1.3.2.1 Wettability of Solids

The wettability of clays plays an important role in stabilizing emulsions. The wettability can be determined by contact angle measurement. As shown in Figure 1-3, contact angle θ is measured through the aqueous phase. Figure 1-4 [29] illustrates the role of solids with various wettbility in stabilizing emulsion systems. Solids with a contact angle much less than 90^o are hydrophilic and tend to stay in the aqueous phase, working as a stabilizer for oil-in-water emulsions. During a bitumen production process, most of the fine solids are rendered or partially rendered hydrophobic by asphaltenes, and tend to stay at the water-oil interface. Biwettable solids stabilized water-in-diluted bitumen emulsions by forming a rigid protective layer at the water-oil interface or making an existing interfacial layer more rigid to prevent water droplets from flocculation and/or coalescence.

Therefore, modification of the surface properties of bi-wettable fine solids is necessary in order to enhance demulsification.

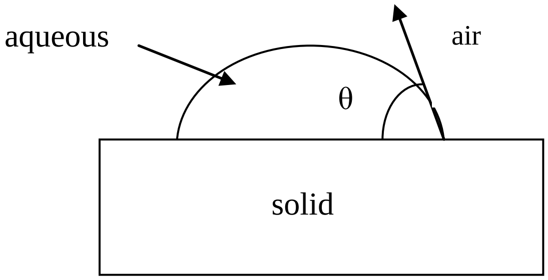

Figure 1-3. A schematics of contact angle determined through the aqueous phase.

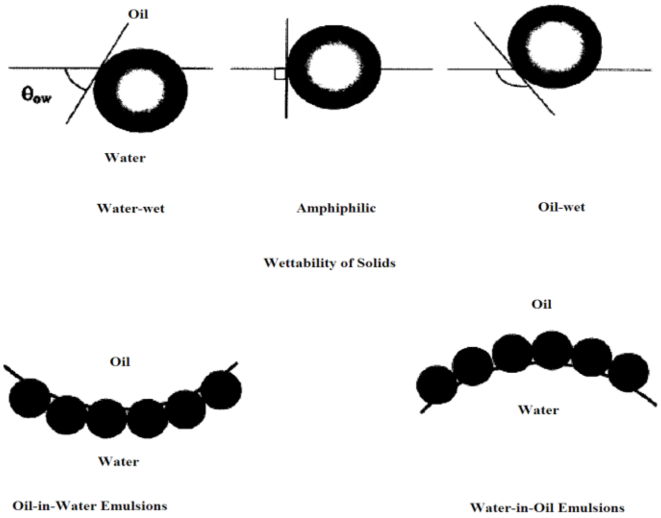

Figure 1-4. Wettability of solids and the types of emulsions [29].

1.4 Demulsification and Demulsifiers

1.4.1 Demulsification

Creaming or sedimentation, flocculation and coalescence are the three main stages in a phase separation process of an emulsified system [18, 41]. Sedimentation occurs as a result of the density difference between two phases. In contrary to sedimentation, creaming takes place when the droplets rise to the top instead of settling out to the bottom of the system. Creaming in oil-in-water emulsions is the analog of sedimentation in water-in-oil emulsions [55]. Usually creaming and sedimentation produce two separated layers of emulsions. Because Brownian motions usually dominate over gravitational forces for emulsified droplets smaller than 1 µm, sedimentation has no effect on droplets smaller than 1 um. For this reason, sedimentation is not an effective pathway for a complete phase separation. Flocculation depends to a large extent on the relative strength of the attractive and repulsive forces among the droplets. When the attractive force overcomes the repulsive force, droplets are linked together to form a larger cluster of droplets with no change in total surface area. In this case, droplets flocculate, and the clusters of emulsified water droplets settle easily. However, flocculation is reversible, and it can be broken by strong agitation. Coalescence occurs when the interfacial films of nearby or flocculated droplets rupture. The rupture of protective films allows droplets to combine with each other, forming a larger single droplet with a reduced surface area. Successful removal of droplets through settling requires either flocculation and/or coalescence of emulsified droplets.

Removal of water from bitumen has been attempted by a number of methods since the start of oil sands processing. Using an absorbent to remove water from oil phase was a well-established method. In this method, water was absorbed by absorbents pre-coated filter and was excluded from the system. However, disposal of the filter cake and associated residual oil was a problem. Washing oil with additional fresh water was another attempt to strip small water droplets from oil. The use of heat to break w/o emulsions by reducing the viscosity of the oil and changing the solubility of the natural emulsifiers in the oil was also an effective method [56]. The only drawback of this method is that some interfacial materials such as solids still exist in the treated oil after evaporation of water, which lowers bitumen quality.

In the recent decades, more water removal techniques have been developed. A successful demulsification mechanism should contain one or more of the steps of limiting, altering or neutralizing the emulsifying agents. Methods for breaking w/o emulsions fall into three categories: mechanical, electrical and chemical demulsification [46, 56]. Mechanical approaches break the emulsion by applying an additional force to increase the collision rates of droplets or to crack the physical barrier between the aqueous and oil phases. Either mechanism drives the coalescence of droplets. Alternatively, electrical approaches apply an electrical field across emulsions to cause polar molecules to reorient themselves. As a result, the polar molecules are no longer concentrated around the droplet’s surface, which eventually weakens the interfacial films. In addition, the applied electric field induces and re-orientates charges on the emulsified particles [41]. This brings the oppositely charged particles closer to each other. Overall, electrical method causes coalescence of water droplets by weakening the interfacial film and re-orientating the charges on the surface of water droplets to make the water droplets electrically attractive to each other.

Chemical demulsification works by modifying the properties of the interfacial film [57, 58] by adding chemical aids to the emulsion system. Chemical demulsification consumes less energy than other demulsification methods. It is the most economical and commonly used demulsification method in the oilfield [46, 59].

1.4.2 Demulsifiers

To successfully break w/o emulsions, demulsifiers must have [59-64]: 1) strong attraction to the water-oil interface with the ability to destabilize the protective film around the droplet and/or change the wettability of solids; 2) the ability to flocculate the droplets; 3) the ability to promote film drainage and droplets coalescence.

Studies from Sjoblom et al. [65] and Wasan et al. [58] showed that long chain alcohols can modify the rigidity of the interfacial film and long chain amines can interact with the interfacial materials in the interfacial film. These authors concluded that these simple organic chemicals function as co-surfactants and improve demulsification.

Polymeric surfactants are the most commonly used commercial demulsifiers for destabilizing w/o emulsions [64]. High molecular weight amphiphilic polymers have been used as demulsifiers since the 1930s [66]. These polymeric demulsifiers are capable of promoting flocculation and coalescence of water droplets [64]. They are able to soften, break and displace the rigid interfacial film or to modify the interfacial properties of the interfacial film through for example changing the wettability of the film materials [49]. Mohammed et al. [67] studied the interfacial rheological properties of a water-crude oil interface. They found that with the addition of an amine-based ethylene oxide polymeric demulsifier, the surface viscosity of a well-aged film decreased by an order of magnitude. Zhang et al. [46] captured the AMF images of an asphaltene interfacial film with and without a commercial EO-PO copolymer demulsifier addition. With increasing demulsifier addition, larger asphaltene aggregates instead of a uniform asphaltene film were observed from the AMF images. This finding indicates that the continuity of the asphaltene film has been disrupted by the demulsifier, leading to a less rigid film. Wu et al. [66] compared the performance of high molecular weight polymeric surfactants and low molecular weight non-ionic surfactants in removing water from diluted bitumen. They found that the polymeric surfactants with an ethylene oxide (EO)-propylene oxide (PO) structure are promising in removal of water from diluted bitumen. Here PO blocks provide hydrophobicity, and EO blocks provide the necessary hydrophilic portion of the demulsifier. With an increase of the PO portion in the structure, a demulsifier becomes more hydrophobic and more soluble in the continuous oil phase, and vice versa for the EO portion. Without EO portion, the above polymers have no demulsification functionality [67]. An effective demulsifier must have both components, with EO chains penetrating into water droplets while hydrophobic PO chains remain in the oil phase. A combination of the two with a suitable degree of polymerization will give intermediate solubility in water and oil phases. Such property allows the demulsifier staying at the interface to either soften or break the interfacial films. The PO-EO ratio in a demulsifier is therefore usually tuned to achieve the best performance.

The performance of demulsifiers is dependent on the properties of emulsions and the HLB (RSN) value, structure and molecular weight of demulsifiers. In the following text, these will be addressed in detail.

1.4.2.1 HLB and RSN

Hydrophile-lipophile balance (HLB) is a widely used standard for characterizing a surfactant in terms of its hydrophilicity to hydrophobicity ratio. The concept of HLB was initially introduced by W. C. Griff in 1949 [68] for nonionic surface-active agents. According to Griffin, HLB value is calculated as:

$$HLB = \frac{\%ethoxylation}{5} \qquad (1.1)$$

An increase in the HLB value of a surfactant suggests an increase in its solubility in the aqueous phase. For nonionic surfactants, HLB values range from 0 (completely hydrophobic) to 20 (completely hydrophilic). Table 1-1 [68] summarizes the range of HLB values for desired functions of surfactants.

Table 1-1. The HLB values and the associated functionalities of surfactants

HLB	Functionality
3-6	w/o emulsifier
7-9	Wetting agents
8-18	o/w emulsifier
13-15	Detergent
15-16	Solubiliser

Abdel-Azim et al. [32] found that demulsification was favored by an increase in the number of polar groups and aromaticity of a demulsifier with HLB values from 6 to 14. The authors claimed that such changes in the structure of the demulsifiers favor their adsorption at the water-oil interfaces and therefore the displacement/solubilization of asphaltene clustered in this region. Zaki et al. [69] discovered that a propoxylated polyethylene-glycols based demulsifier with a molecular weight of 5–7.5 kDa and an HLB value of 16 was the most effective in demulsifying an asphaltene-stabilized water-in-benzene emulsion. The authors [70] also found that a polyoxypropylenated-poloyethylentaed amine based demulsifier with an HLB value in the range of 6–10 and a molecular weight less than 1.5 kDa yielded the best demulsification result in a clay-asphaltene-stabilized water-in-benzene emulsion.

For commercial demulsifiers, it is hard to know their HLB values because they are formulated products whose composition is not disclosed. Thus relative solubility number (RSN) concept is developed as an alternative criterion to characterize the hydrophilicity of demulsifiers [66]. The standard RSN value is defined as the volume of water in milliliter necessary to produce a persistent turbidity in a 30 ml benzene-dioxane solvent mixture, containing one gram of the demulsifier sample [13]. A linear relationship has been found between HLB and RSN for the demulsifiers of the same family. Similar to HLB, RSN values directly correlate to demulsifier's PO-EO composition. A linear correlation has been found between the RSN values and EO numbers for demulsifier families containing the same number of POs [71]. A higher RSN value represents a more water-soluble demulsifier, and a lower RSN value represents a more oil soluble demulsifier. Moreover, the surfactants with a RSN value <13 are typically insoluble in water, and surfactants with a RSN value >17 are soluble in water. The surfactants with a RSN value between 13 and 17 are dispersible in water at low concentration and form gels at high concentration [14]. Both Krawczyk [72] and Berger [73] concluded that the demulsifiers with a unity partition coefficient gave the best demulsification performance regardless of their structures. However, demulsifiers with the same HLB or RSN value may not necessary have the same partition efficiency [73].

1.4.2.2 Structure

The efficiency of a demulsifier is determined by its structure. Wu et al. [66] found that a demulsifier with a PO-EO-PO structure does not break a solid free, water-in-toluene diluted bitumen emulsion regardless of its EO content. This finding suggests that for a water-in-bitumen emulsion, the demulsifer must have an EO chain as the terminal group. Zhang et al. [74] demonstrated that demuslfiers with a dendrimer-structure such as diethylene-triamine-based EO-PO copolymer are more efficient in demulsification of w/o emulsions than demulsifiers with a linear structure. The dendimers have better penetrability than the non-branched polymers. Once they enter the solution, they pervade and dominate the water-oil interface. Berger et al. [73] compared the ability of promoting water droplets coalescence by various polyoxypropylene, polyoxyethylene esters of the same molecular weight. They found that demulsifiers of the same molecular weight but increased number of branches led to better demulsification performance. Based on their findings, they concluded that an increase in molecular weight and degree of branching improved the performance of the demulsifier. However, a demulsifier with a bulky structure, i.e., a larger number of branches may diffuse slowly to the interface, and hence it is less efficient than a demulsifier with a straight chain structure. Wang et al. [61] compared the effect of a straight chain demulsifier and a branched chain demulsifier on the dilational property of water-oil interface. They concluded that the demulsifier with a straight chain structure exhibits stronger adsorption at water-oil interface and gives a better performance on decreasing the dilational elasticity of water-oil interface, which contains surface-active materials.

1.4.2.3 Molecular Weight

Molecular weight of demusifiers also plays an important role in demulsification. Bhardwaj et al. [75] tested demulsification efficiency of water-in-crude oil emulsions using five commercial nonionic surfactants. Their study showed that a demulsifier of molecular weight less than 2 kDa was not effective for demulsification. Wu et al. [66] evaluated the demulsification performance of five commercial demulsifiers and found that the performance of a demulsifier is related to its RSN and molecular weight. They claimed that the most effective demulsifiers are those of high molecular weight (7.5 kDa–15 kDa) and a RSN between 7.5 and 12.5. Surfactants of a low molecular weight (<4 kDa) could not break emulsions with a dosage as high as 300 ppm regardless of their RSN values. Berger et al. [73] compared the ability of two demulsifiers having the same number of branches but different molecular weight in promoting coalescence of water droplets. They found that the performance of demulsifiers increased with increasing molecular weight. However, there is no clear correlation between RSN or HLB and demulsification performance. Ese et al. [76] studied the effect of adding some high molecular weight complex block copolymers on the properties of asphaltene interfacial film. They found that the presence of these high molecular weight demulsifiers made interfacial film more compressible, and some of the high molecular weight chemical additives could work as an inhibitor to prevent the formation of a rigid asphaltene film at water-oil interface. Pena et al. [77] investigated the demulsification efficiency of an EO-PO alkyphenolformaldehyde resin, which was dosed along with polyurethane block copolymers of various molecular weights. They found that 100% dewatering efficiency was achieved within 30 min by using a 200 ppm alkyphenolformaldehyde resin and a high molecular weight (20 kDa) block co-polymer. However, it took 2 h for a low molecular weight (12 kDa) block co-polymer to achieve similar demulsification result. Zaki et al. [69] found that a EO-PO block copolymer with an HLB of 16 and molecular weight of 5 kDa was the most effective in promoting coalescence of water droplets. Follotec et al. [51] reported that a triblock polymer with a molecular weight of 1.8 kDa was the best in demulsification. Zaki et al. [70] found that polyoxyalkylenated amines with HLB value of 6–10 and molecular weight of 0.5–1.1 kDa were the most effective in breaking an asphaltene and clay stabilized emulsion. Pereira et al. [78] showed that a triblock copolymer of a polyethylene oxide-polypropylene oxide-polyethylene oxide structure and an intermediate molecular weight (4.6 kDa) was more effective than polymers with the same structure and either higher (8 kDa) or lower (1.8 kDa) molecular weight in destabilizing water-in-oil emulsions. In contrast, it was reported that a polymer of molecular weight < 2 kDa was ineffective in water removal from water-in-oil emulsions regardless of its structure [75] and RSN value [66].

In general, low molecular weight demulsifiers (typically below 3 kDa), such as conventional surfactants, exhibit high interfacial activity [79]. These demulsifiers can suppress interfacial tension gradient present during the deformation of the interface between approaching droplets, leading to film rupture and coalescence of water droplets. Demulsifiers of molecular weight between 3–10 kDa, such as polyalkoxylated alkylphenolformaldehyde resins and complex block copolymers, are usually used for separation of a large volume fraction of the dispersed aqueous phase [77]. These molecules penetrate the stabilizing film at the water-oil interface and alter its compressibility [46] and rheological properties [79] by disrupting the structure of adsorbed asphaltenes at the interface, leading to coalescence of water droplets. Demulsifiers such as ethoxylated/propoxylated amine polyols of molecular weight above 10 kDa, adsorb at the water-oil interface and are able to flocculate nearby water droplets [30]. They are effective in removing small water droplets.

1.4.3 Operating Conditions

The ideal demulsification involves three stages. First, demulsifier is introduced and mixed with emulsion. Second, water droplets are flocculated and/or coalesced. Finally, the aqueous phase is separated from the oil phase.

It is important to distribute demulsifiers evenly in the emulsion in order to achieve the best demulsification results. For this reason, a mixing stage is required. Little [80] indicated that demulsification was dependent on the collision rate between droplets after a demulsifier had been introduced to the system. Demulsification of smaller droplets requires more intense agitation [81]. Graham et al. [82] claimed that the efficiency of demulsification increased with an increase in the energy of mixing. It is, however, also important not to stir or mix the emulsion too vigorously to make it more stable.

On the other hand, temperature also plays an important role in a demulsification operation. An increase in temperature leads to a decrease in emulsion stability by increasing the rate of adsorption, accelerating the movement of Brownian motion, and decreasing the viscosity of the interfacial film [83]. Some rigid interfacial films "relax" at temperatures higher than 60 ^{o}C [29]. Gillespie and Rideal [84] studied the probability of interfacial film rupture at various temperatures. They found that the lifetime of the water droplets was greatly affected by a minor change in temperature.

1.5 The Value of a Demulsifier in a Flotation Process

A demulsifier is used in the froth treatment stage to separate the emulsified water droplets from the continuous oil phase. On the other hand, chemical aids are usually added during flotation to enhance bitumen recovery and froth quality. The residual flotation aids remaining in the froth will be carried into the froth treatment process. If a demulsifier does not stabilize w/o emulsions, it might be beneficial to add the demulsifier in the flotation process. With potential improvement in bitumen froth quality, the resultant froth may be treated more easily, which has been enhanced by the demulsifier carried into the froth treatment stage from the flotation process.

1.6 Objectives

Recently, a low cost, commercially available polymer, ethyl cellulose (EC) was found to be effective in destabilizing water-in-diluted bitumen emulsions. The nontoxic and biodegradable characteristics of EC make it an outstanding candidate as a chemical demulsifier. However, the ethyl cellulose used in this study was a commercial product and its detailed biodegradable property was unfortunately not provided. The objective of this study is to investigate the role of molecular weights and hydroxyl contents of EC in terms of its demulsification efficiency and to evaluate the demulsification performance of EC at various temperatures and under mixing condition. The behavior of EC at the water-oil interface and the interactions between EC and the interfacially active materials from bitumen that stabilize w/o emulsions will be also studied. The Finally EC is attempted to be used as a flotation aid for improving bitumen recovery.

1.7 Outline of Thesis

This thesis consists of six chapters.

Chapter1: This chapter provides the background of this study. The causes of stable w/o emulsion formation were presented and the functionalities of a demulsifier were introduced. Previous studies on demulsification by various demulsifers were reviewed. Finally, the objectives of this study were listed in this chapter.

Chapter 2: The demulsification performance of six ethylcellulose samples of various hydroxyl content and molecular weights were evaluated in this chapter.

Chapter 3: This chapter focused on studying the effect of operating parameters on four various molecular weight EC samples in demulsifying water-in-diluted bitumen emulsions.

Chapter 4：The behavior of EC at water-oil interface and the interactions between EC and asphaltene/bitumen were investigated in Chapter 4.

Chapter 5: EC was attempted to use in a flotation process in this chapter. The effect of EC addition on bitumen recovery and froth quality was discussed.

Chapter 6: Major conclusions and suggestions for future work were listed in this chapter.

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Chapter 2

Effect of Hydroxyl Content and Molecular Weight of Ethylcellulose on Demulsification of Water-in-Diluted Bitumen Emulsions*

2.1 Introduction

Stable water-in-oil (w/o) emulsions are often encountered in the production of conventional crude oil and bitumen. These w/o emulsions create many operational problems for the oil production. For example, chlorides in the emulsified water are converted to corrosive hydrochloric acid in the downstream crude oil refining or bitumen upgrading, leading to corrosion of the processing equipment.

As an economical and efficient method, chemical demulsification has been widely used in the petroleum industry to break up w/o emulsions. The chemicals used for this purpose include low and high molecular weight polymeric surfactants. These surfactants, known as demulsifiers, have a stronger affinity for the water-oil interface than the emulsion stabilizers, e.g., asphaltenes and other naturally surface-active molecules indigenous to the crude oil [1-6], and have the ability to weaken and/or displace the protecting interfacial film at the water-oil interface [7-10].

In general, demulsification efficiency of demulsifiers is dependent on the hydrophile-lipophile balance (HLB) of demulsifier molecules. To attain high demulsification efficiency, demulsifiers must possess appropriate HLB values. The contributors for hydrophilicity of demulsifier molecules are usually polar functional groups such as hydroxyl, carboxyl, ethylene oxide (EO), amine, and sulfonate, whereas hydrophobicity of demulsifier molecules is controlled by the

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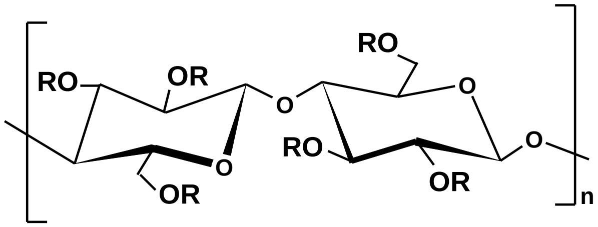
number (or length) of hydrocarbon or propylene oxide (PO) chain. Aveyard et al. [11] studied demulsification of a water-in-crude oil emulsion using a series of octylphenyl polyethoxylates $R(EO)_n$ (n = 3–30). They observed a maximum demulsification efficiency at n = 9–10, corresponding to an HLB value of 12–14, calculated using the Griffin equation [12]. Zaki et al. [13] investigated effect of HLB value of demulsifiers on the demulsification efficiency of an asphaltene-stabilized water-in-benzene emulsion using propoxylated polyethylene glycols, i.e., EO-PO block copolymers, as demulsifiers. They concluded a demulsifier with an HLB value of 16 was the most effective in the demulsification of asphaltene-stabilized water-in-benzene emulsions. For the clay and asphaltene-stabilized water-in-benzene emulsions, however, the HLB value required for demulsifiers to completely break up the emulsions was found to be 6–10 [14]. This finding indicates that presence of fine particles would change interfacial properties of w/o emulsions and consequently the required HLB values for an effective demulsifier. This finding calls for caution on the choice or design of demulsifiers for water-in-diluted bitumen emulsions as fine particles are always present in those emulsions. Zaki et al. [14] also found that phenylenediamine or naphthylamine-based EO/PO copolymer demulsifiers were more effective than diethylenetriamine or other non-aromatic, amine-based EO-PO copolymer demulsifiers for demulsifying the clay and asphaltene stabilized water-in-benzene emulsions.

Recently, Xu et al. [15] systematically studied the effect of EO/PO molar ratio on demulsification of a water in 5% toluene diluted, solids free bitumen emulsion by diethylenetriamine-based EO-PO copolymer demulsifiers. The demulsifiers with an EO/PO of about 0.14 were found to be ineffective even at a dosage as high as 300 ppm. The demulsification efficiency increased with increasing EO/PO molar ratio. As the EO/PO molar ratio approached unity, the demulsifiers were able to break up the emulsions rapidly at a dosage as low as 50 ppm. Further increase in demulsifier dosages did not further improve the performance of demulsification. However, by increasing the EO/PO molar ratio to about 1.4, the demulsifiers became less effective at high dosages, although their performance at low dosages was similar to those with an EO/PO ratio of about unity. For a given emulsion system, it is therefore highly desirable to finely tune HLB values of demulsifiers by controlling the number ratio of hydrophilic chain (EO) and the hydrophobic (PO) blocks to achieve optimal demulsification performance.

Demulsification efficiency depends not only on the HLB value of demulsifiers but also on their molecular structure. Wu et al. [16] studied the relationship between the structure of EO-PO copolymers and their demulsification performance. They found that in order for EO-PO block copolymer demulsifiers to effectively destabilize water in 5% toluene diluted, solid-free bitumen emulsions, the demulsifiers must possess an EO-PO-EO type structure as the active group and a EO content above 10%. The demulsifiers with a PO-EO-PO structure were unable to break up the emulsions regardless of the EO content. This finding suggests that effective EO-PO copolymer demulsifiers must have hydrophilic EO chains as the terminal groups.

It has been found that demulsifiers with starlike structure are more effective than the demulsifiers with a linear structure in demulsification of water-in-oil emulsions [17, 18]. The starlike structure can be achieved, for example, through reaction of molecules having multiple amine functional groups with PO, followed by EO addition. The demulsifiers with starlike structure could flocculate water droplets more effectively than demulsifiers of linear structure, eventually leading to more effective coalescence of water droplets [18]. In comparison, there are relatively few publications describing the influence of molecular weight of demulsifiers on demulsification. Wu et al. [19] investigated demulsification of water-in-diluted bitumen emulsions using conventional low-molecular-weight surfactants and polymeric surfactants. They found that low-molecular-weight surfactants removed only 10% of the water at 400 ppm dosage, whereas use of polymeric surfactants such as polymerized polyols and alkylphenol formaldehyde resin-based EO-PO copolymers removed about 90% water at a much lower dosage of 300 ppm. On the basis of their findings, the authors concluded that demulsifiers with a molecular weight of 7500−15,000 Da were the most effective in demulsification. Unfortunately, since the demulsifiers of a molecular weight higher than 15,000 Da were not tested in their study, the effect of higher molecular weight on demulsification of water-in-diluted bitumen emulsions remains unknown. In demulsification of water-in-crude oil emulsions using acrylate-acrylic acid-styrene copolymer demulsifiers, Shetty et al. [20] observed more effective demulsification by demulsifiers of lower molecular weight than by demulsifiers of higher molecular weight. However, the authors did not report the optimal molecular weight although they pointed out that the molecular weight of their demulsifiers was in the range of 10,000−100,000 Da. Moreover, the demulsifiers in their study were added to the aqueous phase, as the demulsifiers used in their study were water-soluble. This is in great contrast to conventional demulsification practice of water-in-oil emulsions in which demulsifiers are added to the oil phase.

Recently, we reported a novel biodegradable polymer, ethylcellulose (EC), for effective demulsification of water-in-diluted bitumen emulsions [21]. By using in situ visualization of water droplet interactions via micropipette technique and atomic force microscopy imaging of Langmuir-Blodgett interfacial films, we found that EC is able to break up water-in-diluted bitumen emulsions through flocculation-assisted coalescence of water droplets as a result of lowering the interfacial tension and disrupting the interfacial film [22]. Although EC is a linear polymer, its molecular chain contains many six-member-ring repeating units connected to each other by an oxygen atom. Each ring is composed of five carbons and one oxygen atom, as shown schematically in Figure 2-1. The hydroxyl and oxyethyl side groups are either equatorial or axial, locating at both sides of the ring. This structure of EC makes it distinguishable from conventional linear or starlike EO-PO copolymer demulsifiers. In this study, we synthesize a series of EC polymers of varying hydroxyl content and molecular weight to study the role of the hydroxyl content and the molecular weight of biodegradable EC polymers in the demulsification of water-in-diluted bitumen emulsions.



R = H or CH_2CH_3

Figure 2-1. Molecular structure of EC

2.2 Experimental

2.2.1 Materials. Vacuum distillation feed bitumen, being the product stream from the diluent recovery unit, and industrial grade naphtha were provided by Syncrude Canada Ltd. The heptane-insoluble asphaltene content in the bitumen was determined to be 11 wt%. The fine solids content of the bitumen was about 1 wt%. The water used to prepare water-in-diluted bitumen emulsions was industrial plant recycle process water from Syncrude Canada Ltd. The process water of pH 8.9 contained 25 ppm magnesium, 41 ppm calcium, 79 ppm sulfate, 527 ppm sodium, 22 ppm potassium, 407 ppm chlorine, and 793 ppm bicarbonate. Milli-Q water was used as subphase for interfacial tension measurement and for purification of demulsifiers. Cellulose (powder, ~20 μm) and sodium hydroxide (99.5%) were purchased from Sigma-Aldrich. Sodium hydroxide was pulverized and dried under vacuum. Dimethyl sulfoxide (DMSO, >99.7%; water content <50 ppm), tetrabutyl ammonium fluoride trihydrate (TBAF $3H_2O$, 99%), iodoethane (>99.5%), methanol (optima), and acetic acid (99.8%) were purchased from Fisher Scientific.

The silicon wafers purchased from Ultrasil, Hayward, CA, were used as substrate onto which interfacial materials were transferred by Langmuir-Blodgett method. They were 0.5 mm in thickness and 10 cm in diameter, polished on one side. Prior to their use as a substrate, the wafers were cut to $1 \times 3\text{cm}^2$ pieces and cleaned by soaking them in a 70/30 solution by volume of 96% sulfuric acid and 30% hydrogen peroxide at 90 ^{o}C for 30 min, followed by a thorough rinse with Milli-Q water. The cleaned silicon wafers were stored in Milli-Q water before use.

2.2.2 Experiment

2.2.2.1 Synthesis of Ethylcellulose-Based Demulsifiers. The first step of synthesis was mercerization of cellulose. Typically, 6 g of cellulose were added to 300 ml of 20% NaOH at 0 ^{o}C. The mixture was magnetically stirred for 4 h at this temperature, followed by filtration under vacuum and washing repeatedly with Milli-Q water to pH 7. The mercerized cellulose was dried overnight under vacuum at 50 ^{o}C. The ethylation of the mercerized cellulose was then performed. In this study, 0.3 g of mercerized cellulose and 3.2 g of TBAF $\cdot 3H_2O$ were added to 30 ml of dry DMSO in a three-neck flask. The mixture was magnetically stirred for 30 min at room temperature and for 1 h at 60 ^{o}C under reflux with nitrogen purge. After the mixture turned to a clear solution, 1.33 g of sodium hydroxide powder was added to the mixture. The mixture was stirred for 30 min, followed by the addition of 3.46 g of iodoethane. The ethylation reaction was performed at 70 ^{o}C for 5 h. The resultant EC was purified using the following procedure. The mixture was allowed to cool to the room temperature and then poured into 100 ml of 80:20 (v/v) water/methanol solution. The solution was neutralized to pH 7 with acetic acid and filtrated under vacuum. The filter cake was then thoroughly washed with 80:20 (v/v) water/ methanol solution. Finally, the product was dried under vacuum at 50 ^{o}C overnight.

The obtained EC polymers were characterized as follows. Their molecular weight was determined by viscosity measurement, following the same procedure described elsewhere [21]. The molecular structure was analyzed by Fourier transform infrared spectroscopy (FTIR) using a Bio-Rad FTS 6000 spectrometer and diffuse reflectance method. The hydroxyl content of EC polymers was determined by elemental analysis. The standard deviation of elemental analysis is ±3%.

2.2.2.2 Interfacial Tension Measurement. The interfacial tension of naphtha-diluted bitumen-water interface in the presence and absence of EC demulsifiers was measured using a Processor Tensiometer K12 (Kruss, Hamburg, Germany) equipped with a Pt-Ir ring. Milli-Q water was used as aqueous phase. All measurements were performed at 20.0 ± 0.5 ^{o}C with a precision of ±0.1 mN/m.

2.2.2.3 Demulsification Test. Water-in-diluted bitumen emulsions were prepared using industrial process water from oil sands extraction operations and naphtha-diluted bitumen. The diluted bitumen was prepared at 60:40 (w/w) bitumen to naphtha ratio. After the diluted bitumen was shaken in a mechanical shaker for 4 h at 200 cycles/min, an emulsion was prepared by emulsifying 2.2 g of process water in 42 g of naphtha-diluted bitumen using a homogenizer (PowerGen homogenizer, 125 W) running at 30,000 rpm for 3 min. The resultant emulsion contained 5 wt% water.

The emulsion prepared freshly each day using the procedure above was found stable and it was used for the demulsification tests. Typically, 0.3 ml of 0.5 wt% demulsifier dissolved in toluene/ethanol mixed solvent was added to 8.7 g of prepared emulsions in a 20 ml vial. The mixture was homogenized by the homogenizer operating at 8000 rpm for 30 s. In this particular case, the concentration of the demulsifier in the total emulsion was 145 ppm by weight.

To evaluate the effectiveness of demulsification, 9 ml of the emulsion with added demulsifier was transferred immediately after the homogenization into a 12 ml polypropylene test tube. The tube was capped and sealed with a Teflon tape. A plastic rack was used to hold all of the test tubes and placed in a water bath at 80 ^{o}C for gravity settling of 1 h. The demulsification efficiency of EC was evaluated by determining the change in water content of the emulsions at 2.5 cm below the emulsion top surface. As well, the water drops at the bottom of the tubes were photographed [21]. The water content was measured with a Karl Fischer titrator. Blank tests were performed for emulsions without demulsifier addition as a control. The reported water content was the average of three repeats. The water drop size was visualized with a Carl Zeiss Axioskop 40 Pol microscope equipped with a video camera that is connected to a computer. The emulsion sample was placed on a glass slide and covered by a 25 mm × 25 mm × 0.2 mm thin glass cover slide. The image of the emulsion was taken under transmittance light.

2.2.2.4 Preparation of Langmuir Blodgett Film. Langmuir-Blodgett (LB) films were prepared using a Langmuir interfacial trough (KSV Instruments, Espoo, Finland). The trough and barriers were rinsed with HPLC grade toluene prior to each measurement. The interfacial pressure was measured by a Wilhelmy plate (filter paper Whatman 1 CHR) attached to a microbalance. Heptol (60:40 toluene/heptane by volume) instead of naphtha was used as the top phase to avoid influence of the impurities in the industrial-grade naphtha to the interfacial LB films.

In the preparation of the interfacial films, the lower compartment of the Langmuir trough was filled with 120 ml of Milli-Q water as subphase. The water subphase was considered clean if the pressure sensor reading is below 0.1 mN/m upon barriers compression to the closest possible position. After achieving the appropriate cleanliness, a clean and dry hydrophilic silicon wafer was immersed in the aqueous subphase, followed by dropwise addition of 20 μL of 1 g/L solid-free bitumen in toluene solution. The bitumen in toluene solution was added evenly on the water surface using a gastight Hamilton microsyringe. Following a 20 min evaporation of toluene to allow the formation of a uniform bitumen film on top of the subphase, 100 ml of heptol was slowly added as top phase using a glass funnel, and the interface was allowed to equilibrate for 10 min. The formed interfacial bitumen film represents the “toughest” interfacial film to break and is used as reference bitumen interfacial film. For investigating the molecular mechanism of a demulsifier in breaking protective interfacial bitumen films, 40 μL of 0.1 g/L EC in toluene/ethanol solution was injected evenly into the heptol top phase. EC was allowed to diffuse through the top phase to the heptol-water interface for 2 h prior to compression of interfacial films. The interfacial film was compressed at 10 mm/min to 2 mN/m interfacial pressure at which the interfacial film was transferred onto the hydrophilic silicon wafer under constant interfacial pressure as the substrate was pulled upward through the interface at a 10 mm/min pulling rate [23, 24].

2.2.2.5 Atomic Force Microscope (AFM) Imaging. Images of LB films were obtained using Agilent 5500 atomic force microscope (AFM; Agilent Technologies, Inc., Chandler, AZ) operating under AAC mode in air. Silica cantilevers (RTESP, Veeco, Santa Barbara, CA) with a nominal resonance frequency of 300–350 kHz were used for imaging at a scan rate of 1 Hz. Images were obtained at several locations for each sample. At least two individual samples prepared under identical deposition conditions were imaged. AFM imaging was carried out at room temperature ($20 \pm 0.5\ ^{o}$C).

2.3 Results and Discussion

Cellulose is a renewable natural polymer. Due to strong intra- and intermolecular hydrogen bonding interactions, cellulose is insoluble in water and organic solvents [25]. However, cellulose is soluble in ionic liquids [26]. In the presence of TBAF, cellulose becomes soluble in DMSO. Therefore, etherification of cellulose is much faster in TBAF/DMSO medium than in DMSO [27, 28]. By controlling cellulose/sodium hydroxide/iodoethane molar ratio in the etherification reaction, EC polymers of varying hydroxyl contents were obtained. Listed in Table 2-1 are six samples with hydroxyl content ranging from 1.51 to 14.23 wt%, corresponding to degrees of hydroxyl substitution (DHS) of 2.79 to 1.33. On the basis of the monomer unit of EC, the hydrophile-lipophile balance value of EC1 to EC6 was estimated using the modified Davies formula [29], given as follows:

$$HLB=7+0.5(3-DHS)+1.3(2+DHS)-0.475(6+2DHS) \qquad (2.1)$$

The calculated HLB values given in Table 2-1 show a negligible effect of hydroxyl content over the DHS range studied on the HLB value of the resultant EC, suggesting that the hydrophilicity of EC is mainly contributed from the ether linkage of the polymer backbone. The HLB values of the prepared EC are fairly constant. The molecular weights of EC1 to EC6 as determined by viscosity are also given in Table 2-1. EC1 was modified from EC2 based on literature method [30]. EC2 was purchased from Sigma-Aldrich.

Table 2-1. Properties of Ethylcellulose polymers in this study

Polymer	OH, wt%	DHS	HLB	MW, Da
EC1	1.51	2.79	7.83	45,000
EC2	4.48	2.40	7.89	45,000
EC3	6.55	2.14	7.93	143,000
EC4	10.57	1.70	8.00	143,000
EC5	14.23	1.33	8.05	143,000
EC6	5.38	2.29	7.91	177,000

Figure 2-2 shows FTIR spectra of the six EC polymers. The broad band at 3500 cm^{-1} is assigned to hydrogen-bonded OH stretching vibrations. The stretching vibration of ether linkage at the backbone appears at 1100 cm^{-1}. The bands at 2900 cm^{-1} and 1400 cm^{-1} are stretching vibration and deformation vibration of CH, respectively [27, 28]. Although OH content can be judged from FTIR spectra, accurate content was determined by elemental analysis.

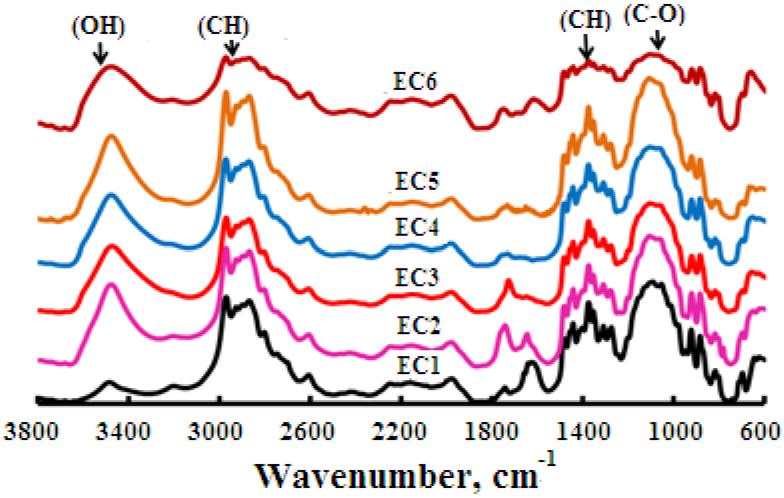


Figure 2-2. FTIR spectra of EC polymers.

To study the effect of molecular weight and hydroxyl content on the demulsification performance of EC, the water-in-diluted bitumen emulsions prepared with the plant process water at 5 wt% were demulsified using the synthesized ECs. The demulsification efficiency of was evaluated by measuring the water content and size of water droplets after settling at 80 ^{o}C for 1 h. A lower water content and larger water droplet size would represent a higher demulsification efficiency.

Figure 2-3 shows water content as a function of EC dosage for the six ECs in the range of 50–290 ppm. Although the HLB value of EC does not depend on the hydroxyl content, demulsification performance of EC was found to depend significantly on hydroxyl content. As shown in Figure 2-3, EC1 gives only a marginal effect on demulsification, whereas EC2 and EC3 were the most effective on a parts per million basis in demulsification. At polymer dosage about 100 ppm, EC2 and EC3 show a similar demulsification performance. As for EC4 and EC5, their demulsification performance is similar over the entire polymer dosage range covered in this study, falling between the two extremes on a parts per million basis. EC6 was slightly less effective than EC3, but more effective than EC4. At 300 ppm dosage, all ECs except EC1 exhibit a similar performance of demulsifying water-in-diluted bitumen emulsions. However, as shown in the inset of Figure 2-3, although EC1 is still the most ineffective, EC3 and 6 appear to be the most effective in water removal on a mole basis. This finding suggests that demulsification performance of EC demulsifiers depends on both hydroxyl content and molecular weight. This observation will be discussed later in detail.

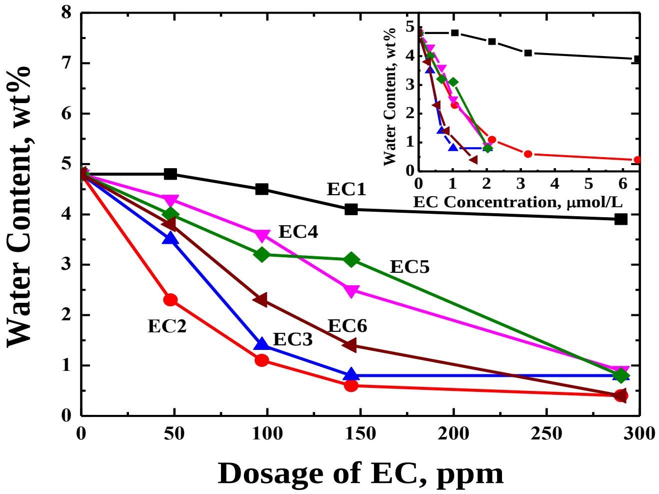


Figure 2-3. Water content at 2.5 cm from the top of the emulsion surface as a function of EC dosage for six EC polymers. Emulsions having 60 wt% naphtha-diluted bitumen and an initial 5 wt% plant process water were treated with EC and settled under gravity at 80 °C for 1 h.

For ECs of molecular weight of 143,000 Da, Figure 2-4a shows a general trend of increasing water removal efficiency with increasing DHS from 1.33 to 2.14, in particular at EC dosage of 145 ppm. The water removal efficiency is defined as the percent of water that settled out at 2.5 cm below the top surface of the original emulsion within 1 h. At higher EC dosages of 290 ppm, increasing DHS showed a negligible effect on water removal efficiency as, at the lowest DHS value of 1.33, the water removal efficiency was already high. Although increasing water removal efficiency with increasing DHS is anticipated as increasing DHS increases interfacial activities of EC due to decreased hydroxyl content of EC, one would expect the existence of an optimal DHS for water removal as excessive hydroxyl substitution of EC would make EC more soluble in oil and hence less effective in partition at the water-oil interface. To confirm this hypothesis, further increasing DHS to 2.79 was attempted with an EC of molecular weight of 45,000 Da. The results in Figure 2-4b indeed show a decrease in water removal efficiency from 55% to 5% at EC dosage of 48 ppm and from 90% to 18% at EC dosages of 145-200 ppm when DHS increased from 2.4 to 2.79. From the results in Figure 2-4, the optimal DHS appears to be around 2.4 (i.e., 4.5 wt% OH).

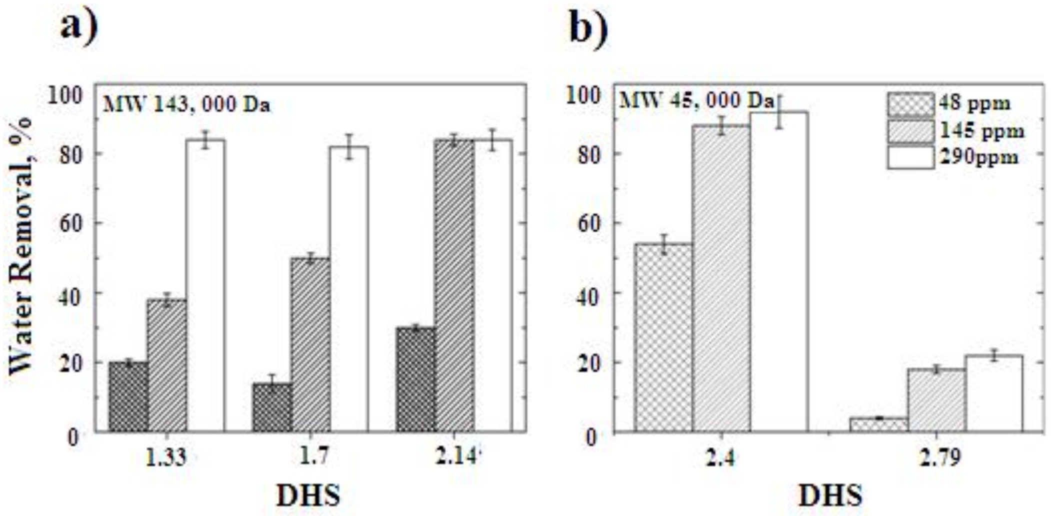
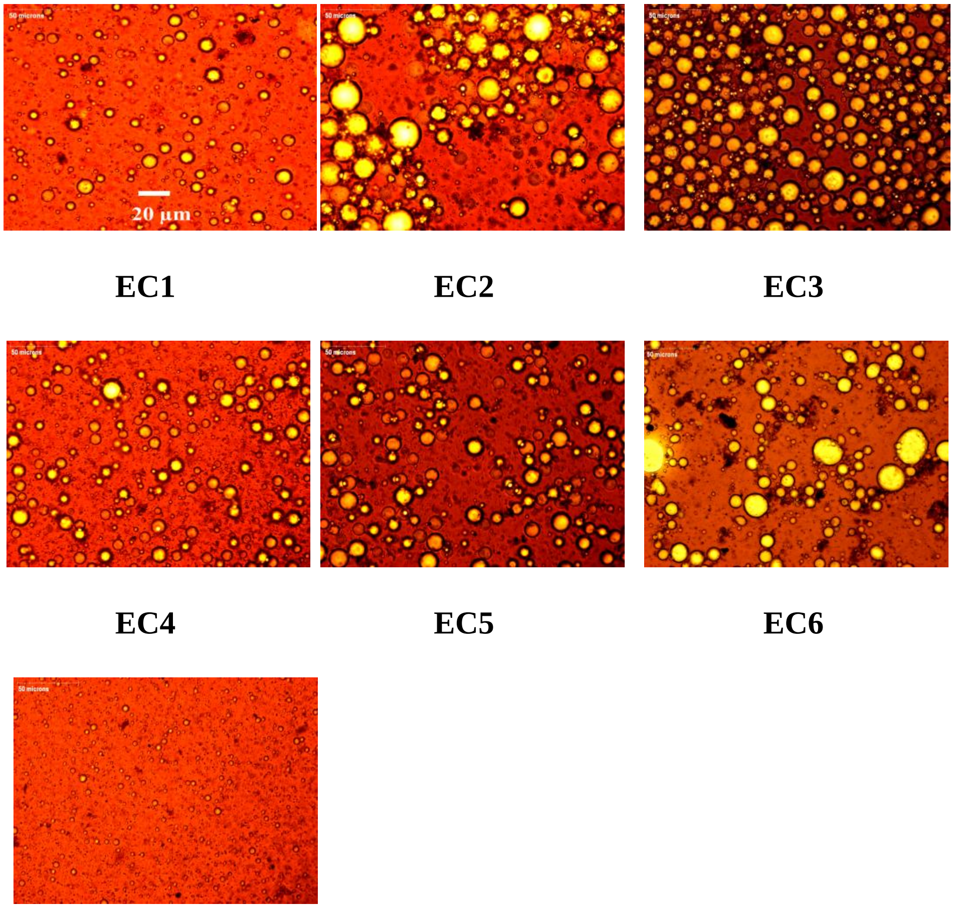


Figure 2-4. Water removal as a function of the degree of hydroxyl substitution at various EC dosages: (a) ECs of molecular weight 143,000 Da and (b) ECs of molecular weight 45,000 Da.

The micrographs in Figure 2-5 further revealed the demulsification mechanism of EC addition. Without demulsifier addition, water droplets are ~ 3 µm in size. In the presence of 145 ppm EC, the size of the water droplets becomes much larger. The average size of the water drops increases to about 10, 20-30, 15 and 20 µm for the emulsions treated with EC1, EC2 or EC3, EC4 or EC5, and EC6, respectively. The greatest increase in water drop size (~8-fold) in the emulsions treated with EC2 or EC3 corresponds well with the highest removal of water from the emulsions by EC2 and EC3, as shown in Figure 2-3. Increasing DHS from 1.33 for EC5 to 2.14 for EC3 is seen to increase the average water drop sizes from 15 to 30 µm, corresponding to an increase in water removal efficiency from 40% to 80% at 145 ppm dosage. Compared with blanks, the addition of 145 ppm EC1 only leads to a 3-fold increase in water drop size, which is the smallest among all six ECs, corresponding to the lowest water removal by EC1 of the highest DHS.

This is in great contrast to 145 ppm EC2 addition, which leads to the largest increase in average drop size and a water removal efficiency of 85%. It is also interesting to note the presence of small water droplets attaching to a large water droplets when EC was added, indicating effective flocculation, but incomplete coalescence of water droplets.



EC1 **EC2** **EC3**

EC4 **EC5** **EC6**

No Demulsifier

Figure 2-5. Micrographs of emulsions destabilized by six EC polymers at 145 ppm dosage. The emulsions for imaging were taken from the bottom of the test tubes after the emulsions of 5 wt% initial water content were allowed to settle under gravity for 1 h at 80 ^{o}C. All micrographs have the same magnification.

The molecular mechanism of demulsifying water-in-diluted bitumen emulsions by EC addition is further revealed by nanoscale AFM imaging of interfacial films. Figure 2-6 shows the morphology of LB films formed at the heptol-water interface with the addition of various ECs. The interfacial film was transferred to silicon substrate after formation of bitumen interfacial film at the heptol-water interface followed by diffusion of EC through the heptol top phase to the interface. In the absence of EC, bitumen forms a continuous, close-packed interfacial film. The addition of EC is seen to partially break bitumen interfacial films, forming a few microdomains of similar nanostructures but of much greater film thickness. At the same EC dosage, EC2 is found to be the most effective and EC1 the least effective in breaking bitumen interfacial films. For a given molecular weight of ECs, EC3 of higher DHS is found to be more effective in breaking interfacial bitumen films than EC4 and EC5 of smaller DHS. The AFM images of bitumen films prepared with the addition of EC3 and EC6, which are of similar DHS and molecular weight, show similar morphology as anticipated. The critical role of hydroxyl substitution in EC in demulsification of water-in-diluted bitumen emulsions is clearly seen to effectively disrupt interfacial films with an appropriate balance of hydroxyl groups with ethyl groups in ethyl celluloses. Excessive substitution of hydroxyl groups as in EC1 (DHS=2.79) is undesirable, as it makes EC less effective in breaking interfacial films. It is interesting to note that the effectiveness of breaking interfacial bitumen films by EC correlates well with the corresponding dewatering efficiency as shown in Figure 2-3. It is due to the breakup of bitumen interfacial film that allows water droplets to coalesce, thereby resulting in effective demulsification of water-in-diluted bitumen emulsions.

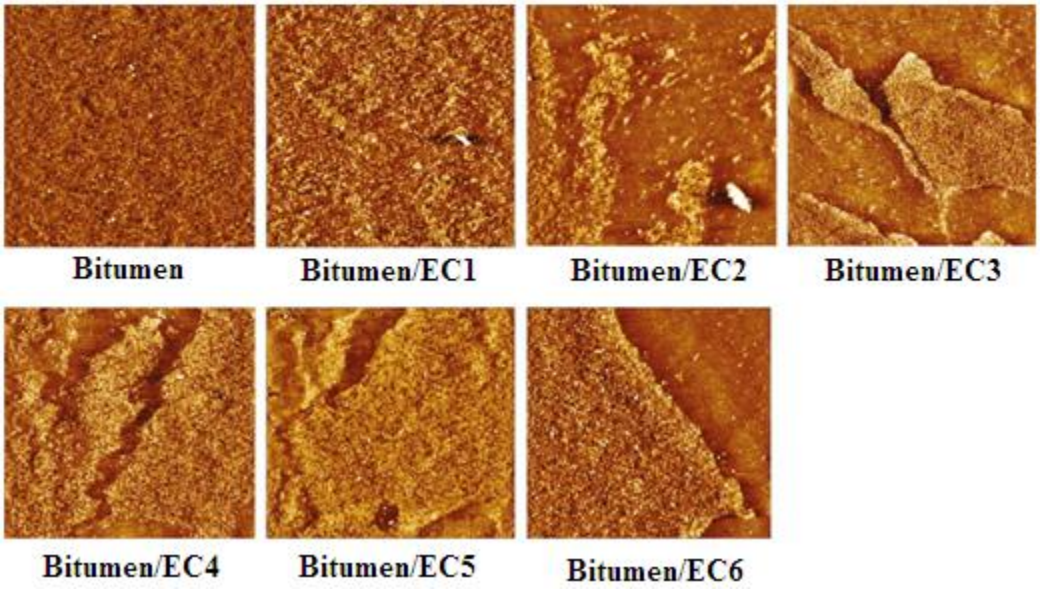


Figure 2-6. AFM images of bitumen and bitumen/EC LB interfacial film transferred from the heptol-water interface at 2 mN/m interfacial pressure. The film was prepared by dispersing 40 μL of 0.1 mg/ml EC through the heptol top phase to the interface in which a film was already formed by 20 μl of 1mg/ml bitumen. The scale of the images is 5 μm × 5 μm.

It is important to note that the molecular weight of the six EC demulsifiers varies over a wide range. The molecular weight of conventional polymeric demulsifiers is usually in the range of 2,000–50,000 Da [20], in most cases being less than 10,000 Da [8, 31, 32]. Since EC was synthesized from cellulose, the molecular weight of EC depends on the molecular weight of available cellulose. In this study, we were unable to obtain cellulose of lower molecular weight. To examine the effect of molecular weight on demulsification, it is desired to use molar concentration instead of mass concentration for comparison. As seen in the inset in Figure 2-3, EC3 and EC6 have a high but similar molecular weight and similar hydroxyl content show the best demulsification performance. EC4, EC5, and EC2 possess quite similar performance, although EC4 and EC5 have a much higher molecular weight and higher hydroxyl content than EC2. EC1 has the lowest hydroxyl content and lowest molecular weight in the six EC demulsifiers. It appears that, over the molecular weight range of 4×10^4 to 1.8×10^5 Da, higher molecular weight EC on a molar basis exhibits a better demulsification efficiency. The adverse effect of high hydroxyl content for EC4 and EC5 was offset by their high molecular weight effect, which eventually leads to similar demulsification efficiency of EC4 and EC5 as EC2. Usually, low-molecular-weight polymeric demulsifiers possess high interfacial activity and adsorb irreversibly at the water-oil interface, causing film rupture and coalescence of water droplets [33]. High-molecular-weight polymeric demulsifiers are more effective in flocculating water droplets, thereby destabilizing emulsions [32]. From flocculation point of view, high-molecular weight is beneficial to bridging flocculation. For example, to successfully flocculate polystyrene latex particles in water, poly(ethylene oxide) flocculants must have at least a molecular weight of 10^6 Da [34]. However, for demulsifying water-in-diluted bitumen emulsions by coalescence, polymer chains of excessively large molecular weight may be more difficult to diffuse or may even lead to steric stabilization, preventing water droplets from coalescing. In the molecular weight range used for this study, such effect was not observed.

To understand the effect of hydroxyl content and molecular weight of an EC on its interfacial activity and hence its demulsification efficiency, the interfacial tension of diluted bitumen-water interface was measured as a function of EC concentration for the six EC polymers. As shown in Figure 2-7, all six EC polymers are effective in decreasing interfacial tension, although to different extent. Among the six EC polymers on a part per million basis, EC2 is the most effective in reducing the interfacial tension, corresponding to the most efficient removal of emulsified water (Figure 2-3). In contrast, EC1 is the least effective lowering the interfacial tension, corresponding to the least effective in demulsification. However, on a molar basis as shown in the inset of Figure 2-7, ECs of higher molecular weight (EC3 through EC6) are found to be more effective in reducing interfacial tensions, as anticipated. This finding agrees with the demulsification results shown in the inset of Figure 2-3. From a molecular point of view, EC demulsifiers of a higher molecular weight would occupy more interfacial area per molecule, resulting in a lower interfacial tension. However, the ability of EC polymers to decrease interfacial tension could not be simply correlated to their demulsification performance. The absence of correlation between demulsification performance and interfacial tension is shown in Figure 2-8. For a given EC, higher dewatering performance clearly corresponds to lower interfacial tension. However at the same interfacial tension, the dewatering performance of the polymers is very different, depending on both molecular weight and DHS. For example, EC3 and EC4 have the same molecular weight and nearly the same interfacial activity, but their demulsification efficiency is quite different. The difference in demulsification performance between EC3 and EC4 is attributed to their hydroxyl content, which controls molecular conformation and hence its ability of flocculation. It is well-known that intra- and intermolecular hydrogen-bonding interactions prevail for cellulose molecules. Substitution of hydroxyl groups by oxyethyl would break up these hydrogen-bonding interactions and increase its solubility in the organic solvent and flexibility of cellulose molecules. It is expected that ECs of a higher hydroxyl content would lead to stronger intra- and intermolecular interactions, which decreases its ability of bridging flocculation. Therefore, controlling the hydroxyl content of ECs is of critical importance in demulsification of water-in-diluted bitumen emulsions.

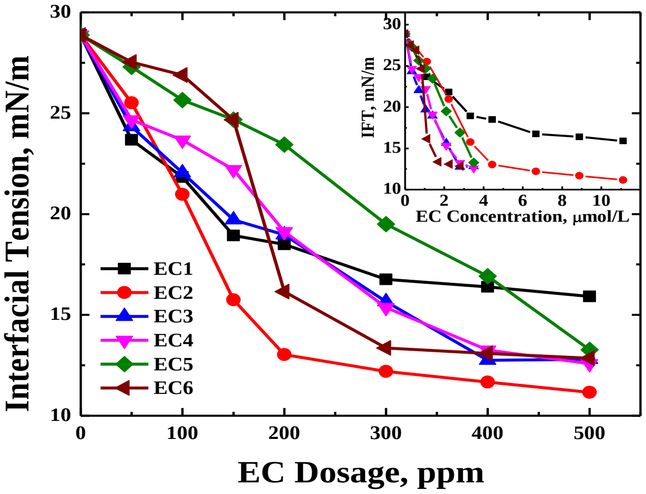


Figure 2-7. Interfacial tension of naphtha-water in the presence of 60 wt% bitumen as a function of EC concentration for six EC polymers at 20 °C.

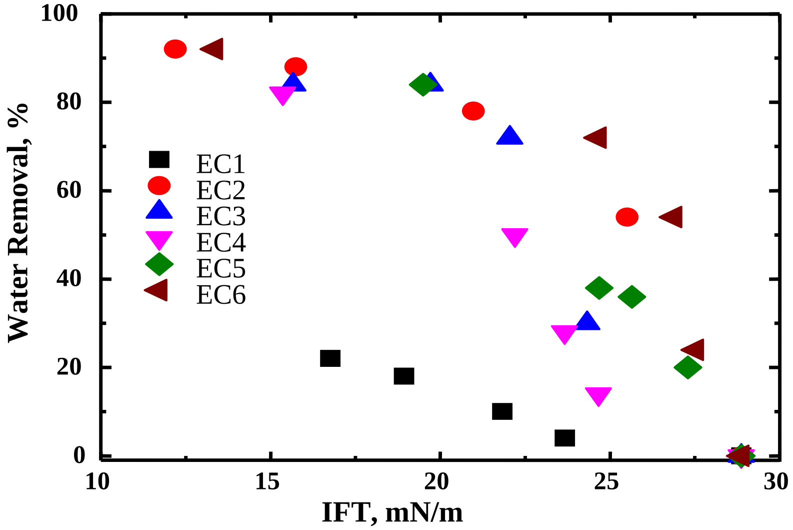


Figure 2-8. Water removal as a function of interfacial tension between naphtha and water in the presence of 60 wt% bitumen for six EC polymers at 20 °C.

The effect of hydroxyl content and molecular weight on demulsification of water-in-diluted bitumen emulsions is schematically shown in Figure 2-9. ECs of high hydroxyl group densities tend to self associate in the organic phase or at the water-oil interface, leading to formation of EC molecular domains and hence steric stabilization and exhibiting poor flocculation and demulsification. ECs of intermediate hydroxyl content and higher molecular weight are more effective for flocculating water droplets, promoting droplets coalescence, and breaking water-in-diluted bitumen emulsions.

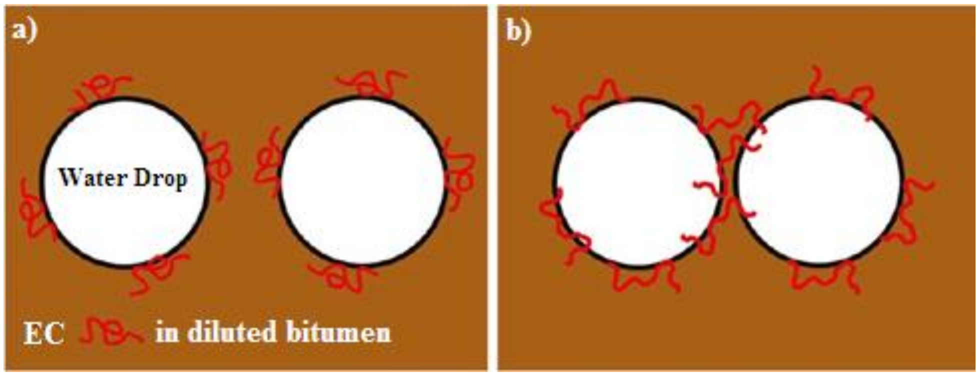


Figure 2-9. Schematic representation of the effect of hydroxyl content and molecular weight on demulsification of water-in-diluted bitumen emulsions: (a) EC with lower molecular weight and/or high hydroxyl content, causing the EC molecules to self-coil due to intra-hydrogen bonding, and (b) EC with intermediate (optimal) hydroxyl content and/or high molecular weight, leading to optimal surface activity and flexible chains of EC molecules for effective flocculation and subsequent coalescence.

2.4 Conclusion

The performance of EC for demulsification of water-in-diluted bitumen emulsions depends on its hydroxyl content, which controls intra- and intermolecular hydrogen bonding and hence conformation of EC at water-oil interfaces. An EC with 4.5 wt% hydroxyl content of higher molecular weight is the most effective in demulsification, removing 90% of the water from the emulsions by gravity settling for 1 h at 80 ^{o}C at optimal dosage. Effective demulsification of water-in-diluted bitumen emulsions by EC relies on its interfacial activity and ability of flocculation. From the practical point of view, ECs of intermediate molecular weights, such as EC2 and EC3, appear to be the most economical as they lead to more effective dewatering at the lowest parts per million dosages, as shown in Figure 2-3, although scientifically the ECs of higher molecular weight are more desirable, as shown in the inset of Figure 2-3.

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Chapter 3

Effect of Mixing and Temperature on Demulsification of Water-in-Diluted Bitumen Emulsions by Ethylcellulose

3.1 Introduction

It has been recognized that water-in-oil (w/o) emulsions are stabilized by a protective interfacial film formed on the surface of the dispersed water droplets [1, 2]. The water droplets cannot coalesce to become sufficiently large in size to settle from the continuous oil phase. The species attributed to the formation of the protective interfacial film are the surface-active materials in crude oils and bitumen, mainly asphaltenes [3] and fine solids [4]. Chemical demulsification is the most commonly approach used to destabilize a w/o emulsion through the alteration of the interfacially active materials and/or rupture of the interfacial film [2, 5]. Since the stability of emulsions depends on a number of factors, such as the type and concentration of solids contained in the crude oil, operating temperature of the system, pH value of the aqueous phase, the size and size distribution of the water droplets [6-9], and the application of demulsifiers [1, 10-13], the operating parameters are usually finely tuned to achieve the best demulsification peromance by a demulsifier.

Temperature is an important factor affecting the stability of emulsions. An increase in temperature reduces the viscosity of oil, increases the mobility of water droplets in the oil phase and amplifies the difference in the density of the fluids, which accelerates the settling of water droplets [14]. It was reported that the thermal treatment weakened or ruptured the interfacial film between water droplets and oil by expanding the volume of water present [15]. Binks et al. [16] investigated the effect of temperature on the stability of wax stabilized w/o emulsions. They observed a more effective water separation from the oil phase at higher temperatures. Microscopy images clearly showed that the resultant water droplets were larger in size at higher temperature than at low temperature. Long et al. [17] observed an accelerated settling rate of emulsified water droplets when they prepared the emulsion at higher mixing temperature. Similar result was also obtained by Gingras et al. [18]. They studied effect of the processing parameters on the stability of water-in-bitumen emulsions, and found that the resultant water droplet was larger in size when the emulsions were prepared at high temperature. On the other hand, they claimed that the droplet size decreased linearly on log-log plot with increasing in mixing speed.

Agitation also has a significant effect on the stability of an emulsion. A mild agitation is beneficial in promoting coalescence, while an excessive agitation would cause the breakage of the flocculated droplets and result in a decrease in droplet size. For this reason, re-emulsification may occur if an emulsion is severely agitated [14]. Owen et al. [19] used a “shear vessel”, developed by Farrow et al.

[20], to study the effectiveness of high molecular weight polyacrylamides in flocculating mineral slurries. They found that the size of the aggregates in the mineral aqueous slurries was reduced under intensive mixing. Serra et al. [21] studied the aggregation and breakage of the particles in a Couette flow system, and found that the model was adjusted by two parameters: the probability of successful collisions and the breakup of the aggregates. They claimed that a higher shear rate led to the formation of smaller size aggregates. Sengupta et al. [22] concluded that the high agitation speed reduced mean floc size and narrowed the size distribution of flocculated kaolinite suspension.

Emulsions can be destabilized by application of demulsifiers. The structure and dosage of demulsifiers determine the performance of demulsification [12, 17, 23-25]. Pena et al. [5] studied the effect of alkylphenol polyalkoxylated resins and cross-linked polyurethanes on the demulsification of brine-in-crude oil emulsions. They found that phenolic resins promoted coalescence of droplets, while polyurethanes promoted flocculation of the droplets but prevented droplet coalescence if overdosed. Mohammed et al. [26] conducted an experiment to determine the demulsification performance of w/o emulsions by a commericial demulsifier, and found that the best demulsification efficiency was achieved with the addition of 800 ppm of the demulsifier.

Previous studies [27, 28] showed that a cellulose derivative polymer, ethylcellulose

(EC) was effective in demulsification, and the demulsification performance of EC depends on its hydroxyl content and molecular weight. In this chapter, the effect of temperature and agitation on demulsification efficiency of water-in-diluted bitumen emulsions by EC demulsifiers of various molecular weights is studied. The objective is to determine the optimal condition of demulsification by EC.

3.2 Experimental

3.2.1 Materials. Vacuum distillation feed bitumen and industrial grade naphtha were provided by Syncrude Canada Ltd. Heavy naphtha from Champion Technologies Ltd was used to make various EC solutions for the focused beam reflectance measurements and demulsification tests. Milli-Q water with a resistivity of 18.2 MQ·cm^{-1} was used throughout the study. The water was prepared with an Elix 5 system followed by a purification process with a Millipore-UV plus system.

Three EC samples, EC-b, EC-c, and EC-d with an ethoxyl content of 48% were purchased from Sigma-Aldrich and used as received. EC-b was further modified by following the procedure that described elsewhere [29] to obtain EC-a. The molecular weight (MW) of EC polymers was determined by applying a viscosity method. Prior to MW measurement, EC samples were dissolved in 1,4-dioxane. The intrinsic viscosity of ECs, η, was determined at room temperature using an Ubbelohde capillary viscometer (Cannon Instrument, PA). Molecular weight of an

EC sample was calculated using equation 3.1:

$$MW = 300\eta(162+28DS) \qquad (3.1)$$

where DS is the degree of ethoxylation per glucose. The detailed procedure for determining a polymer’s molecular weight was described elsewhere [27]. The molecular weights of the four EC polymers are listed in Table 3-1.

Table 3-1. Molecular weight of EC demulsifiers used in this work.

EC sample	EC-a	EC-b	EC-c	EC-d
Molecular weight, kDa	18	45	100	177

3.2.2 Experiment

3.2.2.1 Demulsification Test. The emulsions were prepared by intensively mixing 42 g of 60% naphtha-diluted bitumen with 2.2 g of Milli-Q water using a homogenizer (PowerGen homogenizer, 125 W) running at 30,000 rpm for 3 min. The emulsions made as such contain 5 wt% water. Various amounts of EC-in-heavy naphtha solutions were mildly blended into the emulsions. Water content of the emulsions was determined using a Karl Fisher Titrator after the samples had been settled for a desired period. The detailed emulsion preparation and water content measurement procedures could be found in section 2.2.2.3. The experiment was repeated at various temperatures. The dewatering efficiency of demulsifiers was calculated using the following equation:

$$Demulsification\ Efficiency, \% = \frac{\mathrm{Ci} - \mathrm{C}}{\mathrm{Ci}} \times 100\% \qquad (3.2)$$

where Ci is the water content of the emulsion without demulsifier addition, and C is the water content of the emulsion with demulsifier addition.

3.2.2.2 Focused Beam Reflectance Measurements (FBRM). To evaluate the effect of mixing on demulsification performance by EC samples of various molecular weights, the dynamic change in water droplet size distribution was tracked using an FBRM (Model S400A, Mettler Toleclo, USA). An agitation speed between 300 rpm and 460 rpm was found to be appropriate, and an agitation speed of 400 rpm was used throughout the study. The emulsion was prepared by following the same procedure as described in 3.2.2.1. The sample was stirred at a constant speed of 400 rpm. To prevent evaporation, a piece of aluminum foil was used to cover the surface of the emulsion. Once the emulsion reached 80 ^{o}C, 300 ppm of EC-in-heavy naphtha solution was added into the emulsion. The change in the size of water droplets was monitored by FBRM, which consists of an illumination device and a computer-controlled probe. As the probe scanned a water droplet, the signal of reflected beam was collected and the length of the droplet was recorded simultaneously. The change in size of water droplets as a function of time after demulsifier addition was visualized under an optical microscope (Carl Zeiss Axioskop 40 Pol), which was equipped with a computer-controlled video camera. A micropipette was used to take samples for water droplets size analysis.

3.3 Results and Discussion

3.3.1. The Influence of Operating Temperature in Demulsification Performance by EC. Figure 3-1 shows the demulsification efficiency as a function of time for the three ECs at the same dosage of 650 ppm and at room temperature. It required 55, 120 and 300 min for EC-a, EC-c and EC-b to reach a 90% demulsification efficiency, respectively. This finding suggests that EC-a was a better choice for demulsification at room temperature. A lower molecular weight polymer usually exhibits higher diffusivity [16]. For this reason, EC-a of the lowest molecular weight among the three, diffused fastest to the interface, leading to coalescence of water droplets. Surprisingly, EC-c of a higher molecular weight exhibits a better demulsification efficiency than EC-b. In general, high molecular weight demulsifiers are more effective in water separation by bridging flocculation [5]. The longer chain length of EC-c was an advantage for more effectively flocculating water droplets through bridging than EC-b. For this reason, the addition of EC-c led to a faster demulsification process than EC-b at room temperature. The further effect of temperature on the demulsification performance by ECs is illustrated in Figure 3-2.

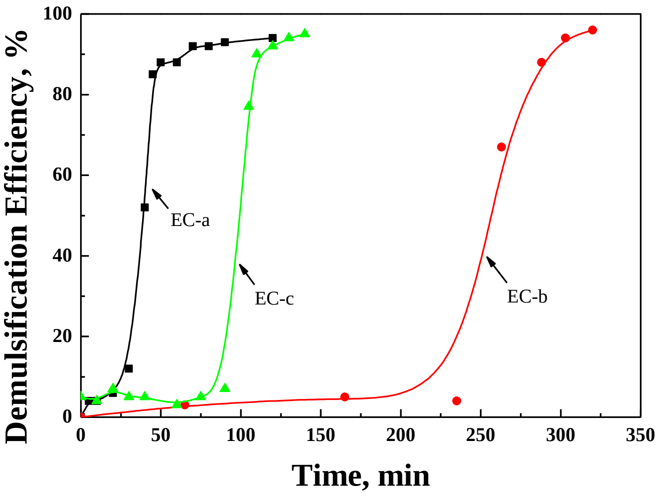
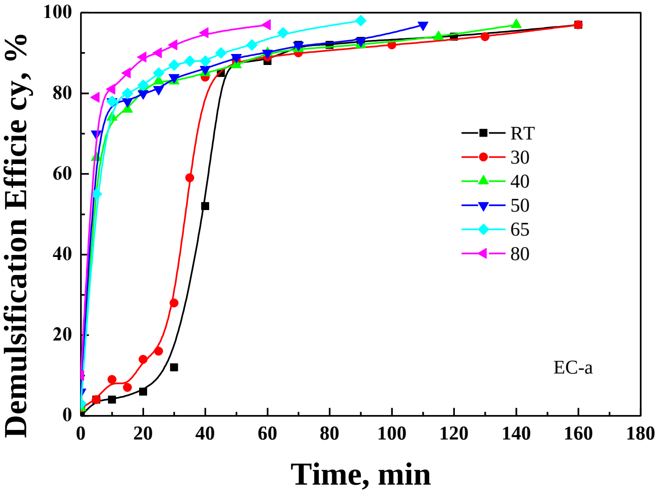


Figure 3-1. Dewatering efficiency of 650 ppm EC-a, EC-b and EC–c as a function of settling time for breaking 5 wt% water-in-diluted bitumen emulsions at room temperature. The testing samples were taken at 2.5 cm from the top of the emulsion surface.



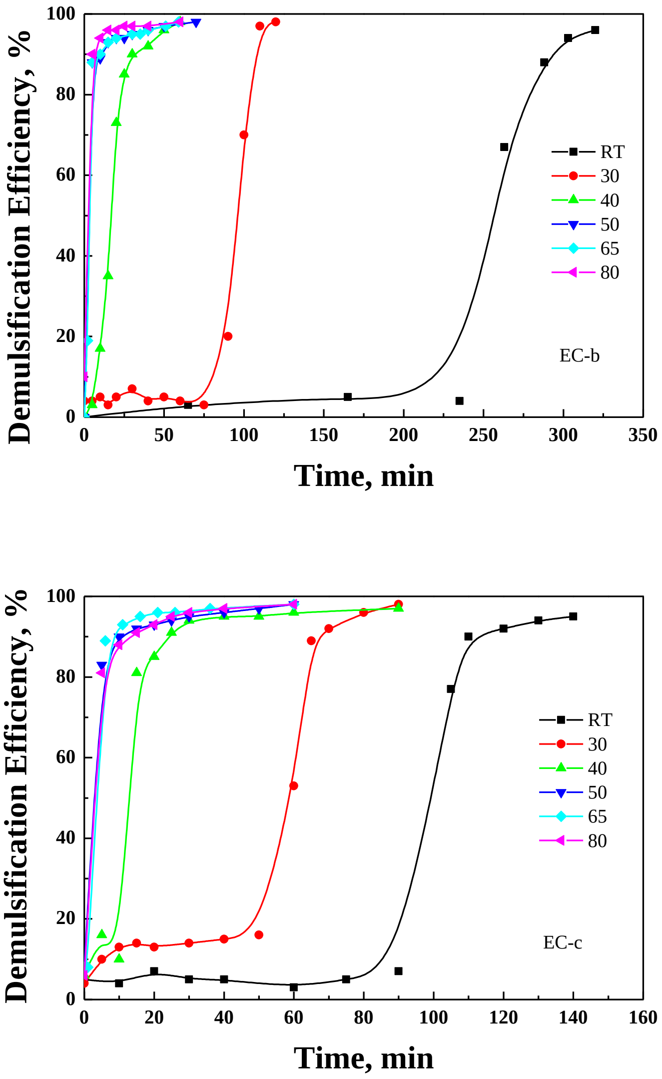


Figure 3-2. Demulsification efficiency of 650 ppm EC-a, EC-b and EC-c as a function of time at various temperatures.

The viscosity of bitumen decreases with increasing temperature. A lower viscosity of bitumen allows EC molecules to more quickly reach the water-oil interface, accelerating the dewatering process. For this reason, demulsification proceeded faster at higher temperatures for all three ECs as shown in Figure 3-2. An increase in temperature from room temperature to 30 °C significantly increased the demulsification efficiency for EC-b and EC-c, but had a negligible impact on the dewatering performance of EC-a. EC-a of a low molecular weight already diffuses very fast at room temperature. Hence, the diffusivity of EC-a was not affected too much by a slight temperature increase. An elevation in temperature accelerated diffusion of EC-b and -c to the surface of the water droplets, leading to a faster demulsification performance. As a result, the time required to achieve 90% demulsificaiton efficiency was shortened from about 300 min to 120 min for EC-b and 120 min to 70 min for EC-c with an increase in temperature from room temperature to 30 °C. Therefore, the effect of temperature on dewatering from diluted bitumen emulsions was in a decreasing order of EC-b > EC-c > EC-a in the temperature range from room temperature to 30 °C. A further increase in temperature to 40 °C accelerated demulsification performance for all ECs. When temperature was increased to above 50 °C, the weak point of slow diffusivity of EC-b and –c counterbalanced the inefficient flocculation due to short molecular chains of EC-a. Therefore, the influence of temperature on dewatering became less significant at high temperatures.

To more clearly demonstrate the effect of temperature on the demulsification performance by EC-a, -b and -c, the time required to achieve 90% demulsification efficiency at various temperatures is shown in Figure 3-3. As expected, an increase in temperature did not shorten the time required for EC-a greatly, as its diffusivity was already high at room temperature. As stated before, below 40 °C, the diffusion of EC-b and EC-c increased with increasing temperature. Hence, the time required for EC-b and EC-c to achieve 90% demulsification efficiency became much shorter with increasing temperature. When temperature was increased to above 50 °C, the influence of temperature on diffusivity became less significant and the time required for achieve 90% demulsification efficiency showed little dependence on temperature.

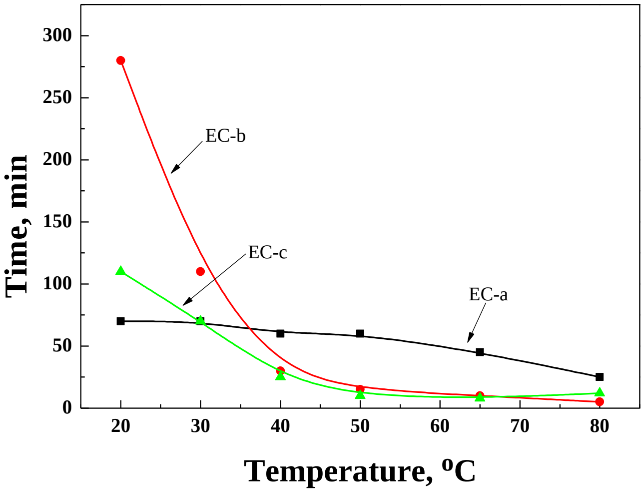


Figure 3-3. The time required to achieve 90% demulsification efficiency as a function of temperatures for demulsifiers EC-a, EC-b and EC-c.

3.3.2. Effect of Mixing on Demulsification. Up to this point of study, EC of higher molecular weight seems to be more effective in dewatering at high temperature by flocculation of water droplets with its longer molecular chains. Further demulsification tests were performed by adding EC-a, EC-b, EC-c and EC-d-in-heavy naphtha solution to emulsions that contain 5 wt% water. The resultant system was allowed to settle at 80 ^{o}C for 1 h prior to water content measurements. The molecular weights of the EC polymers are in the order of EC-a < EC-b < EC-c < EC-d (Table 3-1). The demulsification efficiency as a function of polymer dosage is shown in Figure 3-4. For all polymers, the demulsification efficiency increased with an increase in polymer dosage. In the dosage range of 0−300 ppm used in this work, an optimal dosage was not observed for any of the polymers. At any specific dosage, EC-d of the highest molecular weight was surprisingly not the most effective demulsifier, rather a demulsification efficiency order of EC-c > EC-b > EC-d > EC-a was observed. In contrast to the conclusion obtained in previous section, EC-d with very long polymer chains can only exhibit limited diffusivity, resulting in a less effective demulsification process than EC-c and EC-b, although it has the highest molecular weight. The low demulsification efficiency of EC-a was due to its short molecular chains, which were ineffective in bridging nearby water droplets, leading to a low flocculation ability. Therefore, at an appropriate dosage, EC of an intermediate molecular weight possesses both good diffusivity and good ability of flocculation, which leads to the best dewatering performance. Results in Figure 3-4 indicate that EC-c of a molecular weight of 100 kDa is the most effective in demulsification.

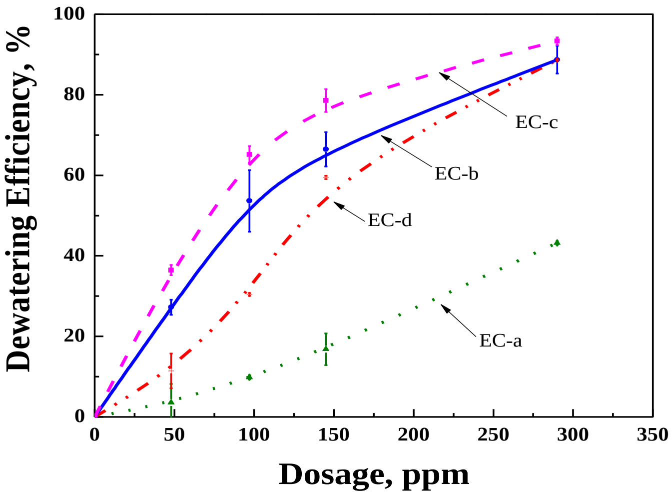


Figure 3-4. Demulsificaiton efficiency as a function of dosage of EC-a, EC-b, EC-c and EC-d. The water content was determined after the emulsions had been settled at 80 ^{o}C for 1 h. The error bars represent the average of at least four measurements.

In a stationary bottle test, the benefit of higher ability of flocculation by high molecular weight EC was offset by its low diffusivity in emulsions. Figure 3-5 illustrates the change in size of water droplets in water-in-diluted bitumen emulsions with EC addition under continuous stirring. In the absence of EC addition, the water droplets were well dispersed and stable in the diluted bitumen phase with a diameter about 2 μm. The addition of EC demulsifiers led to flocculation and/or coalescence of water droplets to a larger droplet size, corresponding to a shift to a longer chord length. It can be seen that the application of EC-c led to a large amount of larger size of water droplets or water droplet clusters. This result agrees with the finding from Figure 3-4, i.e., EC-c is the most effective demulsifier in all EC demulsifiers tested at 80 ^{o}C. As shown in Figure 3-5, the addition of EC-d resulted in an approximately equivalent amount of water droplet clusters with a size larger than 20 μm as EC-b, but led to much more water droplet flocs and/or clusters with a size less than 20 μm. This result may be due to the continuous agitation during demulsification. The effectiveness of any demulsifier is directly dependent its effectiveness of making contact with the emulsion. The agitation enhances contact by improved convection and distribution of EC-d to the surface of the water droplets. As a result, EC-d with longer chains could more effectively flocculate water droplets than EC-b under continuous stirring. The agitation also increased the chance for water droplet flocculation, and hence, the addition of EC-a led to a similar number of counts of enlarged water droplets as the addition of EC-b and EC-d.

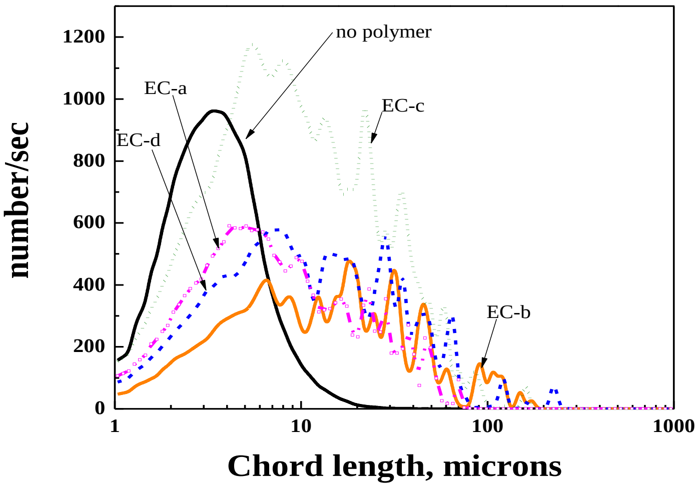


Figure 3-5. Unweighted chord length distribution of water droplets in the absence

and presence of 300 ppm EC demulsifiers. The system was continuously stirred at 400 rpm and 80 ^{o}C before and after demulsifier addition.

The micrographs of emulsions with EC addition are shown in Figure 3-6. Demulsifiers of a higher molecular weight, e.g., EC-b, EC-c and EC-d, were effective in flocculating water droplets. The lower molecular weight demulsifier EC-a showed limited ability for flocculating water droplets, but it had strong ability for coalescing water droplets as the size of water droplets with EC-a addition was the largest.

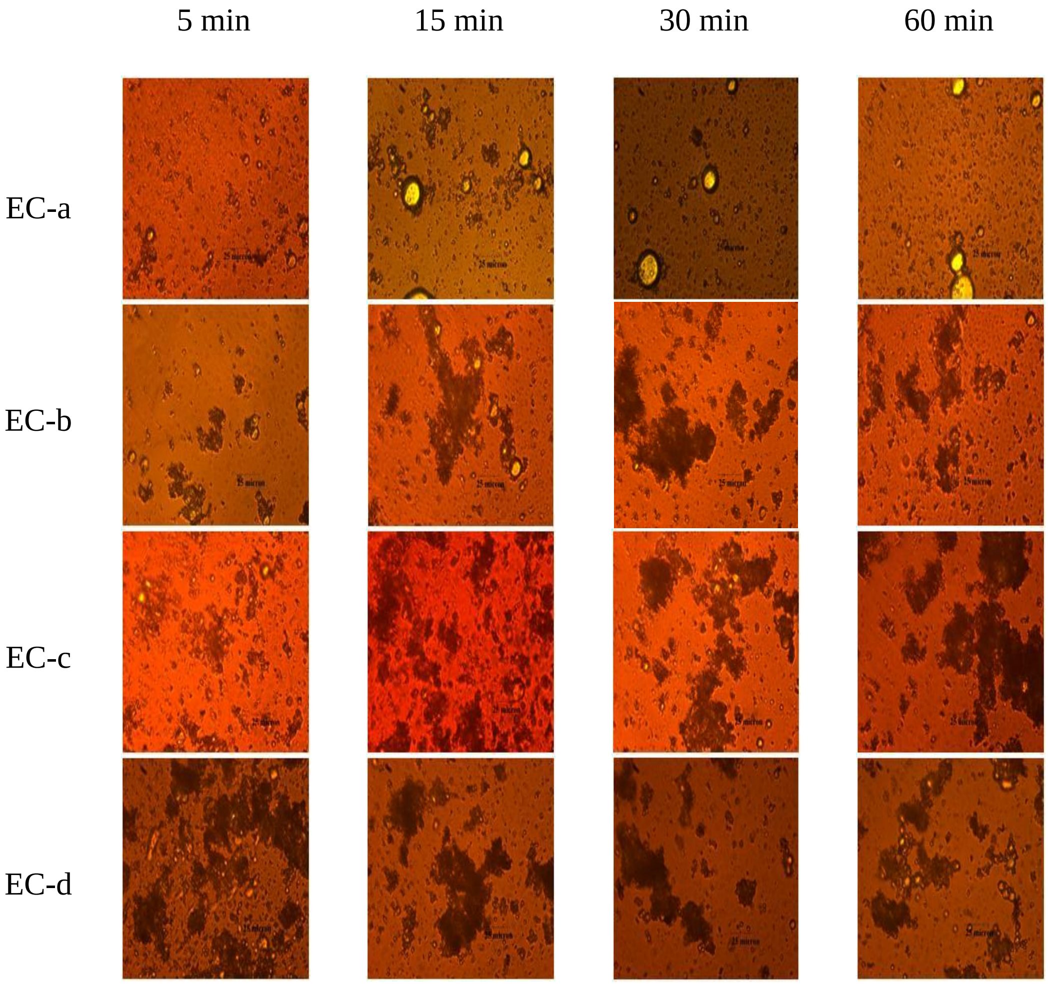


Figure 3-6. Microscopic images of emulsions after treatment with 300 ppm EC-a,

EC-b, EC-c and EC-d for 5 to 60 min. The system was agitated at 400 rpm and 80 ^{o}C.

It is also interesting to note that, within the first 5 min, there were many big clusters of water droplets with the addition of EC-d, but the clusters seem to break-up by continuous stirring to the system. In contrast, the size of water droplet clusters grew with the addition of EC-c as the application of continuous stir. As discussed in Chapter 2, large steric force could be generated between clusters as a result of more high molecular demulsifers with excessively long chains had been brought to the interface, which would prevent small clusters from being re-flocculated into a bigger one. For this reason, the size of water droplet clusters became smaller with the addition of EC-d under continuous stir.

3.4 Conclusions

A lower molecular weight EC exhibited better diffusivity than a high molecular weight EC. An increase in temperature accelerated the diffusion process of demulsifiers, which improved demulsification performance. At low temperature, a low molecular weight EC with high surface activity should be chosen for demulsification of water-in-diluted bitumen emulsions. On the other hand, EC of an intermediate molecular weight, 100 kDa in this case, should be used to achieve the best flocculation at high temperature. Agitation enhanced the demulsification efficiency of a low molecular weight polymer by increasing the collision rate of the water droplets. Greater flocculation and coalescence of water droplets were observed upon collision, which led to more effective demulsification. Under continuous stirring, higher molecular weight polymers were more effectively brought to the water-oil interface, enhancing flocculation of the water droplets, whereas low molecular weight polymers were more effective in coalescing water droplets due to better contact of water droplets resulting from agitation. Both increase in temperature and the application of mild agitation can accelerate demulsification of w/o emulsions.

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Chapter 4

Understanding Interfacial Behaviour of Ethylcellulose at Water-Diluted Bitumen Interface*

4.1 Introduction

There are two common types of emulsions: oil-in-water (o/w) emulsions in which oil droplets are dispersed in water and water-in-oil (w/o) emulsions in which water droplets are dispersed in a continuous oil phase. Emulsions encountered in the petroleum industry are predominately w/o emulsions [1, 2]. Since water is emulsified by asphaltenes and other naturally interfacial active materials in the petroleum oil, the w/o emulsions encountered in petroleum industry are extremely stable [2-6]. These emulsions must be destabilized to remove water and associated chloride ions， which often cause corrosion of the downstream upgrading equipment [3, 4, 7-10].

Although many techniques, such as centrifugation, sonication, high-voltage electrostatic treatment and chemical demulsification have been used to break w/o emulsions [3, 11, 12], chemical demulsification has been proven to be the most efficient and cost effective method [3, 13, 14]. It is generally accepted that demulsifiers are able to adsorb at the water-oil interface and to cause rupture of interfacial films, resulting in coalescence of water droplets and hence more effective separation of emulsified water from the oil phase.

In water-in-crude oil and water-in-diluted bitumen emulsions, asphaltenes are known to adsorb irreversibly at the water-oil interface [7, 15]. Demulsifiers are

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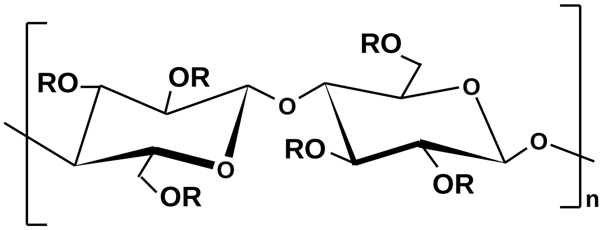
required to interact with the asphaltene molecules adsorbed at water-oil interface to cause destabilization of the emulsions. Applying Langmuir trough technique, a number of researchers have shown that in the presence of demulsifiers, asphaltene and bitumen interfacial films become more compressible [3, 5, 6, 16]. The observed increase in compressibility suggests the reduced rigidity of the interfacial film. A less rigid interfacial film would facilitate the coalescence of water droplets upon collision with each other. The interaction of demulsifiers with interfacially active molecules has been determined by atomic force microscopy (AFM) imaging. Follotec et al. [6] studied demulsification of water-in-crude oil emulsions using poly(ethylene oxide)-poly(dimethyl siloxane)-poly(ethylene oxide) triblock copolymers as demulsifiers. From AFM imaging of the Langmuir-Blodgett films, asphaltene aggregates were observed to be pushed to form larger aggregates occupying much less interfacial area in the presence of demulsifiers. This indicated the addition of demulsifiers broke down the organized network of asphaltene molecules in the film. The presence of demulsifiers could also reduce the viscosity of the interfacial film. Mohammed et al. [17] studied the interfacial rheology of a water-crude oil interface. They found that the viscosity of an aged film decreased by an order of magnitude with the addition of an amine-based ethylene oxide polymeric demulsifier.

Recently, a cost-effective and environmentally friendly natural polymer-ethylcellulose (EC) was found to be an effective demulsifier for breaking water-in-diluted bitumen emulsions [4, 8, 18]. At an optimal dosage, EC addition can remove 90% of water from the emulsions. From AFM imaging of interfacial films transferred to a silicon substrate by Langmuir-Blodgett (LB) method and in-situ visualization of the demulsification via micropipette technique, EC was shown to break water-in-diluted bitumen emulsions by disrupting the original interfacial materials and promoting coalescence of water droplets after flocculation [4, 8]. Wang et al. [19] used the quartz crystal microbalance with dissipation (QCM-D) to determine the adsorption of EC on silica or alumina, which already has a thin layer of asphaltene contaminant. The authors confirmed the possible use of EC to modify the wettability of hydrocarbon-contaminated inorganic solids (clays) to improve heavy oil processing. This communication focuses on the study of the behavior of EC at the water-oil interface using Langmuir trough technique, and properties of interfacial films through polarization modulation infrared reflection absorption spectroscopy (PMIRAS), film thickness and contact angle measurements. This work enables us to achieve a better understanding of demulsification mechanisms by EC. The molecular structure of EC is shown in Figure 4-1.



R = H or CH_2CH_3

4-1. Molecular structure of ethylcellulose

4.2 Experimental

4.2.1 Materials. Vacuum distillation feed bitumen with approximately 1 wt% fine solids was provided by Syncrude Canada Ltd. In this study, fine solids contained in the bitumen were not removed when used to prepare bitumen-in-toluene solutions. ACS grade acetone, and optima grade toluene and n-heptane were purchased from Fisher Scientific. EC from Sigma-Aldrich with an ethoxyl content of 48% was used as received. Asphaltenes used in this study were obtained by precipitation at a 40:1 heptane to bitumen volume ratio, following the procedures reported elsewhere [3]. The solids in bitumen were removed by ultracentrifugation of toluene-diluted bitumen prior to asphaltene precipitation. The amount of asphaltenes precipitated out as such was found to be about 10–11 wt% in bitumen. Milli-Q water prepared with an Elix 5 system followed by a purification process was used as the subphase in the LB interfacial film experiment.

To improve the sensitivity of analysis on interfacial materials using PMIRAS, plain beveled glass slides with a dimension of 75 mm × 25 mm × 1 mm were coated with a layer of gold by thermal vapor deposition method. Before and after gold deposition, the slides were cleaned in hot and cold piranha solution, respectively. The deposited gold was controlled to a thickness of 300 nm. The slides coated with gold were used as substrates for deposition of LB films.

4.2.2 Experiment

4.2.2.1 Interfacial Pressure-Area Isotherm. The molecular behaviors of asphaltenes, bitumen and EC at the water-oil (-toluene) interface were characterized through interfacial pressure-area isotherm measurements using a

Langmuir interfacial trough. The Langmuir trough experiments were carried out using a computer controlled KSV trough (KSV instruments, Finland) with a trough area of 17,010 mm^2. The interfacial pressure was monitored by a Wilhelmy plate made by a piece of Whatman 1 CHR filter paper. Prior to each measurement, the trough was cleaned thoroughly with toluene and acetone. The lower part of the trough was filled with 120 ml of Milli-Q water as the subphase. When the pressure sensor reading reached below 0.1 mN/m upon barrier compression of the water phase to a position of less than 20 mm, the trough was considered clean. After setting the interfacial pressure to zero, the asphaltene-, bitumen- or EC-in-toluene solution was evenly spread on the water surface while the trough area was wide-open, followed by a 15 min evaporation of the toluene to allow the formation of a uniform asphaltene, bitumen or EC film. Finally, 100 ml of optima-grade toluene was added as the top phase. After 30 min of toluene stabilization, the compression of the interfacial film started.

To investigate the effect of EC on the physical properties of bitumen/asphaltene interfacial films, a diffusion protocol of EC was used. Subsequent to covering the interfacial asphaltene or bitumen thin films with 100 ml of toluene, 20 μl of 1mg/ml of EC-in-toluene solution was immediately added on the toluene top phase. A 30 min of EC diffusion was allowed before compression. This diffusion time is chosen to reflect the typical residence time of demulsification in real oil field applications. However, it is important to note that the temperature in our tests is much lower than the temperature operated at industrial applications. Caution should be exercised when apply the results obtained in this study to selection of demulsifiers for industrial operations. For comparison purpose, experiments were also conducted after 90 min of toluene evaporation. As a control test, EC solution was also added to the toluene top phase in the absence of asphaltene or bitumen interfacial films and was allowed to diffuse for 30 min. In all the cases, the interfacial pressure was recorded right before the compression. The interfacial film was compressed at 10 mm/min for each barrier. Tests were also conducted with 5 mm/min compression rate and the difference in the resultant interfacial isotherms was negligible. All the experiments were performed at room temperature.

4.2.2.2 Langmuir-Blodgett (LB) Film. The interfacial films formed by asphaltene and bitumen individually were transferred onto the substrates at a constant interfacial pressure of 10 mN/m. The pulling speed of the substrate was kept at 5 mm/min. To simulate industrial demulsification operations, EC-in-toluene solution was added on the toluene top phase in the presence of either bitumen or asphaltene interfacial film. The interfacial film formed using this method was also transferred onto the substrates by following the same procedures as described above.

4.2.2.3 Polarization Modulation Infrared Reflection Absorption Spectroscopy (PMIRAS). The LB interfacial films transferred from toluene-water interface onto gold-coated slides were characterized using PMIRAS (Nexus 670, Thermo Nicolet, USA) with p- and s-polarizations. The polarization of the IR light was modulated using a Photoelastic Modulator (PEM) with a ZnSe crystal.

4.2.2.4 Atomic Force Microscopy (AFM) Imaging. AFM images of the LB interfacial films were obtained using a molecular imaging microscope (Agilent 5500, Agilent Technologies, Inc., Chandler, AZ). The substrates were fixed by a piece of double sided tape on a sample platform, which was magnetically held in place on the AFM stage. Images were captured under AAC mode in air at room temperature using a silicon nitrate cantilever (Veeco, Santa Barbara, CA). The vendor-supplied SPM software was used to control the probe and scan the sample, producing a 5 μm × 5 μm cross-section view image. Images were taken at different locations of the sample to ensure the unbiased representation of the results.

4.2.2.5 Film Thickness Measurement by Ellipsometry. The thickness of the LB films was determined using a spectroscopic ellipsometer (Sopra GESP-5, Sopra, France). By detecting the changes in polarization of a probing light beam upon reflection from a sample surface, the ellipsometer allows accurate measurement of the thickness of the film. The measurement was performed at an incident angle of 75^o with an incident beam of 450 nm wavelength. The analyzer was set at 45^o. The thickness was determined by fitting the results with Levenberg-Marquardt regression Cauchy Law. At least three measurements were performed at various locations for each sample and the thickness of the film reported was the average of these measurements.

4.2.2.6 Contact Angle Measurement. The characteristic of the LB films was further studied using a drop shape analyzer (DSA100, Kruss, Germany). The DSA includes a source of illumination, an optical microscope equipped with a goniometer eyepiece, and a horizontal stage. The sample was placed on the stage. About 10 µl of Milli-Q water was placed on the sample surface, and the contact angle was determined by the Sessile drop shape analysis method. The results reported are the average of six measurements conducted at various locations of the sample.

4.3 Results and Discussion

4.3.1 Interfacial Behavior of EC. The behavior of interfacially active materials can be characterized by the Langmuir interfacial pressure-area (∏−A) isotherms. The interfacial pressure (∏) is defined as [3, 7, 14, 20]

$$\Pi = \gamma_0 - \gamma \qquad (4.1)$$

where γ_0 and γ are the interfacial tensions in the absence and presence of interfacially active materials, respectively. In our study, γ_0 is the interfacial tension of a water-toluene interface. The change in the interfacial pressure of a water-toluene interface upon compression was determined and is indicated as reference in Figure 4-2.

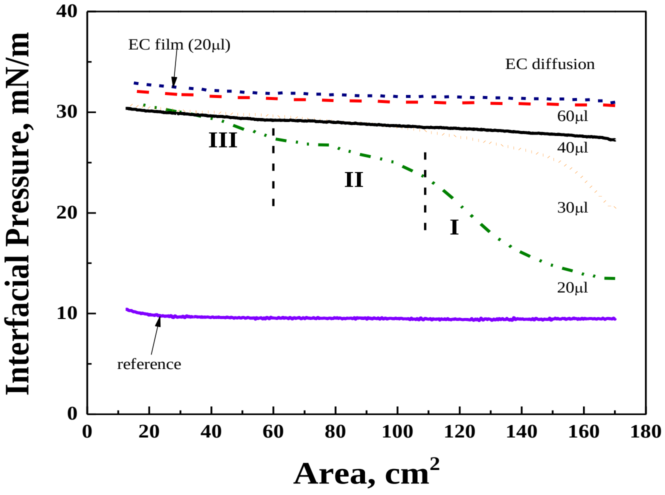


Figure 4-2. Interfacial pressure-area isotherms of EC interfacial films formed by spreading 20 µl of 1 mg/ml EC at the interface and by diffusing 20 – 60 µl of 1 mg/ml EC through 100 ml toluene top phase to the interface. Reference curve was obtained by compressing water-toluene interface in the absence of any added interfacial materials. A 30-min stabilization was allowed prior to each compression.

When the interfacially active materials either brought or migrated to the interface are compressed, the surface tension, γ reduces, resulting in an increase in Π. The compressibility of the interfacial film can be determined from the $\prod-$A isotherm. In this study, the compressibility of interfacial film (C^s) is calculated by [[3, 21]]

$$C^s = -\frac{1}{A\cdot\frac{d\Pi}{dA}} \qquad (4.2)$$

where A is the trough area and $\frac{d\Pi}{dA}$ is the slop of the $\prod-$A isotherm. A smaller change in the interfacial pressure upon compression, i.e., smaller $\frac{d\Pi}{dA}$, represents a more compressible interfacial film. In this case, the film is considered soft. On the other hand, if the $\frac{d\Pi}{dA}$ is large, the compressibility of the interfacial film is small and the film is considered rigid. Figure 4-2 shows the isotherms of EC interfacial films obtained by both spreading and diffusion methods. EC is an amphiphilic polymer of many hydrophilic groups. Once EC molecules adsorbed at the interface, multiple point occupancy of EC molecules at the water-oil interface makes them difficult to migrate back to the toluene top phase. For this reason, the shape of the isotherms obtained by spreading 20 μl of 1 mg/ml of EC is similar to those obtained by diffusing 40−60 μl of 1 mg/ml EC from the toluene top phase to the interface. This result does not only point out that all of EC molecules stay at the interface, but also indicates the irreversible adsorption of EC molecules at the interface. The interfacial pressure increased only marginally when the film area was reduced by compression. This finding suggests an extremely soft nature of EC films even though the absolute pressure of 30 mN/m is relatively high at high interfacial EC concentrations. In contrast, the interfacial isotherms obtained at lower EC interfacial concentration by diffusion from 20 to 30 μl EC-in-toluene solution showed a significant increase in interfacial pressure before leveled off at 30 mN/m pressure with reducing the interfacial area. When 20 μl of 1 mg/ml EC was diffused to the interface, for example, the interfacial pressure increased first from 14 mN/m to 30 mN/m with decreasing interfacial area. There exist three distinction interfacial areas: I) from A=170 cm^2 to 110 cm^2; II) from 110 cm^2 to 60 cm^2; and III) from 60 cm^2 to 10 cm^2. The first region (I) corresponds to a gas phase behavior of EC characterized by low EC concentrations at the interface. The second region (II) corresponds to gas to condensed gas phase transition, featuring significant EC molecular interactions. As the area further reduces to region III, the EC molecules at interface become liquid-like or form a network with relatively soft characteristics and low resistance to the further compression. When 30 μl of 1 mg/ml EC was diffused to the interface, the gas phase region reduced significantly while condensed gas phase disappeared when compared with the diffusion from 20 μl of 1 mg/ml EC solution. It is interesting to note a progressive increase in initial interfacial pressure ($\prod_0$) with diffusion of EC from progressively increasing volume of EC-in-toluene solutions, i.e., $\prod_0$ (20 µl diffusion) < $\prod_0$ (30 µl diffusion) < $\prod_0$ (40 µl diffusion) < $\prod_0$ (60 µl diffusion) ≈ $\prod_0$ (20 µl spreading). This finding suggests that the initial interfacial concentration (C_{in}) of EC before compression was higher for interface formed from high volume addition of EC-in-toluene solutions, i.e., C_{in} (20 µl diffusion) < C_{in} (30 µl diffusion) < C_{in} (40 µl diffusion) < C_{in} (60 µl diffusion) ≈ C_{in} (20 µl spreading). This observation suggests that only a portion of EC molecules was able to migrate to the interface during the diffusion.

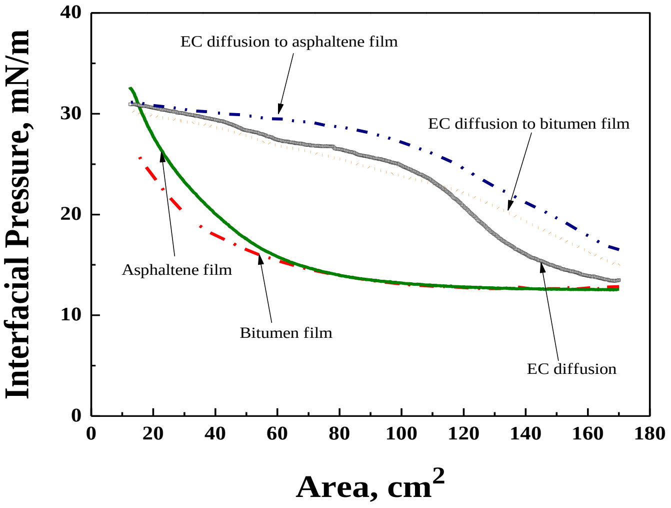


Figure 4-3. Interfacial pressure-area isotherms of bitumen/asphaltene interfacial films formed by spreading 200 µl of 1 mg/ml bitumen or 20 µl of 1 mg/ml asphaltene to the interface, and interfacial pressure-area isotherms of interfacial films formed by diffusing 20 µl of 1 mg/ml EC through toluene top phase to the interface at which 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.

Figure 4-3 shows a significant change in interfacial behavior of bitumen or asphaltene films at the toluene-water interface with EC addition. With the same amount of interfacially active materials, i.e., 20 µl of 1 mg/ml species spread at the interface, interfacial film formed from EC solutions in Figure 4-2 is much more compressible than the asphaltene interfacial films as revealed by equation 4.2. The results indicate that the interfacial EC film is soft while the interfacial asphaltene/bitumen films are rigid. It is interesting to note that the isotherms of asphaltene/EC and bitumen/EC interfacial films are quite similar to the isotherm of EC interfacial film by diffusion, but significantly different from the isotherms of asphaltene/bitumen interfacial films. The similarity of asphaltene and bitumen films with EC addition to EC films clearly indicates that EC dominates the interfacial behavior, significantly reducing the rigidity of the asphaltene/bitumen interfacial films. Since EC is more interfacially active than asphaltene/bitumen as indicated by its stronger ability of decreasing the interfacial tension [4], it is able to adsorb at the defect (void) sites or penetrate into the asphaltene/bitumen network, leading to the displacement of asphaltene/bitumen from the interface by EC. Eventually, this leads to the rupture of the asphaltene/bitumen interfacial films.

4.3.2 Interfacial Film Properties. To further understand the interaction between EC and asphaltene/bitumen at the interface, the LB films obtained by diffusing EC through toluene top phase to the interface at which an asphaltene or bitumen film was already formed were characterized by the polarized IR and AFM, along with determination of film thickness by ellipsometry and contact angle measurements by a drop shape analyzer. Figure 4-4 shows the IR spectra of EC, asphaltene and asphaltene/EC LB films. For all the spectra, the bands at 2920 and 2850 cm^{-1} are stretching vibrations of C-H bonds, and the bands at 1450 and 1370 cm^{-1} correspond to the deformation vibrations of C-H bonds. For the spectrum of bitumen, the band at 1700 cm^{-1} corresponds to C=O stretching vibration in the carboxylic acid group and the band at 850 cm^{-1} is bending vibration of aromatic C-H bonds. For EC, the band at 1100 cm^{-1} corresponds to the stretching vibration of ether linkage on EC backbone. This band can be used as an indicator of EC's presence. Since the spectrum range in this study was limited between 3000 to 800 cm^{-1}, the vibrations of O-H bond at 3500 cm^{-1} were not shown in all the spectra [18]. As seen in Figure 4-4, the 1100 cm^{-1} band appears on the spectra of EC and asphaltene/EC films, indicating the presence of EC in the asphaltene/EC LB film. Similarly, from Figure 4-5, the presence of EC in the bitumen/EC LB film can be concluded from the presence of bands at 1100 cm^{-1} for ether linkage in the bitumen/EC LB film. Although IR spectra clearly show the presence of EC in the asphaltene/EC and bitumen/EC LB films, they cannot distinguish whether EC displaced asphaltene/bitumen films or simply adsorbed on the asphaltene/bitumen films.

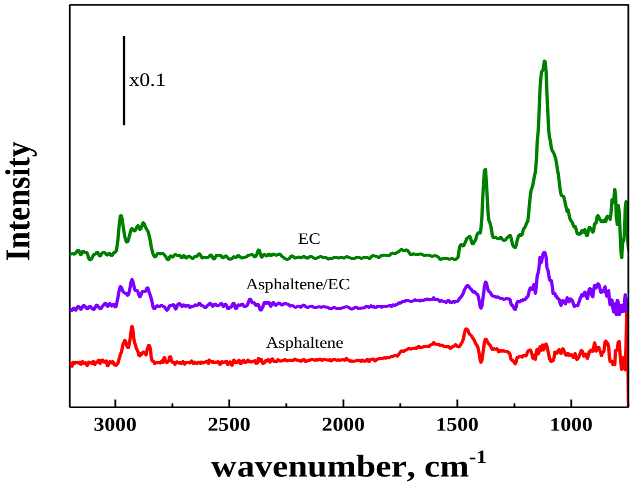


Figure 4-4. PMIRAS spectra of EC, asphaltene, and asphaltene/EC LB interfacial films. The EC film was formed by spreading 20 µl of 1 mg/ml EC-in-toluene solution to the interface. The asphaltene film was formed by spreading 20 µl of 1 mg/ml asphaltene-in-toluene solution to the interface. The asphaltene/EC film was formed by diffusing 20 µl of 1 mg/ml EC-in-toluene solution to the interface where an asphaltene film was already formed by spreading 20 µl of 1 mg/ml asphaltene-in-toluene solution.

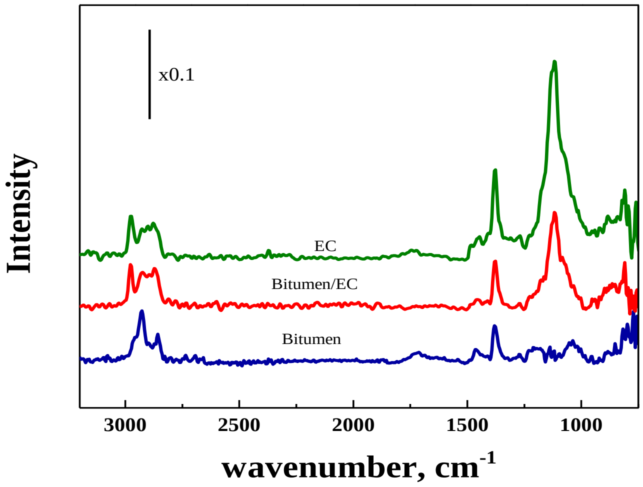


Figure 4-5. PMIRAS spectra of EC, bitumen, and bitumen/EC LB interfacial films. The EC film was formed by spreading 20 µl of 1 mg/ml EC-in-toluene solution to the interface. The bitumen film was formed by spreading 200 µl of 1 mg/ml bitumen-in-toluene solution to the interface. The bitumen/EC film was formed by diffusing 20 µl of 1 mg/ml EC-in-toluene solution to the interface where a bitumen thin film was already formed by 200 µl of 1 mg/ml bitumen-in-toluene solution.

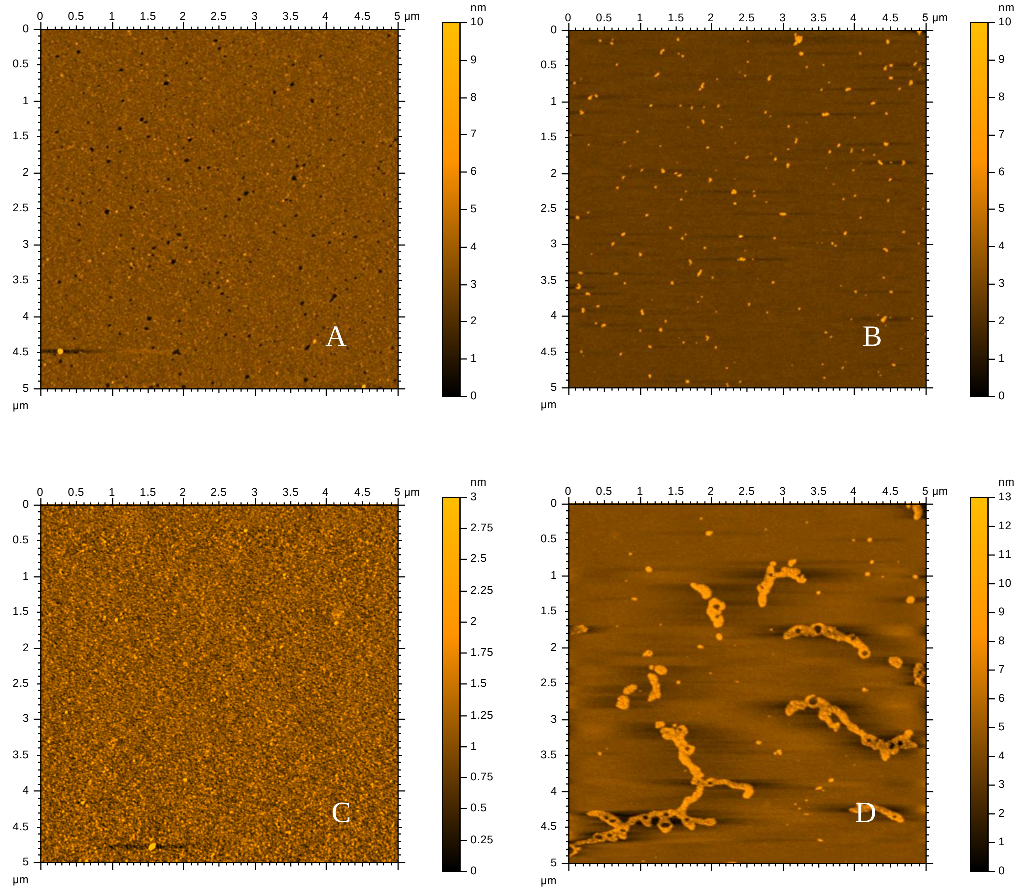


Figure 4-6. AFM images of interfacial LB films. (A) asphaltene film prepared by spreading 20 µl of 1 mg/ml asphaltene at the interface; (B) asphaltene/EC film prepared by diffusing 20 µl of 1 mg/ml EC through toluene top phase to the

interface in which a film was already formed by 20 μl of 1 mg/ml asphaltene; (C) bitumen film prepared by spreading 200 μl of 1 mg/ml bitumen at the interface; and (D) bitumen/EC film prepared by diffusing 20 μl of 1 mg/ml EC through toluene top phase to the interface in which a film was already formed by 200 μl of 1 mg/ml bitumen.

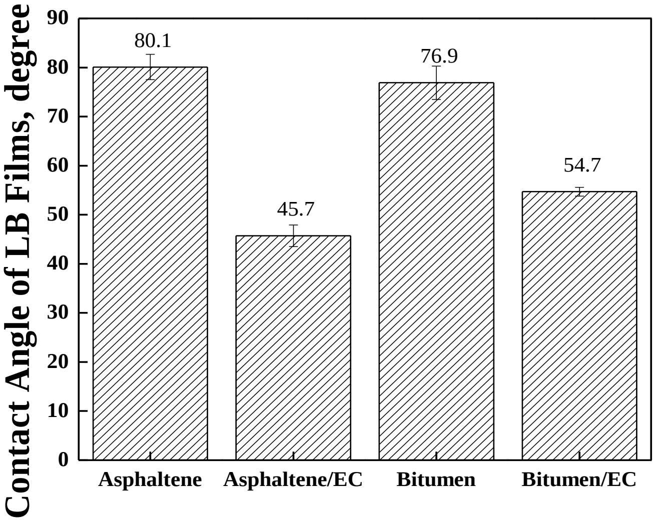


Figure 4-7. Contact angle measurements of LB films (A) to (D) as described in Figure 4-6. All the measurements were performed using a shape drop analyzer. Each value is an average of at least six measurements at various locations of the film.

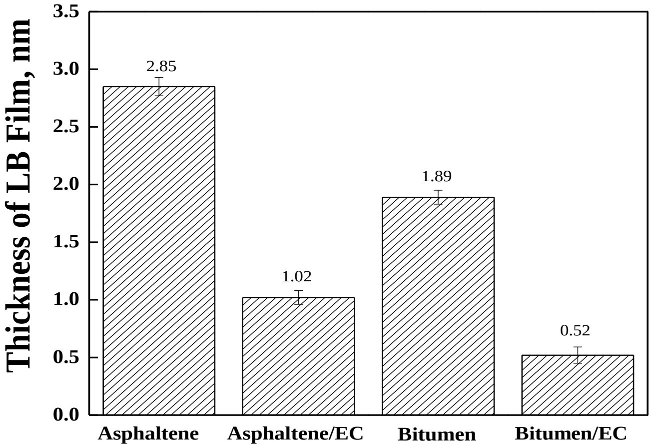


Figure 4-8. Film thickness measurements of the associated LB films (A) to (D) as described in Figure 4-6. All the measurements were determined by an ellipsometer, and each value was an average of at least three measurements at various locations of the samples.

To clarify the above issue, the effect of EC penetration to a pre-existed asphaltene or bitumen interfacial film was studied via AFM imaging, contact angle and film thickness measurements of the corresponding LB films. AFM images in Figures 4-6A and 4-6C show uniform interfacial films formed by the active materials from asphaltenes and bitumen, respectively. In contrast, lumps were seen in AFM images of Figure 4-6B and 4-6D corresponding to asphaltene or bitumen interfacial films with EC addition. Figure 4-7 shows the contact angle values of the corresponding LB films. In the absence of EC, the contact angles were 80.1^o and 76.9^o for the asphaltene and bitumen films, respectively, which were reduced respectively to 45.7^o and 54.7^o with EC addition. Since pure EC film has a contact angle of 36.2^o, these contact angle values indicate a partial replacement of original asphaltene/bitumen films from oil-water interface by EC. This finding is consistent with the results from IR analysis, both showing the presence of EC molecules in the asphaltene/bitumen films at the oil-water interface. To further confirm the displacement action, the thickness of the LB films was measured and the results are shown in Figure 4-8. Should EC simply adsorbed on the asphaltene film, the thickness of the asphaltene/EC film would be at least as thick as the asphaltene films alone. The thickness of the asphaltene films transferred from the water-toluene interface by LB method reduced from 2.85 nm to 1.02 nm with the addition of EC. This reduction in film thickness with EC addition clearly indicates partial displacement of asphaltene molecules from the interface, forming an asphaltene/EC mixed film. Similar displacement of bitumen film by EC was observed, as shown by a significant decrease in bitumen interfacial film thickness from 1.89 nm to 0.52 nm. It should be noted that in the presence of EC, the original interfacial materials, mainly asphaltenes formed larger aggregates as shown in Figures 4-6B and 4-6D, mostly from the occupation of the interface by EC, pushing the asphaltenes together.

It appears that the irreversible displacement of asphaltenes by EC from the water-oil interface breaks the protecting asphaltene films at the water-oil interface. When two water droplets approach each other by mechanical or thermal mixing, EC molecules at the water-oil interface further aid their contact through bridging effect, causing flocculation of water droplets. The flocculation eventually leads to the coalescence of the water droplets, as shown by a significant increase in droplet size of water-in-diluted bitumen emulsions by EC addition as shown in Figure 4-9.

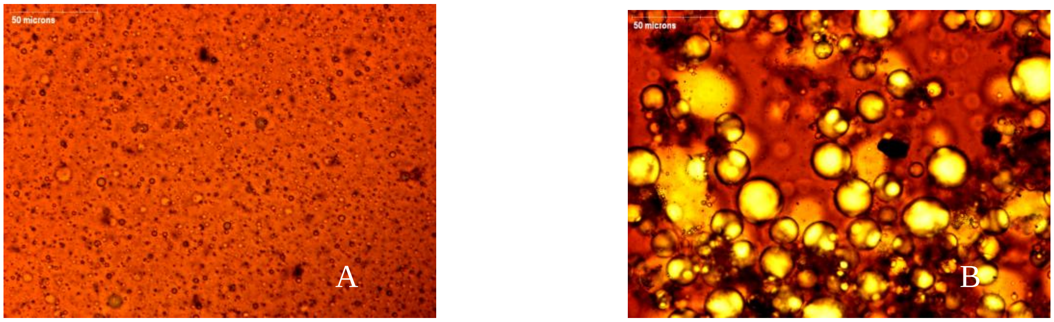


Figure 4-9. Micrographs of emulsions without (A) and with 300 ppm EC addition (B). The emulsions prepared with 5 wt% initial water content in 60 wt% naphtha diluted bitumen were settled under gravity at 80 °C for 1 h. The scale bar of 50 μm is the same for both images.

It should be noted that although the focus of this work is to study interfacial properties of EC at water-oil interface and to understand its role in demulsification of water-in-diluted bitumen emulsions, EC diffusion to the interface and displacement of original interfacial materials by EC are time dependent as revealed in previous studies [19]. As shown in Figure 3-1 in Chapter 3, at least 90 min were required for EC (EC-c) to demulsify water-in-diluted bitumen emulsions at room temperature. The interfacial pressure-isotherm experiment was also conducted after 90 min of EC diffusion through the toluene top phase to the interface at which a film was already formed by 200 μl of 1mg/ml bitumen-in-toluene solution, and the result is shown in Figure 4-10.

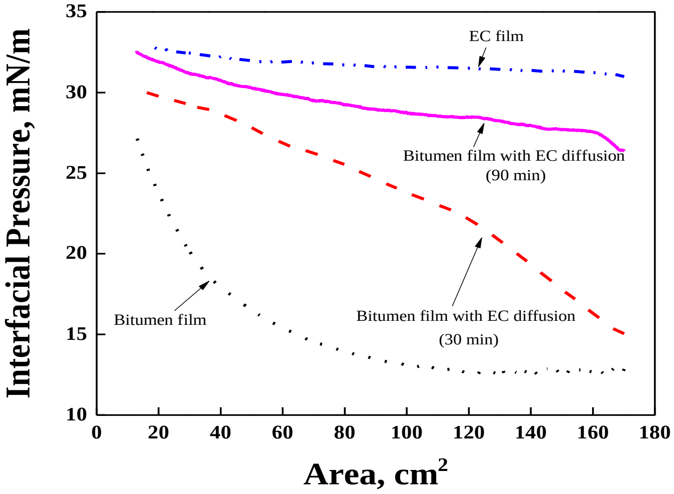


Figure 4-10. Interfacial pressure-area isotherms of bitumen interfacial films formed by spreading 200 µl of 1 mg/ml bitumen or 20 µl of 1 mg/ml EC, and interfacial pressure-area isotherms of interfacial films formed by 90 and 30 min of diffusing 20 µl of 1 mg/ml EC through toluene top phase to the interface at which a film was already formed by 200 µl of 1 mg/ml bitumen.

Higher initial interfacial pressure $\prod_0$ was obtained when EC was allowed to diffuse for 90 min, suggesting the initial interfacial concentration (C_{in}) of species before compression was higher for interface formed at 90 min of EC diffusion than 30 min of EC diffusion, i.e., C_{in} (90 min diffusion) > C_{in} (30 min diffusion). This finding indicates that a complete EC diffusion process takes much more than 30 min, which is consistent with the result of the demulsification performance of EC at room temperature. Although the interfacial film became much softer as more EC molecules adsorbed at the interface at 90 min of diffusion, the pressure-area isotherm obtained by 90 min of EC diffusion exhibits similar characteristics as the isotherm obtained by 30 min of EC diffusion to an interfacial bitumen film upon compression. This finding indicates that 30 min of EC diffusion was enough for the purpose of testing the ability of EC in changing the rigidity of the protective interfacial film. However, longer diffusion time is required for EC to actual demulsify water-in-diluted bitumen emulsions at room temperature. More effective demulsification of water-in-diluted bitumen emulsion by EC addition could achieve at higher operating temperature as shown in Figure 3-2.

4.4 Conclusions

In this study, EC molecules were found to irreversibly adsorb at the water-oil interface subsequent to diffusion through the oil phase, and form a highly compressible interfacial film. Polarized IR, ellipsometry (thickness) and contact angle measurements of the interfacial films clearly show that in water-in-diluted bitumen emulsions, EC participates in the formation of the interfacial film through displacement or disrupture of the existing interfacial film formed by surface-active components of bitumen. As a result of the displacement, the rigid interfacial film formed by surface-active components of bitumen becomes more compressible, which is beneficial to coalescence of water droplets. The results obtained in this study further reinforce the demulsification mechanisms of EC proposed earlier and provide directions for designing new demulsifiers.

4.5 Reference

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Chapter 5

The Role of Ethylcellulose in Bitumen Flotation

5.1 Introduction

With the depletion of conventional crude oil and the increase of worldwide demand on oil, recovery of bitumen from oil sands becomes increasingly important. Oil sands contain sands, bitumen and water. Oil sands ore with 6−8 wt% bitumen is considered as a low grade (poor processing) ore, whereas the one with 8−10 wt% and above 10 wt% bitumen is an average grade and a high grade (rich) oil sands ore, respectively [1, 2]. One of the major challenges in oil sands industry is to improve the processibility of poor processing ore. This type of ore has a low bitumen content and a high fine solids content (more than 30 wt% of solids have a diameter less than 44 µm) [3].

Flotation has been widely used to recover bitumen from Canadian Athabasca oil sands [2, 4]. However, processing of the low grade ore under conventional bitumen flotation conditions (pH 8.5 at 35 ^{o}C) leads to a very low bitumen recovery and poor froth quality. As a result, there are many challenges in the processing of this type of ore [5].

Two processes are involved in bitumen flotation: liberation and aeration. In the liberation process, bitumen is liberated from sand grains. The liberated bitumen attaches to air bubbles and floats to the top of the processing vessel during aeration.

Liberation is controlled by the interactions between bitumen and sand grains. The attachment of bitumen to air bubbles depends on the hydrophobicity of bitumen surface. It has been reported that bitumen recovery through flotation is determined by the grade and fine solids content of ore, water chemistry, temperature, and agitation [2, 5-9]. For example, attachment of fine solids to bitumen surface, i.e., slime coating, could lead to poor processibility of low grade ores, decreasing the attachment of bitumen to air bubbles [10]. In a hot water extraction process, caustic is commonly applied to improve bitumen recovery for low grade and high fines ores [9, 11, 12]. Dai et al. [13] studied the coverage of a bitumen surface by sands of different size in 0.005 M NaCl solution at various pH values. These authors observed a decrease in the coverage of bitumen surface by solids with increasing pH to above 6. An increase in alkalinity also led to an increased detachment of fine solids from bitumen due to the increased repulsive force between bitumen and solids in caustic solution. Wallwork et al. [14] found that increasing in temperature and aeration rate enhanced bitumen recovery regardless of fine solids content of the oil sands ores.

Recently, extraction aids have been applied to flotation in order to improve bitumen recovery. Li et al. [15] studied the effect of water soluble polymers, i.e., a hybrid $Al(OH)_3$-polyacrylamide (Al-PAM) and a partially hydrolyzed polyacrylamide (HPAM) on bitumen flotation. These authors found that the application of Al-PAM alone improved bitumen froth quality and increased tailings settling rate, but reduced bitumen recovery. However, the application of 5 ppm Al-PAM and 5 ppm HPAM together increased bitumen recovery, bitumen froth quality and tailings settling rate. Previous studies showed that an amphiphilic polymer, ethylcellulose (EC) is an effective demulsifier. With our research approach to holistically link flotation, froth cleaning and tailings, the role of EC addition in bitumen flotation was considered. EC-in-toluene solution was added to flotation using two protocols to explore whether it can enhance processibility of oil sands ores. The idea is to couple the addition of EC or other demulsifiers with aqueous-nonaqueous hybrid extraction process, so that the interfacially active demulsifiers may enhance bitumen recovery and froth quality. If EC addition can indeed improve bitumen extraction in terms of bitumen recovery and/or bitumen froth quality, we would maximize its value in oil sands process, not only in froth treatment, but also in bitumen recovery, as the residual EC from the flotation process can further function as demulsifiers.

5.2 Experimental

5.2.1 Materials. EC from Sigma-Aldrich with an ethoxyl content of 48% was used as received. The oil sands ore (CN912) provided by Canadian Natural Resources Ltd. with 8.3 wt% bitumen, 7.4 wt% water and 84.3 wt% solids with 38.2 wt% of solids being fines was used in the flotation experiment. Due to its high fines content, this ore is considered to be a low processing ore. The oil sands ore samples were enclosed in plastic bags and stored in a freezer to prevent oxidization. The process water provided by Syncrude Canada Ltd. contains 35.3 mg/L Ca^{2+}, 13.2 mg/L Mg^{2+}, 20.3 mg/L K^{+}, 700.9 mg/L Na^{+}, 399.2 mg/L Cl^{-}, 2.8 mg/L NO^{3-} and 410.6 mg/L SO_4^{2-}. NaOH or HCl solution was used to adjust the pH of process water to 8.5. Reagent grade toluene purchased from Fisher Scientific was used to extract bitumen from collected froth. Optima grade toluene from Fisher Scientific was used to make EC-in-toluene solutions for the flotation tests. The dosage of the EC-in-toluene solution was calculated as such that 100 ppm EC was referring to 100 ppm EC in the slurry (ore and water). Sodium dodecyl sulfate (SDS) purchased from Sigma-Aldrich was used to make a 2% SDS solution for cleaning purposes in the QCM-D experiments.

The vacuum distillation feed bitumen and industrial grade naphtha were provided by Syncrude Canada Ltd. The heavy naphtha from Champion Technologies Ltd. was used to make EC solutions to study the role EC in stabilizing water-in-oil emulsions. Milli-Q water with a resistivity of 18.2 MQ·cm^{-1} was used to prepare the emulsions.

5.2.2 Experiment

5.2.2.1 Flotation. Bitumen batch flotation tests were carried out in a 1 L Denver flotation cell. A water jacket connected to a temperature-controlled thermal bath was attached to the Denver cell to maintain a constant operating temperature. For each extraction test, 300 g of the oil sands sample was allowed to defreeze at room temperature for 2 h prior to each test. Then, 900 g process water at 50 °C was added to the oil sands ore, with the resultant slurry at 33 ± 2 °C. After the oil sands slurry had been conditioned at 1500 rpm for 5 min, air was introduced at 150 ml/min. The bitumen froth was collected at time intervals of 0–3, 3–5, 5–10 and 10–20 min.

To investigate the effect of EC on bitumen recovery and froth quality, EC-in-toluene solutions were added to the system. Two experimental protocols were followed to introduce EC to the flotation system. In protocol I, 100 ppm, 200 ppm or 300 ppm (based on the total mass of slurry) EC-in-toluene solution was spread into the slurry as soon as the conditioning initiated. In protocol II, EC-in-toluene solution was directly added to the oil sands ore before process water was introduced. The schematics of the two protocols are shown in Figure 5-1.

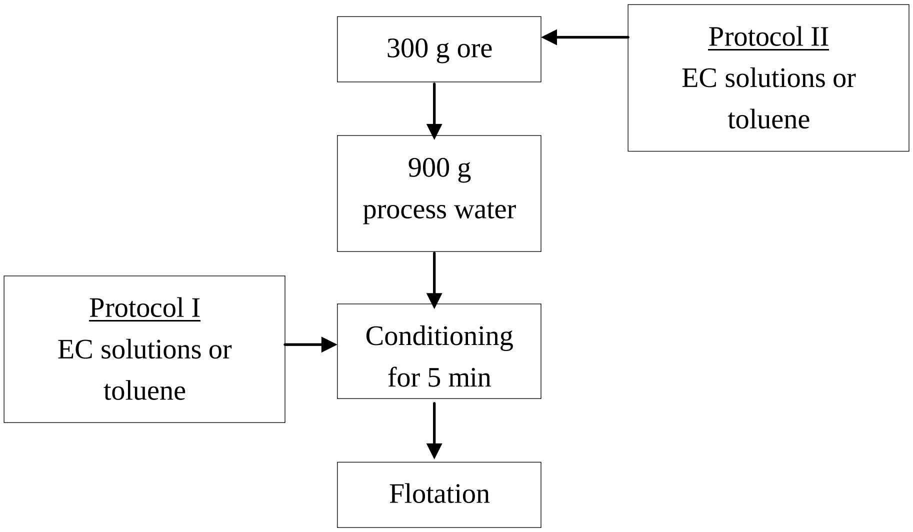


Figure 5-1. Schematics of two protocols of EC-in-toluene solution or toluene

addition in flotation, I) EC prepared in toluene is added during 5 minutes conditioning prior to flotation and II) EC prepared in toluene is added directly to the oil sands ore prior to slurrying.

Since the change in bitumen recovery and froth quality by adding EC-in-toluene solutions could be simply due to the effect of bitumen dissolution by toluene, a test was conducted by adding 12 g of toluene instead of EC-in-toluene solution as process aids following the above two protocols. As a reference, the extraction experiments were performed in the absence of toluene and EC. After extraction, the remaining slurry in the Denver flotation cell was collected as tailings. The bitumen froth collected from the flotation tests was analyzed for its bitumen, solids and water content using the Dean Stark extraction method. The mass ratio of bitumen in froth to bitumen in the oil sands ore represents bitumen recovery. The mass ratio of bitumen to solids (B/S) and bitumen to water (B/W) in froth are used as a measure of froth quality. Higher B/S and B/W values represent a better froth quality.

5.2.2.2 Quartz Crystal Microbalance with Dissipation (QCM-D). QCM-D (Q-sense E4 system, Sweden) was applied to measure the adsorption of bitumen/asphaltene and EC on a silica (QSX 303) coated quartz crystal sensor. Gold electrodes on both sides of this piezoelectric plate sensor allowed the crystal to oscillate at specific resonance frequencies corresponding to a specific mass of the sensor. A decrease in resonance frequency implies an increased amount of materials being adsorbed to the sensor surface. Shifts in dissipation reflect the rigidity of the adsorbed layer. An increase in dissipation suggests a more elastic nature of the adsorbed layer. Prior to each experiment, the quartz crystal sensor, solvent resistant Kalrez O-rings, gaskets and GORE pump tubing were sonicated in a 2% SDS solution for 30 min, followed by thoroughly rinsing with Milli-Q water. After blow drying with nitrogen, the sensor was exposed to UV radiation for 20 min to remove any remaining organic contaminants. The sensor was considered clean if the contact angle of the sensor was less than 10^o. The clean sensor was held in place by the O-ring inside the flow module, which was mounted into the instrument chamber. The cleanness level of the sensor was double checked by flowing air through the sensor surface prior to each measurement. Once the sensor reached appropriate level of cleanness, a stable baseline of optima-grade toluene had to be obtained first at the beginning of each run to set up a reference. A 1000 ppm asphaltene-in-toluene solution (equivalent to 1 wt% bitumen-in-toluene) was allowed to flow over the sensor surface by a peristaltic pump (Ismatec, Switzerland) at a constant rate of 0.15 ml/min. The operating temperature was kept at 22 ± 0.02 ^{o}C by a built-in thermoelectric device in the chamber platform. Once the adsorption equilibrium was established, optima-grade toluene was allowed to pass through the system to remove any loosely attached asphaltene (bitumen). A 300 ppm EC-in-toluene solution was then pumped through the system until a new set of stable frequency and dissipation was achieved. After rising with fresh toluene, another 1000 ppm of asphaltene-in-toluene solution as allowed to pass through the system. Contact angle measurements were conducted before and after the last injection of asphaltene solution using a drop shape analyzer (DSA100, Kruss, Germany). The detailed procedure of contact angle measurements was described in 4.2.2.6 of this thesis.

5.2.2.3 Emulsion. 0, 50 and 100 ppm of EC-in-heavy naphtha solutions were added to 60% naphtha-diluted bitumen at 8000 rpm for 30 s using a homogenizer (PowerGen homogenizer, 125 W). The resultant samples were mixing with Milli-Q water at 30,000 rpm for 3 min to make a 5 wt% water-in-diluted bitumen emulsion. The sample for water content measurement was taken at 2.5 cm from the surface of the resultant emulsion sample, and the water content in the sample was determined using a Karl Fisher Titrator.

5.3 Result and Discussion

5.3.1 Effect of EC on Bitumen Extraction. Figure 5-2 shows bitumen recovery in the presence of toluene and EC using two protocols. It can be seen that adding toluene to the slurry had a negligible effect on bitumen recovery, but the addition of toluene directly to the ore significantly improved bitumen recovery. As it is well known, toluene is a good solvent for bitumen. Direct addition of toluene to the ore helped to reduce the viscosity of bitumen and hence release of bitumen from the sand grains. In contrast, adding toluene to the slurry was unable to deliver toluene through water phase to the surface of the oil sands ore. As a result, the addition of toluene to the slurry had a negligible effect on bitumen extraction. In the case of EC addition, both protocols improved bitumen recovery, but protocol I was a little more effective than protocol II. EC is an amphiphilic polymer, which prefers to stay at the water-oil interface. Direct addition of EC to the ore would only bring EC on a portion of the oil sands surface. With limited EC adsorbed in protocol II, EC addition would still show an improvement in bitumen recovery. In contrast, adding EC to the slurry made it possible for EC to be adsorbed on a larger surface of oil sands ore during agitation. However, due to limited solubility of EC in water, this action was partially offset, resulting in a similar improvement in bitumen recovery for both protocols. Figure 5-2 shows that spreading 100 or 200 ppm EC to the slurry resulted in an increase of bitumen recovery from 60% to above 70%. Surprisingly, a further increase in EC dosage to 300 ppm made bitumen recovery drop back to the original 60% recovery. It appears that access of EC at bitumen-water interface makes bitumen less hydrophobic and hence poor aeration. This finding also accounts in protocol II for higher bitumen recovery with toluene addition than with EC-in-toluene solution addition.

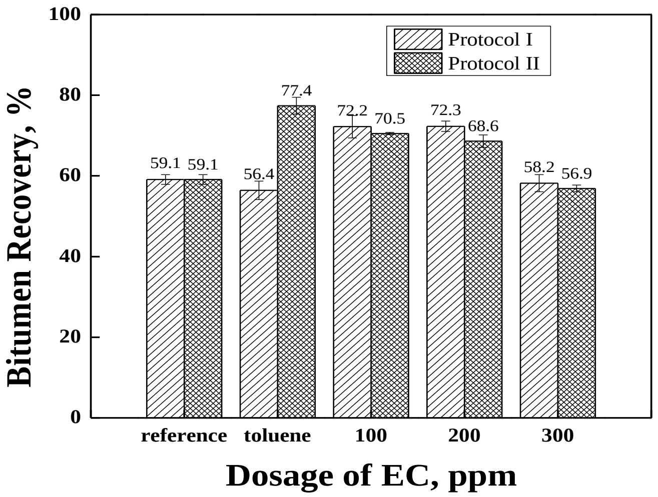


Figure 5-2. Bitumen recovery in the presence of toluene and various dosages of EC-in-toluene solution. Two different protocols were used: I) EC prepared in toluene was added during 5 minutes conditioning prior to flotation and II) EC prepared in toluene was added directly to the oil sands ore prior to slurrying. The bitumen recovery in the absence of toluene and EC addition was used as a reference. The error bars represent a standard deviation from 2-3 times repeated tests.

Figure 5-3 illustrates the appearance of the froths collected under various conditions. In the absence of polymer and toluene (Figure 5-3 (A)), the froth was grayish-brown in color, suggesting a high solid content, and its appearance was sponge-like, indicating a poor froth quality. With application of toluene alone to the ore (Figure 5-3 (B)), the froth was brown-black, suggesting a better froth quality than the froth quality shown in Figure 5-3 (A). When 300 ppm EC was applied, the froth was thick and shiny-black, indicating a good froth quality, which was better than the froth shown in Figure 5-3 (B).

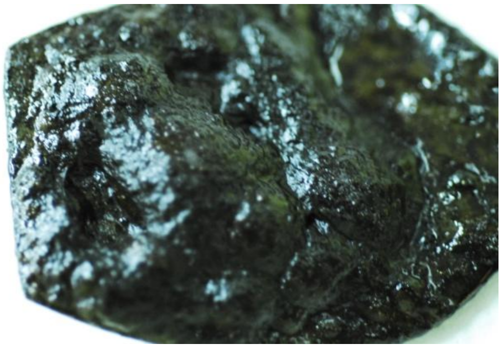
Froth Images	Condition
	(A) Bitumen froth collected within the first 3 min in a flotation process without EC or toluene addition.
	(B) Bitumen froth collected within the first 3 min in a flotation process with toluene added to the oil sands ore before flotation.
	(C) Bitumen froth collected within the first 3 min in a flotation process with the addition of 300 ppm EC-in-toluene solution to the ore.

Figure 5-3. Photographs of the bitumen froth collected within the first 3 min in a flotation tests: (A) without chemical addition (B) toluene addition using protocol II, and (C) EC-in-toluene solution addition using protocol II.

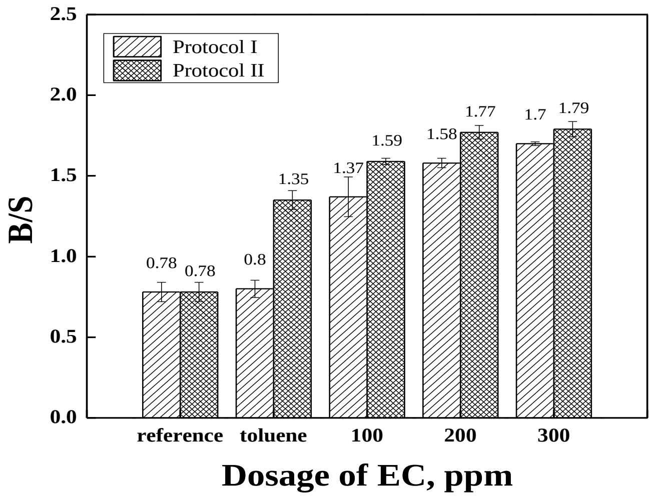


Figure 5-4a. Bitumen to solids ratio of the froth collected over 20 min flotation at 33±2 °C using: I) EC prepared in toluene was added during 5 minutes conditioning prior to flotation and II) EC prepared in toluene was added directly to the oil sands ore prior to slurrying.

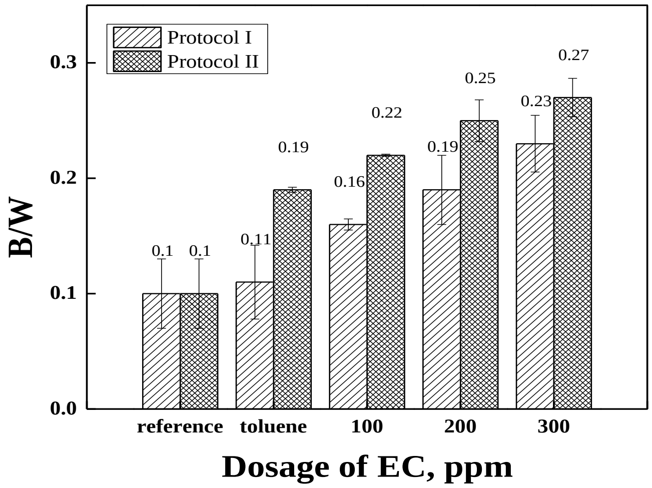


Figure 5-4b. Bitumen to water ratio of the froth collected over 20 min flotation at 33±2 °C using two different protocols: I) EC prepared in toluene was added during

5 minutes conditioning prior to flotation and II) EC prepared in toluene was added directly to the oil sands ore prior to slurrying.

The effect of EC and toluene application on the froth quality was further characterized by B/S and B/W ratios, as shown in Figure 5-4. The B/S and B/W ratios for toluene addition (protocol I) were similar to that for no chemical application. This finding corresponds well to negligible effect of toluene addition to slurry on bitumen recovery. The B/S and B/W ratios for toluene addition (protocol II) were enhanced compared to no chemical application. Using protocol I, B/S increased from 0.8 to 1.4 with the addition of EC from 0 to 100 ppm, and the B/S ratio jumped to 1.6 and 1.7 with further increasing EC dosages to 200 and 300 ppm, respectively. A slightly more increase in B/S ratio was observed by using protocol II than by using protocol I. Adding EC directly to the oil sands ore helped the diffusion of EC to the bitumen-sand grain interface, which resulted in more clean bitumen release from the oil sands. For this reason, the addition of EC solutions directly to the ore yielded higher B/S ratios. The addition of EC led to an increase in B/W ratio as well. As shown in Figure 5-4b, the B/W ratio increased from 0.11 to 0.23 with the addition of 300 ppm EC during slurrying. Addition of toluene and 100 ppm of EC solution directly to the ore led to a B/W ratio of 0.19 and 0.22, respectively. A further increase in the EC dosage resulted in a higher B/W ratio.

5.3.2 QCM-D measurements.

With the silica sensor representing the sand grain surface, QCM-D measurement illustrates the effect of toluene/EC addition to the interactions between bitumen/asphaltene and oil sand grains. As shown in the region I in Figure 5-5, a sudden drop in frequency and elevation in dissipation were observed during injection of an asphaltene solution into the system. This change indicates an adsorption of asphaltene (bitumen) onto the sensor surface, representing a sand grain surface covered with asphaltene (bitumen). An increase in frequency was observed as toluene was introduced into the system, suggesting that asphaltene (bitumen) was dissolved by toluene and released from the sand grain surface. This result correlates well with a higher bitumen recovery and a better froth quality obtained by the addition of toluene directly to the oil sands ore (protocol II) in the flotation experiment. The decrease in dissipation upon toluene rinsing suggests that the asphaltene (bitumen) film became more rigid as it being removed by dissolution of asphaltene (bitumen) molecules by toluene. The remaining asphaltene layer was irreversibly adsorbed to the sand grains. This layer is very hard to remove from the oil sand grain by simple dissolution of toluene.

As shown in region II of Figure 5-5, the addition of 300 ppm EC-in-toluene solution led to a dramatic decrease in frequency, corresponding to adsorption of EC onto the surface. Accompanied was a sharp increase in dissipation right after a slight decrease. It should be noted that the drop in frequency does not provide any indication that the bitumen had been squeezed out from the sand grain surface by EC. However, EC has been previously proven to be able to irreversibly displace bitumen/asphaltene from a hydrophilic (water)-hydrophobic (toluene) interface in Chapter 4. In addition, the increase in dissipations suggests that the resultant film was softer, in line with the results from the previous Langmuir experiment. As more EC molecules were added to the system, they could fracture the asphaltene (bitumen) film and finally squeeze asphaltene (bitumen) out of the sand grains, leading to the formation of a film that only contained EC, which was much softer than an asphaltene film. This finding suggests that the addition of 300 ppm EC to the system led to further release of clean bitumen from the sand grain. However, EC addition might make the bitumen surface less hydrophobic, leading to a lower bitumen recovery.

The raise in frequency and reduction in dissipation in region III indicate a loss of EC molecules due to the rinse of the film by asphaltene-in-toluene solution. However, the contact angle of the resultant film was 38^{o}, which is very similar to the one (37^{o}) obtained before the injection of asphaltene-in-toluene solution, suggesting EC molecules were not completely removed from the silica surface by asphaltene molecules. This result indicates that the displacement of asphaltenes (bitumen) by EC from the sand grains is irreversible. This finding is consistent with the results obtained by Wang et al. [16], suggesting the possible use of EC to modify the wettability of hydrocarbon-contaminated inorganic solids.

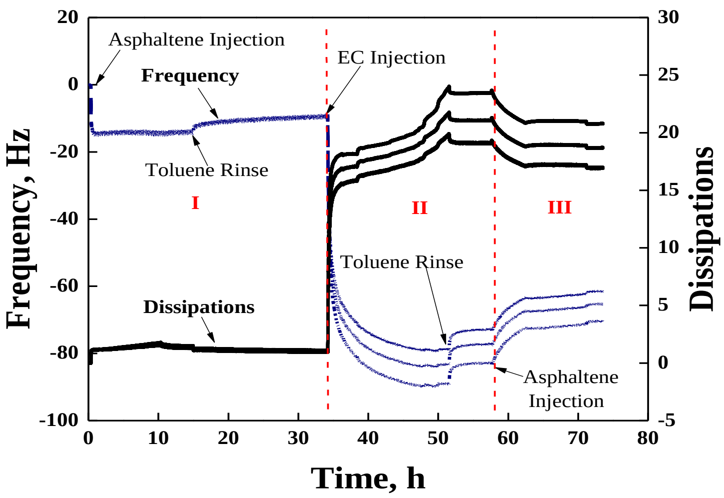


Figure 5-5. QCMD result of silica sensor rinsed with toluene to set up a reference, followed by the injection of 1000 ppm asphaltene-in-toluene solution, toluene rinsing, 300 ppm EC-in-toluene solution and another rinse of fresh toluene and 1000 ppm of asphaltene-in-toluene solution. All the solutions were introduced at 2.5 μl/s and the measurement was operated at 22 °C.

5.3.3 Ability of EC in Stabilizing Water-in-Oil Emulsions. EC has been proven to be an effective demulsifier in froth treatment as described in the previous chapters. However, whether the EC carried in bitumen froth when it was applied during flotation would help removal of water from bitumen froth remains a concern. To answer this question, EC was added to bitumen prior to the emulsion preparation, and its ability in stabilizing water-in-diluted bitumen emulsion was investigated. As shown by the result in Figure 5-6, less water formed water droplets with the addition of EC prior to the preparation of emulsions. The addition of 100 ppm of EC prevented 87% of water from the formation of water droplets, suggesting that the EC carried in bitumen froth could indeed reduce the emulsification of water during froth treatment.

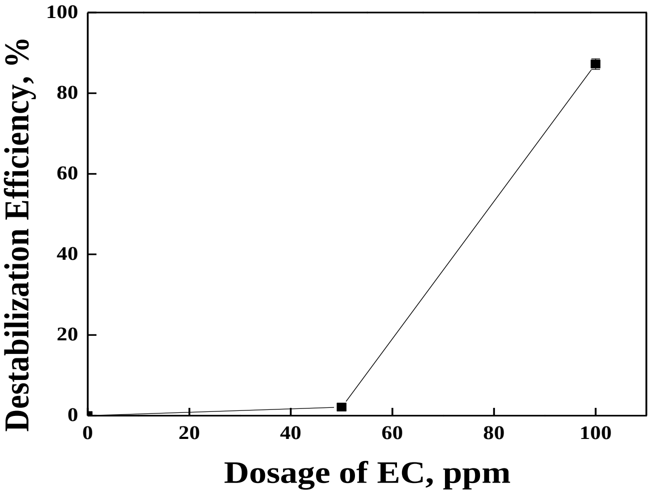


Figure 5-6. The effect of EC addition to bitumen on the formation of a water-in-diluted bitumen emulsion. EC was added to naphtha-diluted bitumen prior to the preparation of emulsions at room temperature. For water content measurement, the sample was taken at 2.5 cm from the surface of the emulsions.

5.4 Conclusions

In this study, 0 to 300 ppm of EC-in-toluene solution or pure toluene was introduced into the flotation system using two different protocols. Due to the dissolution of bitumen by toluene, addition of toluene directly to the oil sands ore led to a higher bitumen recovery and froth quality by reducing viscosity of bitumen.

As EC has a stronger affinity to the bitumen-sand grain interface, it helped squeeze bitumen out from the sand grains. The addition of EC led to a higher froth quality. An overdose of EC to 300 ppm led to a release of cleaner and more condensed froth (much better froth quality). The QCM-D results correlate well with the flotation tests. The addition of toluene dissolved loosely attached bitumen from the sand grains, and the further addition of 300 ppm EC squeezed out the remaining bitumen and led to the formation of a much softer EC film covering the hydrophilic sand grains.

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Chapter 6

Conclusions and Future Work

Water removal from water-in-diluted bitumen emulsions remains a challenge to the oil sands industry. It is generally accepted that surface-active materials in bitumen form a protective interfacial film, which prevents water droplets from coalescence. In this study, ethylcellulose (EC), a biodegradable polymer, was used to destabilize water-in-diluted bitumen emulsions. The role of hydroxyl content and molecular weight of EC on demulsification has been investigated. The effects of temperature and mechanical agitation on demulsification by EC of various molecule weights have also been explored. The behavior of EC at water-diluted bitumen interface and the interactions between EC and the interfacial materials from bitumen have been studied using Langmuir trough technique, AFM, IR, contact angle and film thickness measurements. Finally, the application of EC as a bitumen recovery aid was attempted.

6.1 Major Conclusions

Temperature and mechanical agitation have a great influence on the demulsification of water-in-diluted bitumen emulsions by EC demulsifiers. Higher temperature and appropriate agitation could accelerate diffusion of EC molecules and facilitate contact of demulsifiers with water droplets, leading to higher demulsification efficiency. The diffusion rate of an EC molecule depends on its molecular weight.

Lower molecular weight EC diffused fast. However, this advantage was partially offset by its poorer ability of flocculation due to its short polymer chains. In contrast, high molecular weight EC was beneficial in flocculating water droplets, but its diffusion rate was lower due to long polymer chains. Lower molecular weight EC mainly helped to coalesce water droplets, whereas high molecular weight EC could also flocculate water droplets. EC with a low hydroxyl content also exhibited a poor demulsification efficiency due to non-sufficient interactions with water droplets. An increase in hydroxyl content of EC led to a stronger intra- and intermolecular hydrogen bonding interactions, which reduced the interactions between EC and water droplets and resulted in lower demulsification efficiency. However, the adverse effect of high hydroxyl content could be offset by a demulsifier of high molecular weight, which was beneficial in flocculating water droplets. Therefore, EC with an intermediate molecular weight and desirable hydroxyl content exhibited the best demulsification results.

Using Langmuir trough technique, the interfacial pressure−area isotherms show that the interfacial film formed by the surface-active materials in bitumen became much more compressible by either diffusing of EC through toluene to the toluene-water interface or spreading of EC directly at the interface, where an interfacial film already formed by the surface-active materials in bitumen. The infrared analysis, thickness and contact angle measurements of the interfacial films revealed an irreversible nature of the adsorption of EC at the interface. AFM imaging on interfacial films transferred to a solid substrate by LB method revealed displacement of original protective interfacial films by micron size EC domains, allowing the coalescence of emulsified water droplets in contact. These results allow us to make a conclusion that EC can diffuse to the water-oil interface and reduce the rigidity of the interfacial film by irreversibly displacing/disrupting the interfacial film formed by surface-active materials in bitumen, and facilitating flocculation of water droplets through bridging.

Since EC has proven ability to modify the wettability of hydrocarbon-contaminated inorganic solids [1], EC was added in attempt to enhance bitumen recovery in flotation processes. Fresh toluene was added as a control, and led to an approximate 15% increase in bitumen recovery. While EC addition to toluene did not show too much advantage in bitumen recovery, it did improve bitumen froth quality, in particular when EC-in-toluene solution was added in the ore (protocol II). Comparing to add EC to the oil sands slurry, a slightly better froth quality was obtained when EC solutions were directly added to oil sands ore. This approach allowed EC to have more effective diffusion to bitumen in oil sands. Considering the recovery data and enhancement in froth quality, toluene addition with 100 ppm EC (both protocols) leads to an optimal performance. This dosage is remarkably consistent with the optimal dosage for bitumen froth cleaning, confirming that EC addition prior to flotation would be more effective. The EC remaining in the froth will be carried to froth treatment process. In froth treatment process, EC addition does not stabilize water droplets, and hence it can function as a demulsifier to improve demulsification of bitumen froth.

6.2 Future Work

1) Demulsification experiment can be carried out using the fresh froth collected from the flotation experiment. It would be more practical to investigate the effect of the EC carried to the froth treatment stage from extraction.
2) Ideally, EC could be modified to become temperature responsive water soluble at extraction temperature and less water soluble at froth treatment temperature. This allows EC to be directly added to the process water during flotation, which may lead to increase in both froth quality and bitumen recovery. In addition, the water soluble EC remained in the tailing stream could become a flocculant to facilitate aggregations of fines and enhance tailings settling rates.

6.3 Reference

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