Biodegradable Polymer for Demulsification of Water-in-Bitumen Emulsions

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A Biodegradable Polymer for Demulsification of Water-in-Bitumen Emulsions

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Abstract: A non-toxic and biodegradable polymer, ethylcellulose, was used to break up emulsified water from naphtha-diluted bitumen. At 80 ^{o}C of gravity settling for one hour, it was found that the ethylcellulose polymer at 130 ppm dosage removed 90% of the emulsified water in the diluted bitumen or in a bitumen froth containing about 10 wt% fine solids. Ethylcellulose also assisted in the removal of the fine solids present in the diluted bitumen. It was confirmed by micropipette technique and atomic force microscopy imaging that flocculation and coalescence, as a result of weakening of the interfacial film, are the demulsification mechanism of the water-in-bitumen emulsion.

Keywords: demulsification, water-in-bitumen emulsion, ethylcellulose, bitumen froth treatment, asphaltene, flocculation, coalescence, Langmuir-Blodgett film, atomic force microscopy imaging

1. INTRODUCTION

In bitumen extraction from oil sands using warm water, bitumen is liberated from the sand grains and attaches to air bubbles. The aerated bitumen rises to the top of the separation vessel, forming a bitumen froth which typically contains 60% bitumen, 30% water and 10% solids by weight. To facilitate further separation of water and solids from the bitumen froth, naphtha or paraffinic solvents are used in the bitumen froth treatment (cleaning) step. In the naphtha-based bitumen froth treatment, a solvent-to-bitumen ratio of about 0.7 (wt/wt) is used and typically 1−4 wt% water and 0.3−1 wt% solids remain in the diluted bitumen product (Long *et al.*, 2005).

Removing residual water and solids from the diluted bitumen remains a challenge. In common practice, ethylene oxide/propylene oxide (EO/PO) copolymer-based demulsifiers are used to assist the removal of water from the naphtha diluted bitumen. In this study, we investigate a new biodegradable polymer−ethylcellulose as a potential dewatering aid for naphtha diluted bitumen or diluted bitumen froth, focusing on demulsification mechanism of ethylcellulose.

In the petroleum industry, chemical demulsification has been widely employed to break up water-in-oil emulsions. For example, Wu *et al.* (2003) reported the performance of many conventional low molecular weight surfactants and high molecular weight polymeric surfactants in removing water from diluted bitumen by gravity settling. They found that low molecular weight surfactants removed only 20% of the water at optimal dosage. However, use of polymeric surfactants including polymerized polyols, EO/PO copolymers, and alkylphenol formaldehyde resins modified with EO/PO removed about 90% water. Xu *et al.* (2004) reported dewatering of the naphtha diluted bitumen froth with diethylenetriamine-based EO/PO copolymers. A diluted bitumen froth was treated with 100 ppm EO/PO copolymer and was allowed to settle under gravity at 80 ^{o}C for 3 h. The demulsifiers with an EO/PO molar ratio of 1−1.8 removed about 85% water. It was proposed that polymers with such dentrimer structure broke up water-in-oil emulsions by flocculation and coalescence of the water droplets (Zhang *et al.*, 2005).

In the diluted bitumen, water is present as dispersed droplets of several microns in size which are extremely difficult to coalesce. The water droplets in diluted bitumen are believed to be stabilized by an interfacial skin layer consisting mainly of asphaltenes and fine solids. This steric interfacial film prevents water droplets from flocculating and coalescing (Yan *et al.,* 1999; Angle, 2001; Gafonova and Yarranton 2001; Spiecker *et al.,* 2003; Wu, 2003; Czarnecki and Moran, 2005; Angle *et al.,* 2007). Demulsifiers can destabilize emulsions by changing the properties of interfacial films such as surface tension, mechanical strength, elasticity and thickness of interfacial regions to promote coalescence, or through flocculation of water droplets (Urdahl *et al.,* 1993; Singh, 1994; Kumar *et al.,* 2001; Sjoblom *et al.,* 2001; Zhang *et al.,* 2003).

The properties of interfacial films have been widely investigated using the Langmuir balance and their morphology can be observed by AFM imaging following the transfer of the film onto a solid substrate by the Langmuir-Boldgett (LB) techniques. Zhang *et al.* (2003) reported that in the presence of a commercial alkylphenol formaldehyde resin modified with EO/PO demulsifier, the water/oil interface became significantly less elastic and that the packing of the asphaltene aggregates becomes looser. The properties of interfacial films have also been investigated by using micropipette technique (Yeung *et al.*, 2000). With this technique, the interfacial properties of individual emulsified water droplets can be investigated and the interactions between two water droplets in emulsion can be visualized *in situ*.

In this communication, we intend to study the demulsification mechanism of a promising dewatering aid − ethylcellulose. The properties of ethylcellulose (EC) at oil/water interface are determined. The demulsification mechanism of ethylcellulose for water-in-bitumen emulsions is studied by LB technique and AFM imaging, along with microscopic observation and micropipette technique.

2. EXPERIMENTAL

Materials. Vacuum distillation feed bitumen and industrial grade naphtha were provided by Syncrude Canada Ltd. The heptane insoluble asphaltene content in the bitumen was determined to be about 17 wt%. Heavy naphtha was supplied by Champion Technologies Inc. HPLC grade toluene was purchased from Fisher Scientific. Asphaltene was obtained by following reported extraction procedure of Zhang *et al.* (2003). Mill-Q water was used as the subphase of the toluene/water interface. The water used to prepare water-in-diluted bitumen emulsions was plant recycle process water. The process water had a pH of 8.9 and contained 25 ppm Mg^{2+}, 41 ppm Ca^{2+}, 79 ppm SO_4^{2-}, 527 ppm Na^+, 22 ppm K^+, 407 ppm Cl^- and 793 ppm HCO_3^-. Ethylcellulose with 48% ethoxyl was purchased from Sigma-Aldrich and used as received. The molecular weight of the polymer was 46 kDa which was determined from intrinsic viscosity. Ethylcellulose was dissolved in heavy naphtha or toluene for 24 h prior to its use. The oil sands ores used in this study are summarized in Table 1.

Table 1 Composition (wt%) of Oil Sands Ores

	Good Processing Ore	Medium Processing Ore	Weathered Ore
Bitumen	14.8	13.2	12.1
Water	2.3	1.9	3.8
Total solids	82.9	84.7	84.1
Fines[*]	1.3	13.4	3.1

[*]The percentage of solids with a diameter less than 44 μm in the total solids.

Preparation of Water-in-Bitumen Emulsions. The emulsions were prepared with plant process water and naphtha diluted bitumen with a naphtha-to-bitumen mass ratio of 0.65. After shaking in a mechanical shaker at 200 cycles/min for 4 h, 42 g diluted bitumen was mixed with 2.2 g process water using a homogenizer running at 30,000 rpm for 3 min. The resultant emulsion contained 5 wt% water.

Demulsification Test. In the demulsification test, 9.7 g emulsion and 0.3 ml of 0.5 wt% polymer dissolved in heavy naphtha were homogenized in a 20 ml vial by the homogenizer operating at 8,000 rpm for 30 s. In this case, the concentration of polymer in the emulsion was 130 ppm by weight. Then 9 ml of the mixture was transferred into a 12 ml polypropylene test tube. The tube was capped and sealed with a Teflon tape. All test tubes were collected in a plastic rack and placed in a water bath at a controlled temperature for gravity settling of 1 h. After settling, the water content of the emulsion at 2.5 cm from the top of the emulsion surface was measured with a Karl Fischer titrator. Control tests were also performed for emulsions without demulsifier addition.

Observations by Optical Microscopy. Micrographs of emulsions were obtained using a Carl Zeiss Axioskop 40 Pol microscope equipped with a video camera which was connected to a computer. The emulsion sample without further dilution was placed on a glass slide and covered by a thin glass slide (25 mm × 25 mm × 0.2 mm). The image was taken under halogen light. Unless otherwise stated, all the samples were taken at the bottom of the test tube.

Other Characterization Methods. The interfacial tension of ethylcellulose at the toluene/water interface was determined by using a tensiometer. The demulsification process of water-in-diluted bitumen emulsions was visualized *in situ* by a micropipette technique (Yeung *et al.*, 2000). Monolayers of asphaltenes and ethylcellulose and asphaltenes/ethylcellulose mixture were prepared using a Langmuir interfacial trough (KSV Instruments, Finland), following the reported procedures (Zhang *et al.*, 2003; Chandra *et al.*, 2008). Images of LB films were obtained using a Nanoscope IIIa atomic force microscope (Digital Instruments, Santa Barbara, CA) operating in tapping mode.

3. RESULTS AND DISCUSSION

3.1 Demulsification of water-in-bitumen emulsions

Model Systems: The demulsification efficiency of the polymer was evaluated by measuring the water content at 2.5 cm depth and the water droplet size at the bottom of the emulsion test tube after settling. A lower water content and larger size of water droplets represent a higher demulsification efficiency. Figure 1 shows dewatering performance of ethylcellulose, measured by water content at 2.5 cm depth from the top of the emulsion surface as a function of polymer dosage. Without polymer addition, the water content of the emulsion was reduced from the original 5% to about 4.5%. The addition of ethylcellulose to the emulsion led to a rapid decrease in the water content. When 130 ppm ethylcellulose was added, the water content decreased to as low as 0.5%. Further increase in polymer dosage did not cause additional significant reduction in the water content. The results of Figure 1 show that for the chosen system at optimal dosage of ethylcellulose, the water removal efficiency could reach as high as 90%. The demulsification efficiency of ethylcellulose was also visually observed. The micrographs in Figure 1 show that without polymer addition, the water droplets in the emulsion were about 3 µm in diameter. The size (diameter) of the water droplets increased when the emulsions were treated with increasing dosage of ethylcellulose. At 130 ppm EC, the water droplet size increased to 20−30 µm. It is clear that ethylcellulose promoted coalescence of water droplets. As noted in Figure 1, water droplets appeared as flocs in the emulsions treated with ethylcellulose. A higher polymer dosage led to the formation of more flocs, suggesting flocculation assisted coalescence of water droplets.
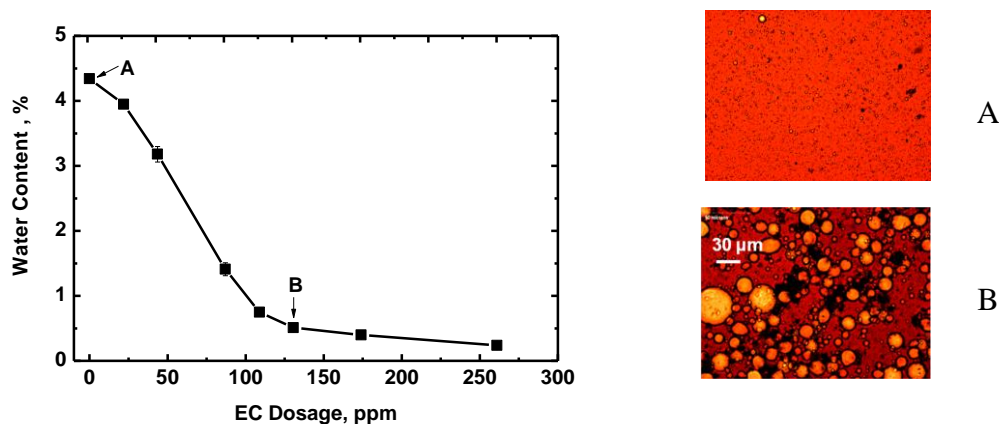

Fig. 1. Water content at 2.5 cm depth from the top of emulsion surface as a function of polymer dosage. Emulsions having an initial 5% water were treated with ethylcellulose and settled under gravity at 80°C for 1 h. The micrograph images of emulsion A (no polymer addition) and emulsion B (with 130 ppm EC added) were shown. The emulsions for imaging were taken from the bottom of the test tubes. The two micrographs have the same magnification.

Bitumen Froth: Ethylcellulose was further applied to dewatering of diluted bitumen froth. The results were shown in Figure 2. For the bitumen froth derived from a good processing ore, the water content could be reduced to 0.5 wt% at 130 ppm EC. However, the addition of ethylcellulose had negligible effect on reducing the water content of the bitumen froth obtained from the weathered ore. The effect of ethylcellulose on dewatering of bitumen froth obtained

3

from the medium processing ore lied between the two extremes: a continuous decrease in water content with increasing polymer dosage, but at a reduced rate as compared with the bitumen froth obtained from the good processing ore. The poor dewatering efficiency for the bitumen froth obtained from weathered ore was attributed to the high content of hydrophobic fine solids in the weathered ore (Liu *et al.*, 2005), which decreases the amount of ethylcellulose available for dewatering. For industrially produced bitumen froths which were produced from blend of good and poor processing oil sands ores, the addition of ethylcellulose reduced the water content to below 0.5% at 130 ppm dosage.
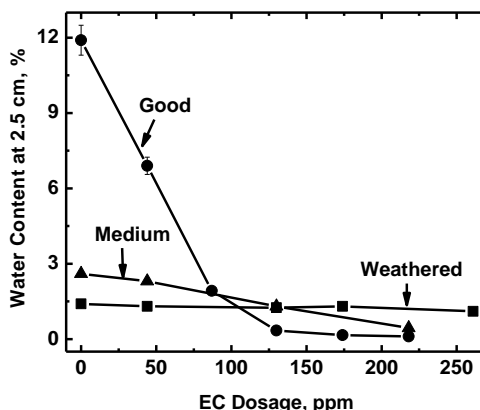

Fig. 2. Water content at 2.5 cm depth from the top of diluted bitumen froth surface as a function of polymer dosage. The settling was carried out under gravity at 80 $^{\circ}$C for 1 h.

3.2 Mechanism of demulsification with ethylcellulose

Ethylcellulose is amphiphilic in nature because of its hydrophilic cellulose backbone and hydrophobic ethyl substitution. It can adsorb at the oil/water interface. The measurement of toluene/water interfacial tension showed a significant decrease in the interfacial tension with the addition of ethylcellulose. The measurement of interfacial pressure−area isotherms of ethylcellulose and asphaltenes using Langmuir trough revealed that ethylcellulose addition led to a greater interfacial tension reduction than by asphaltene addition. Due to its stronger affinity for interfacial adsorption, ethylcellulose can replace partially asphaltenes that have adsorbed at the oil/water interface when it is introduced into water-in-bitumen emulsions. Such displacement will cause destabilization of the emulsion and eventually results in demulsification.

To understand demulsification mechanism of ethylcellulose from a molecular view point, monolayers of asphaltenes and ethylcellulose and asphaltene/ethylcellulose mixture at the toluene/water interface were investigated using AFM imaging. Unlike pure asphaltene films which are characterized by random, close-packed discoid nanoaggregates (Zhang *et al.,* 2003), ethylcellulose did not form such aggregates. Instead, they formed a network-like structure at the interface. When asphaltene and ethylcellulose were mixed, ethylcellulose prevented asphaltenes from forming a continuous interfacial film by segregated polymer domains within the asphaltenes matrix. This characteristic of molecular imaging explains why ethylcellulose can break up water-in-bitumen emulsion.

The demulsification mechanism was further revealed by the visualization of demulsification process *in situ* with a micropipette technique. When two water droplets were brought into contact in the emulsion having no polymer addition, no significant change was observed for both water droplets. The water droplets could be pulled apart from each other without significant deformation. In the presence of 35 ppm EC, however, water droplets flocculated and coalesced. The whole process of flocculation and coalescence occurred within about 15 s. The coalescence speed increased with polymer dosage. At a polymer dosage greater than 130 ppm, for example, the coalescence completed within 1to 2 s.

4. CONCLUSIONS

Under gravity settling at 80°C for 1 h, the addition of 130 ppm ethylcellulose polymer reduced water content from original 2−20% by weight in naphtha diluted bitumen by 90%. At the same polymer dosage and settling conditions, ethylcellulose polymer removed 90% of the water in bitumen froth containing about 10 wt% solids. Ethylcellulose broke up the water-in-bitumen emulsions by flocculation and coalescence, as evidenced by micrographic images and real time visualization of the demulsification process using a micropipette technique. The ethylcellulose polymer addition decreased interfacial tension significantly and was capable of displacing asphaltene aggregates at the interface.

REFERENCES

Angle, C. W. (2001). Chemical demulsification of stable crude oil and bitumen emulsions in petroleum revovery−A review. In: Encyclopedic Handbook of Emulsion Technology. J. Sjoblom (Ed.). 541-594, Marcel Dekker. New York.

Angle, C. W., T. Dabros and H. A. Hamza (2007). Demulsifier effectiveness in treating heavy oil emulsion in the presence of fine sands in the production fluids. Energy Fuels 21, 912-919.

Chandra, M. S., Z. H. Xu and J. H. Masliyah (2008). Interfacial films adsorbed from bitumen in toluene solution at a toluene-water interface: A Langmuir and Langmuir-Blodgett film approach. Energy Fuels 22, 1784-1791.

Czarnecki, J. and K. Moran (2005). On the stabilization mechanism of water-in-oil emulsions in petroleum systems. Energy Fuels 19, 2074-2079.

Gafonova, O. V. and H. W. Yarranton (2001). The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins. J. Colloid Interface Sci. 241, 469-478.

Kumar, K., A. D. Nikolov and D. T. Wasan (2001). Mechanisms of stabilization of water-in-crude oil emulsions. Ind. Eng. Chem. Res. 40, 3009-3014.

Liu, J., Z. Xu and J. Masliyah (2005). Processability of Oil Sand Ores in Alberta. Energy Fuels 19, 2056-2063.

Long, Y. C., J. Kan, A. Walker and T. Dabros (2005). Process for treating heavy oil emulsions using a light alphatic solvent-naphtha mixture. CA 2435113.

Singh, B. P. (1994). Performance of demulsifiers - prediction based on film pressure-area isotherms and solvent properties. Energy Sources 16, 377-385.

Sjoblom, J., E. E. Johnsen, A. Westvik, M. H. Ese, J. Djuve, I. H. Auflem and H. Kallevik (2001). Demulsification in the oil industry. In: Encyclopedic Handbook of Emulsion Technology. J. Sjoblom (Ed.). 595-619, Marcel Dekker New York.

Spiecker, P. M., K. L. Gawrys, C. B. Trail and P. K. Kilpatrick (2003). Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation. Colloids and Surfaces A 220, 9-27.

Urdahl, O., A. E. Movik and J. Sjoblom (1993). Water-in-crude oil-emulsions from the Norwegian continental-shelf .8. Surfactant and macromolecular destabilization. Colloids and Surfaces A 74, 293-302.

Wu, J., Y. Xu, T. Dabros and H. Hamza (2003). Effect of demulsifier properties on destabilization of water-in-oil emulsion. Energy & Fuels 17, 1554-1559.

Wu, X. (2003). Investigating the stability mechanism of water-in-diluted bitumen emulsions through isolation and characterization of the stabilizing materials at the interface. Energy Fuels 17, 179-190.

Xu, Y. M., J. Y. Wu, T. Dabros, H. Hamza, S. Y. Wang, M. Bidal, J. Venter and T. Tran (2004). Breaking water-in-bitumen emulsions using polyoxyalkylated DETA demulsifier. Can. J. Chem. Eng. 82, 829-835.

Yan, Z. L., J. A. W. Elliott and J. H. Masliyah (1999). Roles of various bitumen components in the stability of water-in-diluted-bitumen emulsions. J. Colloid Interface Sci. 220, 329-337.

Yeung, A., T. Dabros, J. Masliyah and J. Czarnecki (2000). Micropipette: a new technique in emulsion research. Colloids and Surfaces, A: Physicochemical and Engineering Aspects 174, 169-181.

Zhang, L. Y., Z. H. Xu and J. H. Masliyah (2003). Langmuir and Langmuir-Blodgett films of mixed asphaltene and a demulsifier. Langmuir 19, 9730-9741.

Zhang, Z. Q., G. Y. Xu, W. Fang, S. L. Dong and Y. J. Chen (2005). Demulsification by amphiphilic dendrimer copolymers. J. Colloid Interface Sci. 282, 1-4.