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Bitumen-silica interactions in the presence of hydrophilic ionic liquids

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ABSTRACT

Ionic liquids have been considered for application in petroleum separation (especially in unconventional oil production) as interfacial functional materials at pure state or aqueous solution state. Herein, the interactions between bitumen and silica in ionic liquids (i.e., [Emim][BF_4]) aqueous solution and pure ionic liquids have been investigated by dynamic contact angle, atomic force microscopy (AFM) and sum-frequency generation spectroscopy (SFG). Results show that the addition of ionic liquids in water enhances the equilibrium degree of bitumen recession from silica surface, while negligible change has been observed when the bitumen coated plate was put into the pure ionic liquids. The force measurements by AFM demonstrate that the bitumen-silica adhesion force in different systems are in the order of: DI water > 1 mM [Emim][BF_4] > pure [Emim][BF_4]. Results of SFG detection show that the addition of [Emim][BF_4] in the aqueous solution strengthens the orientation of water molecules on the silica surface, while making the water molecules more disordered on the bitumen surface. Consequently, a positively charged Helmholtz-like layer is formed by the [Emim]$^+$ cations on negatively charged silica and bitumen surfaces.

1. Introduction

The unconventional petroleum ores (about 70% of total world oil reserves) are naturally a mixture of heavy hydrocarbons (or bitumen), mineral solids and water. As a major part in unconventional oil reserves, oil/tar sands are playing an increasingly important role in global energy supplying. However, characterized by extremely high viscosity, high density and complex chemistry, petroleum production from oil/tar sands is much difficult and costly. The hot water-based extraction (HWBE) is one of the commercial technologies applied in Canadian oil sands industry for many decades. However, a series of issues are impeding its development, including extensive water/energy consumption and environmental pollutions due to the loss of bitumen, exposure of PAHs/naphthenic acids, emission of green-house gases (GHG), etc. [1,2].

To recover the heavy hydrocarbons/bitumen from oil sands in a much easier and more environment-friendly way, some novel technologies have been proposed, such as aqueous-non aqueous hybrid process, solvent extraction, pyrolysis, etc. [3–7]. Ionic liquids (ILs) are reported to be a promising assistant for the enhancement of heavy hydrocarbons recovery from oil sands. Because, compared with the conventional methods (e.g., solvent extraction, water based extraction), ILs-enhanced techniques are known for higher bitumen recovery and bitumen product quality with less solids entrainment, negligible ILs remaining in the residual solids, and high performance of ILs recycling [8,9]. Generally, the ionic liquids are applied in two different ways for the oil recovery enhancement: i) working together with the solvents as additive [8–13], and ii) being added into the solution as functional chemicals for process intensification [14]. It is found that a relatively more complete separation could be achieved during the Canadian oil sands processing when a small amount of ILs (e.g., 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]), 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate ([Bmim][CF_3SO_3]), 1-butyl-2,3-dimethyl-imidazolium tetrafluoroborate ([Bmmim][BF_4])) are added together with the solvents, resulting in higher bitumen recovery at ambient temperatures [8,9,12]. When the ionic liquids (e.g., trihexyl (tetradecyl) phosphonium chloride) act together with water solution, a decrease in oil–water interfacial tension could be obtained, which in turn enhances the oil recovery from ores [1,14].

Basically, the whole production of heavy hydrocarbons from unconventional oil ores could be divided into several sub-steps, including the oil liberation from host rocks surfaces, flotation or dissolution (in

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solvent extraction), etc. [2]. These steps are often strongly influenced by the properties of additives and operational parameters, such as temperature, agitation, etc. [1,3]. Charles and co-workers investigated the bitumen-sand interactions in pure ionic liquid by atomic force microscopy (AFM). Their results indicated that the adhesion force between bitumen and silica was almost an order of magnitude smaller in [Bmmim][BF_4] than that in an 1 mM KCl aqueous solution at ambient conditions [15]. Paul Painter et al. compared the bitumen–silica interactions in a deep eutectic ionic liquid analogue and the de-ionized water, the results showed that the adhesion force between the probe tip and the bitumen surface in deep eutectic mixture were significantly smaller than that in water. Although some work has been done to measure the bitumen-silica interaction in pure ionic liquids, the bitumen recession and force measurement in aqueous solution of ILs are still lack of experimental evidence. Despite recent progress in force measurement, it remains a challenge to obtain the behaviors of water or IL molecules at mineral-bitumen interfaces in aqueous solution or solvent condition during oil sands processing.

Accordingly, in this study, the specific objectives are to: (i) find out the effect of hydrophilic ILs on the bitumen liberation behavior in aqueous solution and at its pure state; (ii) investigate the bitumen-silica interactions in different states of the hydrophilic ILs; (iii) obtain the molecular orientation of ILs and water molecules on silica and bitumen surfaces, as well as the exact mechanisms of ILs enhanced oil recovery from unconventional oil ores.

2. Materials and methods

2.1. Materials

Bitumen used for coating was extracted from the Athabasca oil sands by toluene. Toluene and nitrogen gas were purchased from Tianjin Jiangtian Technology Co. Ltd., China. The IL, named 1-ethyl-3-methyl-imidazolium tetrafluoroborate ([Emim][BF_4]), was obtained from Lanzhou Institute of Chemical Physics, CAS, China. The physiochemical properties of [Emim][BF4] was shown in Table 1. The silica slides and single-crystal silica wafers were provided by Zhongjingkeyi Technology Co., Ltd., China. The silica spheres (~10 μm) were obtained from Knowledge & Benefit Sphere Tech. Co., Ltd., China. The deionized (DI) water used in the whole experiment was at an ultrapure level (18.5 MΩ).

2.2. Contact angle measurements

The contact angle of bitumen on a glass slide in the prepared solution (including pure [Emim][BF_4], 1 mM [Emim][BF_4] aqueous solution, and DI water) was measured to investigate the effect of ILs on bitumen liberation. To simplify the analysis, glass plates were used as model solids to mimic host rocks or sand grains. A detailed procedure of how to prepare the glass slides and bitumen sample, as well as the measurements has been given elsewhere [16]. The whole recession process of bitumen on the glass plate was recorded by a drop shape analyzer (DSA).

2.3. Zeta potential measurements

Emulsion droplets of bitumen were prepared using an ultrasonic method. Approximately 1 g of bitumen was placed in 200 mL of the solution (DI water, 1 mM KCl or 1 mM IL) and then sonicated for about 30 min. The emulsified suspension was allowed to cream for 30 min.

Zeta potentials of the bitumen droplets were measured with a Nano ZS (Malvern Instruments Ltd.). Before the measurements, the rectangular electrophoresis cell was washed by DI water and then filled with about 40 mL of the prepared emulsion. Through the laser-illuminating and video-viewing system, the movement of particles in the stationary layer was traced, 10 times for each direction by alternating positive and negative electrode potentials. The data were then analyzed by a built-in software and converted to zeta potential distributions as desired. Each test was repeated at least twice. The measurement error was less than 10%.

2.4. Bitumen-silica interactions test by AFM

2.4.1. Probe particle preparation

The silica sphere (Φ10 μm), instead of real sand grain, was glued onto a silicon nitride V-shaped cantilever (Bruker) by A&B adhesives. The spring constant of the prepared probe was calibrated by thermal tune method.

2.4.2. Bitumen substrate preparation

Bitumen solution was centrifuged at 7000 rpm for 30 min to remove the residual fine/clays. After that, a toluene-diluted bitumen solution with concentration of 2.5 mg/mL was used for bitumen coating. The silica wafer, as substrate (cutting into 10 × 10 mm^2 pieces), was ultrasonic cleaned by being immersed in chloroform and ethanol for 30 min respectively, followed by washing with DI water and dring by high purity nitrogen, and then it was put onto a Spin Coater to prepare the bitumen film as described above in contact angle measurements.

2.4.3. Force measurement

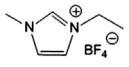
Prior to force-distance measurement by AFM (Multimode 8, Bruker), both probe and bitumen film/silica wafer were immersed in the test liquid to equilibrate for at least 30 min. A suitable ramp rate was chosen to eliminate the effluence of the drag force caused by fast moving of the probe in the liquid. For each approach/retraction cycle of the AFM force-distance measurement, the cycle lasted for 2 s in DI water, while lasted 60 s in [Emim][BF_4] and 1 mM [Emim][BF_4] aqueous solution because of the high viscosity of the IL and low cantilever spring constant. Take the uneven bitumen-coated surface into consideration, a total of 100 force-distance curves (10 curves at 10 different spots) were collected for each system and adhesion force distribution diagram was reported.

To obtain the effect of IL on the interaction between bitumen and sand, the force curves between bitumen and silica wafer were determined under the environments of DI water, 1 mM [Emim][BF_4] and pure [Emim][BF_4] respectively.

2.5. Water molecules structure on mineral and bitumen surfaces detected by SFG

Sum-frequency generation (SFG) spectroscopy has emerged as a novel technique to gain insight of the noncentrosymmetric mineral interfacial structure at a molecular scale, as a result of extreme sensitivity to the interface [17–19]. SFG is also the only non-invasive

Table 1
Physiochemical properties of [Emim][BF4].

Name	Molecular formula	Molecular structure	Molecular weight	Density, 20 °C ($g·cm^{-3}$)	Viscosity, 20 °C (cP)	Melting point (°C)
1-ethyl-3-methyl-imidazolium tetrafluoroborate	$C_6H_{11}N_2BF_4$		197.97	1.294	45	11