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Ionic liquids as viscosity modifiers for heavy and extra-heavy crude oils

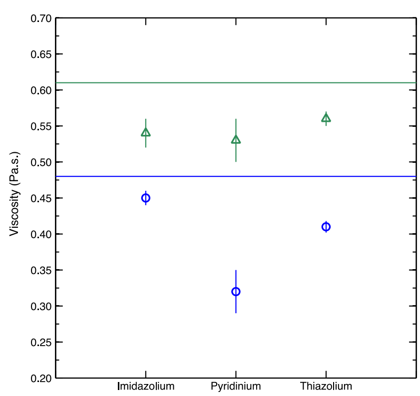
Deepa Subramanian [a], Kathleen Wu [a], Abbas Firoozabadi [a,b,*]

[a] Department of Chemical and Environmental Engineering, Yale University, 9 Hillhouse Avenue, New Haven, CT 06511, United States
[b] Reservoir Engineering Research Institute, 595 Lytton Ave, Palo Alto, CA 94301, United States

HIGHLIGHTS

- Ionic liquids are used to reduce the viscosity of heavy oil and bitumens.
- Viscosity reduction up to 35% is observed using 5 ppm of dodecylpyridinium chloride.
- Ionic liquids seem to interact with asphaltenes to decrease their aggregate size.
- Decrease in asphaltene aggregate size seems to lower the crude viscosity.
- Intermolecular interactions include π–π, aliphatic, acid–base, and charge-transfer.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy oils and extra-heavy oils (bitumens) are difficult to produce and transport due to problems associated with the aggregation of asphaltene molecules. Asphaltenes, a primary component of heavy oils and bitumens, affect the viscosity significantly. Traditional methods of viscosity reduction for heavy petroleum fluids include thermal or dilution methods. In this work, we employ an alternative method for viscosity reduction, by using functionalized molecules that could interact with the asphaltenes and change the properties of the crude oil at the molecular level, reducing viscosity. Ionic liquids, having favorable thermophysical properties such as low vapor pressure, are the functionalized molecules tested in this work. Various properties of the ionic liquids such as alkyl tail lengths (C2, C4, C6, C8, C10, and C12), counter-ion charge density (chloride, thiocyanate, and tetrafluoroborate), and type of head group (imidazolium, pyridinium, and thiazolium) are tested with a Mexican heavy oil and Canadian and Venezuelan bitumens. Small amounts of the additives (between 1 and 10 ppm), dissolved in toluene, are used. Viscosity reduction up to 35% is observed for the crude oils, with dodecylpyridinium chloride showing the maximum reduction. Various molecular interactions between the ionic liquids and the asphaltene molecules, such as aromatic, acid–base, and charge-transfer interactions, seem to hinder the asphaltene aggregate formation, which consequently reduces the viscosity. These results set the stage for further research on the viscosity reduction of heavy oil and extra-heavy oils by using functionalized molecules.

1. Introduction

Petroleum is amongst the most widely used natural resource available to man. It is a heterogeneous mixture of many organic compounds with varying molecular weights [1]. Conventional petroleum (oil), consists of free flowing liquid hydrocarbons

* Corresponding author at: Department of Chemical and Environmental Engineering, Yale University, 9 Hillhouse Avenue, New Haven, CT 06511, United States.
E-mail address: abbas.firoozabadi@yale.edu (A. Firoozabadi).

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extracted from reservoirs. Oil is an indispensable part of our modern world, used for almost all activities ranging from transportation to industrialization [1,2]. The economies of several countries are dependent on oil [3]. In 2012, the amount of oil consumed world wide totaled 90 million barrels per day, a 1% increase as compared to 2011 [4,5]. At the end of 2012, the proven world reserves of oil was about 1700 billion barrels, an increase of about 25% over the past decade [5]. The current reserves are projected to last for about 50 years at the present level of world oil demand, but the global oil requirement is steadily rising [4]. Driven by the energy consumption of emerging markets such as India and China, the world oil demand is projected to rise by 20–25% over the next decade [4].

Heavy oils, bitumens, oil sands, and shale deposits are all alternatives to conventional oil [4]. The Middle East leads the world in reserves of conventional oil, while the unconventional oil reserves are abundant in the Americas, with Venezuela leading the reserves of heavy oil, and Canada leading the reserves of extra-heavy oil [5]. Oils are classified based on the American Petroleum Institute (API) Standard. According to this standard light oil is defined as having an API gravity greater than 31.1°, medium oil is defined as having an API gravity between 22.3° and 31.3°, heavy oil has an API gravity between 10° and 22.3°, and extra-heavy oil (bitumen) has an API gravity less than 10° (API gravity is inversely related to specific gravity) [4]. The higher the API index of oil, the greater is the commercial value.

Heavy oils and bitumens, two unconventional oil resources explored in this work, are characterized by high viscosities, which require prodigious methods to extract them from the subsurface and make them transportable across long distances [4,6,7]. These oils are extracted via two methods: (1) thermal and (2) non-thermal [4]. Thermal methods include techniques such as insitu combustion, cyclic steam stimulation, and steam assisted gravity drainage. Non-thermal methods include techniques such as dilution, chemical flooding and formation of oil in water emulsion. Thermal methods, although very effective, require huge amounts of energy and involve high monetary expenditures. On the other hand, the non-thermal methods are not energy intensive, but require bulk amounts of chemicals.

In this work, we implement an alternative approach for viscosity reduction: our goal is to use functionalized molecules that can interact with the asphaltene molecules in crude oils, and lower the viscosity of the oil. Asphaltenes, the most polar fraction of crude oils, seem to be a primary factor contributing to the high viscosity of heavy oils and bitumens [8,9]. The interactions between the functionalized molecules and the asphaltene molecules could change the properties of crude oil at a molecular level, which could then reduce the viscosity of the crude. With this outlook, we investigate the scope of using ionic liquids as the functionalized molecules to reduce the viscosity of heavy oils and bitumens.

Ionic liquids are salts with melting points below 100 °C [10]. They have low vapor pressures and are environmentally more benign than other organic solvents, such as volatile aromatics and alkanes. Properties of ionic liquids can be customized by choosing the appropriate combination of anion and cation for specific applications [11]. The most important reason for the choice of ionic liquids is that they exhibit a wide variety of functionalities, such as aromatic and acid–base interactions. These functionalities cause the ionic liquids to interact with the asphaltenes and lower the asphaltene aggregate size, which leads to a reduction in the viscosity of the crude oil.

Various researchers have used functionalized molecules to enhance stability and lower the viscosity of crude oil. Ionic liquids were first tested by Hu et al. in 2005 to reduce the precipitation of asphaltenes and enhance the stability of crude oils [12]. Many features of the ionic liquids, such as effect of alkyl tail length, charge density of cation head group, and counter-ion charge density were investigated. They observed that ionic liquids having high anion charge density and low cation charge density were effective at inhibiting asphaltene precipitation. They also noted that as the concentration of the ionic liquid is increased, from about 0.5 to about 5 wt.%, the stability of crude oil increased. They attribute this to electrostatic interactions between the ionic liquid and the asphaltene molecule, which lowers the asphaltene aggregate size and reduces precipitation.

In 2009 Boukherissa et al. investigated the use of ionic liquids as efficient dispersants of crude oil [13]. Imidazolium ionic liquids consisting of the boronic acid functionality or the propenyl group functionality in the cation head group, with bromide anions, were tested. Model oils containing around 2% asphaltenes in a 2:1 heptane:toluene mixture were treated with the ionic liquids, whose concentration varied from about 2% to 8%. It was observed that the ionic liquids with the boronic acid head group, and having a tail of at least 8 carbon atoms, reduced the viscosity of the model oil by about 80% (from 16 to about 3 Pa s). They attribute this effect to polar interactions between the Lewis-acid moiety of the boronic acid head group and the basic regions of the asphaltene molecules, which limits the growth of asphaltene aggregates and reduces the viscosity.

Recent experimental work by Chàvez-Miyauchi et al. show the effect of adding polyisobutylene succinimides, consisting of long branched alkyl tail lengths and a boronic acid head group, on the viscosity of Mexican crude oil [14]. They observed that mixing about 0.2 wt.% of the additive (with a tail of 16 carbon atoms) and 0.3 wt.% xylene with 99.5 wt.% of a Mexican crude oil, lowered the viscosity by 11% (change is compared to 99.5 wt.% crude oil containing 0.5 wt.% xylene) [14]. They ascribe this effect to π–π interactions and the formation of hydrogen bonds between the functionalized molecule and the asphaltenes, which lowers the asphaltene aggregate size and reduces the viscosity of the crude. The presence of a branched tail leads to further disorder in the system and hinders aggregate formation. The same group then investigated the effect of adding another novel chemical additive, n-aryl amino alcohol - a tetrameric complex with cyclopentanes, benzene rings, amino, and hydroxyl groups with long alkyl tails and the boronic acid head group. This complex, with a tail of 16 carbon atoms, was mixed with a different Mexican crude oil to determine viscosity reduction. They noted that adding 0.3 wt.% of the additive to 1.2 wt.% heptane and 98.5 wt.% crude, reduces the viscosity of the crude by about 8 wt.% (the reference being 98.5 wt.% crude containing 1.5 wt.% heptane) [15]. They attribute these effects to the interactions between the functionalized molecules and the asphaltene molecules [15]. The additive seems to inhibit the growth of asphaltene aggregates, by either associating with the asphaltenes through the formation of hydrogen bonds, or by creating a steric interference that prevents the assemblage of asphaltene molecules, thus lowering the viscosity of the crude oils.

Motivated by the successful results on the application of ionic liquids to enhance stability and lower viscosity of crude oils, this work is focused on investigating the commercially available ionic liquids for the same purpose. The effect of 1-alkyl-3-methyl imidazolium salts, with varying alkyl tail length (from C2 to C12), and varying anion charge density (chloride, thiocyanate, and tetrafluoroborate) are tested in this work. The ionic liquid with the dodecyl tail and the chloride anion are tested with various head groups, imidazolium, thiazolium, and pyridinium. Very small concentrations, between 1 and 10 ppm, of the ionic liquids are used, keeping in view environmental and economic considerations. Results indicate that there exists a non-monotonic relationship between the tail length of the ionic liquid and the observed reduction in viscosity of the crude oils. Ionic liquids with higher tail lengths (C8–C12) are more effective at viscosity reduction com-