



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



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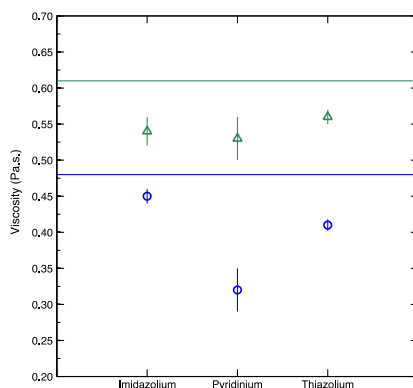
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HIGHLIGHTS

- 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. Asphaltene, 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 asphaltene 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.

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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

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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-

pared to ionic liquids with smaller tail lengths (C2–C6). Anions with higher charge density, such as chloride, seem to be more effective at viscosity reduction compared to anions with lower charge density. Ionic liquid with the pyridinium head group is the most effective in reducing the viscosity (with a maximum reduction of about 35%) as compared to ionic liquids with imidazolium or thiazolium head groups. All these results are ascribed to specific non-covalent interactions between the ionic liquid and the asphaltenes.

2. Materials and methods

2.1. Materials

Three different oils, heavy oil from Mexico and bitumens from Canada and Venezuela, are investigated in this work. The 1-alkyl-3-methyl imidazolium chlorides are purchased from Sigma Aldrich, (C2-ethyl, C4-butyl, C6-hexyl, and C10-decyl) and Iolitech Inc. (C8-octyl and C12-dodecyl). The ionic liquids 1-butyl-3-methyl imidazolium with anions chloride, thiocyanate, and tetrafluoroborate are from Sigma Aldrich. Dodecylpyridiniumdinium chloride is purchased from Santa Cruz Biotechnology while dodecylthiazolium chloride is purchased from Celestial Specialty Chemicals. All ionic liquids have a purity > 98%. Toluene, ethanol, isopropanol, anhydrous KOH, and glacial acetic acid are from Avantor Chemicals (ACS grade reagents), heptane is from Fisher Scientific (ACS grade reagent), and 0.1 M perchloric acid in glacial acetic acid is from Sigma Aldrich.

2.2. Characterization methods

The three oils are characterized to determine properties such as asphaltene content, density, total acid number (TAN), and total base number (TBN). The asphaltene content of the oils is measured by mixing 1 g of the oil with 40 mL of heptane. The samples are then sonicated for about 15 min and left to rest for about 24 h. Next, they are vacuum filtered with 200 nm cellulose-nitrate filters (purchased from Whatman) and the residue is left to dry over night. Subsequently, the residue is collected and weighed to determine the amount of asphaltenes per gram of oil. Results are based on 8–10 measurements.

The densities of the heavy and the extra-heavy oils are determined by diluting them with various concentrations of toluene, and extrapolating the values to 0 wt.% toluene. The density of oil-toluene mixtures is measured by using an Anton Paar densitometer at $T = 25^\circ\text{C}$. Multiple density measurements (3–4) are carried out for each concentration and 4–5 concentrations are tested for each oil. The API gravity is computed from the density, as given in Eq. (1). The results are summarized in Table 1.

$$\text{API gravity} = \frac{141.5}{\text{Specific gravity}} - 131.5 \quad (1)$$

The acidity and basicity of the crude oils are measured by determining the total acid number (TAN) and the total base number

Table 1
Properties of the crude oils.

Name	Asphaltene content (wt.%)	Density (g/cc)	API gravity (°)
Mexican heavy Oil	34 (±1)	0.978 (±0.0002)	13.2
Canadian bitumen	14 (±2)	1.000 (±0.0002)	10.0
Venezuelan bitumen	14 (±1)	1.001 (±0.0006)	9.9

(TBN). TAN and TBN values of crude oils seem to be correlated with the asphaltene content of the oils [16]. TAN and TBN are determined by using a potentiometric titrator unit (Metrohm 916 Ti-touch) combined with a glass electrode (Metrohm Solvotrode). The TAN is determined in accordance with ASTM D664, while the TBN is determined in accordance with ASTM 2896. The titrating solvent in TAN measurements is 0.1 M KOH dissolved in ethanol, while the titrating solvent in TBN is 0.1 M perchloric acid in glacial acetic acid. The samples are sonicated for about 45 min at 40°C before the measurements to ensure homogeneity. Each measurement is repeated 4–6 times to ensure reproducibility of results. The resultant TAN and TBN values are given in Table 2.

The critical (reverse) micelle concentration, CMC, of the ionic liquids, in solvents toluene and heptol (1:1 by volume of toluene and heptane), is determined by static light scattering (SLS) experiments. The light scattering intensity of samples containing varying concentrations of the ionic liquid, ranging from 1 ppm to 1000 ppm (solubility limit), are measured at a scattering angle of 90° and $T = 25^\circ\text{C}$. The concentration at which the derivative of the intensity exhibits a maximum is taken as the CMC concentration. These results are summarized in Table 3. Solubility experiments in heptane indicate that the solubility of the ionic liquids in heptane is below 1 ppm. As a result, due to practical limitations of sample preparation, CMC measurements are not carried out in heptane.

2.3. Sample preparation for rheology

A small amount of the crude oils, about 5 g, is weighed out in a glass vial and mixed with appropriate amounts of the ionic liquid, which is previously dissolved in toluene. The sample is then sonicated for 20 min at room temperature, after which it is manually mixed for about 30 s. The sample is further sonicated for 40 min at about 40°C and cooled to room temperature before performing rheology measurements. Before each rheology measurement, the sample is vigorously agitated for about 30 s to ensure homogeneity. Multiple rheology runs (3–4) are carried out from each sample, and 2–4 samples, for each concentration, are tested to confirm reproducibility of results.

2.4. Rheology experiments

Rheology experiments are carried out in an Anton-Paar MCR302 Rheometer. The MCR302 functions on an air-bearing technology, employing parallel-plate and cone-and-plate techniques to measure viscosity. Most of the experiments in this work use the parallel-plate system, which requires a small volume of sample for each run, and works ideally at varying temperature gradients as compared to the cone-and-plate system. To maintain temperature after loading the sample, the sample and the tool-system are enclosed with a thermo-protecting hood, which is an inherent part of the MCR302 rheometer. The thermo-protecting hood also contains a "solvent trap" provision, which leads to a controlled environment around the sample and prevents drying or evaporation of the solvent and the sample. In this work, n-decane is used as the "solvent trap" fluid.

3. Results

Fig. 1 depicts the viscosity of heavy oil and the bitumens as a function of shear rate. This figure shows that these oils exhibit Newtonian behavior at low shear rates, and seem to be shear-thinning at higher shear rates. In order to investigate the effect of functionalized molecules on the viscosity of these oils, rheology

Table 2
Total acid number (TAN) and total base number (TBN) of the crude oils.

Name	TAN ^a (mg/g)	TBN ^b (mg/g)
Mexican heavy oil	35 (±0.008)	4.1 (±0.13)
Canadian bitumen	3.30 (±0.04)	4.5 (±0.12)
Venezuelan bitumen	5.0 (±0.12)	5.9 (±0.16)

^a As per ASTM D664.

^b As per ASTM 2896.

Table 3
Critical (reverse) micelle concentration (CMC) of ionic liquids in various solvents.

Name	Toluene (ppm)	HepTol ^a (ppm)
1-Octyl-3-methyl-imidazolium chloride	550	170
1-Decyl-3-methyl-imidazolium chloride	420	60
1-Dodecyl-3-methyl-imidazolium chloride	170	15
Dodecylpyridinium chloride	110	10

^a Equivolume mixture of heptane and toluene.

experiments are carried out in the low shear regime, where the oils exhibit Newtonian behavior.

Toluene, which acts as a carrier fluid for the functionalized molecules, has a dilution effect on the viscosity of the crude oils. Fig. 2 shows the effect of toluene on the viscosity of the crude oils, at $T = 25^\circ\text{C}$, measured over a fixed shear range, where Newtonian behavior is observed. The concentration of toluene chosen in this work is such that it facilitates a homogeneous mixing of the additive and the crude oil. The toluene concentration in the Mexican heavy oil is maintained at 1 wt.%, while it is 10 wt.% in the Canadian and Venezuelan bitumens.

Fig. 3 shows the effect of temperature on the viscosity of the crude oils. The temperature dependence of viscosity seems to follow an Arrhenius law,

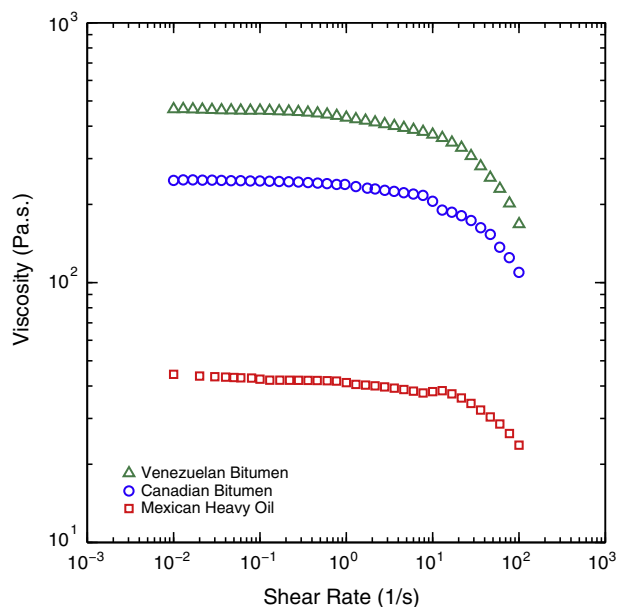


Fig. 1. Viscosity of heavy oil and the bitumens as a function of shear rate at $T = 25^\circ\text{C}$. At low shear rates the oils behave like Newtonian fluids, while at higher shear rates, they seem to be shear thinning.

$$\eta = \eta_0 \exp\left(\frac{E}{k_B T}\right), \quad (2)$$

where η is the viscosity, η_0 is a constant, E is the activation energy, k_B is Boltzmann's constant, and T is temperature.

In order to investigate the effect of alkyl tail length on the viscosity of the crude oils, imidazolium ionic liquids with tail lengths C2, C4, C6, C8, C10, and C12 are tested. Chloride is maintained as the anion. Fig. 4a shows the normalized viscosity of the Mexican heavy oil containing toluene (1 wt.%) and 1 ppm (w/w) of the various ionic liquids. Since the Mexican heavy oil is observed to be heterogeneous, normalized viscosity is shown here (normalization is done with respect to the viscosity of heavy oil, 60 Pa s.). Fig. 4b shows the effect of adding 5 ppm of the imidazolium chlorides with varying alkyl tail lengths on the viscosities of the Canadian and Venezuelan bitumens (toluene concentration is maintained at 10 wt.%).

Next, the effect of the anion charge density of the ionic liquid on the viscosity of the crude oil is determined. Fig. 5 shows the normalized viscosity of heavy oil, containing the 1-butyl-3-methyl imidazolium cation with anions of varying charge densities, chloride, thiocyanate, and tetrafluoroborate (anion radii given in Table 4). The temperature is maintained at $T = 25^\circ\text{C}$ and toluene concentration is maintained at 1 wt.%.

The effect of the cation head group on the viscosity reduction of the crude oils is investigated next. Fig. 6 shows the effect of adding 5 ppm of dodecyl chloride with varying head groups, imidazolium, pyridinium, and thiazolium, on the viscosity of the Canadian and Venezuelan bitumens, at three different temperatures. Experiments are also carried out by adding 1 ppm of dodecylpyridinium chloride to the Mexican heavy oil but no change in viscosity is observed.

The effect of concentration of the ionic liquid on the viscosity reduction of the oils is also probed. Fig. 7 shows the effect of C8 and C10 imidazolium chlorides, at varying concentrations on the viscosity of the Canadian bitumen, at $T = 25^\circ\text{C}$.

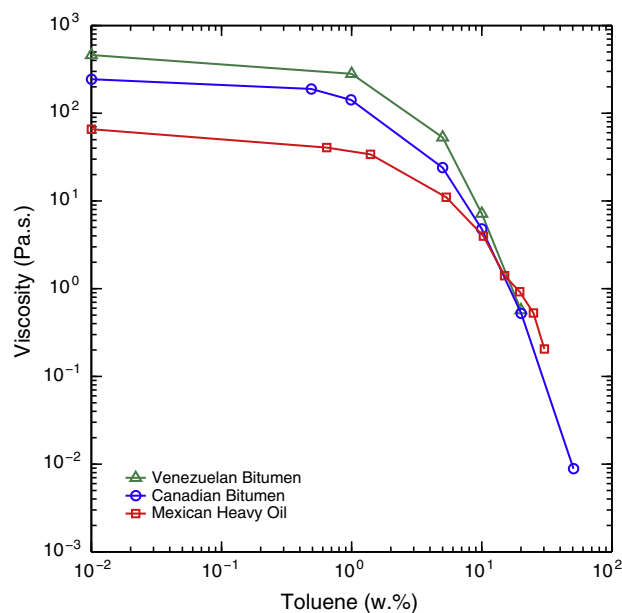


Fig. 2. Viscosity of heavy oil and bitumens, in mixtures of toluene, at $T = 25^\circ\text{C}$. The shear rate has been maintained constant at a value where the oils exhibit Newtonian behavior. The average viscosity of the Venezuelan bitumen, Canadian bitumen, and the Mexican heavy oil, without any toluene, is about 460 Pa s., 240 Pa s., and 60 Pa s. respectively.

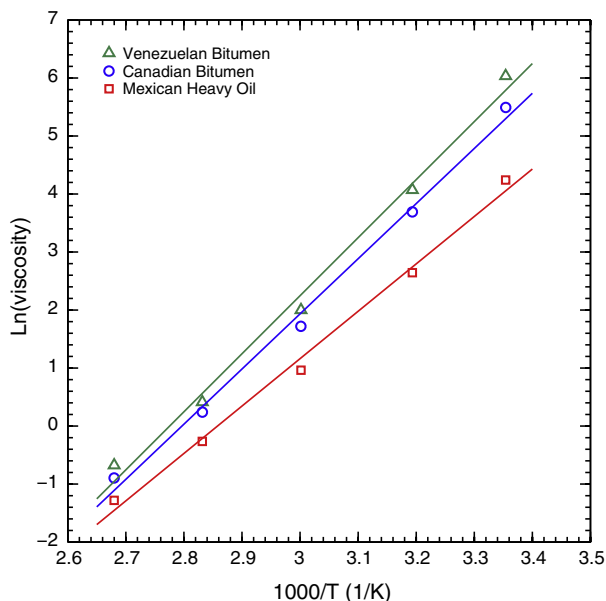


Fig. 3. The temperature dependence of the viscosity of the three oils studied in this work. Viscosity is measured in SI units. The shear rate is maintained at a constant value where the oil exhibits Newtonian behavior. The solid lines are a fit to Eq. (2).

4. Discussion

In this work, the effect of ionic liquids on the viscosity reduction of heavy and extra-heavy crude oils is explored. In order to interpret the results, we first need to understand the various interactions occurring in the system. As stated earlier, a primary contributor to the high viscosity of heavy oils and bitumens is the asphaltene [4,8,9]. Asphaltenes are defined as the fraction of crude oil, which are soluble in aromatics such as toluene and insoluble in aliphatics such as heptane [4,8]. They have a polyaromatic core consisting of fused benzene rings, surrounded by aliphatic chains [8]. Asphaltenes contain heteroatoms such as nitrogen, oxygen, and sulfur on the periphery, and transition metals such as iron, vanadium, and nickel on porphyrin-like structures [8]. Fig. 8 shows the schematic of hypothetical asphaltenes.

Asphaltenes exhibit a wide variety of interactions, ranging from π - π interactions between the polyaromatic cores, aliphatic interactions between the side-chains, acid-base interactions involving heteroatoms such as nitrogen in pyridine or pyrrolic form, hydrogen-bonding interactions exhibited by carboxyl or hydroxyl group, and possibly charge-transfer interactions involving metals [8,20–23]. These interactions are responsible for the aggregation of asphaltenes, which affects the viscosity of the crude oil [8,24].

In order to reduce the viscosity of the heavy oil and bitumens, we have chosen functionalized molecules such that they would interact with the asphaltenes via π - π , aliphatic, acid-base, or charge-transfer interactions. As a result, the size of the asphaltene aggregate could decrease, which would in turn lower the viscosity. With this viewpoint in mind, ionic liquids, which exhibit aromatic, aliphatic, acid-base, and charge-transfer interactions [25], are chosen.

Viscosity reduction ranging up to 35% (with reference to the oil containing toluene) is observed for the crude oils tested in this work. Favorable properties of the ionic liquids, which lead to a higher viscosity reduction, are identified. Fig. 4 indicates a non-monotonic relation between the tail length of the ionic liquid and viscosity reduction. Ionic liquids with larger tail lengths (C8–C12) are more effective at viscosity reduction than those with smaller tail lengths (C2–C6). This trend can be explained by under-

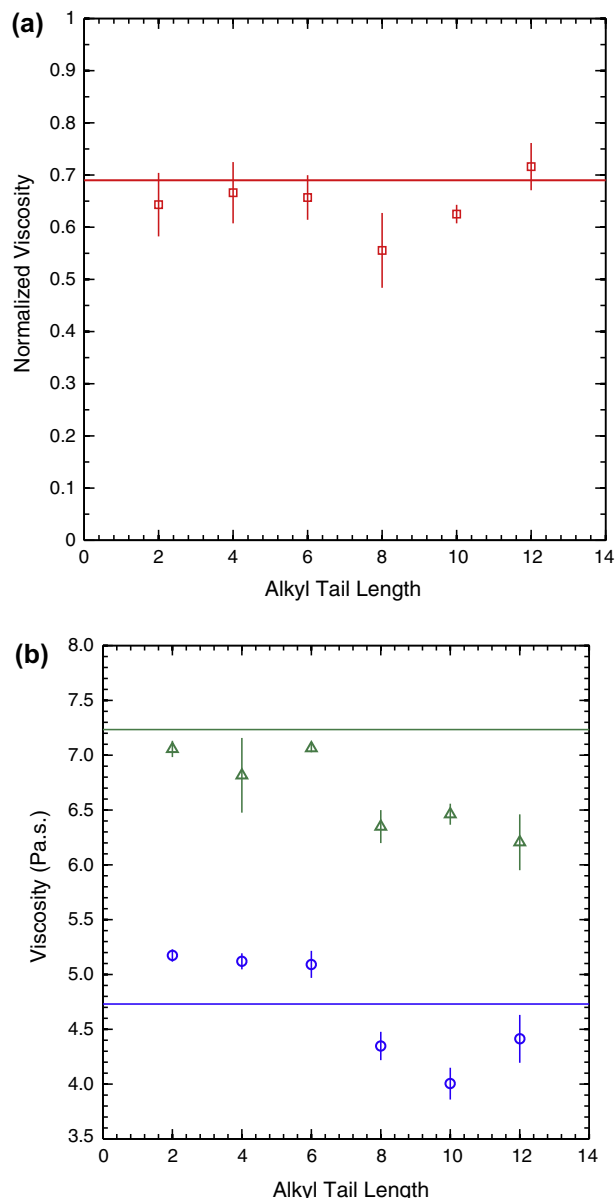


Fig. 4. (a) Normalized viscosity of the Mexican heavy oil, containing 1 wt.% toluene and 1 ppm (w/w) of ionic liquid. Data are normalized with the viscosity of heavy oil, 60 Pa s. (b) Viscosity of Venezuelan bitumen (triangles) and Canadian bitumen (circles), containing 10 wt.% toluene and 5 ppm (w/w) of ionic liquids. The solid lines represent the viscosity with only toluene. The ionic liquids added are imidazolium chlorides with varying alkyl tails, from ethyl (C2), butyl (C4), hexyl (C6), octyl (C8), decyl (C10), to dodecyl (C12). The temperature is maintained at $T=25^\circ\text{C}$, and the shear rate is maintained at a range where the oil exhibits Newtonian behavior.

standing the mechanism of interactions within the system. Experimental and simulation studies show that π - π interactions amongst the polyaromatic cores of asphaltene molecules are a primary cause of asphaltene aggregation [20,24,21]. However, if the asphaltene molecules or the externally added functionalized molecules contain aliphatic side chains, then these side chains can create a steric hindrance to the π - π stacking of asphaltene molecules that inhibit the growth of asphaltene aggregates [21–23]. The trend observed in Fig. 4 indicates that at small tail lengths (less than C8), the strength of the alkyl tails of the ionic liquids are not strong enough to cause steric hindrance to the π - π stacking of asphaltene molecules, while at higher alkyl lengths (C8–C12), the tails of the ionic liquid seem to inhibit the π - π inter-

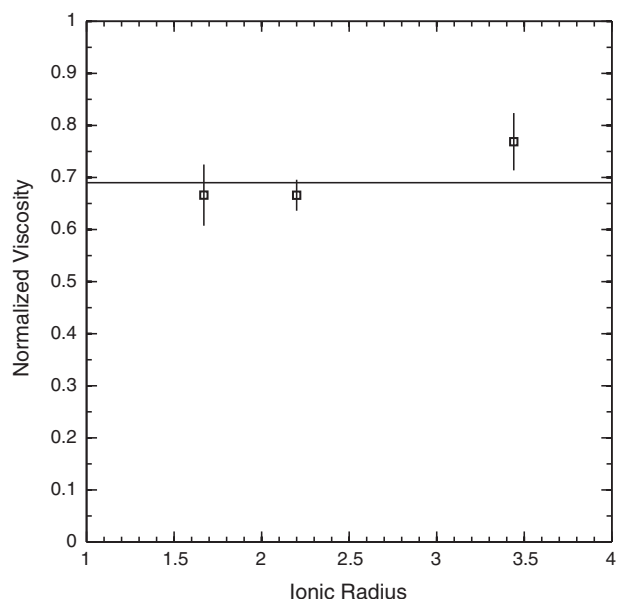


Fig. 5. Normalized viscosity of heavy oil + 1 wt.% toluene + 1 ppm (w/w) of 1-butyl-3-methyl imidazolium ionic liquids with increasing anion size, ranging from Chloride, Thiocyanate, to Tetrafluoroborate. The solid line represents the normalized viscosity of heavy oil with 1 wt.% toluene. Data are normalized with the viscosity of heavy oil, 60 Pa s.

Table 4
Ionic radii of various anions.

Name	Radius (Å)
Chloride (Cl ⁻)	1.67 ^a
Thiocyanate (SCN ⁻)	2.20 ^b
Tetrafluoroborate (BF ₄ ⁻)	3.44 ^c

^a Ref. [17].

^b Ref. [18].

^c Ref. [19].

actions between asphaltene molecules by creating a steric interference. This seems to lead to smaller aggregate sizes and thus higher viscosity reduction. The recent findings of Jian et al., who have studied the effect of tail length on asphaltene aggregation via molecular dynamics simulations [22], can further corroborate these findings. They show that there is indeed a non-monotonic relationship between the length of the side chain and the amount of asphaltenes aggregated.

Next, we comprehend the effect of the counter-ion (anion) charge density on the viscosity of crude oils. Fig. 5 indicates that anions with higher charge density, such as chloride, seem more effective at viscosity reduction as compared to anions with lower charge density, such as tetrafluoroborate. Anions with smaller charge density may exhibit weaker interactions with the asphaltene molecules and do not associate strongly with the electron deficient regions of the asphaltene molecules. Thus, weaker anions do not hinder asphaltene self-association, and therefore do not cause viscosity reduction. Similar evidence is seen in the work of Swatloski et al. wherein they have solubilized cellulose in imidazolium ionic liquids with increasing anion charge density [26].

Subsequent to the effect of the anion, we look at the effect of the cation head group on the viscosity reduction of crude oils. From Fig. 6, we see that the ionic liquid with pyridinium head group causes higher viscosity reduction in the bitumens as compared to the ionic liquids with imidazolium and thiazolium head groups.

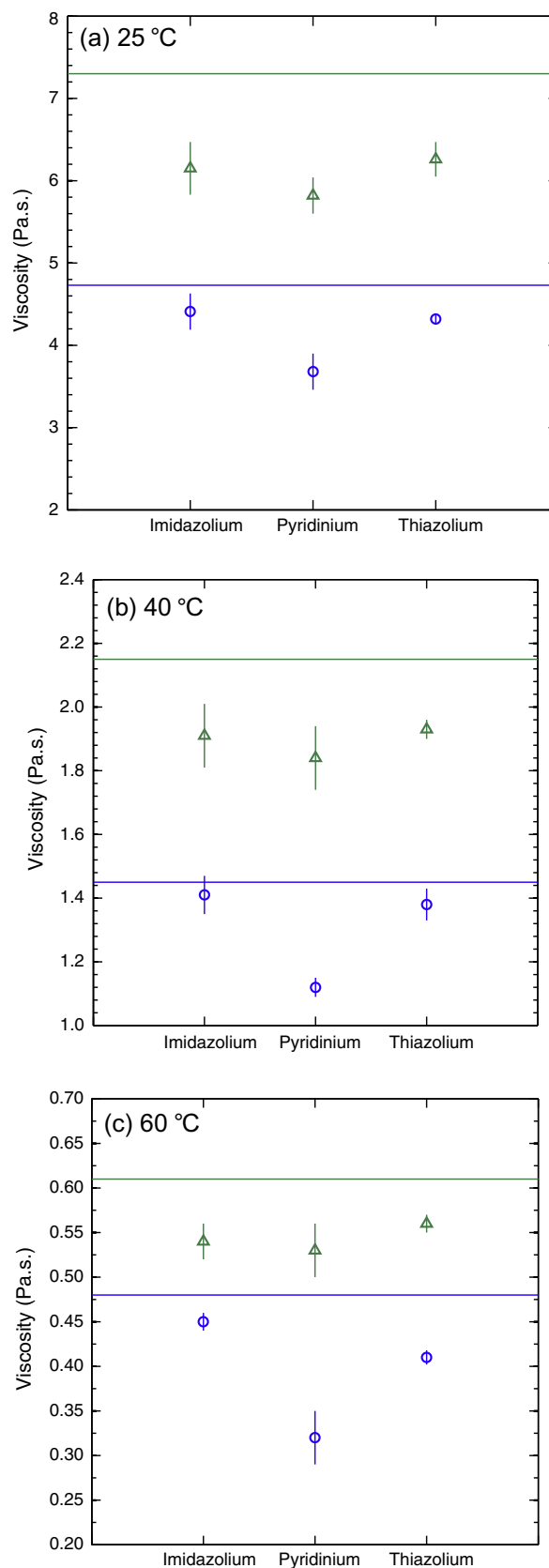


Fig. 6. The viscosity of Canadian (circles) and Venezuelan (triangles) bitumens containing 10 wt.% toluene and 5 ppm (w/w) of dodecylchlorides with varying head groups: imidazolium, pyridinium, and thiazolium. The solid line represents the viscosity of bitumen + 10 wt.% toluene. (a) 25 °C, (b) 40 °C and (c) 60 °C.

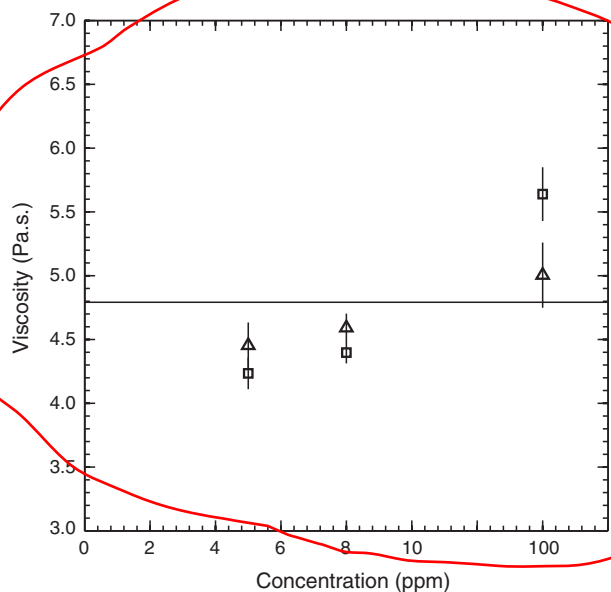


Fig. 7. The viscosity of Canadian bitumen containing 10 wt.% toluene and various concentrations of C8 (triangles) and C10 (squares) imidazolium chloride, at $T = 25\text{ }^{\circ}\text{C}$. The solid line represents the viscosity of bitumen + 10 wt.% toluene.

This effect is seen at all the temperatures studied. To comprehend this trend, we investigate the acid–base interactions between the ionic liquids and the crude oils. Table 2 indicates the acidity and basicity of the crude oils, while Table 5 indicates the change in pH of DI water on the addition of 1 wt.% of the ionic liquid. It is

observed that the TBN of the Mexican heavy oil is much higher than its TAN, while the TAN and TBN values of the Canadian and Venezuelan bitumens are of the same order of magnitude. It is also seen that pyridinium ionic liquid causes the most change in the pH of DI water, while thiazolium causes the least change. These results explain the inefficacy of the pyridinium ionic liquid to reduce the viscosity of the Mexican heavy oil, as well as the effectiveness of the pyridinium and imidazolium ionic liquids on the viscosity reduction of the bitumens. The results further indicate that the higher viscosity reduction observed in the bitumens by using the pyridinium ionic liquid could be attributed to the stronger acid–base interactions occurring in the system, as compared to the system containing imidazolium or thiazolium ionic liquids.

Another interesting feature to note here is the effect of concentration of the ionic liquid on the viscosity reduction of the heavy oil and bitumens. Fig. 7 indicates that adding 100 ppm of the C8 and C10 imidazolium chlorides to the Canadian bitumen increases the mixture viscosity, rather than decreasing it. To comprehend this, we investigate whether the ionic liquids exhibit self-association, as has been suggested in the literature [27]. This could prevent them from interacting with the asphaltenes and causing viscosity reduction. We carry out static light scattering experiments to determine the critical (reverse) micelle concentration, CMC, of the ionic liquids in solvents toluene and heptol (1:1 by volume of heptane and toluene). The results from Table 3 show that the larger the tail length, the smaller the CMC. Results also indicate that the CMC in heptol is smaller than the CMC in toluene. This suggests that the weaker solvent leads to a lower CMC. These results confirm that at higher concentrations (>10 ppm w/w), the ionic liquids could self-associate and may no longer interact with

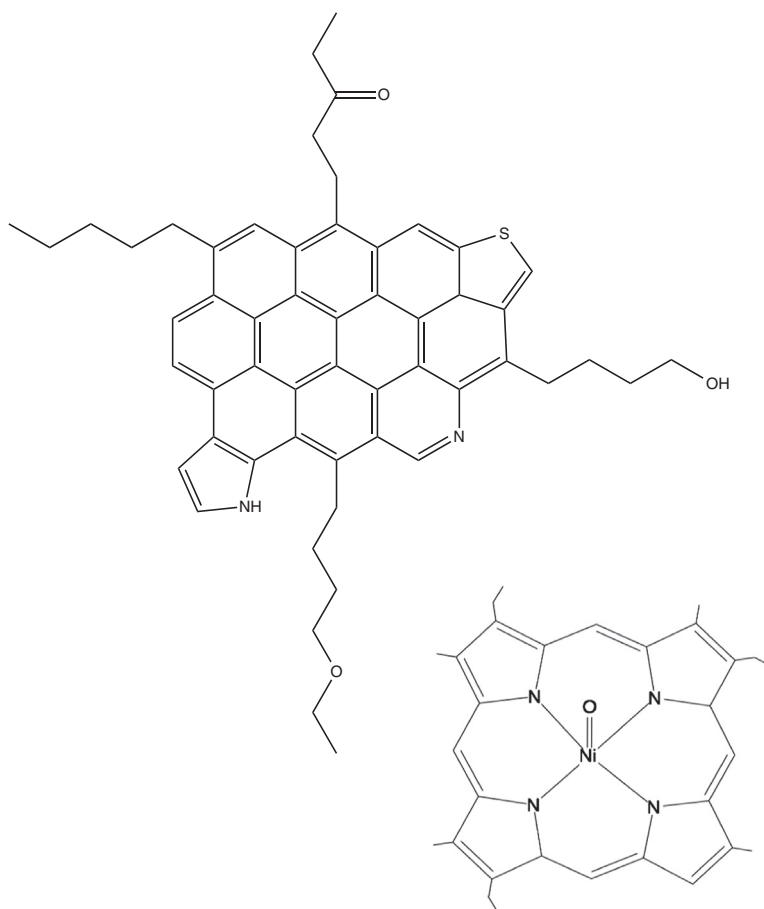


Fig. 8. Structure of hypothetical asphaltenes. Asphaltenes have a polyaromatic core surrounded by aliphatic side-chains. They may also have heteroatoms, such as nitrogen, oxygen, and sulfur on the periphery. Petro-porphyrins containing transition metals such as iron, nickel, and vanadium, also constitutes asphaltenes.

Table 5
Change in the pH of DI water on the addition of 1 wt.% of ionic liquid.

Name	Δ pH
Dodecylthiazolium chloride	–1.5
1-Dodecyl-3-methylimidazolium chloride	–1.8
Dodecylpyridinium chloride	+2.4

the asphaltenes. Low concentrations of the ionic liquid (below the CMC) are thus preferable for the viscosity reduction of the crude oils.

A common question that arises on the use of ionic liquids in the viscosity reduction of crude oils is their cost vis-à-vis the cost of a dilutant, such as toluene. For our lab scale experiments, involving small quantities of chemicals, the cost of dodecylpyridinium chloride (which shows the maximum viscosity reduction amongst all the ionic liquids tested) is about \$ 0.96/g vs. toluene which is about \$ 0.03/g. Toluene is almost 30 times cheaper, but for a viscosity reduction of about 35%, one would need about 10,000 ppm of toluene (see Fig. 2), while we achieve the same result by using only 5 ppm of the ionic liquid. Another factor to account for in this discussion is the innovation in process development and manufacturing of ionic liquids. Recent works have shown that it is possible to mass-produce ionic liquids in an economically efficient and safe way [28].

5. Conclusions

In this work, the consequence of adding functionalized molecules to reduce the viscosity of heavy oils and bitumens is studied. The functionalized molecules are chosen such that they can interact with asphaltene molecules in the crudes and lower the asphaltene aggregate size, which consequently lowers the viscosity of the crude. Small amounts of various ionic liquids, with toluene as a carrier fluid, are tested in a Mexican heavy oil and Canadian and Venezuelan bitumens. The results, dependent on the properties of the functionalized molecule, are summarized as follows:

1. *Alkyl tail length*: There exists a non-monotonic relation between the alkyl tail length of the ionic liquid and its ability to reduce viscosity. Ionic liquids with higher tail lengths (C8–C12) are more effective at viscosity reduction as compared to ionic liquids with smaller tail lengths (C2–C6). This non-monotonic relation has been attributed to the subtle balance of aliphatic and aromatic interactions occurring in the system.
2. *Counter-ion (anion) charge density*: The higher the anion charge density, the stronger is its interactions with the asphaltene molecules. Such interactions could lower asphaltene aggregate size and this leads to viscosity reduction.
3. *Cation head group*: Highest viscosity reduction is obtained by using dodecylpyridinium chloride (35%) as compared to ionic liquids containing the imidazolium or thiazolium head groups. This is attributed to the strong acid–base interactions occurring in the system, which seem to hinder asphaltene aggregate formation and thus reduce the viscosity of the crude.
4. *Concentration*: Small concentrations of the ionic liquid, between 1 and 10 ppm, show a stronger effect in viscosity reduction as opposed to larger concentrations such as 100 ppm, wherein the ionic liquids themselves self-associate.

The results obtained in this work set the stage for further research on the use of functionalized molecules to reduce the viscosity of heavy oils and bitumens. Molecular simulations could add

further light on the mechanism of interaction between the ionic liquids and the asphaltenes, and could help us design optimally functionalized molecules.

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