Effect of imidazolium-based ionic liquids on the asphaltenes average size in crude oil and water-in-oil emulsions

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Efecto de los líquidos iónicos a base imidazol en el tamaño promedio de los agregados de asfaltenos en emulsiones de crudo y agua-crudo

Efecte dels líquids iònics a base d'imidazol en el volum mitjá dels agregats d'asfaltens en emulsions de cru i aigua-cru

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ABSTRACT

Water-in-oil emulsions are ubiquitous in the oil industry due to the presence of polar compounds like asphaltenes and resins that act as natural surfactants. A key parameter in flow properties is viscosity, mainly when its value is high a practical solution use of viscosity reducers. In this work, two imidazolium-based ionic liquids with long alkyl chains inserted into their structures was used to simulate the natural interaction and to evaluate the aggregation behavior of asphaltenes in water-in-oil (W/O) emulsions. Dynamic light scattering (DLS) results showed that both the added ionic liquid and alkyl chain length of imidazolium cations modified the asphaltene average size. These changes in aggregates size was observing viscosity changes induced by concentration of ionic liquids According to zeta potential study, alkyl chain length of imidazolium cation affected the stability and surface charge of asphaltenes; although surface charge test suggest interaction between asphaltenes and ionic liquids, is not enough to achieve its complete dispersion and decreases viscosity of W/O emulsions. Flocculated asphaltenes from crude oil solutions was study by TEM. The result shows that the asphaltenes are constituted of nanoparticles. Aggregation behavior of asphaltenes revealed the complex molecular structure and interaction of asphaltenes in solution.

Keywords: Crude oil, Dynamic light scattering, Ionic liquids, Rheology, Water-in-oil emulsions.

RESUMEN

Las emulsiones de agua-crudo están omnipresentes en la industria petrolera, debido a la presencia de compuestos polares como asfaltenos y resinas que actúan como tensioactivos naturales. Un parámetro clave en las propiedades de flujo es la viscosidad, principalmente cuando su valor es alto, una solución práctica es utilizar reductores de viscosidad. En este trabajo, se utilizaron dos líquidos iónicos a base de imidazolio con largas cadenas de alquilo insertadas en su estructura para simular la interacción natural y evaluar el comportamiento de agregación de los asfaltenos en emulsiones de agua en crudo (W/O). Los resultados de la dispersión dinámica de la luz (DLS) mostraron que tanto el líquido iónico, como la longitud de la cadena de alquilo de los cationes de imidazolio modificaron el tamaño medio de los asfaltenos. Estos cambios en el tamaño de los agregados producen cambios en la viscosidad, inducidos por la concentración de los líquidos iónicos. De acuerdo al estudio de potencial zeta, la longitud de la cadena de alquilo del catión imidazolio afectó la estabilidad y la carga superficial de los asfaltenos; aunque la prueba de carga superficial sugiere interacción entre asfaltenos y líquidos iónicos, no es suficiente para lograr su completa dispersión y disminuye la viscosidad de las emulsiones W/O. En TEM se estudiaron los asfaltenos floculados de las soluciones de petróleo crudo. El resultado mostró que los asfaltenos están constituidos por nanopartículas. El comportamiento de agregación de

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los asfaltenos reveló la compleja estructura molecular y la interacción de los asfaltenos en solución.

Palabras clave: petróleo crudo, dispersión dinámica de luz, líquidos iónicos, reología, emulsiones de agua en crudo.

RESUM

Les emulsions d'aigua-cru estan omnipresents en la indústria petroliera, a causa de la presència de compostos polars com asfaltens i resines que actuen com tensioactius naturals. Un paràmetre clau en les propietats de flux és la viscositat, principalment quan el seu valor és alt. Una solució pràctica és utilitzar reductors de viscositat. En aquest treball, es van utilitzar dos líquids iònics a base d'imidazolio amb llargues cadenes d'alquil inserides en la seva estructura per simular la interacció natural i avaluar el comportament d'agregació dels asfaltens en emulsions d'aigua en cru (W/O). Els resultats de la dispersió dinàmica de la llum (DLS) van mostrar que tant el líquid iònic, com la longitud de la cadena d'alquil dels cations d'imidazolio van modificar el volum mitjà dels asfaltens. Aquests canvis en el volum dels agregats produeixen canvis en la viscositat, induïts per la concentració dels líquids iònics. D'acord a l'estudi de potencial zeta, la longitud de la cadena d'alquil del catió imidazolio va afectar l'estabilitat i la càrrega superficial dels asfaltens; encara que la prova de càrrega superficial suggereix interacció entre asfaltens i líquids iònics, no és suficient per aconseguir la seva completa dispersió i disminueix la viscositat de les emulsions W/O. En TEM es van estudiar els asfaltens floculats de les solucions de petroli cru. El resultat va mostrar que els asfaltens estan constituïts per nanopartícules. El comportament d'agregació dels asfaltens va revelar la complexa estructura molecular i la interacció dels asfaltens en solució.

Paraules clau: petroli cru, dispersió dinàmica de llum, líquids iònics, reologia, emulsions d'aigua en cru.

INTRODUCTION

Crude oil is one of the major forms of non-renewable fossil fuel and fundamental raw material for a wide variety of products in the petrochemical industry. During its extraction it is usually accompanied by residual water as well as a combination of organic and inorganic compounds[1]. Due to the depletion of conventional light crudes, the oil industry is increasingly turning to unconventional oil resources such as heavy crude oil (HCO)[1,2]. Estimates indicate that about 80% of the exploited crude oil exists in an emulsion state, mainly as water-in-oil (W/O) type due to the presence of water in the extractions wells[3].

Although the chemical composition of the oil is very variable and complex, it is usually grouped into four major fractions according to their solubility and aromaticity: saturates, aromatics, resins and asphaltenes, traditionally known as the acronym of SARA fraction[4]. Consequently, the viscosity of crude oil at given temperature and pressure is a function of its composition, and the stability of W/O emulsions is related to the amount of asphaltenes and resins present in crude oil, which act as natural surfactants[5,6]. These surface-active components prevent water-droplet coalescence by the formation of an adsorption layer at the water-oil interface[7].

Asphaltenes are aromatic compounds of higher polarity and molecular weight in the crude oil, besides presenting a high tendency to self-aggregation; whereas the resins are defined as the fraction of crude oil constituted by aromatic-ring aggregates, with similar structure that asphaltenes but much lower molecular weight[5]. Several authors have pointed out that asphaltenes content is the most important factor in the formation of emulsions[3,8,9]. However, resins also play a key role in emulsion-stability since they act as peptizing agents of asphaltenes[9,10], favoring their dispersion as has been shown in works on the stability of emulsion through different evaluation techniques used, such as electrical conductivity measurements[11], light scattering methods[12] as well as observations by optical an electron microscopy[13]. In addition, the amount of asphaltenes and resins determines and limits the viscosity and processing of the oil, since they constitute an important part of the dispersed phase of the crude oil, impacting their rheological properties[8,14].

In this context, the oil industry has been investigated the use of solvents and dispersants of aromatic aggregates to improve the viscosity of heavy oils. To date, various viscosity reducing agents have been employed. The efficiency of the dispersants depends on their polarity and structure, i.e. the dispersants must have an double polar and non-polar affinity, and must be adsorbed on the surface of asphaltenes aggregates or bound to the polar group of asphaltenes molecules[15]. Various ionic liquids that may interact with asphaltenes have been reported, and 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 ionic liquids to interact with asphaltenes, leading to modification on the properties of crude oil at the molecular level, reducing its viscosity[16,17].

Several researchers have used functionalized molecules to enhance stability and lower viscosity of crude oil. The ionic liquids were first tested by Hu and Guo in 2005 in order to reduce the precipitation of asphaltenes and improve stability of crude oil[18]. Subramanian et al., (2015) tested different ionic liquids in order to reduce viscosity of heavy and extra-heavy crude oils[17]. Their results showed that ionic liquids with higher tail lengths are more effective to reduce viscosity, but there are not exist a complete relation between alkyl tail length and the ability to reduce viscosity. Also anion charge density and type of head group influences through stronger interactions with the asphaltenes molecules. Finally, a high concentration of ionic liquid increases its self-associate effect, with an opposite effect in viscosity reduction. Sakthivel et al., (2016) investigated the dissolution behavior of heavy crude oil in presence of eleven ionic liquids from lactam, alkyl ammonium and hydroxyl ammonium families by using organic solvents, through spectroscopic investigations[19]. They show that a very low concentration of ionic liquids has an effect on the heavy crude oil dissolution, and the interactions between ionic liquid and polar moieties of heavy crude oil are responsible of this efficient dissolution of heavy crude oil when ionic liquids were added.

The purpose of this work was to evaluate the effect of two imidazolium-based ionic liquids with linear carbon chain (12 and 14 carbons) in the asphaltenes aggregation and their rheological behavior in water-in-oil emulsion. The ILs were added based on a standard solution of crude oil in cyclohexane, and aggregation state of the resulting solutions was monitored by DLS testing. The results were corroborated with rheology study of W/O emulsions and the type of interactions between asphaltenes and both ILs was determined with zeta potential measurements.

MATERIAL AND METHODS

Materials

The Mexican crude sample used in this work has a density of 0.9696 g cm^{-3} with API degree of 14.40, and SARA fractions of 21.66 wt% saturate, 30.57 wt% aromatic, 24.35 wt% resin and 23.41 wt% asphaltene content, respectively.

The ionic liquids 1,3-dodecylimidazolium bromide, (C_{12}Im) and 1,3-tetradecylimidazolium bromide, (C_{14}Im) are show in Table 1 and were synthesized according to a reported procedure[20] The chemicals used were; imidazole (ReagentPlus®, 99% purity), 1-bromododecane (97% purity), 1-bromotetradecane (97% purity), sodium ethanoate (99% purity), ethyl ether (≥ 99% purity) and ethanol (99.5% purity) were purchased from Sigma Aldrich, México. And used in the dispersion of asphaltenes. Cyclohexane (99.9% purity) was used as solvent for oil-emulsion preparation and supplied by Tedia Company (USA).

EXPERIMENTAL METHODS

Extraction of asphaltenes from heavy crude oil was performed by precipitation method, according to ASTM D2007-80 1983 standard method of the American Society for Testing and Materials (ASTM).

The water-in-oil emulsions were prepared at room temperature and containing 30% (v/v) aqueous solutions. Once the mixture was homogenized, the ionic liquids were added at two different concentrations of 200 and 400 mg L^{-1}, respectively. The average aggregate size and zeta potential measurements were carried out using a Zetasizer Nano ZS ZEN 3600 system (He-Ne laser, 633 nm, 4 mW) from Malvern Instruments. Scattering light was detected at 173 degrees by the automatically adjusted laser attenuation filters in a cell. All measurements were performed at 25°C in order to maintain constant viscosity ($\eta = 1.0200$ cP and the refractive index of 1.427).

The aggregation state of oil-in-cyclohexane and water-in-oil emulsions were determined based on a standard solution of 100 mg L^{-1} of oil in cyclohexane, to which the additives were added and homogenized by ultrasonic for 20 min (Crest Ultrasonics Powersonic™) for their immediate evaluation. Average aggregate size was monitored during the first 100 minutes. Figure 1 shows the experimental procedure followed for the preparation of heavy crude oil dissolution with ionic liquids. Zeta potential measurements were conducted at constant temperature of 25°C. The measured electrophoretic mobility and zeta potential was estimated according to the Smoluchowski model[21-23].

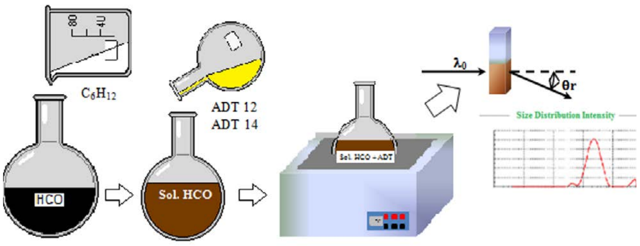
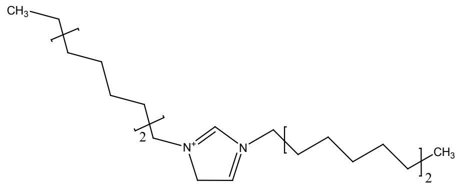
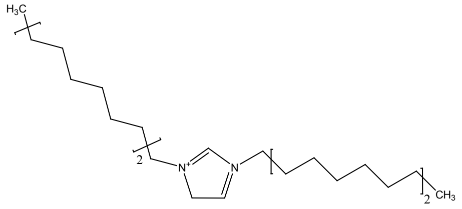


Figure 1. *Scheme of methodology for preparation of oil-ionic liquid-cyclohexane solutions.*

Table 1. *Structure and label of the evaluated ionic liquids.*

Ionic liquid	Label	Cation	Anion
1,3-dodecylimidazolium bromide	C_{12}Im		Br^-
1,3-tetradecylimidazolium bromide	C_{14}Im		Br^-

Shape and size of flocculated asphaltenes were examined through HRTEM using a JEOL JEM-2200FS equipment. Crude oil suspensions in ethanol were prepared by applying 5 min of ultrasound. Subsequently the solution was dripped onto the grid and left to dry with an incandescent lamp. The rheological behavior of the solutions was analyzed by a rheometer (MCR 301 Physica Anton Paar), with parallel plate geometry (4.958 mm diameter). Measurements were performed at constant temperature of 25°C and a shear rate from 1 to 100 s^{-1}. All experimental measurements were performed in triplicate.

RESULTS AND DISCUSSION

Solvent-oil and ionic liquid-solvent-oil emulsions dispersion

In asphaltenes precipitation assessment, DLS is the more used experimental technique. This technique involves direct measurement of the effective diffusion coefficient from a set of suspended particles following Brownian movement within a viscous medium. When the particles grow slow enough, it is possible to record its kinetics. However, application of DLS to crude oil and asphaltene solutions has its challenge since opacity of these systems hiders light to pass through them. Asphaltenes are operationally defined as the crude oil fraction soluble in toluene and insoluble in n-heptane. The solubility must be understood here as not generating a precipitate and not as molecular solubility, since asphaltenes are known to form aggregates in toluene[24] and in cyclohexane[25].

DLS is based on determining the diffusion coefficient of colloidal particles by measuring the spectral composition (correlation function) of scattered light[26]. Assuming a spherical particle, the radius of the particle can be calculated by the Stokes-Einstein equation, which relates the diffusion coefficient (D; m^2 s^{-1}), the shear viscosity η of the medium (η; Kg m^{-1} s^{-1}) and the average hydrodynamic radius of the R_H particles (R_H; m)[27]:

$$D_t = \frac{K_B T}{6\pi\eta R_H} \qquad (1)$$

where K_B is the Boltzmann constant (K_B = 1.380648 x 10^{-23} J K^{-1}) and T is the absolute temperature (T; K).

Figure 2 shows the aggregation behavior of crude oil-in-cyclohexane. The initial average size of crude aggregates in cyclohexane (ZAV) was 55 nm with a standard deviation of 5.24 nm, and this value remained stable over the analyzed time range. These results show that cyclohexane favors aggregation of asphaltene as a diluents as suggested by Pereira et al., (2011)[28] because it maintains the asphaltene in molecular state, favoring the association of higher molecular weight species while the lower molecular weight fraction remains as individual molecules or in states of lower aggregation.

Banda et al., (2017) evaluated the aggregation state of Mexican crude oil solutions by DLS and they concluded that this phenomenon is influenced by crude oil composition, specifically by the amount of resins[29]. In this work, results indicant that the addition of ionic liquids modifies the aggregation behavior of the crude in cyclohexane. The presence of C_{12}Im and C_{14}Im at a concentration of 200 mg L^{-1} induces an increase in aggregate size by about 660-761 nm and 600-680 nm, respectively. However, when the concentration of both ILs increased to 400 mg L^{-1}, there was a decrease in the size of the aggregates at values between 280-220 nm for C_{12}Im and 410-460 nm for C_{14}Im.

The difference in aggregate size by DLS was attributed to the effect of alkyl chain length in the presence of both C_{12}Im and C_{14}Im ILs. Wang et al., (2011) have pointed out that a higher alkyl chain length decreases the value of the critical micellar concentration, by solvophobic effects of the alkyl chain of the ionic liquid[30]. Pino et al., (2009) reported that the micellar behavior of two ionic liquids in the presence of organic solvents is affected by the alkyl chain length and a greater amount of organic solvent[31]. This effect allows to explain the decrease of the aggregate size by increasing the concentration of C_{12}Im and C_{14}Im, since an increase in the concentration of the ILs affects the micellar dynamics of the aggregates and, therefore, the size observed by DLS[32-35]. At this point our results may suggest an interaction between ILs and crude, however, perhaps solubility of asphaltenes is also affected by the solvent effect[9].

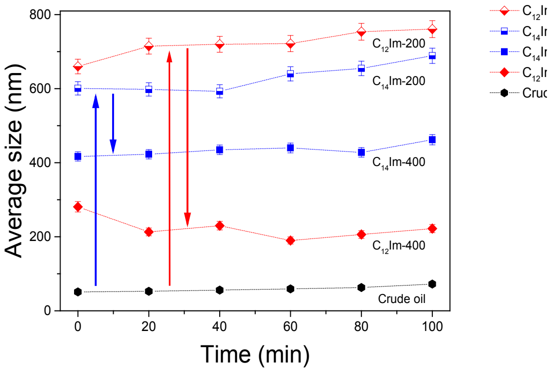


Figure 2. *Measurements of aggregate size of the crude oil in cyclohexane at a concentration of 100 mg L^{-1} and effect of the addition of C_{12}Im and C_{14}Im at concentrations of 200 and 400 mg L^{-1} in the average size of the aggregates.*

Evaluation of water-in-oil emulsions

The rheological properties of a substance provide information regarding flow and deformation characteristics. Viscosity characterizes flow resistance while elasticity is a measure of system-response to stresses. Water-in-oil emulsions exhibit both characteristics: the typical behavior of viscoelastic fluids[8,36].

Figure 3 shows the relationship between viscosity of as-prepared emulsions and shear rate (viscosity curves). Viscosity of native crude oil in the evaluated shear rate range was kept constant, and the addition of 30 vol% of water to the crude oil to produce the emulsion, induces an increase in viscosity, which decreases with increasing shear rate. This feature reflects a non-Newtonian shear-thinning behavior[8]. Similar results were reported by Ariffin et al., (2016)[37] where an increase in the water content produces an increase in the viscosity of the emulsion with a viscoelastic behavior.

The addition of ionic liquids at a concentration of 200 mg L^{-1} into the emulsion increased the viscosity. The increase in viscosity under these conditions is related to the increase in average aggregate size as indicated by DLS results, with maximum viscosities of ~9 Pa.s for C_{12}Im and ~8.1 Pa.s for C_{14}Im respectively; that is, a higher viscosity increase in presence of ionic liquid with shorter alkyl chain. When the concentration of ILs increased to 400 mg L^{-1}, a decrease in viscosity occurred (~6.8 Pa.s for C_{12}Im and ~6.3 Pa.s for C_{14}Im), which is associated to aggregate size decreasing. In addition, the shape of the curves showed that as the shear rate increases, emulsion viscosities are reduced. As the shear rate increase, the molecules tend to break down into individual flocs, thus resistance to spindle rotation is less and eventually reducing the emulsion viscosity. This phenomenon is also known as non-Newtonian shear thinning behavior[37]. Similar result was reported by Subramanian et al., (2015)[17] where the addition of the ILs in the emulsions shows a non-Newtonian shear thinning behavior of the emulsion. From the physical point of view, it means that the resistance to flow decreases when the spill velocity increases.

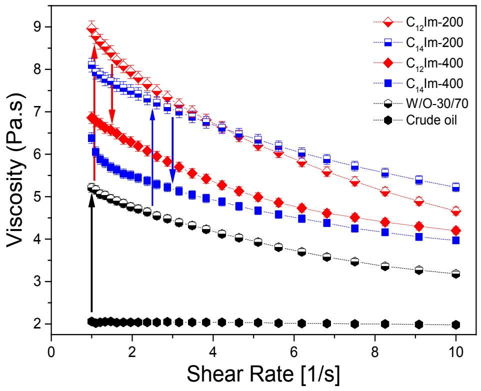


Figure 3. *Viscosity vs shear rate dependence of crude oil, water-in-oil emulsions and effect of C_{12}Im and C_{14}Im ionic liquids. The addition of C_{12}Im and C_{14}Im was carried out at concentrations of 200 and 400 mg L^{-1}.*

The results showed that the addition of ILs preserves non-Newtonian rheological behavior with differences in viscosities in the investigated domain. Different rheological behavior of emulsions can also be observed in the flow curve (Figure 4), since the relationship between the shear rate and the shear stress is not linear.

In general, the rheological behavior depends on the chemical composition of the material, its molecular structure and its microstructural organization at the interface. Due both evaluated ILs have an amphiphilic character and similar composition with only different alkyl-chain length, the observed rheological differences may suggest a different microstructural organization[38], which result from the solubility/compatibility level between both ILs and asphaltenes in the emulsion. In other words, the behavior of the emulsion is controlled primarily by the properties of amphiphilic molecule surrounding the water droplets in the oil solution. The increase in viscosity is indicative of a certain level of interactions in the system asphaltenes aggregates-water, but is not sufficient to create a complete dispersion of asphaltenes by the effect of both ILs.

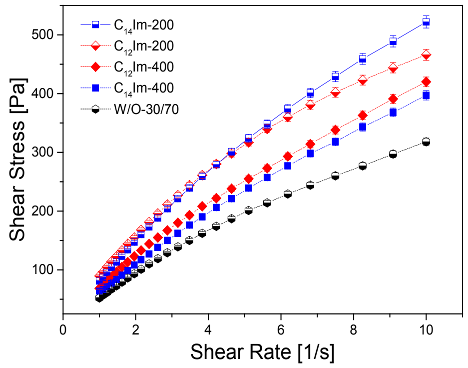


Figure 4. *Shear stress versus shear rate for crude oil, W/O emulsion and effect of the addition of ionic liquid C_{12}Im and C_{14}Im emulsion at room temperatures. Flow curves the characteristic non-Newtonian shear-thinning behavior.*

Transmission electron microscopy (TEM)

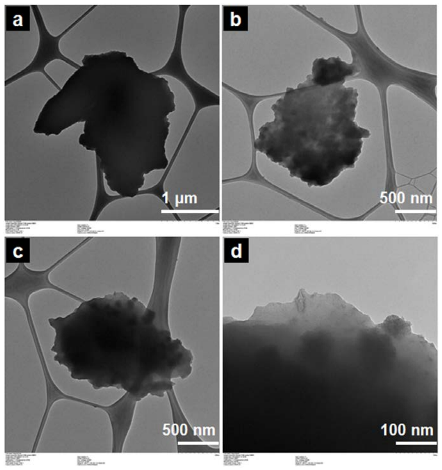


Figure 5. *Representative transmission electron microscopy of precipitated crude oil asphaltenes.*

Figure 5 shows the transmission electron microscopy images of precipitated asphaltenes. A thick, irregularly-shaped sheet similar to stacked-carbon flakes[39] is shown in Figure 5a. This phenomenon may result from the high aggregation tendency of asphaltenes with a resulting in average size in the micrometric scale. Banda et al., (2016) report a similar morphology of asphaltene aggregates, which details their stacked-flakes structure[25].

Figure 5b and 5c allows observing that these aggregates of asphaltenes are constituted by nanometric agglomerates. It is possible to appreciate them in various shapes and sizes as shown in Figure 5d. In the upper part of this image, the typical lamellar morphology with irregular edges is observed, suggesting the presence of layered structures resulting from the asphaltenes stacking. Although it was not possible to analyze the size distribution given the contrast, the range of these particles lies in the 300-500 nm size. Similar aggregate sizes have been reported by Banda et al., (2017)[29]. These results show the complex structure that asphaltenes possess both in topology and composition and with amorphous structure, since the images did not shown the characteristic discernible order of a crystalline material.

According to DLS results, the range of these aggregates lies at 300-700 nm. The difference in size according to the TEM results can be explained on the basis that both techniques provide different information about the size of particles. DLS provides aggregate sizes from hydrodynamic radius of the particle in solution. In contrast, TEM measurement provides real information of dried particle size distributions.

Zeta potential measurements

The zeta potential (ζ) is a key parameter for characterizing the stability of colloidal dispersion and provides information about surface charge associated with the double layer around the colloidal particle[40]. Figure 6 shows the zeta potential of asphaltenes dispersed in an aqueous solution of 1.0 mM NaNO3. The zeta potential of the asphaltene solution is negative in the pH range from 3 to 10, which decreases slightly as the pH increases, and an isoelectric point (IEP) around pH 3 (~2.7). This value of IEP is close to that reported in the literature[41]. The surface charge ζ of asphaltene aggregates is a consequence of ionization of the different surface functional groups which depending on the pH value. According to these results, the asphaltene surface is negatively charged for lower values that pH 3, and positively charged for higher pH values.

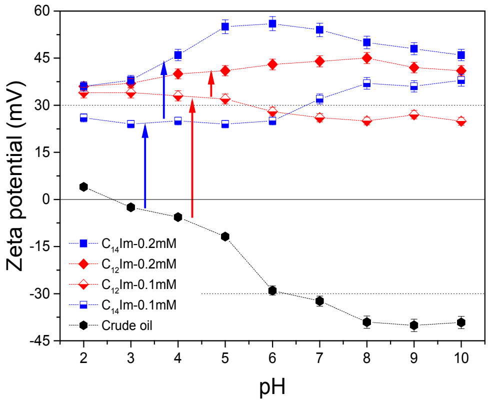


Figure 6. *Effect of different concentrations of C_{12}Im and C_{14}Im (0.1 y 0.2 mM) on zeta potential of crude oil solution.*

These results indicate a favorable electrostatic adsorption of imidazolium cations on negatively charged asphaltene surfaces, and indeed, the addition of C_{12}Im and C_{14}Im at different concentrations (0.1 and 0.2 mM) modifies the surface charge of asphaltenes in solution to positive values of zeta potential, in the all evaluated pH range (from 2 to 10), without observable IEP.

This electrokinetic behavior implies electrostatic interactions between imidazolium cations of C_{12}Im and C_{14}Im molecules and asphaltene aggregates in the double layer. However, the effect of the alkyl chain also contributes to the adsorption mechanism, because the difference in magnitude of ζ apparently affect the electrical properties at the interface. At a concentration of 0.1 mM C_{12}Im and C_{14}Im, the zeta potential is positive and oscillates at a value of 30 mV and without a defined trend in the investigated range. This electrokinetic potential value suggests a moderately stable colloidal stability. For oil solutions with 0.2 mM of both ILs, a stable dispersion was formed because the magnitude of the zeta potential is greater than +30 mV. This result indicates that at a higher concentration of ILs in the solution, the effect of the alkyl chain length can also modify the electrostatic interactions between the polar sites of the asphaltenes aggregates and the imidazolium cations. So, zeta potential is dependent on the length of the alkyl chain[42], and suggest that the length of the alkyl chain of the imidazolium cation affect the stability and surface charge of asphaltenes aggregates in solution.

On the other hand, these interactions increased the aggregation state of crude oil in cyclohexane. Although DLS results were performed under different experimental conditions compared to the zeta potential test (n-heptane-crude); experimental results indicate that the electrokinetic behavior of asphaltenes can be manipulated in the presence of ionic liquids containing imidazolium cations and different alkyl chains lengths. Therefore, the use of these amphiphilic molecules can give indications on the phenomena of aggregation and precipitation of asphaltenes, as well as the stabilization of water-in-oil emulsions.

CONCLUSIONS

Through the addition of two imidazolium-based ionic liquid with different alkyl length chain in crude oil solutions and water-in-oil emulsions, the asphaltenes aggregation behavior and its rheological features was analyzed. Particular insights of this work are the following:

The addition of ionic liquids modified the aggregation behavior of the crude in cyclohexane, the presence of C_{12}Im and C_{14}Im at a concentration of 200 mg L^{-1} induced an increase in aggregate size but when ILs concentrations increased, a decreased in aggregate sizes was observed. The difference in aggregation behavior by DLS results is attributed to the effect of alkyl chain length between of both evaluated ILs.

The initial increase and later decrease water-in-oil viscosity in the rheological tests were related by the ionic liquids-induced change in aggregate size.

The emulsion behavior was main controlled by the molecular properties of both used ionic liquids, although viscosity change indicative certain level of interactions in the system, apparently is not enough to achieve a complete dispersion of the asphaltenes in solution.

TEM results showed difference in asphaltene aggregate size both in size and shape but they do not allow to differentiate the effects of the ionic liquids in the aggregation behavior, due to the their molecular complexity of asphaltenes.

Zeta potential measurements revealed that the alkyl chain length of the imidazolium cation affect the stability and surface charge of asphaltenes aggregates in solution, possibly through electrostatic interactions between asphaltenes polar sites and imidazolium cations.

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REFERENCES

1. Alboudwarej, H.; Felix, J.; Taylor, S.; Badry, R.; Bremner, C.; Brough, B.; Skeates, C.; Baker, A.; Palmer, D.; Pattison, K.; Beshry, M.; Krawchuk, P.; Brown, G.; Calvo, R.; Triana, J.; Hathcock, R.; Koerner, K.; Hughes, T.; Kundu, D.; Cárdenas, J.; West, C. Highlighting heavy oil, *Oilfield Review* **2006**, 18, 34-53.
2. Abdurahman, N.; Rosli, Y.; Azhari, N.; Hayder, B. Pipeline transportation of viscous crudes as concentrated oil-in-water emulsions, *Journal of Petroleum Science and Engineering* **2012**, 90, 139-144.
3. Kilpatrick, P. Water-in-Crude Oil Emulsion Stabilization: Review and Unanswered Questions, *Energy & Fuels* **2012,** 26, 4017-4026.
4. Qiao, P.; Harbottle, D.; Tchoukov, P.; Masliyah, J.; Sjoblom, J.; Liu, Q.; Xu, Z. Fractionation of Asphaltenes in Understanding Their Role in Petroleum Emulsion Stability and Fouling, *Energy & Fuels* **2017,** 31, 3330-3337.
5. Mousavi, M.; Abdollahi, T.; Pahlavan, F.; Fini, E. The influence of asphaltene-resin molecular interactions on the colloidal stability of crude oil, *Fuel* **2016,** 183, 262-271.
6. Wong, S.; Lim, J.; Dol, S.; Crude oil emulsion: A review on formation, classification and stability of water-in-oil emulsions, *Journal of Petroleum Science and Engineering* **2015,** 135, 498-504.
7. Tchoukov, P.; Yang, F.; Xu, Z.; Dabros, T.; Czarnecki, J.; Sjöblom, J. Role of Asphaltenes in Stabilizing Thin Liquid Emulsion Films, *Langmuir* **2014,** 30, 3024-3033.
8. Maia-Filho, D.; Ramalho, J.; Lucas, G.; Lucas, E. Aging of water-in-crude oil emulsions: Effect on rheological parameters, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2012,** 405, 73-78.
9. Langevin, D.; Argillier, J. Interfacial behavior of asphaltenes, *Advances in Colloid and Interface Science* **2016,** 233, 83-93.
10. Spiecker, P.; Gawrys, K.; Trail, C.; Kilpatrick, P. Effects of petroleum resins on asphaltene aggregation and water-in-oil emulsion formation, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2003,** 220, 9-27.
11. Varka, E.; Ampatzidis, C.; Kostoglou, M.; Karapantsios, T.; Dutschk, V. On the use of electrical conductance measurements for the stability of oil-in-water Pickering emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2010,** 365, 181-188.
12. Makan, A.; Spallek, M.; Du Toit, M.; Klein, T.; Pasch, H. Advanced analysis of polymer emulsions: Particle size and particle size distribution by field-flow fractionation and dynamic light scattering, *Journal of Chromatography A* **2016,** 1442, 94-106.
13. Ma, L.; Xu, X.; Zhang, C.; Luo, J. Direct observation of the formation and destruction of the inverted continuous oil phase in the micro-outlet region achieved by the confined diluted O/W emulsion stream, *Soft Matter* **2014,** 10, 7946-7951.
14. Ghannam, M.; Hasan, S.; Abu-Jdayil, B.; Esmail, N. Rheological properties of heavy & light crude oil mixtures for improving flowability, *Journal of Petroleum Science and Engineering* **2012,** 81, 122-128.
15. Rezaee-Nezhad, E.; Heidarizadeh, F.; Sajjadifar, S.; Abbasi, Z.; Dispersing of petroleum asphaltenes by acidic ionic liquid and determination by UV-visible spectroscopy, *Journal of Petroleum Engineering* **2013**, 1-5.
16. Boukherissa, M.; Mutelet, F.; Modarressi, A.; Dicko, A.; Dafri, D.; Rogalski, M.; Ionic Liquids as Dispersants of Petroleum Asphaltenes, *Energy & Fuels* **2009,** 23, 2557-2564.
17. Subramanian, D.; Wu, K.; Firoozabadi, A. Ionic liquids as viscosity modifiers for heavy and extra-heavy crude oils, *Fuel* **2015,** 143, 519-526.
18. Hu, Y.; Guo, T. Effect of the Structures of Ionic Liquids and Alkylbenzene-Derived Amphiphiles on the Inhibition of Asphaltene Precipitation from CO2-Injected Reservoir Oils, *Langmuir* **2005,** 21, 8168-8174.
19. Sakthivel, S.; Gardas, R.; Sangwai, J. Spectroscopic investigations to understand the enhanced dissolution of heavy crude oil in the presence of lactam, alkyl ammonium and hydroxyl ammonium based ionic liquids, *Journal of Molecular Liquids* **2016,** 221, 323-332.
20. Gallardo-Rivas, N.; Moreno-Guerrero, A.; Mendoza-Martínez, A.; Reyes-de la Torre, A.; Díaz-Zavala, N.; Domínguez-Esquivel, J. Efecto de la longitud de las cadenas hidrocarbonadas de moléculas iónicas en las propiedades reológicas de crudos pesados, *Innovación y desarrollo tecnológico* **2014,** 6, 10-19.
21. Frenklach, M. Dynamics of discrete distribution for Smoluchowski coagulation model, *Journal of Colloid and Interface Science* **1985**, 108, 237-242.
22. Parra-Barraza, H.; Hernández-Montiel, D.; Lizardi, J.; Hernández, J.; Urbina, R. H.; Valdez, M. A. The zeta potential and surface properties of asphaltenes obtained with different crude oil/n-heptane proportions, *Fuel* **2003**, 82, 869-874.
23. Collini, H.; Li, S.; Jackson, M. D.; Agenet, N.; Rashid, B.; Couves, J. Zeta potential in intact carbonates at reservoir conditions and its impact on oil recov-

ery during controlled salinity waterflooding, *Fuel* **2020**, 266, 116927.
24. Xu, J.; Liu, H. The growth and development of asphaltene aggregates in toluene solution, *Petroleum Science and Technology* **2015,** 33, 1916-1922.
25. Banda-Cruz, E.; Rivas-Gallardo, N.; Páramo-García, U.; Estrada Moreno, I.; Pozas-Zepeda, D.; Reyes-Gómez, J. Crude oil aggregation by microscopy and dynamic light scattering, *Petroleum Science and Technology* **2016,** 34, 1812-1817.
26. Maltseva, E.; Gorshkov, A.; Chekantseva, L.; Shishmina, L.; Yudina, N. Influence of aggregation of asphaltenes on the rheological properties of oil, *Russian Journal of Applied Chemistry* **2013,** 86, 1370-1375.
27. Rahdar, A.; Almasi-Kashi, M. Dynamic light scattering of nano-gels of xanthan gum biopolymer in colloidal dispersion, *Journal of Advanced Research* **2016,** 7, 635-641.
28. Pereira, J.; Delgado-Linares, J.; Briones, A.; Guevara, M.; Scorzza, C.; Salager, J. The Effect of Solvent Nature and Dispersant Performance on Asphaltene Precipitation from Diluted Solutions of Instable Crude Oil, *Petroleum Science and Technology* **2011,** 29, 2432-2440.
29. Banda-Cruz, E.; Gallardo-Rivas, N.; Páramo-García, U.; Mendoza-Martínez, A.; Melo-Banda. J. Physicochemical Characterization of crude Oils and the precipitated asphaltenes fraction using UV spectroscopy, *Dynamic Light Scattering and Microscopy.* Mansoor Zoveidavianpoor (Ed.), InTech, **2017,** Chap. 6, 117-135.
30. Wang, J.; Zhang, L.; Wang, H.; Wu, C. Aggregation Behavior Modulation of 1-Dodecyl-3-methylimidazolium Bromide by Organic Solvents in Aqueous Solution, *Journal of Physical Chemistry B* **2011,** 115, 4955-4962.
31. Pino, V.; Yao, C.; Anderson, J. Micellization and interfacial behavior of imidazolium-based ionic liquids in organic solvent–water mixtures, *Journal of Colloid and Interface Science* **2009,** 333, 548-556.
32. Baltazar, Q.; Chandawalla, J.; Sawyer, K.; Anderson, J. Interfacial and micellar properties of imidazolium-based monocationic and dicationic ionic liquids, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2007,** 302, 150-156.
33. Liu, X.; Dong, L.; Fang, Y. Synthesis and Self-Aggregation of a Hydroxyl-Functionalized Imidazolium-Based Ionic Liquid Surfactant in Aqueous Solution, *Journal of Surfactants and Detergents* **2011,** 14, 203-210.
34. Blesic, M.; Marques, M.; Plechkova, N.; Seddon, K.; Rebelo, L.; Lopes, A. Self-aggregation of ionic liquids: micelle formation in aqueous solution, *Green Chemistry* **2007,** 9, 481-490.
35. Łuczak, J.; Hupka, J.; Thöming, J.; Jungnickel, C. Self-organization of imidazolium ionic liquids in aqueous solution, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008,** 329, 125-133.
36. Fingas, M.; Fieldhouse, B. Studies on crude oil and petroleum product emulsions: Water resolution and rheology, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2009,** 333, 67-81.
37. Ariffin, T.; Yahya, E.; Husin, H. The rheology of light crude oil and water-in-oil-emulsion, *Procedia Engineering* **2016,** 148, 1149-1155.
38. Merola, M.; Carotenuto, C.; Gargiulo, V.; Stanzione, F.; Ciajolo, A.; Minale, M. Chemical–physical analysis of rheologically different samples of a heavy crude oil, *Fuel Processing Technology* **2016,** 148, 236-247.
39. Li, K.; Vasiliu, M.; McAlpin, C.; Yang, Y.; Dixon, D.; Voorhees, K.; Batzle, M.; Liberatore, M.; Herring, A. Further insights into the structure and chemistry of the Gilsonite asphaltene from a combined theoretical and experimental approach, *Fuel* **2015,** 157, 16-20.
40. Bhattacharjee, S. DLS and zeta potential – What they are and what they are not?, *Journal of Controlled Release* **2016,** 235, 337-351.
41. Parra-Barraza, H.; Hernández-Montiel, D.; Lizardi, J.; Hernández, J.; Herrera-Urbina, R.; Valdez, M. The zeta potential and surface properties of asphaltenes obtained with different crude oil/n-heptane proportions, *Fuel* **2003,** 82, 869-874.
42. Markiewicz, M.; Mrozik, W.; Rezwan, K.; Thöming, J.; Hupka, J.; Jungnickel, C. Changes in zeta potential of imidazolium ionic liquids modified minerals – Implications for determining mechanism of adsorption, *Chemosphere* **2013,** 90, 706-712.