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# Anion and cation effects of ionic liquids and ammonium salts evaluated as dehydrating agents for super-heavy crude oil: Experimental and theoretical points of view

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ABSTRACT

One series of ionic liquids (IL), $[TOA]^+$ [Y] (where $[Y]^- = [Cl]^-$, $[HSO_4]^-$ or $[H_2PO_4]^-$), and new ammonium salts, $[OCD]^+$ $[Y]^-$ (where $[Y] = [HSO_4]^-$, $[MeSO_3]^-$ or $[MePhSO_3]^-$), were evaluated as demulsifying agents for super-heavy crude oil, at API = 6.39° (MO1) and API = 7.13° (MO2), with 8.46 and 8.94 wt.% of asphaltenes, respectively, at dosages of 1000 and 1500 ppm, using a conventional heating bottle test. At 1000 ppm, the ranking of water removal efficiency for the $[TOA]^+$ $[Y]^-$ series (in MO1 and MO2, in order to reach 96.7% and 95.4%, respectively) was $[Cl]^- > [HSO_4]^- > [H_2PO_4]^-$. For the $[OCD]^+$ $[Y]^-$ series, the rankings for efficiency at 360 min were $[HSO_4]^- > [MeSO_3]^-$, reaching approximately 27% in MO2, whereas $[MePhSO_3]^-$ reached 1% in MO2.

At a dosage of 1500 ppm, the $[TOA]^+$ $[Y]^-$ series achieved 100% water removal, showing the same order at 1000 ppm. For $[OCD]^+$ $[Y]^-$, the order at 24 h was $[HSO_4]^- > [MeSO_3]^- > [MePhSO_3]^-$ for MO1 and MO2 at maximums of 85.5% and 92.3%, respectively. $[OCD]^+$ $[HSO_4]^-$ was an efficient demulsifier in tests of long duration. Quantum parameters were obtained at the semiempirical RM1 level, in order to establish a correlation with the experimental results. The molecular volume ($V_M$), molecular refractivity ($MR$), dipolar moment ($\mu$) and mean polarizability ($\alpha$) of the cation and anion fragments were important factors driving the dewatering process. $V_M$, $MR$ and $\alpha$ were shown to have a direct relationship with water removal efficiency. Furthermore, absolute softness and the electrophilicity index of the cation fragments were calculated at the density functional theory (DFT) level. An increase in the softness and electrophilicity of the cations correlated with lesser effectiveness as demulsifiers. Finally, the partition coefficient of the cations showed that if the viscosity of the crude oil is low, it is possible to use ILs with a low partition coefficient (log $P$), but if the viscosity is high, the log $P$ of IL should be near the $[TOA]^+$ $[Cl]^-$ value.

## 1. Introduction

During its extraction, crude oil is produced as an emulsion with water. There are different types of such emulsions: water/oil (W/O), oil/water (O/W), and even ternary emulsions (W/O/W and O/W/O). These emulsions are stabilized by natural surfactants that are present in crude oil, as well as by resins, clays of colloidal size, asphaltenes, carboxylic derivatives, and transition metal salts.

From the economic and operational points of view, it is imperative that these emulsions be broken down into their constituents. This is done in order to reach two targets: diminishing, as far as possible, corrosion damage in refinery installations, and preparing the oil for exportation [1].

To break up crude oil emulsions, it is common to add mixtures of chemical products known as demulsifiers. Different families of these products have been used, as well as alkylphenol aldehyde resin [2], polyoxypropylenated–polyoxyethylenated amines [3], alkoxylated polyhydric alcohols [4], polyalkylene oxide-modified polydimethylsiloxane chains [5], aromatic sulfonic acids [6], alkoxylated polyethyleneimines [7], orthoester-based polymers [8], hyperbranched polymers (polycarbonates, polyesters, polyethers, polyurethanes, polyureas, polyamides, polyetheramines, polyesteramides) [9], phosphoric ester composition [10], and magnetic demulsifiers [11]; all of these are formulations which consist mainly of three components: breaking, coalescing, and clarifying agents. The aim of such agents is

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to break up the emulsion in the shortest possible amount of time, as well by using microwave heating technology [12].

Ionic liquids (ILs) are a new class of chemical products; they are considered "green solvents," due to their low-pressure vapor, and recent reviews give an overview of their potential utilization. A large number of these molecules have been synthesized and are available on the market, while some are made only for laboratory use [13,14].

ILs have also been applied in the oil industry — for example, as asphaltene dispersants [15]; as potential solvents for extracting asphaltenes from coal residue [16]; as agents in the oxidative desulfurization of fuel oil [17], in the desulfurization of natural gasoline [18], and in naphthenic acid removal from crude oil by forming ILs [19]; and as agents for upgrading heavy oil through the separation of asphaltenes [20], for removing mercaptan from hydrocarbon streams [21], and for inhibiting clathrate hydrate [22]. Recently, the effect of 1-dodecyl-3-methylimidazolium chloride $[C_{12}mim]^+$ $[Cl]^-$ was measured for its dynamic interfacial tension with heavy crude oil [23]. ILs have also been used in oil dehydration. In this vein, two research groups, in the same year, recently described the application of ILs as demulsifying agents for crude oil, using microwave (MW) irradiation [24,25], which has been employed to enhance the demulsification rate and to provide high efficiency in the breaking up of W/O emulsions under conventional heating procedures [26–30].

On the other hand, reactivity descriptors such as absolute electronegativity, $\chi$; absolute hardness, $\eta$; and absolute softness, $S$, have been widely used to illuminate the nature of molecules in terms of their stability, and consequently, their reactivity [31,32]. Moreover, electrophilicity, as a descriptor of reactivity, provides a quantitative classification of the global electrophilic nature of a molecule on a relative scale; it is effectively the power of a system to "soak up" electrons [33].

The aim of this work was to explore the behavior of emulsions of heavy and super-heavy crude oil under the influence of one group of ILs ($[TOA]^+$ $[Y]^-$) and ammonium salts ($[OCD]^+$ $[Y]^-$) in a conventional bottle test. The first group, $[TOA]^+$ $[Y]^-$ (see Fig. 1), was synthesized previously [34]; the second group, $[OCD]^+$ $[Y]^-$ (see Fig. 2), is new — its anion sizes were varied. Theoretical calculations at the semiempirical and density functional theory (DFT) levels were carried out in order to establish the correlation between the quantum parameters and the experimental behavior of the groups, and therefore, to explore the effect of anion size on the efficiency of these substances as demulsifiers.

## 2. Experimental procedure

### 2.1. Materials and methods

The following reagents were purchased from Aldrich: sulfuric acid (98%), methanesulfonic acid (99.5%), *p*-toluenesulfonic acid monohydrate (99.5%), and octadecylamine (97%). These were used with no further purification.

### 2.2. Apparatus

#### 2.2.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded on a Nicolet FT-IR 5DX FT spectrometer.

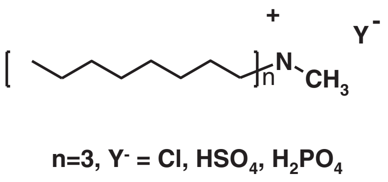

**Fig. 1.** Structures of the $[TOA]^+$ $[Y]^-$ series.

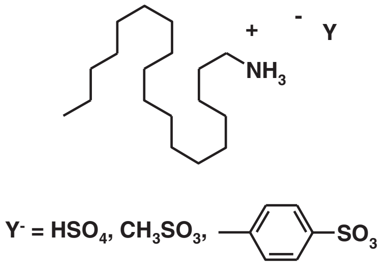

**Fig. 2.** Ammonium salt $[OCD]^+$ $[Y]^-$ series.

#### 2.2.2. Nuclear magnetic resonance (NMR) spectrometry

$^1H$ and $^{13}C$ NMR spectra were collected at 300 K, using a JEOL_Eclipse spectrometer at 300 MHz and 75.4 MHz for $^1H$ and $^{13}C$ nuclei, respectively, using $CDCl_3$ as a solvent. The chemical shifts were referenced to tetramethylsilane (TMS) ($^1H$, $\delta = 0.0$ ppm, and $^{13}C$, $\delta = 0.0$ ppm).

### 2.3. General procedure for the synthesis of ILs and ammonium salts

The trioctylmethylammonium $[Y]^-$ ($[TOA]^+$ $[Y]^-$) series was synthesized according to the procedure described in the literature [33]. The new $[OCD]^+$ $[Y]^-$ series, derivatives of octadecylammonium, was synthesized according to the route of synthesis presented in Fig. 3.

#### 2.3.1. $[OCD]^+$ $[Y]^-$ general synthesis procedure

Toluene (250 mL), with equal mol amounts of octadecylamine and a strong acid (sulfuric, *p*-toluene-sulfonic, or methanesulfonic) were placed in a flask equipped with a magnetic stirrer, thermometer and reflux condenser. The reaction mixture was refluxed for 24 h; after that time, the solvent was removed under reduced pressure. Finally, the solid product was crushed in hexane and vacuum-filtered.

### 2.4. Spectral characterization of synthesized ammonium salts

#### 2.4.1. Octadecylammonium bisulfate ($[OCD]^+$ $[HSO_4]^-$)

IR (KBr, $cm^{-1}$): 3050, 2923, 2849, 2020, 1628, 1470, 1196, 1052; $^1H$ NMR ($CDCl_3$) $\delta$ 2.916 (m, 2H, $J = 7.5$ Hz, $H_1$), 1.652 (m, 2H, $J = 7.2$ Hz, $H_2$), 1.291 (m, 30H, $H_3$–$H_{17}$), 0.905 (t, 3H, $J = 6.6$ Hz, $H_{18}$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 40.96, 33.21, 30.92, 30.61, 30.38, 28.73, 27.59, 23.88, 14.63.

#### 2.4.2. Octadecylammonium mesylate ($[OCD]^+$ $[MeSO_3]^-$)

IR (KBr, $cm^{-1}$): 3040, 2920, 2490, 2000, 1620, 1520, 1460, 1150, 1040; $^1H$ NMR ($CDCl_3$) $\delta$ 3.204 (m, 3H, $J = 7.2$ Hz, $H_T$), 2.916 (m, 2H, $J = 7.5$ Hz, $H_1$), 1.644 (m, 2H, $J = 7.2$ Hz, $H_2$), 1.310 (m, 30 H, $J = 6.3$ Hz, $H_3$–$H_{17}$), 0.900 (t, 3H, $J = 6.3$ Hz, $H_{18}$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 73.86, 40.94, 33.21, 30.93, 30.39, 28.69, 27.61, 23.88, 23.44, 14.61.

#### 2.4.3. Octadecylammonium tosylate ($[OCD]^+$ $[MePhSO_3]^-$)

IR (KBr, $cm^{-1}$): 3060, 3050, 2920, 2360, 1620, 1520, 1470, 1120, 1040, 1010, 717, 690; $^1H$ NMR ($CDCl_3$) $\delta$ 7.709 (d, 2H, $J = 8.1$ Hz, $H_X$), 7.24 (dd, 2H, $J = 8.4$, 0.6 Hz, $H_W$), 2.892 (t, 2H, $J = 6.9$ Hz, $H_1$), 2.374 (s, 3H, $H_U$), 1.628 (m, 2H, $J = 7.2$ Hz, $H_2$), 1.290 (t, 30H, $J = 6.6$ Hz, $H_3$–$H_{17}$), 0.902 (t, 3H, $J = 6.6$ Hz, $H_{18}$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 143.63, 141.86, 129.99, 127.09, 40.92, 33.23, 30.95, 30.69, 30.39, 28.72, 27.60, 23.89, 14.61, 21.49.

### 2.5. Demulsifier evaluation

The Mexican crude oil samples (MO1 and MO2) were characterized as described previously [35]. Tables 1 and 2 list the characteristic physico-chemical properties of the super-heavy Mexican crude oils.

Evaluation by bottle testing was performed roughly as follows: to graduated bottles (150 mL volume), crude oil was added in quantities

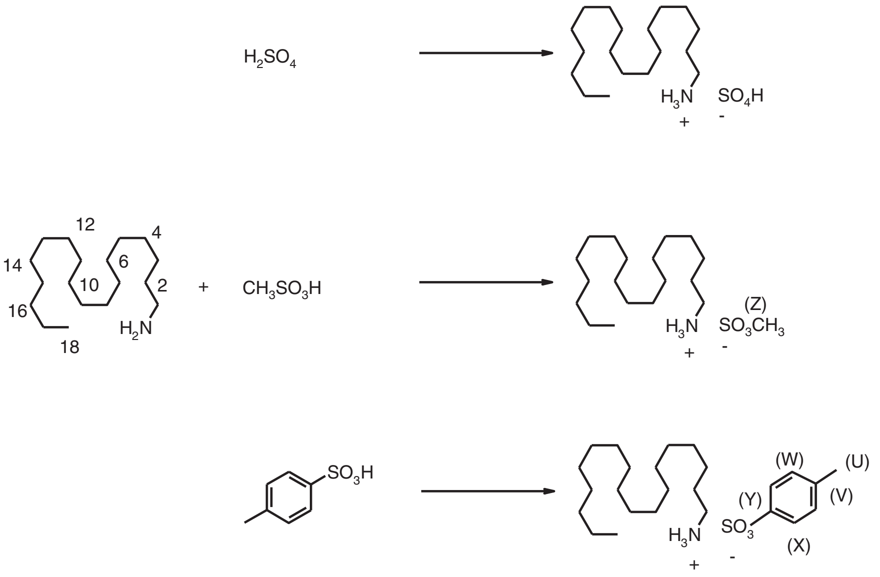

**Fig. 3.** Synthesis of the $[OCD]^+$ $[Y]^-$ series of ILs.

of 100 mL. The bottles were placed in a temperature-controlled water bath at 80 °C for a period of 30 min, after which they were removed. Subsequently, one aliquot of a dissolution of ILs in xylenes, or ammonium salts in methanol, was added; in the case of untreated oil, an aliquot of xylene was added; all the bottles were shaken for 2 min at a rate of 2 shakes per second. After mixing, the bottles were placed in the controlled temperature bath, and the water removal from petroleum was monitored for 360 min at 1000 ppm and for 24 h at 1500 ppm.

### 2.6. Computational procedure

The ILs and ammonium salt structures were fully optimized at the RM1 level, using Hyperchem 8.0 software [36], using a RMS $=$ 1E−06. The quantitative structure-activity relationship (QSAR) parameters of the ILs and ammonium salts were obtained using Hyperchem. Frontier orbital energies were obtained at the B3LYP/6-31G + (*d*,*p*) level, using Gaussian 03 software [37].

## 3. Results and discussion

New ammonium salts, $[OCD]^+$ $[Y]^-$ (where $[Y] = [HSO_4]^-$, $[MeSO_3]^-$ or $[MePhSO_3]^-$), were synthesized according to the established experimental procedures, and the compounds were characterized by FTIR and NMR spectroscopy. Subsequently, the ammonium salts ($[OCD]^+$ $[Y]^-$) and the ILs ($[TOA]^+$ $[Y]^-$) were evaluated as demulsifying agents for super-heavy crude oil. The anion size was modified in both series to evaluate the effect on water removal efficiency (WRE). Figs. 4 and 5 show the WRE patterns of the $[TOA]^+$ $[Y]^-$ and $[OCD]^+$ $[Y]^-$ series at a dosage of 1000 ppm for MO1 and MO2 crude oils; Fig. 5 shows the WRE patterns for both crude oils at a dosage of 1500 ppm.

At a dosage of 1000 ppm, $[TOA]^+$ $[Cl]^-$ broke up the emulsion of MO1 to an extent of 0.9% at 5 min (Fig. 4a), and the MO2 crude oil to an extent of 23% (Fig. 4b). At 10 min, $[TOA]^+$ $[Cl]^-$ was able to reach 77.4% and 92.3%, for MO1 and MO2, respectively, whereas $[TOA]^+$ $[HSO_4]^-$ and $[TOA]^+$ $[H_2PO_4]^-$ in MO1 were able to reach 35.5% and 69.2%, respectively, and with MO2 were able to reach 32.3% and 61.5%, respectively. The superior effectiveness of $[Cl]^-$ as an anion, as opposed to $[HSO_4]^-$ and $[H_2PO_4]^-$, is significant. The maximum WRE values obtained with MO1 for $[TOA]^+$ $[Cl]^-$, $[TOA]^+$ $[HSO_4]^-$ and $[TOA]^+$ $[H_2PO_4]^-$ were 96.8%, 96.8% and 93.5%, respectively, whereas with MO2 the three ILs reached 95.4%. Regarding the ammonium salts, for MO1 crude oil, the WRE values for $[HSO_4]^-$, $[MeSO_3]^-$, and $[MePhSO_3]^-$ were 3.2%, 1.6% and 0.8%, respectively, and for the MO2 crude oil 27.7%, 22.1% and 0%, respectively.

At 1500 ppm and at 5 min, the WRE values of $[TOA]^+$ $[Cl]^-$, $[TOA]^+$ $[HSO_4]^-$ and $[TOA]^+$ $[H_2PO_4]^-$ with the MO1 crude oil were 80.6%, 77.4% and 35.5%, respectively. $[TOA]^+$ $[Cl]^-$ reached 100% at 10 min, whereas $[TOA]^+$ $[HSO_4]^-$ and $[TOA]^+$ $[H_2PO_4]^-$ reached maximums of 96.7% and 93.5%, respectively, at 180 min. With the MO2 crude oil, the WRE values for $[TOA]^+$ $[Cl]^-$, $[TOA]^+$ $[HSO_4]^-$ and $[TOA]^+$ $[H_2PO_4]^-$ were 93.9%, 92.3%, and 90.8%, respectively. In this case, a WRE of 100% for $[Cl]^-$, $[HSO_4]^-$ and $[H_2PO_4]^-$ was reached at around 15, 25, and 180 min, respectively. In regard to ammonium salts, the emulsion with MO1 broke up at 20 min for $[OCD]^+$ $[HSO_4]^-$ and $[OCD]^+$ $[MeSO_3]^-$, at 4.5% and 4.8%, respectively. $[OCD]^+$ $[MePhSO_3]^-$ started to break up at 40 min, with an efficiency of 3.2%. At 360 min, the WRE values for $[OCD]^+$ $[HSO_4]^-$, $[OCD]^+$ $[MeSO_3]^-$ and $[OCD]^+$ $[MePhSO_3]^-$ were 35.7%, 29.0% and 22.1%, respectively, and at 24 h, 85.5%, 77.3%, and 39.3%. The emulsion of MO2 crude oil broke up at 10 min, with $[OCD]^+$ $[HSO_4]^-$ and $[OCD]^+$ $[MeSO_3]^-$ yielding WRE values of 46.2% and 23.1%, respectively. $[OCD]^+$ $[MePhSO_3]^-$ broke up the emulsion at 45 min. At 360 min, the WRE values for $[OCD]^+$ $[HSO_4]^-$, $[OCD]^+$ $[MeSO_3]^-$ and $[OCD]^+$ $[MePhSO_3]^-$ were 76.9%, 73.8% and 43.1%, respectively; and at 24 h, 92.3%, 76.9%, and 53.8%.

**Table 1**
Physical data for Mexican super-heavy crude oils.

| Parameter | MO1 | MO2 |
|---|---|---|
| API density | 6.39 | 7.13 |
| Salt (lb/1000 bls of oil) | 21,655 | 19,513 |
| Water by distillation (vol.%) | 56 | 60 |
| Kinematic viscosity ($mm^2$ $s^{-1}$) | 35,456 | 16,073 |
| Pour point (°C) | −6 | −6 |
| Asphaltenes from *n*-$C_7$ | 15.71 | 13.78 |

**Table 2**
Chemical properties of Mexican super-heavy crude oils ((wt./wt.%).

| Type | Saturates | Aromatics | Resins | Asphaltenes |
|---|---|---|---|---|
| MO1 | 16.09 | 21.97 | 53.42 | 8.46 |
| MO2 | 16.81 | 22.51 | 51.70 | 8.94 |

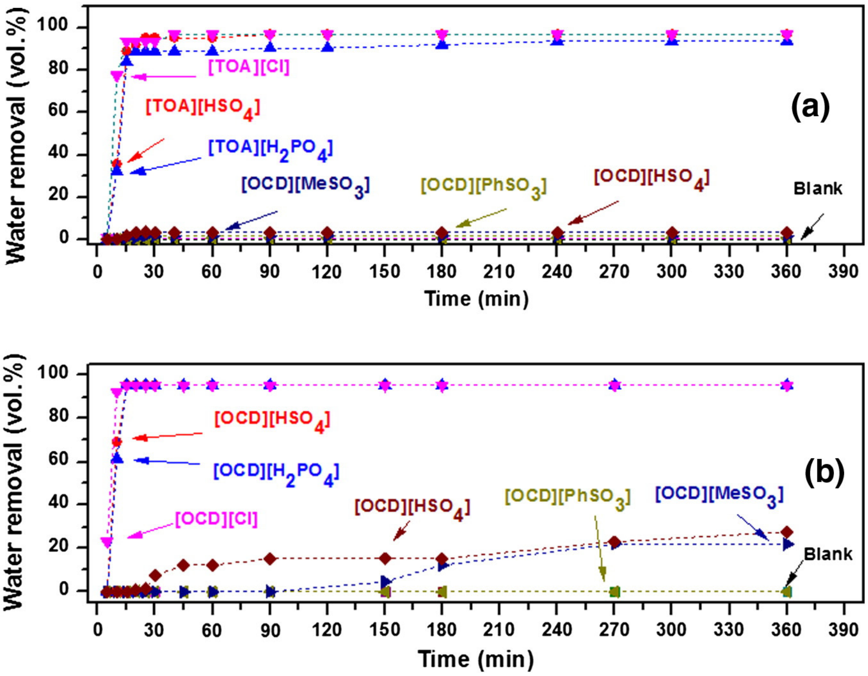

**Fig. 4.** Water removal efficiency of the $[TOA]^+$ $[Y]^-$ series at doses of 1000 ppm: (a) MO1 crude oil; (b) MO2 crude oil.

In contrast to these findings, Guzmán-Lucero et al. [24] carried out an evaluation of ten ionic liquids, cation-containing alkylimidazolium ($[MIM\text{-}C14]^+$ and $[MIM\text{-}C18]^+$), alkylpyridinium ($[Py\text{-}C14]^+$ and $[Py\text{-}C18]^+$), and ammonium – in the form of triethylhexylammonium ($[TEA\text{-}C6]^+$), triethyldodecylammonium ($[TEA\text{-}C12]^+$), triethyloctadecylammonium ($[TEA\text{-}C18]^+$), tripentylmethylammonium ($[TPA]^+$), trihexylammonium ($[THA]^+$) and trioctylmethylammonium ($[TOA]^+$ – using $[TOA]^+$ $[Cl]^-$) as demulsifier at a dosage of 1000 ppm, and using the conventional heating test on medium (API = 29.59°), so-called heavy (API = 21.27°), and super-heavy crude oils (API = 9.88°). $[TOA]^+$ $[Cl]^-$ was the only substance with good performance in super-heavy crude oil after 9 h of heating. With super-heavy crude oil, microwave-heated at the same dosage, $[TOA]^+$ $[Cl]^-$ removed 98% of the volume of water after 30 min of irradiation. However, the super-heavy crude oil used by Guzmán-Lucero had only 1245 lb/1000 bbl of salt, notably lower than the amount of salt present in the MO1 (21,655 lb/1000 bls.) or MO2 (19,513 lb/1000 bls.) crude oils [23]. It is well known that an increase in salt content causes a reduction of water removal in the microwave heating test [29]. Guzmán-Lucero mentioned that the efficiency of the ILs depended only on the alkyl chain size.

In addition, Lemos et al. [25] evaluated the compounds 1-octyl-3-methylimidazolium tetrafluoroborate ($[Omim]^+$ $[BF_4]^-$) and 1-octyl-

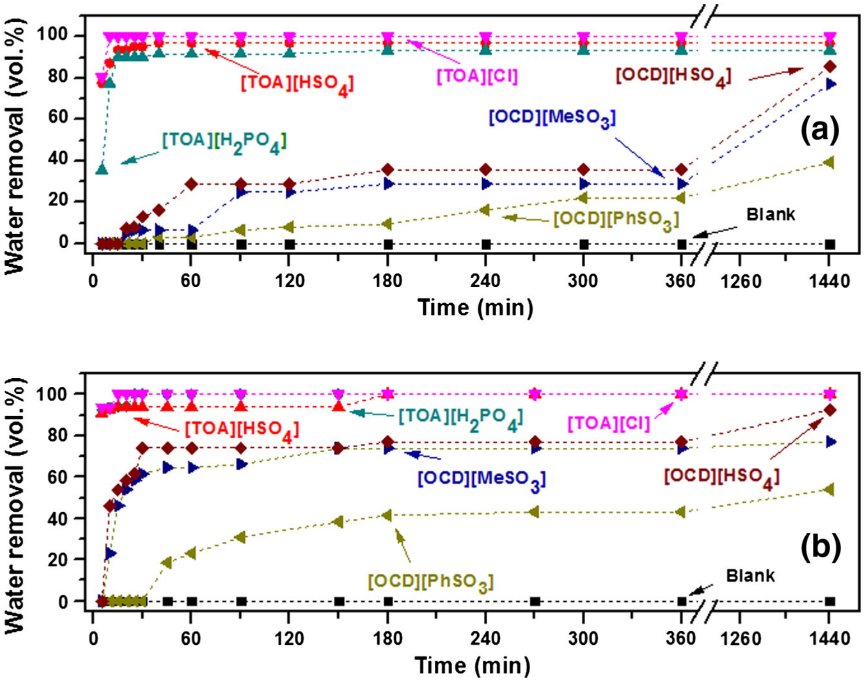

**Fig. 5.** Water removal efficiency of the $[OCD]^+$ $[Y]^-$ series at doses of 1500 ppm: (a) MO1 crude oil; (b) MO2 crude oil.

3-methylimidazolium hexafluorophosphate ($[Omim]^+$ $[PF_6]^-$) as demulsifiers of crude oil, using both microwave heating and conventional heating tests. They used a crude oil of API = 23.3° with a 1.9% weight of asphaltenes, making a stable emulsion with a range of 30–50% (v/v) of water. The conventional heating test yielded WRE values of 24.7% and 42.8% for $[Omim]^+$ $[BF_4]^-$ and $[Omim]^+$ $[PF_6]^-$ at dosages of 5100 and 6200 ppm, respectively. However, using microwave heating at the same dosage, the efficiency values reached 87.4% and 95.6%, respectively.

In order to understand their effectiveness for breaking up water/oil emulsions, the $[TOA]^+$ $[Y]^-$ and $[OCD]^+$ $[Y]^-$ series, as well as the ILs described by Guzmán-Lucero and Lemos, were fully optimized at the semi-empirical RM1 level to obtain the molecular volume ($V_M$), molecular refractivity (*MR*), and polarizability ($\alpha$). *MR* and $\alpha$ parameters are related to molecular volume and steric effects. As the best demulsifying agent for MO1 and MO2 crude oils, $[TOA]^+$ $[Cl]^-$ is considered a reference compound. Thus, Figs. 6 and 7 show a graph of the $V_M$ and *MR* of $[TOA]^+$ $[Cl]^-$ versus the gap of $[TOA]^+$ $[Cl]^-$, compared to other ILs and ammonium salts; this gap value enables us to assess the behavior of ILs and ammonium salts in relation to the reference compound. In Figs. 6 and 7, each IL and ammonium salt is labeled as it appears in Table 3. It is noteworthy, as seen in Fig. 6a, that the gap value is negative, so that the IL or ammonium salt is not efficient as a demulsifier of super-heavy crude oil; conversely, a positive gap value within the 2.3 limit between compounds **6** and **1** is typically considered acceptable. As for cations, $[TOA]^+$ shows higher $V_M$ and *MR* values than the other cations (Fig. 6b). $[OCD]^+$ shows a value near $[THA]^+$, being the lowest negative gap value, and it shows medium performance as a demulsifier, depending on which of the anions is employed. In this case, in the comparisons of $[TOA]^+$ $[HSO_4]^-$ with $[OCD]^+$ $[HSO_4]^-$ and $[TOA]^+$ $[Cl]^-$ with $[THA]^+$ $[Cl]^-$, the effect of cation size on dewatering efficiency is significant, showing that the cation must have a specific $V_M$ or *MR* value to be considered an efficient demulsifier. $[MIM\text{-}C18]^+$ and $[Py\text{-}C18]^+$ show lower negative gap values than those of $[MIM\text{-}C14]^+$ and $[Py\text{-}C14]^+$; therefore, ILs containing $[MIM\text{-}C18]^+$ or $[Py\text{-}C18]^+$ should perform better as demulsifiers. This assertion is contrary to the observations of Guzmán-Lucero; however, because they did not give a water efficiency value for the conventional heating bottle test (only face-scale was given), it is not possible to arrive at a valid comparison [24]. Indeed, other factors can influence WRE; these are discussed below.

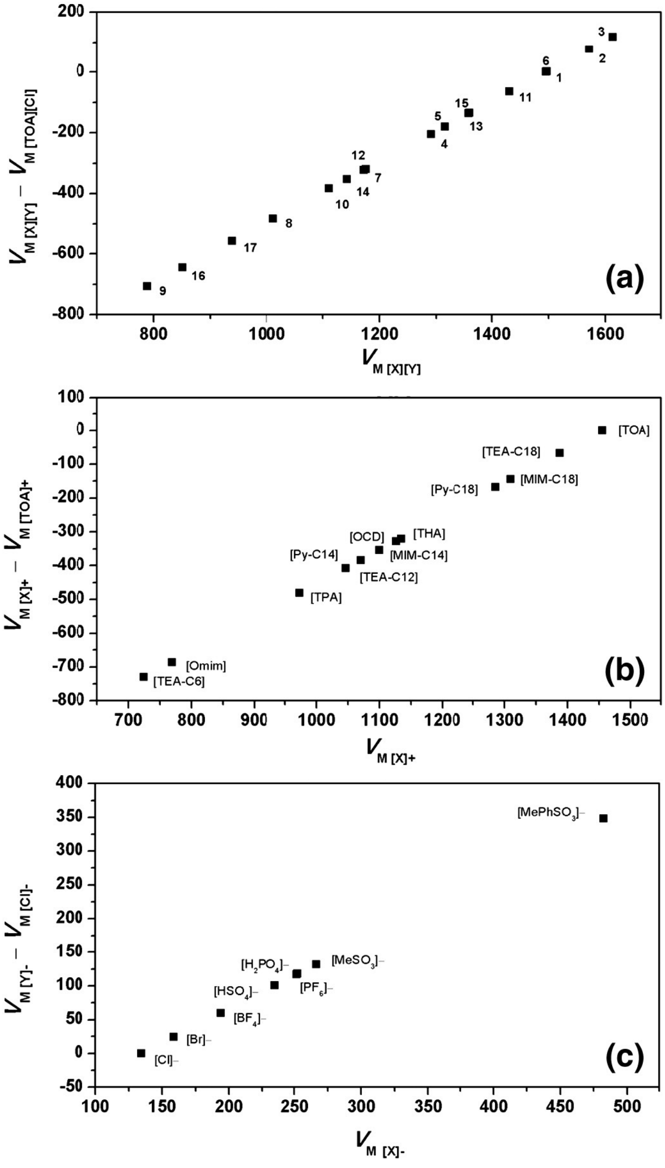

**Fig. 6.** (a) Graph of $V_M$ of $[X]^+$ $[Y]^-$ versus the gap of $V_M$ of $[X]^+$ $[Y]^-$ − $[TOA]^+$ $[Cl]^-$; (b) graph $V_M$ of $[X]^+$ versus the gap of $V_M$ of $[X]^+$ − $[TOA]^+$; (c) graph $V_M$ of $[Y]^-$ versus the gap of $V_M$ of $[Y]^-$ − $[Cl]^-$.

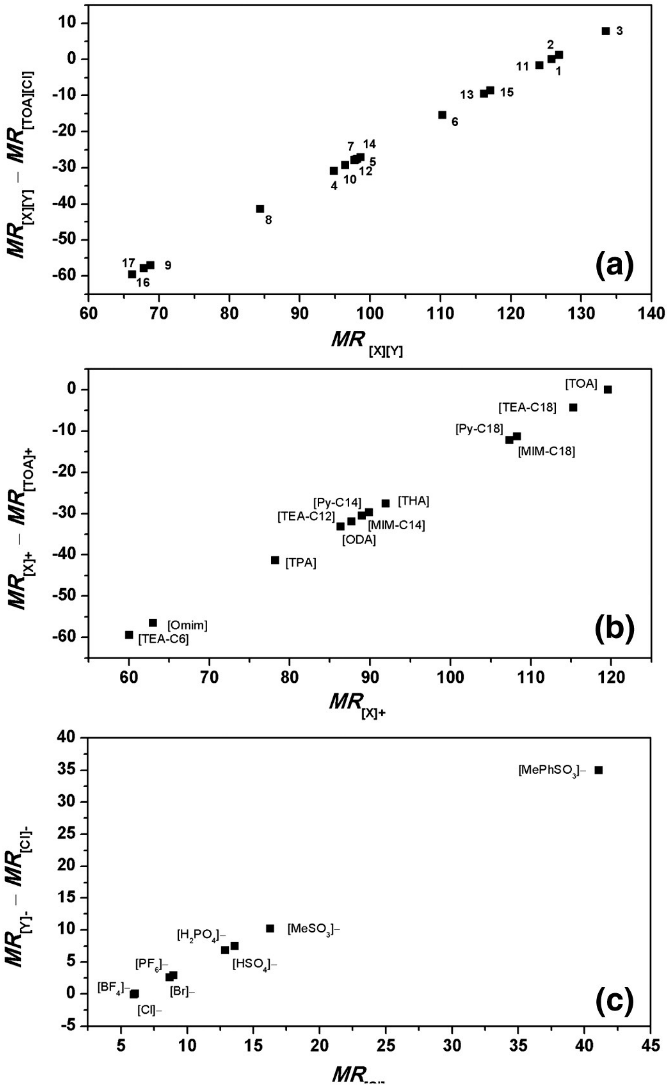

**Fig. 7.** (a) Graph of *MR* of $[X]^+$ $[Y]^-$ versus the gap of *MR* of $[X]^+$ $[Y]^-$ − $[TOA]^+$ $[Cl]^-$; (b) graph *MR* of $[X]^+$ versus the gap of *MR* of $[X]^+$ − $[TOA]^+$; (c) graph *MR* of $[Y]^-$ versus the gap of *MR* of $[Y]^-$ − $[Cl]^-$.

**Table 3**
Polarizability, molecular volume and molecular refractivity values for several ILs.

| LI | | $V_M$ (Å$^3$) | | | α (a.u.) | | | *MR* (Å$^3$) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | LI | Cation | Anion | LI | Cation | Anion | LI | Cation | Anion |
| **1** | $[TOA]^+$ $[Cl]^-$ | 1495.8 | 1454.8 | 134.6 | 212.1 | 204.4 | 0 | 125.8 | 119.6 | 6.1 |
| **2** | $[TOA]^+$ $[HSO_4]^-$ | 1571.6 | 1454.8 | 235.3 | 224.6 | 204.4 | 17.2 | 126.9 | 119.6 | 12.9 |
| **3** | $[TOA]^+$ $[H_2PO_4]^-$ | 1613.5 | 1454.8 | 252.3 | 228.0 | 204.4 | 19.7 | 133.5 | 119.6 | 13.6 |
| **4** | $[OCD]^+$ $[HSO_4]^-$ | 1291.1 | 1126.6 | 235.3 | 167.9 | 146.9 | 17.2 | 94.9 | 86.4 | 12.9 |
| **5** | $[OCD]^+$ $[MeSO_3]^-$ | 1315.8 | 1126.6 | 266.4 | 172.4 | 146.9 | 22.1 | 98.0 | 86.4 | 16.3 |
| **6** | $[OCD]^+$ $[MePhO_3]^-$ | 1497.1 | 1126.6 | 482.6 | 223.2 | 146.9 | 72.0 | 110.3 | 86.4 | 41.1 |
| **7** | $[THA]^+$ $[Cl]^-$ | 1172.9 | 1134.3 | 134.6 | 165.4 | 157.8 | 0 | 98.2 | 92.0 | 6.1 |
| **8** | $[TPA]^+$ $[Cl]^-$ | 1012.0 | 973.3 | 134.6 | 142.1 | 134.4 | 0 | 84.4 | 78.2 | 6.1 |
| **9** | $[TEA\text{-}C6]^+$ $[Br]^-$ | 789.1 | 724.7 | 158.8 | 112.6 | 102.8 | 0 | 68.8 | 60.1 | 8.7 |
| **10** | $[TEA\text{-}C12]^+$ $[Br]^-$ | 1111.3 | 1046.4 | 158.8 | 155.9 | 149.3 | 0 | 96.5 | 87.7 | 8.7 |
| **11** | $[TEA\text{-}C18]^+$ $[Br]^-$ | 1431.1 | 1387.8 | 158.8 | 201.7 | 195.7 | 0 | 124.1 | 115.3 | 8.7 |
| **12** | $[MIM\text{-}C14]^+$ $[Br]^-$ | 1176.1 | 1099.9 | 158.8 | 171.2 | 156.5 | 0 | 97.8 | 89.0 | 8.7 |
| **13** | $[MIM\text{-}C18]^+$ $[Br]^-$ | 1358.7 | 1310.2 | 158.8 | 204.4 | 187.9 | 0 | 116.2 | 107.4 | 8.7 |
| **14** | $[Py\text{-}C14]^+$ $[Br]^-$ | 1142.8 | 1070.4 | 158.8 | 178.1 | 158.6 | 0 | 98.7 | 89.9 | 8.7 |
| **15** | $[Py\text{-}C18]^+$ $[Br]^-$ | 1360.8 | 1285.8 | 158.8 | 203.3 | 189.7 | 0 | 117.1 | 108.3 | 8.7 |
| **16** | $[Omim]^+$ $[BF_4]^-$ | 850.9 | 769.0 | 194.3 | 114.9 | 109.3 | 7.4 | 66.2 | 63.0 | 6.0 |
| **17** | $[Omim]^+$ $[PF_6]^-$ | 938.4 | 769.0 | 251.5 | 119.3 | 109.3 | 10.6 | 67.8 | 63.0 | 9.0 |

In regard to the anions in Table 3, it is worth noting that there is an inverse relationship between the $V_M$ and *MR* values of the anion fragments and the water removal efficiency of ILs and ammonium salts. $[BF_4]^-$ shows a lower positive gap value than $[HSO_4]^-$ (Fig. 6c), which implies that using this anion with an $[OCD]^+$ fragment to obtain the ammonium salt $[OCD]^+$ $[BF_4]^-$ would be more efficient than using $[OCD]^+$ $[HSO_4]^-$. Fig. 7a and b show the same pattern of behavior as Fig. 6a and b, except for $[Py\text{-}C18]^+$ $[Br]^-$ versus $[MIM\text{-}C18]^+$ $[Br]^-$, which shows a less negative gap; this is the same behavior observed for cationic fragments (Fig. 7b). Accordingly, a smaller anion volume presents less steric hindrance to the natural surfactants that stabilize the emulsion in crude oil (asphaltenes and paraffins), making small anions more effective for breaking up the emulsion. In this sense, the steric effect plays an important role in the water removal process, although this behavior is opposite to that observed for cation size, as mentioned above. In ILs containing $[BF_4]^-$ and $[PF_6]^-$, this behavior is not observed; thus, other factors should be considered. In general, these results help us decide whether to select or reject the use of ILs or cationic fragments for dehydrating heavy or super-heavy crude oil without microwave heating. In sum, ILs or ammonium salts, when the cation size is increased and the anion size decreased, can perform more efficiently as dehydrating agents for heavy and super-heavy crude oils.

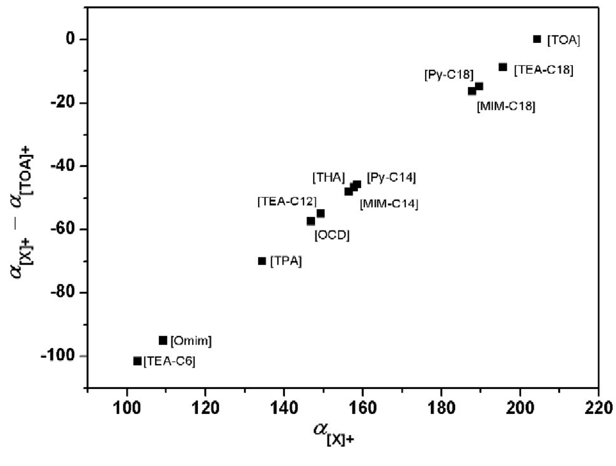

**Fig. 8.** Graph of $\alpha_{[X]+}$ versus the gap of $\alpha_{[X]+} - \alpha_{[TOA]+}$.

Table 3 lists the mean polarizability values for ILs, ammonium salts, cations and anions, and Fig. 8 shows a graph of mean polarizability versus the gap value for cations. If the cation size increases, as in $[TPA]^+$, $[THA]^+$, and $[TOA]^+$, the α values also increase, yielding a high WRE value. $[OCD]^+$ gave a mean polarizability 57.5 a.u. smaller than $[TOA]^+$, reflecting the low efficiency of both as demulsifiers. The mean polarizability of $[Cl]^-$ and $[Br]^-$ anions was zero, whereas for $[BF_4]^-$, $[PF_6]^-$, $[HSO4]^-$, $[H_2PO_4]^-$, $[MeSO_3]^-$, and $[MePhSO_3]^-$ anions, it was 7.4, 10.6, 17.2, 19.7, 22.1, and 72.0, respectively. It is significant that an increase in the polarizability of the anions, mainly in the $[TOA]^+$ $[Y]^-$ and $[OCD]^+$ $[Y]^-$ series, provokes a decrease of WRE values. In addition, quantum parameters of ILs and ammonium salts were obtained to establish a correlation with the experimental results. The dipolar moments (μ) of the ILs and ammonium salts do not show any correlation with the experimental results, whereas the μ of the cations and anions do show a correlation (Table 4). $[OCD]^+$ shows the highest μ value; notwithstanding, the $[OCD]^+$ $[Y]^-$ series is capable of removing emulsified water from crude oil of API < 10°, in comparison with the ILs with $[TEA\text{-}C6]^+$, $[TEA\text{-}C12]^+$, $[TEA\text{-}C18]^+$, $[MIM\text{-}C14]^+$, $[MIM\text{-}C18]^+$, $[Py\text{-}C14]^+$, and $[Py\text{-}C18]^+$, which are inefficient as demulsifiers for super-heavy crude oil. $\mu_{[Omim]+}$ is 8.7 Debye higher than $\mu_{[TOA]+}$. ILs with an $[Omim]^+$ fragment are efficient for removing water (>90%) only at IL dosages higher than 3000 ppm and only with the use of microwave heating for the test; furthermore, the crude oil evaluated has a low viscosity and a low amount of asphaltenes, favoring the water removal process. In the case of the anions, for $[Cl]^-$, $[HSO_4]^-$ and $[H_2PO_4]^-$, the μ value increased to 0, 2.3, and 2.7 Debye, respectively, as the demulsification capability decreased (Table 4). $[Br]^-$, $[BF_4]^-$ and

**Table 4**
Dipolar moment (μ) of the cation and anion fragments of different ILs.

| Cation | μ (Debye) | Anion | μ (Debye) |
|---|---|---|---|
| $[TOA]^+$ | 4.8 | $[Cl]^-$ | 0 |
| $[OCD]^+$ | 50.8 | $[Br]^-$ | 0 |
| $[THA]^+$ | 3.4 | $[HSO_4]^-$ | 2.3 |
| $[TPA]^+$ | 2.6 | $[H_2PO_4]^-$ | 2.7 |
| $[TEA\text{-}C6]^+$ | 6.8 | $[CH_3SO_3]^-$ | 3.5 |
| $[TEA\text{-}C12]^+$ | 20.1 | $[MePhSO_3]^-$ | 10.7 |
| $[TEA\text{-}C18]^+$ | 35.4 | $[BF_4]^-$ | 1.6E−04 |
| $[MIM\text{-}C14]^+$ | 32.4 | $[PF_6]^-$ | 2.7E−04 |
| $[MIM\text{-}C18]^+$ | 44.9 | | |
| $[Py\text{-}C14]^+$ | 29.7 | | |
| $[Py\text{-}C18]^+$ | 40.9 | | |
| $[Omim]^+$ | 13.5 | | |

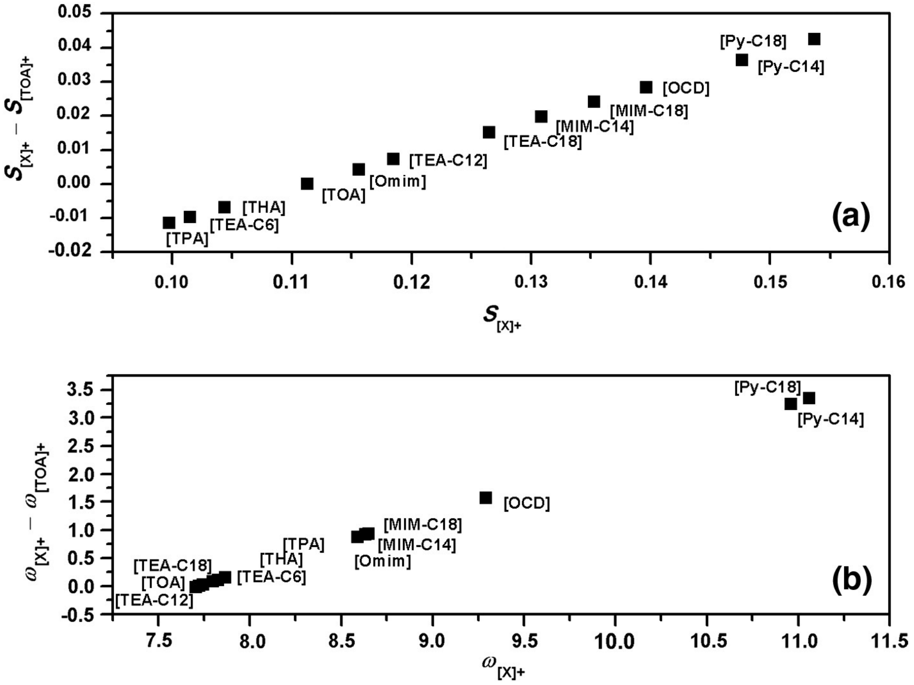

**Fig. 9.** (a) Graph of absolute softness for cations; (b) Graph of electrophilicity for cations.

$[PF_6]^-$ anions have the same $\mu$ value as $[Cl]^-$, but their molecular volume is different, and as previously mentioned, this parameter has an important influence on the effectiveness of ILs.

In regard to reactivity parameters, the absolute softness ($S$) and the electrophilicity index ($\omega$) of the ILs and ammonium salts did not show any relationship with the WRE. However, $S$ and $\omega$ for the cations showed a relationship with the experimental results. Fig. 9 shows the correlation between the $S$ and $\omega$ of $[TOA]^+$ and the gap value. Softer cations than $[TOA]^+$, specifically $[OCD]^+$, are less efficient at removing water from super-heavy crude oil. $[TEA\text{-}C12]^+$, $[MIM\text{-}C14]^+$ and $[Py\text{-}C14]^+$ are regular demulsifiers for so-called heavy crude oil, being harder cations than those with a larger alkyl-chain, which are ineffective for this type of crude oil. Thus, the WRE values with $[MIM\text{-}C14]^+$ should be higher than with $[MIM\text{-}C18]^+$; unfortunately, because of the lack of values, it is not possible to corroborate this. In addition, if the hardness increases with $[THA]^+$, $[TEA\text{-}C6]^+$, and $[TPA]^+$, the WRE decreases. Even when $V_M$ or $MR$ are important factors to be considered in respect to the ILs employed, the absolute softness parameters seem to be important parameters to take into account for ILs and ammonium salts.

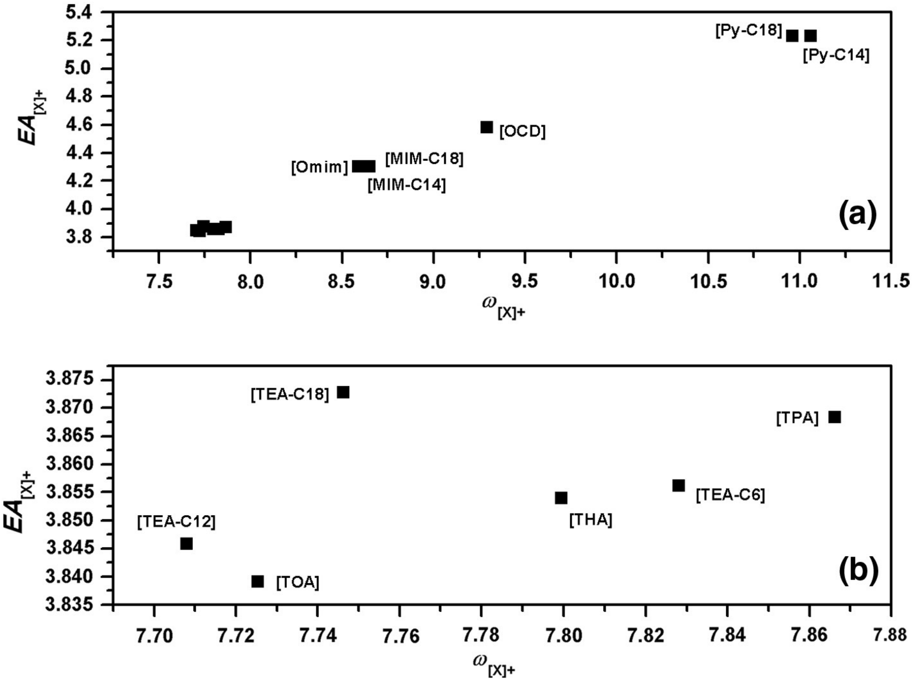

**Fig. 10.** (a) Graph of $\omega$ versus $EA$ for cation fragments; (b) amplification of the 7.70–7.88 region. Both graphs are in eV.

On the other hand, the electrophilicity index, $\omega$, measures the capability of an agent to accept electrons. In this sense, cation-containing imidazolium and pyridinium structures present high electronic delocalization via resonance effects, and therefore, they show high $\omega$ values. Parr et al. have noted that $\omega$ should be related to electron affinity (*EA*), because both parameters measure the capability of an agent to accept electrons; in particular, *EA* reflects a capability to accept only one electron from the environment [33]. Considering this correlation between both parameters, Fig. 10a shows a graph of $\omega$ versus *EA* for cationic fragments where $R^2 = 0.9928$. Fig. 10b shows an amplification of the 7.70–7.88 region; it is noteworthy that [TOA]$^+$ showed the lowest *EA* values for cations with alkyl-fragments. A correlation was also made for ILs; however, in this case $R^2 = 0.6645$. In sum, an increase in the capability for accepting electrons (high *EA* and $\omega$ values) reduces the effectiveness of the ILs and ammonium salts as demulsifying agents, mainly due to the cation-containing imidazolium and pyridinium structures.

Recently, Hezave et al. [38] carried out a study of the surfactant effect of 1-dodecyl-3-methylimidazolium chloride on water/oil interfacial tension; the partition coefficient (log *P*) was calculated for the cations, and it was observed that they were more lipophilic than the cationic heads of conventional surfactants such as dodecyl(trimethyl)azanium bromide (DTAB). Considering this study, log *P* was obtained for the ILs, ammonium salts, cations and anions (Table 5). There was no lineal relationship of log *P* versus WRE; however, if the ILs or ammonium salts have a log *P* value lower or higher than 8.69, corresponding to [TOA]$^+$ [Cl]$^-$, the WRE is low. In the case of the anions for the [TOA]$^+$ [Y]$^-$ series, if the log $P_{[Y]-}$ value is near zero, the WRE is higher; thus, when the anion fragment is more hydrophilic, the ILs are more efficient demulsifiers. In the [OCD]$^+$ [Y]$^-$ series, this statement obtained for the [HSO$_4$]$^-$ and [MePhO$_3$]$^-$ anions; however, the [MeSO$_3$]$^-$ anion showed a lower log *P* than [HSO$_4$]$^-$, but it was a little less efficient than [HSO4]$^-$; hence, other factors are implicated in this case. In the comparison of [TOA]$^+$ [HSO4]$^-$ with [OCD]$^+$ [HSO4]$^-$, it is noteworthy that with a more hydrophobic alkyl cation, the IL is more capable of diffusing into the oil phase, but being less compatible with the hydrophilic phase, it has a low removal efficiency. Other factors involved, such as π–π interactions of aromatic rings, could also affect the WRE. Hydrophobic anions, such as [PF6]$^-$ and [BF4]$^-$, show intermediate log *P* values, whereas their respective ILs show low log *P* values and are capable of removing a certain amount of water in a conventional bottle test from crude oil of API = 23.3°. Hence, if the crude oil is lighter, it is possible to use ILs with a low log *P*, but if the viscosity of the crude oil is high, the log *P* of the IL should be near the [TOA]$^+$ [Cl]$^-$ value.

**Table 5**
Partition coefficients of the ILs.

| | Compound | Cation | Anion |
|---|---|---|---|
| [TOA]$^+$ [Cl]$^-$ | 8.69 | 8.06 | 0.63 |
| [TOA]$^+$ [HSO$_4$]$^-$ | 9.55 | 8.06 | 1.41 |
| [TOA]$^+$ [H$_2$PO$_4$]$^-$ | 8.89 | 8.06 | 1.88 |
| [THA]$^+$ [Cl]$^-$ | 6.32 | 5.86 | 0.63 |
| [TPA]$^+$ [Cl]$^-$ | 5.13 | 4.49 | 0.63 |
| [TEA-C6]$^+$ [Br]$^-$ | 3.64 | 2.71 | 0.94 |
| [TEA-C12]$^+$ [Br]$^-$ | 6.02 | 5.09 | 0.94 |
| [TEA-C18]$^+$ [Br]$^-$ | 8.40 | 7.47 | 0.94 |
| [MIM-C14]$^+$ [Br]$^-$ | 6.78 | 5.85 | 0.94 |
| [MIM-C18]$^+$ [Br]$^-$ | 8.37 | 7.43 | 0.94 |
| [Py-C14]$^+$ [Br]$^-$ | 7.75 | 6.81 | 0.94 |
| [Py-C18]$^+$ [Br]$^-$ | 9.33 | 8.40 | 0.94 |
| [OCD]$^+$ [HSO$_4$]$^-$ | 11.95 | 5.70 | 1.41 |
| [OCD]$^+$ [MeSO$_3$]$^-$ | 10.47 | 5.70 | 1.17 |
| [OCD]$^+$ [MePhO$_3$]$^-$ | 13.15 | 5.70 | 3.32 |
| [Omim]$^+$ [BF$_4$]$^-$ | 4.60 | 2.26 | 1.37 |
| [Omim]$^+$ [PF$_6$]$^-$ | 5.77 | 2.26 | 2.06 |

## 4. Conclusion

The IL series [TOA]$^+$ [Y]$^-$ and the ammonium salt series [OCD]$^+$ [Y]$^-$ were evaluated as demulsifying agents for super-heavy crude oil, and the size of the anion was varied. ILs with [TOA]$^+$ were able to reach a WRE greater than 95%, whereas in the case of the ammonium salts, [OCD]$^+$ [HSO$_4$]$^-$ and [OCD]$^+$ [MeSO$_3$]$^-$ were more efficient as demulsifiers than [OCD]$^+$ [MePhSO$_3$]$^-$, which removed 53.8% of water after 24 h.

Quantum parameters at the semiempirical RM1 and DFT levels, such as $V_M$, *MR*, *S*, and $\omega$, enabled us to establish a correlation with the experimental results, and the data reported in the literature evaluating ILs as demulsifier agents were included. Therefore, it is important to consider the following: For an IL or an ammonium salt to serve as an effective demulsifier, it must have: a) a high molecular volume of IL and cations, b) a high polarizability value for the cations, and c) low molecular refractivity and molecular volume values for the anions.

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