



## Short communication

## Ionic liquid enhanced oil recovery in sand-pack columns



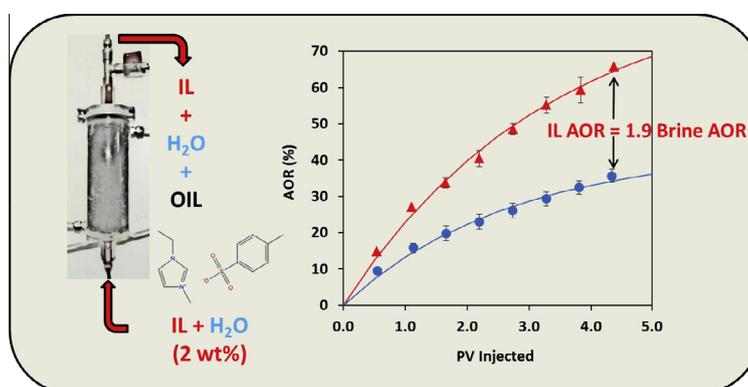
Jorge F.B. Pereira, Rita Costa, Neusa Foios, João A.P. Coutinho\*

CICECO, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal

## HIGHLIGHTS

- IL-EOR at Lab scale using a sand-pack column model was studied.
- 1-ethyl-3-methylimidazolium tosylate ( $[\text{C}_2\text{mim}][\text{OTs}]$ ) was used to recover an aromatic oil.
- Injection of a 2 wt% IL solution produced a twofold increase of the oil recovery than a brine solution.
- The use of ILs could be a constitute alternative or a complement to the conventional CEOR techniques.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 21 October 2013

Received in revised form 19 May 2014

Accepted 20 May 2014

Available online 2 June 2014

## Keywords:

Ionic liquids

1-ethyl-3-methylimidazolium tosylate

CEOR

Water-flooding

## ABSTRACT

Studies on the ionic liquids (ILs) for Chemical Enhanced Oil Recovery (CEOR) processes are limited. This work aims at fulfilling a gap in the research on IL-based CEOR processes (hereby designated by IL-EOR), showing the possibility to use the ILs as an alternative to the conventional chemicals widely studied for this purpose. Results application of ionic liquids are here reported, for the first time, on IL-EOR at Lab scale using a sand-pack column model. A 2 wt% aqueous solution of 1-ethyl-3-methylimidazolium tosylate ( $[\text{C}_2\text{mim}][\text{OTs}]$ ) was used to recover an aromatic oil. The results show that a flooding processes using only 4 pore volumes (PV) could recover 65.7% ( $\pm 1.0$ ) of the oil in place, almost the double of what was recovered with a brine solution (NaCl, 2 wt%). These preliminary results, requiring further optimization of the IL characteristics and concentration, and other process parameters, suggest that water-flooding with aqueous solutions of ILs can contribute to enhance the oil recovery in mature reservoirs.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

There is nowadays an increasing interest for enhanced oil recovery (EOR) techniques as a result of the oil scarcity and the increasing oil prices. Among the EOR techniques most attention has been focused on CO<sub>2</sub> injection and Chemical Enhanced Oil Recovery [1–3]. Chemical Enhanced Oil Recovery (CEOR) technology uses surfactants, polymers, acids, gases, salts, and conventional

solvents in order to foster the recovery of unrecoverable oil from mature reservoirs [4]. It is generally accepted that about 30% of the oil contained in the reservoirs can be recovered using current CEOR technology [5]. Although the CEOR processes have been widely studied during these last decades, the use of ILs as alternative solvents or surfactants in enhanced oil recovery techniques is quite limited [5].

By definition ionic liquids (ILs) are purely ionic materials with melting temperatures lower than 100 °C [6]. Unlike conventional solvents constituted by molecules, these are formed by ions as typical salts; yet, a large range of ILs are available allowing the

\* Corresponding author. Tel.: +351 234401507; fax: +351 234 370 084.

E-mail address: [jcoutinho@ua.pt](mailto:jcoutinho@ua.pt) (J.A.P. Coutinho).

combination of properties afforded by their dual, salt and organic solvent, nature. These compounds have attracted a vast attention from both academia and industry since the late 1990s due to a series of interesting features that they exhibit, namely an extremely low vapour pressure, low melting temperatures, wide liquid temperature range, good chemical and thermal stabilities, and in particular their ability to solvate a broad range of compounds, and the capability of tailoring their properties by a judicious selection of the constitutive ions [7,8].

In the last few years the petroleum industry has been looking carefully for the ILs properties, namely, to apply these compounds as solvents in the processes of refining, recovery or upgrade of oil [5]. Among all the applications of these compounds in oil industry, studies on the use of ILs in oil recovery processes are still scarce. Painter and collaborators [9–11] have reported some works aiming at the bitumen recovery from oil sands. In these studies several imidazolium-based ILs are used in combination with non-polar solvents and, after successive extractions, more than 90% of bitumen is released from the sand [9–11]. Although, these processes showed higher rates of oil recovery from the sands, they use large amounts of organic solvents, whereas several extraction steps were needed. Recently Arce and collaborators [12] suggested the possibility to use ILs as alternative to the conventional surfactants. Using trihexyl(tetradecyl)phosphonium chloride as surfactant, they determined its liquid–liquid phase equilibrium with dodecane, and water and reported the ability of the IL to act as surface active agent, and also to increase the viscosity of the aqueous phase. A similar study was performed by Hezave et al. [13], which used 1-dodecyl-3-methylimidazolium chloride, in order to reduce the interfacial tension between an Iranian crude oil and formation brine. The authors further demonstrated the effectiveness of ILs as surfactants to retrieve the oil trapped in core flood experiments. However, both of these studies only addressed the study of ILs with surfactant properties, in order to replace the commercial surfactants used by the oil industry.

Beside these approaches aiming the ILs application in EOR processes, it was not reported any other work aiming at the use of non-surfactant ILs nor, with the exception of Hezave et al. [13], have any other authors attempted any Lab-scale flooding experiments, in particular the use of sand-pack columns. The EOR sand-pack column assay is a suitable bench-scale approach to evaluate oil recovery, since it is an easy and economic model for a reservoir, and can be applied at high pressures and temperatures simulating the reservoir conditions. In this work a non-surfactant IL, namely 1-ethyl-3-methylimidazolium tosylate ([C<sub>2</sub>mim][OTs]), is evaluated as a ionic additive to improve to enhance oil recovery in sand-pack columns.

## 2. Experimental

### 2.1. Material

The 1-ethyl-3-methylimidazolium tosylate ([C<sub>2</sub>mim][OTs]), was acquired from Iolitec with a purity of 99 wt%. The chemical structure of the [C<sub>2</sub>mim][OTs] is presented in the Fig. 1. The NaCl (99.9 wt% purity) was acquired from VWR BDH Prolabo. A commercial chemical surfactant (Petrostep) commonly used in CEOR was kindly supplied by SNF Floereger, S.A. France. All the reagents were used as received.

A heavy aromatic crude oil from a sandstone reservoir in Brazil, kindly supplied by Partex, S.A. (Portugal), was used in this study. The oil viscosity and API of the oil was determined using a viscometer/densimeter Anton Paar (model SVM 3000). The wax content quantification was done according to a modified UOP 46-64 [14] methodology described previously [15]. A SARA

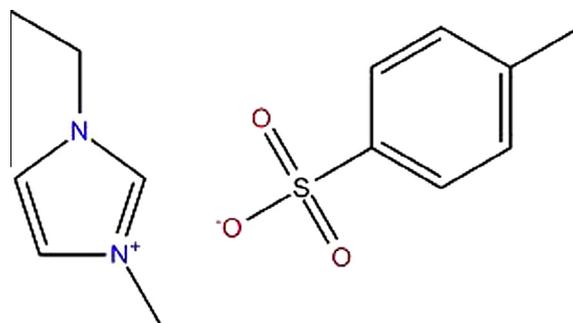


Fig. 1. Chemical structure of 1-ethyl-3-methylimidazolium tosylate ([C<sub>2</sub>mim][OTs]).

analysis was performed using the method proposed by Musser and Kilpatrick [15]. All the properties of the oil are presented in the Table 1.

The sand used in the sand-pack column was collected in a Portugal beach, and the respective particles size and surface charge characterized. The average size of the sand particles was determined by sieving, in which 75% of the particles showed a diameter between 0.25 and 0.50 mm. The surface charge (zeta potential, ZP) was determined by the streaming potential method using an electrokinetic analyser Anton Paar surpass with cylindrical cell. For the ZP measurements two aqueous solutions (1 mM) of NaCl (pH = 5.5) and [C<sub>2</sub>mim][OTs] (pH = 4.95) were used. In both cases the sand surface charge was negative exhibiting ZP values of  $-43.36 \pm 0.68$  mV and  $-42.53 \pm 3.08$  mV, respectively for sand rinsed with the salt and IL aqueous solutions. Additional supplementary data according the sand particles size and surface charge are presented in Figs. S1 and S2.

### 2.2. Methods

The sand-pack columns used to perform the IL-EOR tests in this work were previously developed and described in a work where they were used to evaluate various microorganisms in microbial enhanced oil recovery studies [16]. The vertically oriented acrylic columns, with a volume of 250 cm<sup>3</sup>, were uniformly packed with dry sand (previously sterilized). After packing the sand tightly, a top sieve and cap were fixed. The caps on both the ends of the column were provided with holes for insertion of inlet and outlet tubes. Rubber 'O' rings surrounded the caps to hermetically seal the column.

The experiments were carried out at 40 °C (this being temperature of the oil reservoir), as described below. A schematic representation of this process is shown in Fig. 2.

The column was first flooded with water at a constant flow rate of 3 cm<sup>3</sup>/min. Pore volume (PV, cm<sup>3</sup>), defined as the empty volume of the model, was calculated by measuring the volume of water required to saturate the column. The porosity (%) of the column

Table 1

Properties of the heavy aromatic oil used in sand in sand-pack columns studies: viscosity ( $\eta$ ), density ( $\rho$ ), API gravity, wax content and SARA composition. Viscosity and density values were measured at 40 °C.

	Heavy aromatic oil
$\eta$ @ 40 °C (mPa s)	50.92
$\rho$ @ 40 °C (g/cm <sup>3</sup> )	0.87
API	27.6°
Wax content (wt%)	26.9
SARA composition (wt%)	Saturated
	Aromatic
	Resins
	Asphaltenes
	2.0

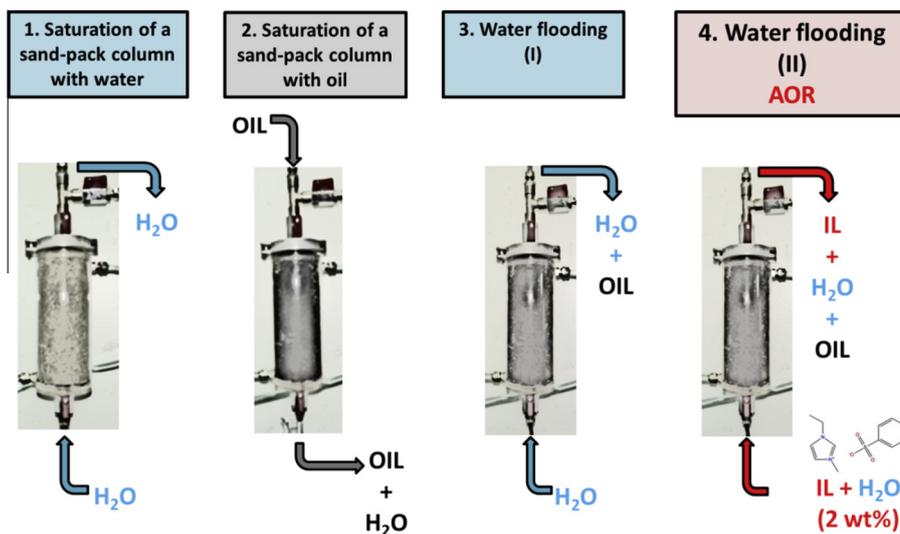


Fig. 2. Schematic representation of the sand-pack column process.

was calculated as the PV divided by the total volume of the column ( $250 \text{ cm}^3$ ). In the second step, the crude oil was injected into the column to replace water, until there was no more water coming from the effluent. Original oil in place (OOIP,  $\text{cm}^3$ ) was then calculated as the volume of oil retained in the column. Initial oil saturation ( $S_{oi}$ , %) and initial water saturation ( $S_{wi}$ , %) were calculated as follows:

$$S_{oi} = (\text{OOIP}/\text{PV}) \times 100 \quad (1)$$

$$S_{wi} = ((\text{PV} - \text{OOIP})/\text{PV}) \times 100 \quad (2)$$

The sand-pack column was maintained at  $40^\circ\text{C}$  for 24 h and afterwards flooded again with water to remove the excess of crude oil, until no more oil was observed in the effluent. The amount of crude oil recovered, here named oil recovered after water flooding ( $S_{orwf}$ ,  $\text{cm}^3$ ) was determined volumetrically. Residual oil saturation ( $S_{or}$ ) was calculated as follows:

$$S_{or} = ((\text{OOIP} - S_{orwf})/\text{OOIP}) \times 100 \quad (3)$$

The residual oil was then subjected to IL-EOR processes. The column was flooded with  $400 \text{ cm}^3$  (approximately 4 PV) of a 2 wt% aqueous solution of  $[\text{C}_2\text{mim}][\text{OTs}]$  and the effluent was collected in fractions of  $50 \text{ cm}^3$  (0.5 PV) using a volumetric graduated cylinder. All the fractions recovered correspond to the oil recovered after IL-EOR flooding ( $S_{orILf}$ ,  $\text{cm}^3$ ). Thus, the Additional Oil Recovery (AOR, %) was calculated as follows:

$$\text{AOR}(\%) = (S_{orILf}/(\text{OOIP} - S_{orwf})) \times 100 \quad (4)$$

Control essays were performed using the same methodology and conditions, but instead of the IL aqueous solution using a brine solution (NaCl, 2 wt%). For comparison purposes an aqueous solution of chemical surfactant (Petrostep, 0.15 wt%) was also used in the sand-pack column tests. The concentration of the chemical surfactant was, according to the supplier, a value above the respective critical micelle concentration ( $\text{CMC} = 1 \text{ g}/\text{dm}^3$ ). All the experiments were performed in triplicate.

### 3. Results and discussion

Initially, in order to choose the IL to be used in the sand-pack column assays, a number of ILs previously used in literature were investigated. Several vials ( $50 \text{ cm}^3$ ) with 5 g of sand + oil (sand previously saturated with oil in a column) were soaked with different ILs aqueous solutions ( $30 \text{ cm}^3$ , at 2 wt%). The vials were stored

during 24 h and then the AOR evaluated by visual analysis, in which the respective AOR was classified using the following nomenclature: no oil recovery (–); small oil recovery (+); high oil recovery (++) (images of the visual analysis are presented Fig. S3). The results of the set of preliminary assays and the respective AOR recovery are presented in Table 2.

Based on the preliminary assays, the IL  $[\text{C}_2\text{mim}][\text{OTs}]$  was selected for further studied. Three CEOR assays using sand-pack columns were performed, the first using a  $[\text{C}_2\text{mim}][\text{OTs}]$  aqueous solution, a second with a brine solution and a third using a chemical surfactant. The results obtained are reported in Table 3 and Fig. 3.

The sand-pack column had a PV in the range of  $90.0\text{--}94.0 \text{ cm}^3$ , and the OOIP was between  $69.5$  and  $83.0 \text{ cm}^3$ . The water-flooding with pure water removed about 60–70% of the oil entrapped in the column, remaining between 30 to 40 wt% of the initial oil in place in the sand-pack column. This water-flooding step corresponds to the simulation of the secondary conventional recovery process. Then the tests corresponding to the EOR processes were performed, in which, as previous described, the column was submitted to a second water-flooding process with an IL, brine solution or chemical surfactant. After the three CEOR flooding processes, with approximately 4 PV injected, were recovered approximately 65.7, 35.7 and 33.3 wt% of the oil entrapped, for the flooding with

Table 2

Set of preliminary oil recovery essays with different IL aqueous solutions (2 wt%). The AOR was evaluated visually according the following classification: no oil recovery (–); small oil recovery (+), high oil recovery (++)

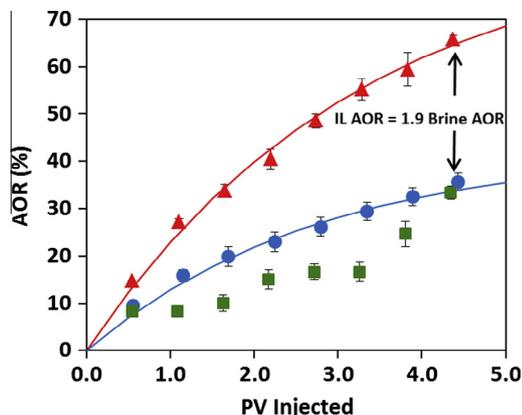
IL aqueous solution (2 wt%) <sup>a</sup>	Visual AOR
$[\text{C}_2\text{mim}]\text{Cl}$	+
$[\text{C}_4\text{mim}]\text{Cl}$	–
$[\text{C}_8\text{mim}]\text{Cl}$	–
$[\text{C}_2\text{mim}][\text{OTs}]$	++
$[\text{C}_4\text{mim}][\text{OTs}]$	+
$[\text{C}_4\text{C}_1\text{py}][\text{N}(\text{CN})_2]$	–
$[\text{Benzyl}]\text{Cl}$	–
$[\text{P}_{66614}]\text{Cl}$	+
$[\text{P}_{4441}][\text{OTs}]$	+

<sup>a</sup> Acronyms of ILs studied: 1-ethyl-3-methylimidazolium chloride ( $[\text{C}_2\text{mim}]\text{Cl}$ ); 1-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}]\text{Cl}$ ); 1-methyl-3-octylimidazolium chloride ( $[\text{C}_8\text{mim}]\text{Cl}$ ); 1-ethyl-3-methylimidazolium tosylate ( $[\text{C}_2\text{mim}][\text{OTs}]$ ); 1-butyl-3-methylimidazolium tosylate ( $[\text{C}_4\text{mim}][\text{OTs}]$ ); 1-butyl-3-methylpyridinium dicyanamide ( $[\text{C}_4\text{C}_1\text{py}][\text{N}(\text{CN})_2]$ ); benzyltrimethyl(2-hydroxyethyl)ammonium chloride ( $[\text{Benzyl}]\text{Cl}$ ); trihexyltetradecylphosphonium chloride ( $[\text{P}_{66614}]\text{Cl}$ ); triisobutyl(methyl)phosphonium tosylate ( $[\text{P}_{4441}][\text{OTs}]$ ).

**Table 3**

Oil recovery in sand-pack columns after flooding with [C<sub>2</sub>mim][OTs] (2 wt%), NaCl (2 wt%) and Petrostep (0.15 wt%) aqueous solutions. Results represent the average of three independent experiments ± standard deviation.

	[C <sub>2</sub> mim][OTs]	NaCl	Petrostep
PV (cm <sup>3</sup> )	92.0 ± 2.0	94.0 ± 6.0	90.0 ± 3.8
Porosity (%)	36.8 ± 0.8	37.6 ± 2.4	36.0 ± 1.5
OoIP (cm <sup>3</sup> )	69.5 ± 10.5	77.0 ± 3.0	93.0 ± 1.5
S <sub>oi</sub> (%)	75.3 ± 9.0	82.5 ± 8.5	92.2 ± 2.7
S <sub>wi</sub> (%)	24.7 ± 9.0	17.5 ± 8.5	7.8 ± 2.7
S <sub>or</sub> (%)	31.3 ± 2.5	40.9 ± 0.0	36.1 ± 3.5
AOR with 4 PV injected (%)	65.7 ± 1.0	35.7 ± 1.8	33.3 ± 2.3



**Fig. 3.** Additional oil recovery (AOR) by flooding at 40 °C with: (▲) [C<sub>2</sub>mim][OTs] (2 wt%); (●) brine solution (2 wt%); (■) Petrostep (0.15 wt%).

[C<sub>2</sub>mim][OTs], NaCl and Petrostep solutions respectively. The AOR in the CEOR processes is dependent of the PV of water-flooded into the reservoir. Fig. 3 presents the oil recovery as function of the volume of aqueous solution injected. The oil recovery according the volume of aqueous solution injected exhibited different behaviors if ionic aqueous solutions (IL and brine) or the commercial chemical surfactant are used. The oil recovery data obtained with chemical surfactant was only used for comparison purposes and in order to show that the mechanism that induces the AOR obtained with non-surfactant IL here reported is different. Thus, considering the main issue of this work (CEOR with a non-surfactant IL), only the experimental oil recovery data for ionic aqueous solutions were correlated using Eq. (5):

$$\text{AOR}(\%) = a \times (1 - e^{(-b \times \text{PV})}) \quad (5)$$

The fitted parameters, and respective standard deviations, are summarized in Table 4.

As observed by the analysis of Fig. 3 the oil recovery increases with the amount of aqueous solution injected, being recovered after 4 PV almost twice as more oil when using the IL solution than with brine. According to the fitted parameters reported in Table 4, the potential AOR recovery with a [C<sub>2</sub>mim][OTs] solution is 88%, more than twice of the oil recovery obtained by flooding with a brine solution. On the other hand, when injected the aqueous solution of the chemical surfactant the oil recovery trend is completely different with the volume of solution injected (see Fig. 3).

As expected the different trends seem to indicate that the CEOR mechanisms when used surfactant or non-surfactant compounds are different. Additional evidences were obtained when evaluating the interfacial tension (IFT) values between binary mixtures of each aqueous solution and the crude oil at 40 °C. These IFT measurements were performed according the procedure previously described by us [17], in which a decrease of IFT was only observed when used an aqueous solution of Petrostep ([Petrostep] = 1.5 g/

**Table 4**

Correlation parameters used in Eq. (5) to describe the AOR (%) in function of PV of the aqueous solution injected (cm<sup>3</sup>) (and respective standard deviations,  $\sigma$ ).

Aqueous solution (2 wt%)	(a + $\sigma$ )	(b + $\sigma$ )
[C <sub>2</sub> mim][OTs]	88.40 ± 6.30	0.30 ± 0.03
NaCl	42.85 ± 3.29	0.37 ± 0.05

dm<sup>3</sup>; IFT = 4.3 ± 0.0 mN/m). The non-surfactant compounds, namely [C<sub>2</sub>mim][OTs] and NaCl solutions (20 g/dm<sup>3</sup>), exhibited IFT equal to 19.1 ± 1.0 mN/m and 17.0 ± 0.4 mN/m, respectively. These high IFT values are clear indications that the EOR mechanism in action with these ionic solutions does not result from a decrease in the adhesion of the oil to the sand due to a decrease in the IFT as is the case for chemical surfactants.

The use of IL to improve the oil recovery in mature reservoirs has been suggested since ILs may have several interesting properties, such as surfactant, emulsifying, and ionic character. Among the several properties of ILs, in this work, two different properties, high electrostatic interactions and aromatic character, seem to be essential. In the first case, as previously reported for other chemical compounds such as polymers or surfactants [18], the electrostatic factor between the aqueous solutions and the surface charge of the sand is an important factor to take into account. When using silica-based particles (sand in this study), they have a negatively charged weak acidic surface (as reported in the materials section). Thus, when an aqueous solution with an IL with strong dipole moment like [C<sub>2</sub>mim][OTs] is injected, there seems to be a favourable electrostatic attraction between the negative charge of sand surface and the ionic groups, allowing an increase of the oil recovery when compared with the brine solution. On other hand, as previously reported [19], the driving force for the aromatics separation or solubility is the  $\pi$ - $\pi$  interactions between aromatics and ILs. The high AOR rates achieved in this work using the [C<sub>2</sub>mim][OTs], and the poor performance of non-aromatic ILs in the preliminary set of experiments presented in Table 2, suggest that the aromatic character of the IL (with both cation and anion with aromatic rings) was important in the enhanced oil recovery of this heavy aromatic oil.

Thus for the first time, and unlike in the few previously reported applying ILs in EOR processes [5,9–12], here is not the ILs surfactant character that induces the oil recovery. The results here reported, albeit requiring more work to clarify the molecular mechanisms involved, seem to indicate that the ionic charge and aromaticity of the [C<sub>2</sub>mim][OTs] play an important role in the EOR process, being the  $\pi$ - $\pi$  interactions between the IL and the aromatic fractions of the oil entrapped in the column crucial to improve the oil recovery, as well as the electrostatic interactions between the negative surface of the sand particles and the IL. Previously, Meindersma and collaborators [20] observed that the existence of  $\pi$ -electrons in the aromatic ring results in a much stronger electrostatic field around the aromatic ILs. Several other studies have been reported [21–25], showing the importance of the ILs aromaticity to improve the selectivity and extraction of aromatic compounds.

Furthermore, the addition of the ILs to water, or seawater could be advantageous to increase the oil recovery rates in the water flooding conventional EOR processes even in carbonated reservoirs since, as demonstrated before by Fathi and collaborators [26], the modification of the salinity and ionic composition may act as improved wettability modifier in a water-based EOR processes in carbonates.

Summing up, the innovative results here presented and discussed show the use of ILs as an alternative to the CEOR processes, or an additive to the conventional flooding EOR techniques, to be a promising approach. Although, the AOR results obtained using

[C<sub>2</sub>mim][OTs] are extremely exciting, those should be considered as a first step in the IL-EOR studies using non-surfactant ILs. Additional tests aiming the use of cheaper and more biodegradable ILs should be addressed, as well the study of other parameters, such as IL recoverability, and the impact of the ILs in the soil/water compartments.

#### 4. Conclusions

In the current work, it was studied the use of [C<sub>2</sub>mim][OTs] as alternative compound to be used in CEOR processes. It was demonstrated that the injection of a diluted solution of [C<sub>2</sub>mim][OTs] (2 wt%) produces a twofold increase of the oil recovery when compared with a brine solution. The results show that it was possible to recover approximately 65% of the oil entrapped in the sand-pack columns with the injection of 4 PV of the IL aqueous solution and up to 88% could be recovered by this method. Furthermore, it seems that the aromatic character of [C<sub>2</sub>mim][OTs] contributes to the increase of the interactions with the aromatic oil fractions allowing a better wettability and consequent removal of the oil from the reservoir. These are preliminary results requiring further optimization of the IL characteristics and concentration, its relation with the oil composition and the nature of the reservoir rock, and other process parameters including the IL recyclability. However the results here reported suggest that water-flooding with aqueous solutions of ILs may constitute an alternative, or a complement, to the conventional CEOR processes currently used by the oil industry.

#### Acknowledgements

The authors would like to acknowledge Prof. Ascensão Lopes and Ana Paula Piedade from CEMUC, University of Coimbra, for assisting in the surface charge measurements. Jorge F.B. Pereira acknowledges the financial support from FCT-Fundação para a Ciência e Tecnologia, Portugal, for the Grant SFRH/BD/60228/2009. CICECO is being funded by FCT through Pest-C/CTM/LA0011/2013. This work was also supported by PARTEX OIL AND GAS, Portugal.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2014.05.055>.

#### References

- [1] Sheng J. *Modern chemical enhanced oil recovery. Theory and practice*. Burlington, MA, USA: Gulf Professional Publishing; 2011.
- [2] Thomas S. Enhanced oil recovery – an overview. *Oil Gas Sci Technol* 2008;63:9–19.
- [3] Aladassani A, Bai B. Recent developments and updated screening criteria of enhanced oil recovery techniques. In: *International oil and gas conference and exhibition in China, Society of Petroleum Engineers, Beijing, China*, 2010.
- [4] Jamaloei BY. Chemical flooding in naturally fractured reservoirs: fundamental aspects and field-scale practices. *Oil Gas Sci Technol* 2011;66:991–1004.
- [5] José-Alberto MH, Jorge A. Current knowledge and potential applications of ionic liquids in the petroleum industry. In: Kokorin PA, editor. *Ionic liquids: applications and perspectives*. InTech; 2011. p. 439–56.
- [6] Wilkes JS. A short history of ionic liquids – from molten salts to neoteric solvents. *Green Chem* 2002;4:73–80.
- [7] Earle MJ, Seddon KR. Ionic liquids. *Green solvents for the future*. *Pure Appl Chem* 2000;72:1391–8.
- [8] Brennecke JF, Maginn EJ. Ionic liquids: innovative fluids for chemical processing. *AIChE J* 2001;47:2384–9.
- [9] Hogshead CG, Manias E, Williams P, Lupinsky A, Painter P. Studies of bitumen-silica and oil-silica interactions in ionic liquids. *Energy Fuel* 2011;25:293–9.
- [10] Painter P, Williams P, Lupinsky A. Recovery of bitumen from Utah tar sands using ionic liquids. *Energy Fuel* 2010;24:5081–8.
- [11] Williams P, Lupinsky A, Painter P. Recovery of bitumen from low-grade oil sands using ionic liquids. *Energy Fuel* 2010;24:2172–3.
- [12] Lago S, Rodriguez H, Khoshkbarchi MK, Soto A, Arce A. Enhanced oil recovery using the ionic liquid trihexyl(tetradecyl)phosphonium chloride: phase behaviour and properties. *RSC Adv* 2012;2:9392–7.
- [13] Hezave AZ, Dorostkar S, Ayatollahi S, Nabipour M, Hemmateenejad B. Investigating the effect of ionic liquid (1-dodecyl-3-methylimidazolium chloride ([C(12)mim][Cl])) on the water/oil interfacial tension as a novel surfactant. *Colloid Surf A* 2013;421:63–71.
- [14] Burger ED, Perkins TK, Striegler JH. Studies of wax deposition in the trans Alaska pipeline. *J Petrol Technol* 1981;33:1075–86.
- [15] Musser BJ, Kilpatrick PK. Molecular characterization of wax isolated from a variety of crude oils. *Energy Fuel* 1998;12:715–25.
- [16] Gudiña EJ, Pereira JFB, Costa R, Coutinho JAP, Teixeira JA, Rodrigues LR. Biosurfactant-producing and oil-degrading *Bacillus subtilis* strains enhance oil recovery in laboratory sand-pack columns. *J Hazard Mater* 2013;261:106–13.
- [17] Pereira JFB, Gudiña EJ, Costa R, Vitorino R, Teixeira JA, Rodrigues LR, et al. Optimization and characterization of biosurfactant production by *Bacillus subtilis* isolates towards microbial enhanced oil recovery applications. *Fuel* 2013;111:259–68.
- [18] Somasundaran P, Huang L. Adsorption/aggregation of surfactants and their mixtures at solid-liquid interfaces. *Adv Colloid Interface Sci* 2000;88:179–208.
- [19] Pandey S. Analytical applications of room-temperature ionic liquids: a review of recent efforts. *Anal Chim Acta* 2006;556:38–45.
- [20] Meindersma GW, Podt A, de Haan AB. Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures. *Fuel Process Technol* 2005;87:59–70.
- [21] Selvan MS, McKinley MD, Dubois RH, Atwood JL. Liquid-liquid equilibria for toluene + heptane + 1-ethyl-3-methylimidazolium triiodide and toluene + heptane + 1-butyl-3-methylimidazolium triiodide. *J Chem Eng Data* 2000;45:841–5.
- [22] Hanke CG, Johansson A, Harper JB, Lynden-Bell RM. Why are aromatic compounds more soluble than aliphatic compounds in dimethylimidazolium ionic liquids? A simulation study. *Chem Phys Lett* 2003;374:85–90.
- [23] Ferreira AR, Freire MG, Ribeiro JC, Lopes FM, Crespo JG, Coutinho JAP. Overview of the liquid-liquid equilibria of ternary systems composed of ionic liquid and aromatic and aliphatic hydrocarbons, and their modeling by COSMO-RS. *Ind Eng Chem Res* 2012;51:3483–507.
- [24] Arce A, Earle MJ, Katdare SP, Rodriguez H, Seddon KR. Application of mutually immiscible ionic liquids to the separation of aromatic and aliphatic hydrocarbons by liquid extraction: a preliminary approach. *Phys Chem Chem Phys* 2008;10:2538–42.
- [25] Poole CF, Poole SK. Extraction of organic compounds with room temperature ionic liquids. *J Chromatogr A* 2010;1217:2268–86.
- [26] Fathi SJ, Austad T, Strand S. Water-based enhanced oil recovery (EOR) by “smart water”: optimal ionic composition for EOR in carbonates. *Energy Fuel* 2005;25:5173–9.