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Short communication

Ionic liquid enhanced oil recovery in sand-pack columns

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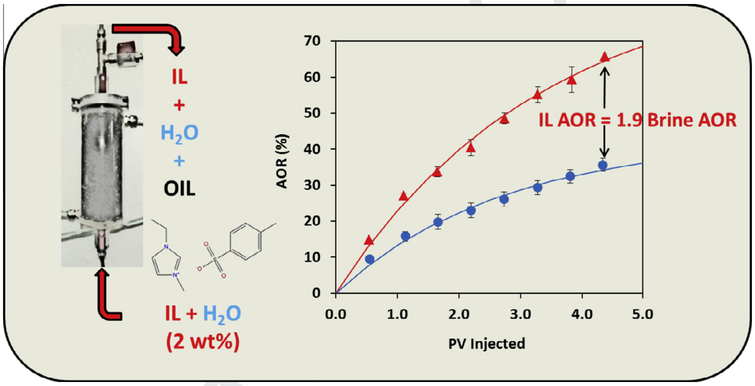
HIGHLIGHTS

- IL-EOR at Lab scale using a sand-pack column model was studied.
- 1-Ethyl-3-methylimidazolium tosylate ($[C_2mim][OTs]$) 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



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ABSTRACT

Studies on the (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 ($[C_2mim][OTs]$) was used to recover an aromatic oil. The results show that a flooding processes using only 4 pore volumes (PV) could recover 65.7% (±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.

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_2 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

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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_2mim][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_2mim][OTs]), was acquired from Iolitec with a purity of 99 wt%. The chemical structure of the [C_2mim][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 Shell, 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 analysis was performed using the method proposed by Musser and Kilpatrick [15]. All the properties of the oil are presented in the Table 1.

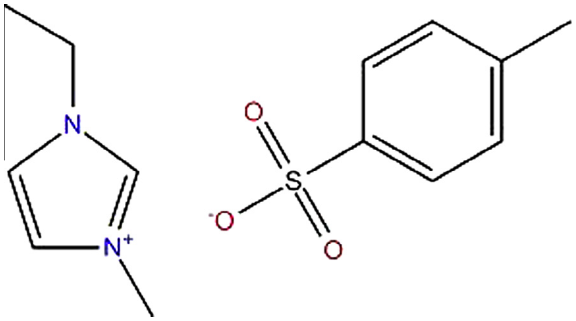

Fig. 1. Chemical structure of 1-ethyl-3-methylimidazolium tosylate ([C_2mim]-[OTs]).

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_2mim][OTs] (pH = 4.95) were used. In both cases the sand surface charge was negative exhibiting ZP values of −43.36 ± 0.68 mV and −42.53 ± 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^3, 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^3/min. Pore volume (PV, cm^3), 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 (η), density (ρ), API gravity, wax content and SARA composition. Viscosity and density values were measured at 40 °C.

		Heavy aromatic oil
η @ 40 °C(mPa s)		50.92
ρ @ 40 °C (g cm^{-3})		0.87
API		27.6°
Wax content (wt%)		26.9
SARA composition (wt%)	Saturated	29.7
	Aromatic	38.3
	Resins	14.4
	Asphaltenes	2.0

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