Introduction

The efficiency of water flooding, as a cost-effective method, in carbonate reservoirs is lower than the sandstones, attributed to the presence of fracture network and oil/mixed-wet matrix which prevents the spontaneous imbibition of water into the matrix (Standnes and Austad 2000). The high interfacial tension (IFT) between the aqueous and oleic phases further increase the oil trapping in the matrices. To address these challenges, chemical enhanced oil recovery (CEOR) methods are considered as a good candidates to alter the properties of the rock and fluids. Surfactants as an appropriate chemical agent have been introduced by several researchers to reduce the IFT between two phases and to alter the wettability of the rock surface toward more water-wet state (Ahsaei et al. 2019; Esfandiarian and Azdarpour 2018; Strand, Puntervold, and Austad 2016). However, surfactants confront the CEOR operation with some limitations such as low stability at high temperatures, high hazardous-nature, high fingering due to low solution viscosity, high cost, and high adsorption on the rock surface. Considering these limitations, finding an appropriate alternative of surfactants has been turned to a real challenge. Recently, ionic liquids (ILs), as a “green chemical”, has immensely attracted the attention of some researchers as an appropriate alternative of surfactants in CEOR processes to overcome the surfactants limitations. The unique properties of ILs including high stability at harsh conditions of high salinity and high temperature, environmental-friendly nature, low toxicity, high viscosity, and the ability of being manipulated structurally make them good enough for improving the oil sweep efficiency. The Imidazolium-based ILs with a halide anion such as chloride, bromide, etc are beneficial for IFT reduction, wettability alteration, and crude oil degradation. Consequently, they are always preferable for oil recovery experiments due to the high-level of surface activities (Bera and Belhaj 2016).

In brief, the main difference between current work versus other water based chemical flooding in the literature is that not only the interactions between ILs, waters with various salinity and crude oil were studied, but also the interactions among dolomite rock and chemical slug were investigated by measuring their physicochemical properties. Moreover, dolomite coated micromodel was used as a porous medium for the first time in purpose of visualization of fluid flow mechanisms on the pore scale. In this study, three different imidazolium-based ILs were synthesized according to a simple procedure and their quality were assessed by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) method. The critical micelle concentration (CMC) of each IL was measured in three different saline solvent. To investigate the fluid-fluid interaction between the IL in different saline solvent and the crude oil, the ATR-FTIR were performed. Moreover, the rock-fluid interactions in the system of IL solutions, crude oil, and the rock surface were analyzed via contact angle (CA) measurement experiments, scanning electron microscope (SEM), ATR-FTIR, and X-ray diffraction (XRD) analysis for both carbonate cross sections and carbonate powder used in micromodel system. Finally, the impacts of fluid-fluid and rock-fluid interactions on EOR were shown by conducting twelve chemical flooding tests in a carbonate coated micromodel.

Material and Methods

1-hexyl-3-methylimidazolium chloride ([HMIM][Cl] or IL6), 1-octyl 3-methylimidazolium chloride ([OMIM][Cl] or IL8) and 1-dodecyl-3-methylimidazolium chloride ([DMIM][Cl] or IL12) have been synthesized and applied in this study, as three cationic ILs according to Bowers et al. method(Bowers et al. 2004). The crude oil with an API of 31.56 and the formation brine (FB) with a total dissolved solid (TDS) of 195,475 ppm were taken from an Iranian oil reservoir. Seawater (SW) with a TDS of 36,250 ppm was provided from Persian Gulf seawater. A low saline water (LSW) was prepared by diluting FB up to 2000 ppm.

Experimental Procedure

The quality of all synthesized ILs were investigated with the ATR-FTIR method between wavenumber of 400 and 4000 cm\(^{-1}\) by Bruker Tensor II device made by Germany. Then the compatibility between several different concentrations of ILs (100, 500, 1000, 5000, and 10,000 ppm) with LSW, SW, and FB was investigated by bottle tests at reservoir temperature of 80 °C. The IFT400 apparatus was used for determining the IFT between different IL solutions and crude oil by pendant drop method for obtaining CMC values at reservoir temperature. The contact angle between the smooth thin section of the rock surface and the crude oil was measured for different IL solutions by sessile drop method to reveal the optimum IL concentrations in the three saline environments. The mineralogy of the smooth thin sections were determined by D500 XRD method (Bruker, Germany). Based on a CT-scan analysis from a
dolomite rock thin section, the micromodel pattern (shown in Figure 1a) was designed by CorelDraw Graphics Suite software. The dimensions of the prepared micromodel were 12 cm length, 6 cm width, and 0.009 mm depth, with a diameter of 0.01-0.05 mm, total volume of 0.5 cc and a porosity of 36.62%. The micromodel was coated with dolomite powder to represent a carbonate media for flooding experiments. The pictures of the non-coated and coated pore structures in micromodel is shown in Figure 1b and the designed micromodel setup in the laboratory is illustrated in Figure 1c. Twelve different solutions including LSW, SW, FB, 5000 ppm IL6+LSW, 1000 ppm IL6+SW, 500 ppm IL6+FB, 5000 ppm IL8+LSW, 1000 ppm IL8+SW, 500 ppm IL8+FB, 4000 ppm IL12+LSW, 500 ppm IL12+SW, and 50 ppm IL12+FB were chosen based on the CMC measurements and the optimum values of CA experiments, to injected into the micromodel at reservoir temperature with a constant rate of 0.1 cc/hr (0.00167 cc/min) until the oil production reaches zero (almost 2 pore volume injection (PVI)).

**Figure 1** (a) Micromodel pattern obtained from dolomite pore structure, (b) coated and non-coated pore structure in micromodel, (c) schematic diagram of the micromodel setup

**Result and Discussion**

**Fluid-fluid interactions**

**FT-IR.** The FT-IR spectrum of the three different imidazolium-based ILs synthesized in this study is shown in Figure 2. Each of the characteristic peak in the FT-IR spectra is related to a specific functional group participate in the IL structure.

**Figure 2** FT-IR spectrum of [HMIM][Cl], [OMIM][Cl] and [DMIM][Cl]

Although the chemical bond number of IL6, IL8, IL12 are approximately the same, their structural differences are in the carbon number of their hydrophobic chain. Hence, almost the same peaks are shown for all ILs with different absorbance intensity. The red line represents the IR spectrum of IL12 which shows two strong peaks at 2849 and 2917 cm⁻¹, representing the –CH₂– and –CH₃ in the hydrophobic chain, respectively. These peaks are more intensive than that of the same peaks for IL6 and IL8, indicating the more concentration of –CH₂– and –CH₃ in IL12.

**IFT.** According to the obtained data from the pendant drop method, the CMC values for IL6, IL8, and IL12 in FB were about 500, 500, and 50 ppm, respectively and the IFT values were about 7.42, 4.54, and 0.34 mN/m, respectively. Some researchers reported that ILs with a longer alkyl chain have a more potential in reducing IFT due to the high surface activity (Bera and Belhaj 2016; Hezave et al. 2013). Hence, IL12 has more effect on IFT reduction compared to the IL8 and IL6. Moreover, the IFT values were decreased by increasing the salinity in a way that the IFT values of IL12 (at CMC value) in LSW, SW, and FB were 2.39, 0.48, and 0.34 mN/m, respectively. The better performance of ILs in saline
environment is due to the tolerance power of these environments. Substantially, when cationic ILs are used in the saline water, the negatively-charged ions neutralize the positive charge of cationic ILs, and as a result, accumulation of ILs molecules at the oil-water interface facilitates the IFT reduction (Bera and Belhaj 2016).

**Rock-fluid interactions**

The great potential of changing wettability for various ILs in three different salinity waters are shown in Figure 3. A shift of the rock surface wettability from oil-wet to water-wet is illustrated for the ILs with a longer carbon chain at the more saline environment. This phenomenon is occurred by ILs as the ion pair is formed between the positive head groups of the ILs and the adsorbed negatively-charged carboxylic groups of crude oil on the rock surface. In the presence of salinity, increasing the carbon bonds in IL improve the wettability alteration ability. The presence of monovalent and divalent cations in the saline water activates the carbon bonds in IL structures and eliminate the crude oil acidic components from the rock surface. According to Figure 3, the aqueous solution of IL12 in SW have the most impact on wettability alteration from oil-wet to water-wet state.

![Figure 3](https://example.com/image3)

**Flooding experiments in micromodel**

Based on the XRD analysis, the carbonate thin section surfaces and also the carbonate powder used in micromodel were both found to be dolomite type. Figure 4a illustrates the displacement of the oleic phase by the aqueous phase in micromodel (porous media) during seven different injection time steps of FB, including at the beginning, 0.1 PVI, 0.2 PVI, 0.3 PVI, 0.4 PVI, breakthrough (BT), and at the 2 PVI. As can be seen, the final recovery factor of water flooding is approximately equal to the recovery factor at the breakthrough time (almost 41%). Viscous fingering phenomenon is occurred during the water flooding, due to the high IFT between two phases, the oil-wet nature of the pore surfaces, and the low viscosity of water, leading to an increment in the mobility ratio and a reduction in the final oil recover.

![Figure 4](https://example.com/image4)

**Figure 4 (a)** The distribution of the aqueous (FB) and oil phases in micromodel during seven different time steps. **(b)** The distribution of the aqueous (IL12 in SW at CMC) and oil phases in micromodel during seven different time steps

The final values of recovery for IL6, IL8, and IL12 (at the CMC value) with FB were about 61.82 %, 63 % and 72.93 %, respectively. The oil displacement by IL12 solution (at CMC value) in SW during seven time steps, from 0.1 PV to BT (Figure 4b) shows an ultimate recovery of 80.28%, attributed to the high potential of IFT reduction and wettability alteration. The amount of oil recovery of the aforementioned twelve different flooding scenarios in a period of 2 PVI are shown in Figure 5. A drastic increment is observed in the recovery values until reaching the BT. After BT, the graph is approximately reaches a plateau, because of the water channelling phenomena.
Figure 5  Pore-scale recovery performance of IL solutions during flooding in the micromodel

Conclusion

In this study, three different imidazolium-based ILs were synthesized and their quality was assessed by ATR-FTIR method. The CMC of each IL was measured in three different salinity solutions to investigate the synergism between ILs and salts for fluid-fluid interactions. Furthermore, the rock-fluid interactions were analyzed with contact angle experiments and XRD analysis for the thin sections. Finally, the impacts of fluid-fluid and rock-fluid interactions on EOR were shown by conducting twelve chemical flooding tests in a dolomite-coated micromodel.

- ILs perform better at high salinity environments such as FB for IFT reduction, attributed to the tolerance power of high saline environment. However, the optimum salinity for wettability alteration was the salinity of SW.
- IL12 with a longer alkyl chain length has a more effect on IFT reduction, wettability alteration, and recovery improvement compared to the IL8 and IL6 at the CMC value.
- Although IL12+FB solution has the most influence on IFT reduction, the maximum recovery of about 80.28 % belongs to the IL12+SW solution, which is because of the mutually role of IFT reduction and wettability alteration as the main mechanisms.
- The amount of ultimate recovery was almost at a constant value after BT time, attributed to the channeling effect.

References


