Introduction

The current trend in oil and gas price shift has challenged the researchers to develop efficient ways to enhance oil recovery and reduce operational costs. From sustainability point of view every attempt made to enhance recovery of existing oil and gas resources from subsurface reservoirs must be environmental friendly as well as commercially viable (Madani et al., 2019). Nearly two-third fraction of initial oil in place still remain in the reservoir as residual oil after primary and secondary recovery (Kumar and Mandal, 2017), thus tertiary oil recovery or EOR methods are employed to recover the residual oil left. Amongst EOR methods used worldwide, chemical flooding including polymer flooding and surfactant flooding techniques has delivered promising results by introducing tailor-made chemicals both in laboratory and field scales (Benzagouta et al., 2013; Madani et al., 2019; Romero-Zerón and Kittisrisawai, 2015). In surfactant flooding technique aqueous solutions of complex mixtures of surface active chemicals are injected in the reservoir which lowers aqueous-oil interfacial tension (IFT) and alters wettability thereby increasing the amount of oil that it is possible to extract from residual oil saturations (Abdullah et al., 2017). The surfactants form micro-emulsion at the flood front by interacting with the crude oil, which is later produced from the pores of the reservoir rock by high viscosity of polymeric fluid (Turosung and Ghosh, 2017).

Ionic liquids (ILs) have gained recognition as a good candidate to be used as surface active agent in chemical slugs in place of surfactants due to their various eccentric properties (Lago et al., 2012; Pillai et al., 2018). The conventional surfactants utilized consists of a polar hydrophilic part and often a long-chain, non-polar hydrophobic part while in a surface active IL system, the surface activity may be associated to the cation, anion or both (Rodríguez-Palmeiro et al., 2015; Turosung and Ghosh, 2017). ILs also exhibit low critical micelle concentration (CMC) and IFT value in comparison to conventional surfactants of same chain length (Manshad et al., 2017). In EOR recovery mechanisms, chemical system’s ability to alter wettability and lower IFT values is considered as an important factor.

In present work, imidazolium based IL has been investigated for application in EOR. Surface and interfacial activity was analyzed with varying concentration, formation water (FW) and temperature. The application of IL for wettability alteration of oil-wet sandstone surface was investigated before applying for core-flooding. These investigations might play an effective role in understanding the mechanism of ILs and its promising application in EOR.

Materials Required

Ionic liquid, 1-dodecyl-3-imidazolium bromide was purchased from TCI chemicals. The crude oil used was of API gravity 25°. Formation water composition and salinity are reported in Table 1 was simulated by distilled water and reagent grade salt.

Table 1. Composition and chemical analysis of formation water

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>4272</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>39</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>116</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>2</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>1830</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>5832</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>38</td>
</tr>
<tr>
<td>Total dissolved solids (TDS)</td>
<td>12129</td>
</tr>
</tbody>
</table>

Methodology

The aggregation behavior of utilized IL was determined using du Noüy ring method with Easy Dyne K20 tensiometer (KRUSS Germany) to obtain critical micelle concentration. The interfacial behavior between crude oil and aqueous IL phase was determined by SVT20 tensiometer (Data Physics, Germany) using spinning drop method with varying concentration of IL and temperature. The contact
angle was conducted with Drop Shape Analyzer (Kruss DSA25, Germany) using Sessile drop method to study the efficiency of IL in altering the wettability from oil-wet to more water-wet. The core flooding experiment was performed in a standard core flooding system, as shown in Fig. 1. Flooding runs were conducted at reservoir conditions of 90 °C (363.15 K) temperature, 1000 psia overburden pressure. The flooding experiment was conducted at a constant flow rate of (0.2 ml/min) and produced fluid was collected in graduated vials.

![Core Flooding System](image)

**Fig. 1. Schematic Diagram of core flooding set-up**

**Results and Discussions**

**Surface activity**

The surface tension variation with increasing concentration was plotted as shown in Fig. 2(a). It can be observed that surface tension values decrease with increasing IL concentrations and attains a minimum value, above which no effect of increasing concentration was seen. The concentration corresponding to the minimum surface tension is termed as critical micellar concentration (CMC), above which IL molecules forms micelles (nano-sized structures) which enables emulsification, dispersion and solubilization of oleic phase. The CMC of IL was found to be 900ppm and corresponding surface tension value was observed to be 26.2mN/m.

The effect of increasing IL concentration on the interfacial behavior of IL solution and crude oil was investigated as shown in Fig. 2(b). The IFT showed a decreasing trend with increasing IL molecules in the bulk solution. On comparing the results in distilled water and FW, the presence of ions has a positive effect on IL, the IFT was observed to reduce from 2.1 mN/m in distilled water to 0.31 mN/m in FW. In the presence of ions, the repulsive forces between the imidazolium head group is reduced, which leads to movement of more and more surfactant molecules to the interface thus reducing IFT (Rodríguez-Palmeiro et al., 2015). The surfactant slug is subjected to elevated temperature while application in EOR, thus effect of increasing temperature on IFT was investigated. The IFT values decreased by a factor of 10, from 0.31mN/m to 0.05mN/m at 70°C, as adsorption of IL molecules at the interface increases, which favors IFT reduction.

![Surface Tension and Interfacial Tension](image)

**Fig. 2. Effect of IL concentration on (a) Surface tension and (b) Interfacial tension**

**Wettability alteration**

The contact angle experiments with increasing IL concentration were studied to determine the wettability alteration behavior of IL in FW as shown in Fig. 3. As the concentration increases the contact angle decreases from oil wet conditions (110°) to water wet conditions (<20°). This wettability
alteration is caused due to formation of ion pair between the adsorbed crude oil components and hydrophilic imidazolium head of IL (Gong et al., 2016). The reservoir with water wet conditions have lower residual oil saturation and considered beneficial for oil recovery.

![Contact Angle vs Time](image1.png)

**Fig. 3. Effect of concentration on contact angle on sandstone rock in the presence of FW at 70℃,**

**Core Flooding**

The core flooding experiment was performed to investigate the practical feasibility of IL in chemical EOR. The cumulative oil production and pressure drop with injected pore volume is as shown in Fig. 4. In secondary flooding, 2.5 PV of FW was injected until residual oil saturation was attained, which was calculated to be 13.22% and secondary flooding accounted for 45.66% of original oil in place. It was observed from the figure that the differential pressure drop decreases from 20 psi and attains a constant value during water flooding, which indicates that the breakthrough of injected flood. The chemical slug (1.25 CMC of IL + PHPA polymer) of 0.5 PV was injected when water-cut percentage exceeded ~95%, and additional oil recovery of 29.11% was accounted. After breakthrough a sudden increment in differential pressure was seen during the chemical slug injection. The IL in the chemical slug reduces the IFT and alters the wettability as explained in previous sections and improves the mobility of the trapped oil which are adhered to the pores due to capillary forces and increases the oil recovery (Pillai et al., 2018). The polymer added in the slug improves the viscosity of the flooding front which improves the sweep efficiency of the flooding (Al-Shakry et al., 2018). Later, pressure drop decreases and attains a constant value during the chase water flooding.

![Production Profile](image2.png)

**Fig. 4. Production profile of core flooding experiments**

**Conclusion**

In present work, an imidazolium based IL, 1-dodecyl-3-imidazolium bromide was utilized to investigate its efficiency in recovering the residual oil from the reservoirs. The CMC of IL was determined to be 900ppm, which is less in comparison to the conventional surfactant counterparts. The IFT value was lowered to a magnitude of $10^{-2}$ in the presence of FW and high temperature, which depicts its thermal tolerance and applicability in harsh conditions. The wettability alteration behavior gave an insight to the capability of IL to alter the wettability towards water wet which is required to recover the residual oil saturations. The core flooding experiments were conducted to conclude the preliminary findings on IFT reduction and wettability alteration and additional recovery of 29.11%
was accounted. Thus, ILs can be considered as new age surface active chemicals that can be employed in EOR, especially for reservoirs with harsh conditions.

References


