

REVIEW

Effect of Aromatic Ring, Cation, and Anion Types of Ionic Liquids on Heavy Oil Recovery

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ABSTRACT

Surfactant/alkali flooding is one of the best chemical flooding methods to enhance the oil Recovery Factor (RF). In this research, Ionic Liquid/Alkali (ILA) mixtures were chosen to represent a form of chemical flooding experiments. The selected Ionic Liquids (ILs), {[EMIM][Cl], [THTDPH][Cl], [EMIM][Ac], [BzMIM][Cl], [DMIM][Cl], [BzMIM][TOS], [dMIM][TOS] and [MPyr][TOS]}, were introduced to investigate their efficiency in improving heavy oil (14o API) RF from the sand packs. Besides, the use of mixtures of the same ionic liquids and brine (3.37 wt. % salts) with an alkali (Sodium Bicarbonate [NaHCO₃]) were also investigated. In this experimental study, the flooding process started with injecting about 3.2 Pore Volumes (PVs) of only brine, followed by one PV of the chemical composites, and flushed with two PVs of formation brine. The study discussed the influence of cation type, anion type, the structure of the ILs, and the effect of combining ILs/alkali on the RF. The results revealed that the proposed chemical mixtures are effective in enhancing the recovery factor. ILs with shorter alkyl chain and more aromatic rings are noticeably more efficient in enhancing the RF. Finding the optimum composition of ([DMIM][Cl] + NaHCO₃) the chemical slug increased the additional RF up to 31.55 (% OOIP). Also, increasing the slug size to two PVs improved the RF to 42.13 (% OOIP). The recovery factor mechanism was explained and supported by measuring the effect of IL types on the viscosity, Surface Tension (SFT), and Zeta Potential (ZP) of the mixture.

1. Introduction

Due to the challenges and high cost that are needed to explore and develop new reservoirs, oil corporations began investigating new ways where the produced oil ratio of the depleted or non-producing reservoirs would be developed.^[1] It is well known that roughly, conventional reservoir forces would produce one-third of

the Oil Initially In Place (OIIP). That is why Enhanced Oil Recovery (EOR) methods are required to produce more of the remaining oil.^[2] One of the suggested methods is to flood the reservoirs with chemicals such as surfactants. Due to the positive results of the chemical EOR techniques, they have been commonly employed for the last three decades.^[3] Surfactants can reduce the interfacial ten-

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sion (IFT) of oil-water systems to ultralow levels, which, in turn, increases the RF.^[4,5]

Surfactants are composites that have hydrophilic (head) and hydrophobic (tail) groups.^[6] They are capable of lowering the IFT and alter the rock wettability.^[7] Recently, a new class of chemicals considered as surfactants were introduced namely Ionic Liquids (ILs). They are made of cation (organic) and anion (organic or inorganic).^[8, 9] The types of cations and anions control their properties.^[10] Besides, ILs have low vapor pressures and are chemically and thermally stable even when injected in reservoirs with high pressures and temperatures.^[11] ILs possess a significant density, polarity, and heat potential.^[12,13] Most of ILs withstand water and have low toxicity.^[14] ILs also can lower the oil-water IFT. It was observed that the IFT reduction increased with developing IL concentration. Even with the presence of salts (NaCl, Mg₂Fl), IL still noticeably decreases the IFT.^[15] The addition of salt (NaCl) to the mixture of the low ratio of surfactant might reduce the surfactant head group area and affect the surfactant interfacial adsorption performance. In opposition, when salt was added to high surfactant ratio, it increased the micelle solubilization. Besides, IL with longer alkyl chain on the cation size has better performance in reducing the IFT.^[16] ILs can alter the wettability to more water wet, which is preferred for improving the RF.^[17,18] The adsorption of surfactant increased as the ratio of surfactant developed to the critical micelle concentration, but exceeding that concentration, no more improvement in the adsorption noticed. The electrostatic interaction between the surfactant's headgroup charge and net charge on the surface of the rock might be the main reason of adsorbing the surfactant and altering the wettability. So IL could adsorb on the rock surface and release the crude oil.^[17]

This work reports chemical enhanced heavy oil recovery (CEHOR) employing ionic liquid/alkali (IL/A). Different chemically structured ILs were mixed, for the first time, with alkali (NaHCO₃) and employed for EHOR. Many properties such as viscosity, SFT and ZP denoted studied and correlated to changes in RF. The upside of IL injection is the fact that it does not demand high pressure or temperature to produce the heavy oil.

2. Materials

Chemical types applied in the study were alkali (Sodium Bicarbonate [NaHCO₃]), 1-Ethyl-3-Methylimidazolium Chloride [EMIM][Cl] (≥ 98 % mass), 1-Benzyl-3-Methylimidazolium Chloride [BzMIM][Cl] (≥ 97 % mass), and TriHexylTetraDecyl Phosphonium Chloride [THTDPh][Cl] (≥ 95 % mass) were obtained from Sigma-Aldrich Company; 1-Ethyl-3-Methylimidazolium Acetate [EMIM][Ac] (≥ 95 % mass), and 1-Dodecyl-3-methyl-

imidazolium Chloride [DMIM][Cl] (> 98 % mass) were purchased from IoLiTech Company, and 1,3-dimethylimidazolium Tosylate [dMIM][TOS] (≥ 98 % mass), 1-Benzyl-3-Methylimidazolium Tosylate [BzMIM][TOS] (≥ 99 % mass), The Tosylate [Mpyr][TOS] (> 98 % mass) were acquired from Shanghai Cheng Jie Chemical Company LTD and used without any further purification. The chemical structures of the ionic liquids are presented in Fig. 1. Also, the composition of Synthesized Pelican Brine (SPB) injected is as shown in Table 1. Pelican Lake pool is the source of the used heavy oil sample. Table 2 presents the properties of the oil sample as reported by the Saskatchewan Research Council (SRC). Centrifuging the oil sample at high speed treated the fine solid particles. Finally, the sand pack samples were prepared using Ottawa sand with mesh size ranges from 40 to 80.

Table 1. The composition of Pelican brine (SPB)

Chloride, mg/l	20,607
Sulfate, mg/l	2
Sodium, mg/l	12,349
Calcium, mg/l	380
Magnesium, mg/l	280
Potassium, mg/l	80
TDS	33,698

Table 2. Pelican oil properties

Density, g/cm ³	@25°C	0.9642
Viscosity, cP	@22°C	1200
SARA, wt. %	Saturates	26.3
	Aromatics	39.7
	Resins	14.4
	Asphaltenes	11.4

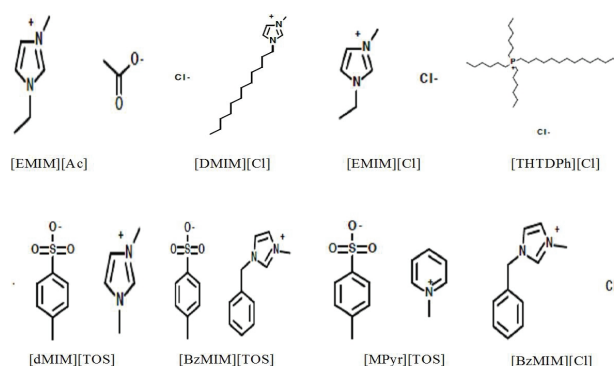


Figure 1. The chemical structure of ionic liquids and commercial surfactant

3. Preparation and Methodology

3.1 Mixture Preparation and Properties Measurements

The samples were prepared at room temperature (21.5 ± 1 oC), and their characteristics were measured. First, type 1 ultrapure water instrument was used to prepare Distilled Water (DW) that were used to formulate the brine (SPB) and the chemical mixtures by mixing them using a stirrer for 20-25 minutes. Solution was checked for stability of the emulsion before the ZP, SFT, and viscosity were measured using Nano Zetasizer-ZS, KRUSS K100, and Brookfield DV-II viscometer, respectively.

3.2 Sandpack Samples Preparation

The traditional core flooding apparatus that consists of a pump, transfer cylinders, pressure gauge, core holder, and tubes was employed for the runs. The holder length and diameter are 7.4 cm and 3.3 cm, respectively. The sample was cleaned, dried, and the sand was dry packed, and the holder was vibrated. Fresh Ottawa sand was used for each experiment to have comparable wettability for all core samples. After vacuuming and saturating the sample with brine, the porosity and permeability were calculated. Pelican oil was then added continuously from the top into the sand pack at a rate of 1 cm³/min till the displaced water ceased to exit the core. The replaced and residual brine describes the initial oil saturation (Soi), and irreducible water saturation (Swirr), respectively. The petrophysical properties of the sand packs are presented in Table 3.

Table 3. Sand pack samples properties

Ka, D	5.36 ± 0.33
PV, cm ³	25.72 ± 0.33
Ø, %	40.61 ± 0.21
Swi, %	10.10 ± 0.38
Vo, cm ³	23.11 ± 0.14
Soi, %	89.90 ± 0.39

3.3 Flooding Procedure

The flooding mode started with injecting about 3.2 PV of brine (SPB), followed by 1 PV of a chemical slug (ionic liquid/alkali) and flushed with 2 PV of SPB. The flooding rate applied for all experiments was 0.75 cm³/min. The produced oil samples were gathered in testing tubes and put in a separator. The produced oil volume out of the original volume in the core sample is considered as the RF.

4. Results and Discussion

4.1 Effect of the Type of Anion/Cation/Alkyl Chain on the Performance of ILs

Several types of ILs were considered regarding enhancing the RF. As shown in Fig. 2, the RFs of flooding the sand packs with 3.2 ± 0.1 PVs of brine (SPB) were comparable (39.29 ± 0.24 % OOIP). Then the RF obtained by injection of 1 PV of chemical slug (1,000 ppm IL + SPB) mixture and 2 PVs of SPB that were used to flush the sample depending on IL type. The performance of the investigated ILs on improving the RF decreases in this order: [EMIM][Cl] (14.75 % OOIP) > [EMIM][Ac] (12.55 % OOIP) > [dMIM][TOS] (11.76 % OOIP) > [DMIM][Cl] (10.89 % OOIP) > [BzMIM][TOS] (10.22 % OOIP) > [MPyr][TOS] (10.00 % OOIP) > [BzMIM][Cl] (8.44 % OOIP) > [THTDPh][Cl] (7.87 % OOIP). Nevertheless, it is clear that the additional RF improvement mainly depends on the IL type. The possible mechanisms for the enhancement could be due to lower SFT, ZP close to zero line, and increased viscosity of the introduced phases comparing to that of just SPB, as shown in Fig. 3 and supplementary material (S1). It is obvious that the addition of IL notably lowered mixture the SFT (73.062 mN/m) and increased both the ZP (-13.10 mV) and slightly the viscosity (1.08 cP) of the aqueous phase. Any of those factors could be the primary mechanism for the enhancement in the recovery factor when IL was combined with brine. Although the SFT represents the interfacial tension between air and liquid, it gives an idea about the efficiency of surfactants in reducing the IFT of two liquids. Tunnish found that [DMIM][Cl] is more active than [EMIM][Ac] in diminishing Pelican oil-brine IFT, and similar performance of these ILs was noticed in SFT measurements.^[19] In this work, it is noticed that all ILs were capable of reducing the SFT. ZP represents the surface charge mechanism, and it completely agrees with the enhancement in the RF, as it is greater for the best RFs. Tunnish et al. noted that the RF enhanced as the ZP of the displacing phase increased.^[20] As known, the zeta potential measures the repulsive or attractive forces between particles that address the stability of disperse systems. Fazullin and his colleagues observed that the gathering of oil products grew as the zeta potential decreased^[21] in the case of cleaning up the produced water. Increasing the zeta potential of the injected mixtures might weaken the aggregation of the oil contents in the produced phase and form an emulsion. As highlighted in this study, the higher the ZP, the better it is for the RF, which represents weak aggregation, and the consequent creation of emulsion and carrying more oil out of the porous medium. The electrostatic interactions mechanism (wettability change)

represented by the ZP could be one of the factors that improved the RF in this study. Recently, Tunnish et al. found that the ZP value of different systems (brine/oil/sand) was mainly affected by the presence of IL. Adding IL to brine-oil and brine-oil-sand systems increased their ZP values. ILs “neutralize” the charge of the tested system, and may, consequently, alter the wettability type.^[22] In a recent study, the addition of the type of an ionic liquid (Deep Eutectic Solvent) altered the rock wettability type and increased the RF, and was considered as a primary mechanism for EOR. Another suggested mechanism that led to an enhancement in RF is the increase in viscous force.^[23] This led to a lower oil-water mobility ratio due to the addition of ILs.^[24] In our case, as displayed in Fig. 3, all combined ILs led to an increase in the viscosity of the displacing phases. Although the difference is not too high to critically change the mobility ratio, it could be partially engaging in the noticed enhancement of the RF. Certainly, the ability of ILs to efficiently change the mobility ratio is stronger with oils with higher API values.

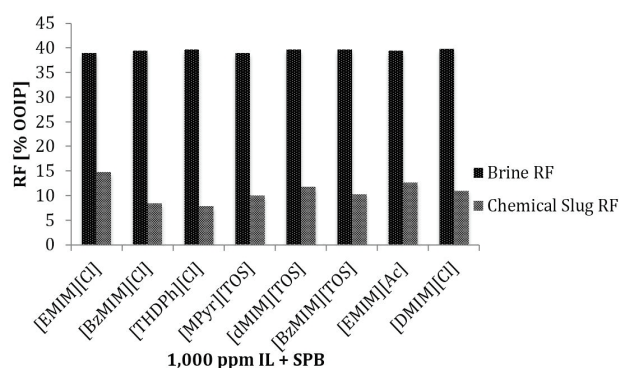


Figure 2. The effect of IL type on the additional RF

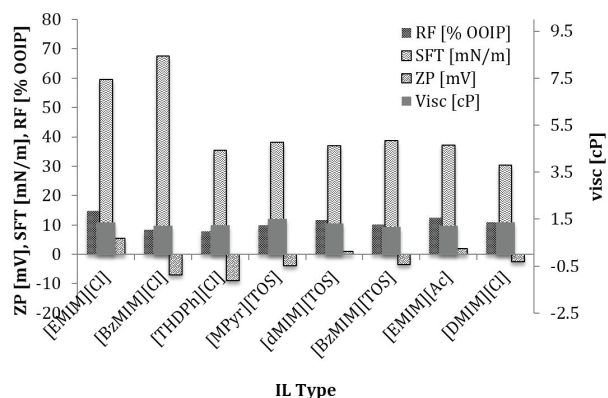


Figure 3. The effect of ionic liquid type on the properties of ionic liquids

[Cl], [TOS] and [Ac] types of anions based ILs were selected to study the effect of the anion type on the RF.

Fig. 2 shows that the efficiency of 1 PV (1,000 ppm) of the selected ILs decreases as following: [EMIM][Cl] (14.75 % OOIP) > [EMIM][Ac] (12.55 % OOIP) > [BzMIM][TOS] (10.22 % OOIP) > [BzMIM][Cl] (8.44 % OOIP). Regarding those results, we can say that when the same cation combined with an aromatic anion ([BzMIM][TOS]) is stronger than the non-aromatic ringed anion-based IL ([BzMIM][Cl]) in improving the RF. It could be because of the interaction between the aromatic compounds in the oil sample and ILs, which supports the effect of the aromaticity (π - π interaction) mechanism.^[25] In comparison to one-sided aromatic IL ([BzMIM][Cl]), the tosylate anion as aromatic anion and the two aromatic rings on the cation may have stronger potential to interact with oil sample aromatics and progresses the RF noticeably. It was noticed that [EMIM] cation-based IL is more efficient when it is combined with [Cl] anion compared to that when it is united with [Ac] anion. It could be due to the high salinity ratio of the employed brine, as the efficiency of [EMIM][Ac] improves with decreases the salinity ratio.^[19]

Three cation types based ILs were chosen to study the influence of cation type on the performance of ILs. As shown in Fig. 2, the enhancement of RF by injecting 1 PV (1,000 ppm) of these ILs declines in the following order: [BzMIM][TOS] (10.22 % OOIP) > [MPyr][TOS] (10.00 % OOIP) > [BzMIM][Cl] (8.44 % OOIP) > [THTDPh][Cl] (7.87 % OOIP). Concerning ILs with the same anion base, the aromatic IL type (imidazolium) is more efficient than the aliphatic (phosphonium) cation IL, and that supports the potential of the aromaticity (π - π) mechanism. Regarding the number of aromatic rings, the IL with three aromatic rings ([BzMIM][TOS]) is more efficient than that of two aromatic ringed IL ([MPyr][TOS]).

The effect of cation alkyl chain type on the additional RF was also studied. Fig. 2 displays the efficiency of the ILs (1 PV and 1,000 ppm) decreases in the following order: [EMIM][Cl] (14.75 % OOIP) > [EMIM][Ac] (12.55 % OOIP) > [DMIM][TOS] (11.76 % OOIP) > [BzMIM][TOS] (10.22 % OOIP) > [DMIM][Cl] (10.89 % OOIP) > [BzMIM][Cl] (8.44 % OOIP). For similar anion-based ILs, the shorter alkyl chain, the better is the RF. For the studied ILs and regardless of the anion type, it was observed that the ethyl type of alkyl chain was more efficient than all others.

This study confirms the great ability of ILs in improving the RF of heavy oil and the influence of ILs structure and composition (anion, cation and alkyl chain types) on their performances. The effect of four mechanisms (IFT/SFT, electrostatic, aromaticity, and viscous force) on the RF was discussed. The reduction in the SFT values somehow confirms the ability of ILs in reducing IFT. The slight

increase of the mixtures viscosity values confirms that the enhancement of RF, in this case, is not due to the contribution, as the primary mechanism, of the viscous forces. The improvement in the additional RF was stronger when highly aromatic, and higher ZP ILs were injected, which supports the contribution of the aromaticity interactions and electrostatic (wettability alteration) mechanisms in enhancing the RF.

4.2 Effect of NaHCO₃ on the Performance of ILs

ILs were finally mixed with alkali (NaHCO₃) and introduced for enhancing the RF. Fig. 4 shows the RF (39.25 ± 0.26 % OOIP) of the first stage of the flooding process that began with injecting about 3.2 PVs of brine (SPB). Then, the additional RF after introducing 1 PV of chemical slug (1,000 (ppm) IL + 0.1 wt. % NaHCO₃ + SPB) and flushing the sand packs with 2 PVs of SPB. The additional RF of the second step declined in the following order: [DMIM][Cl] (31.57 % OOIP) > [EMIM][Cl] (19.48 % OOIP) > [BzMIM][Cl] (18.42 % OOIP) > [THTDPh][Cl] (15.79 % OOIP) > [BzMIM][TOS] (14.13 % OOIP) > [EMIM][Ac] (13.44 % OOIP) > [dMIM][TOS] (13.25 % OOIP) > [MPyr][TOS] (12.61 % OOIP). In comparison to the injection of alkali alone (7.67 % OOIP), it is obvious that the additional RF is enhanced for all cases when IL was introduced. Similar results of adding just ILs to brine were noticed when ILs and alkali were added to the brine, where all mixtures improved the ZP and viscosity and reduced their SFT values, as shown in Fig. 5 and in the table provided in the supplementary material (S2). The anion and cation types control the performance of IL. Based on the additional RF results, RF is better when chloride [Cl] based ILs are injected. Concerning the cation type, it was found that imidazolium-based cation + [Cl] anion is considerably better than IL-based phosphonium cation + [Cl]. Remarkably, [DMIM][Cl] + NaHCO₃ + SPB (31.55 % OOIP) mixture is more effective than all other combinations; one of the factors could be the higher ability of [DMIM][Cl] to increase the mixture viscosity (1.70 cP) further than the other mixtures. Also, the strength of cationic IL ([DMIM][Cl]) to decrease the SFT (28.99 mN/m) and increase ZP (15.21 mV) much more than the other selected ILs, as reported in Fig 5. Also, the potential of cationic IL as [DMIM][Cl] to create an emulsion is surely one of the reasons that led to the noticeable RF.^[26] In another study, it was observed that the hydrophilic anion ([Cl]) based imidazolium IL was not efficient demulsifier,^[27] which good for EOR purposes. Cationic surfactants have a positive head group and get strongly adsorbed in sandstone rocks^[28] and change the wettability, which is another factor of improving the RF in the case of

[DMIM][Cl] (cationic IL). It is known that the addition of alkali to chemical slug helps to keep the ratio of surfactant in the mixture at the same level, which would raise the RF further.^[29] An in situ surfactant is formed when an alkali reacts with the acid groups in the oil sample.^[30,31] The ratio of surfactant adsorption and IFT decreased when alkali and surfactant were combined.^[32,33]

This study proved the efficiency of injecting ILs either alone or combined with other chemical types (alkali) to improve the heavy oil recovery. It is evident that more than one mechanism (IFT/SFT, electrostatic, aromaticity, and viscous force) is controlling the noticeable enhancement in the RF. For ILs with similar cations or anions types, the one with more aromatic rings is better for RF improvement. The optimum slug composition was obtained in this research, where 1 PV of ([DMIM][Cl] + NaHCO₃) improved the RF to 31.55 (% OOIP).

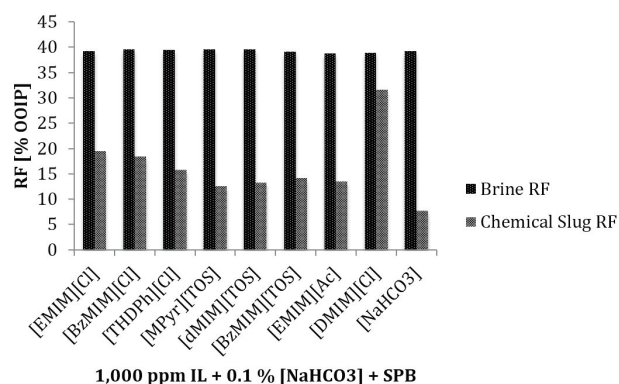


Figure 4. The effect of NaHCO₃ on the efficiency of IL

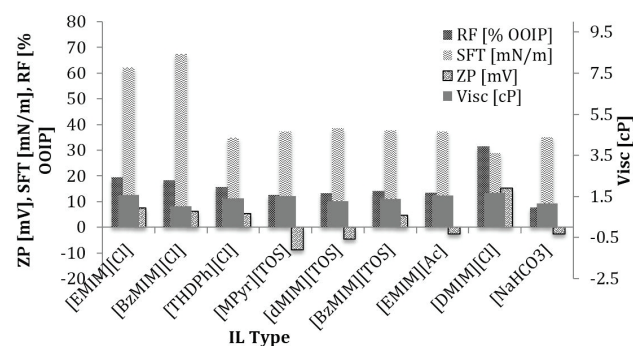


Figure 5. The properties of NaHCO₃/IL mixtures

4.3 Effect of Chemical Slug Size on the Additional RF

1,000 (ppm) of [DMIM][Cl] + 0.1 wt. % NaHCO₃ + SPB chemical mixture was selected for studying the influence of altering the Slug Size (SS) on the additional RF. Three slug sizes of 0.5 PV (18.07 % OOIP), 1 PV (31.55 % OOIP), and 2 PVs (42.13 % OOIP) were investigated, as

reported in Fig. 6. Obviously, the larger the SS, the better the RF. It is apparent from our study that the combination of IL and alkali is better than injecting either of them alone. It was found, from the literature, that the 0.7 PV mixture of surfactant, NaOH, and Na₂CO₃ slug ended with better RF (17.3 % OOIP) than introducing just NaOH or Na₂CO₃ slug (2 % OOIP).^[34] This result confirms the importance of injecting IL and alkali as a mixture.

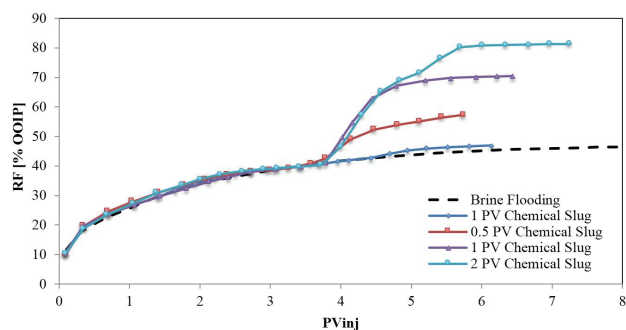


Figure 6. Slug size performance on the extra RF

5. Conclusions

Chemical flooding is a commonly used technique for EOR. The revealed enhancements in additional RF were supported by measurements of changes in zeta potential, surface tension, and viscosity values. The additional RF depends primarily on the IL type; where the weakest IL is [THTDPh][Cl] (7.87 % OOIP), and the most efficient IL is [EMIM][Cl] (14.75 % OOIP) when the studied ILs injected with brine only. For the anion type, it is clear that the RF is better when a strong aromatic ringed IL ([BzMIM][TOS]) is employed. Additionally, it was found that [EMIM][Cl] was better than [EMIM][Ac] because of the anion type efficiency. As for the cation type, it is noticed that imidazolium-based IL is more efficient than phosphonium and pyridinium cations. Higher RF values were obtained when IL with smaller alkyl chain was introduced. Noticeably, the type of the alkyl chain; anion and cation are unquestionably crucial for the performance IL and alkali mixtures. For the injected slug size, the additional RF increased with an increase in the volume of the introduced chemical slug. The improvement in the additional RF was stronger when highly aromatic, and higher ZP ILs were injected suggesting the contribution of the mechanisms based on the aromaticity interactions and electrostatic (wettability alteration) mechanisms.

Nomenclature

AIL	Alkaline + Ionic Liquid
BV	bulk volume
Ka	absolute permeability
ppm	part per million

PV	pore volume
Vo	oil volume
SARA	saturates/aromatics/resins/asphaltenes
μ	viscosity
ρ	density
\varnothing	porosity

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