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ORIGINAL PAPER - PRODUCTION ENGINEERING

Efficiency of ionic liquids for chemical enhanced oil recovery

Mabkhot Bin Dahbag · Abdulrahman AlQuraishi ·
Mohammed Benzagouta

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Abstract Substantial amount of crude oil remains in the reservoir after primary and secondary production. Chemical flooding is one of the enhanced oil recovery (EOR) methods; however, chemicals (i.e., Surfactant) used are sensitive to the harsh environment characterizing the local reservoirs. The current study aimed at investigating the utilization of ionic liquids (ILs), known as environment friendly salt with good solubility, thermal stability and effective surface activity, as an alternative to conventional organic surfactants in enhanced oil recovery process. In this work, screening tests of nine ILs were performed. These ILs were diluted in different brine solutions of different salt compositions at 10 % (w/w) salinity and their solubility, thermal stability and surface activity in presence of Saudi medium crude oil were tested. Tetra alkyl ammonium sulfate known as Ammoeng 102 was found to be the ionic liquid of choice. Further investigations on Ammoeng 102 solutions at 10 and 20 % (w/w) salinity were conducted and IFT measurements indicate enhanced surface activity of Ammoeng 102 with increasing solution salinity. Effects of pressure and temperature on interfacial tension (IFT) were also tested and the results indicate minor effects. Adsorption test indicates high Ammoeng 102 adsorption tendency with more adsorption for higher salinity solution. Different flooding scenarios were conducted in sandstone rock samples to investigate the effectiveness of Ammoeng 102 IL as an EOR chemical. The findings indicate promising results for ionic solution flooding in secondary mode at irreducible water saturation (S_{wirr}). Ultimate recovery obtained is higher than that obtained with combined secondary brine flooding followed by tertiary ionic solution flooding at residual oil saturation (S_{or}). Injection of slug of ionic solution in secondary mode provides lower recovery compared to that recovered with continuous ionic solution injection in the same mode. Rock water content affects recovery efficiency indicating higher oil recovery for secondary brine and tertiary ionic solution flooding at low S_{wirr}. Contact angle and relative permeability measurements demonstrate the role of wettability alteration behind the extra oil recovery which is very much affected by ionic liquid concentration that can be altered by dilution with formation and injected brines.

Keywords Ionic liquids · Ammoeng 102 · Enhanced oil recovery · Wettability

Introduction

Ionic liquids (ILs) have received great environmental and technological attention as a potential alternative to traditional organic solvents. They are known as organic salts having a melting point below 100 °C (Xiao and Malhotra 2005), often found as liquids at ambient temperature (Domanska 2005; Simoni et al. 2008). Typically, ILs molecular composition consists of organic cations such as *N*-dialkylimidazolium, *N*-alkylpyridinium, alkylammonium, alkyl-phosphonium, alkylsulphonium and tiazolium; inorganic anions such as halide (e.g., Br^-, Cl^-), tetrachloroaluminate $[AlCl_4]^-$, tetrafluorborate $[BF_4]^-$, hexafluorphosphate $[PF6]^-$, bis(trifluoro-methyl-sulfonyl)imide

M. Bin Dahbag · M. Benzagouta
Petroleum and Natural Gas Engineering Department, King Saud University, P.O. Box 800, Riyadh 11421, Saudi Arabia

A. AlQuraishi (✉)
King Abdulaziz City for Science and Technology, National Center for Oil and Gas Technology, P.O. Box 6086, Riyadh 11442, Saudi Arabia
e-mail: aqurishi@yahoo.com

[$(CF_3SO_2)2N^-$] and acetate [$CH_3CO_2^-$] and organic anions such as alkylsulfate [R-O-SO3$^-$], tosylate [C_7H_7O3S] and methanesulfonate [R3C-S-O3-]. ILs are known for their negligible vapor pressure and non-flammability under ambient conditions, high thermal conductivity, high polarity, high heat capacity, high density, extremely low volatility and thermal stability (Domanska 2005; Siedlecka et al. 2011; Keith and Johnson 2007; Bermudez et al. 2009). They have many advantages over organic surfactants. Among these advantages are their low cost and commercial availability, water and solvents stability, low toxicity, in addition to their noncorrosive properties and recyclability (Domanska 2005; Dharaskar 2012). The most important attribute of ILs is their potential as tunable solvents with properties that can be tailored according to their application based on their number of cations and anions combination (Siedlecka et al. 2011; Hernández et al. 2011).

ILs were used in petroleum industry to upgrade heavy and extra heavy crude oil by cracking asphaltene chains (Fan et al. 2007, 2009. They are also used to inhibit paraffin and asphaltene aggregation and precipitations in addition to desalting and demulsifying of water in oil emulsions in refining process (Lemos et al. 2010). The role of ILs in inhibiting asphaltene precipitation in simulated CO_2 flooding was investigated (Hu et al. 2004). Minor asphaltene precipitation and deposition were reported in the presence of IL preventing pore plugging problems during flooding process. ILs can replace organic surfactant in breaking water/oil emulsions in oil refining process (Lucero et al. 2010). The self-organization, micelle formation and surface properties of ILs (Hernández et al. 2011, 2009) as well as their ability to dehydrate crude oil have been recently reported (Painter et al. 2010). Lately, the efficiency of ILs in extracting heavy oil from tar sands was evaluated (Painter et al. 2009; Hezave et al. 2013a). Recovery efficiency of 90 % was reported with five times ILs recyclability with no efficiency loss.

The increased demand for energy directed the oil industry to explore different enhanced oil recovery methods to release the trapped oil left behind at the end of the primary injection. Among the EOR methods is the chemical flooding and among these chemicals are the surface acting agents (surfactants). Lowering the aqueous-oleic pair interfacial tension (IFT) and wettability alteration due to adsorption are the main recovery mechanisms for organic surfactant flooding. ILs are known for their surface activity and micelle formation; therefore, they can be of potential for flooding process. The effect of ([C_{12} mim] [Cl]) ionic liquid on interfacial tension in harsh environment (high salinity, high temperature) was investigated to assess its efficiency for chemical flooding Hezave et al. (2013b; Somasundaran and Zhang 2006). Findings indicate promising results demonstrating the effectiveness of ionic solutions as EOR chemical for enhanced recovery of trapped oil.

This work is aimed at screening different ILs based on their solubility in different brine compositions, thermal stability and ability to significantly lower the IFT at high salinity and temperature conditions. The most efficient ionic liquid is further tested in several flooding runs at reservoir conditions to investigate its adsorption tendency and its efficiency as new enhanced oil recovery chemical.

Materials and methods

Materials

Fresh Berea sandstone samples were used for the different flooding runs. Routine core analysis was conducted on the tested samples and their petrophysical properties are listed in Table 1. X-ray diffraction analysis (XRD) shown in Fig. 1 indicates that rock mineralogy is composed mainly of Quartz with Kaolinite clay as cementing material. Aqueous phase used in screening process was distilled water and three synthetic brine solutions at 10 % (w/w) salinity listed as brine I (100 % NaCl), brine II (95 %

Table 1 The petrophysical properties of core samples

Plug #	Diameter (cm)	Length (cm)	Porosity (%)	Permeability (md)
1	3.72	7.285	21.7	263
2	3.745	6.354	21.7	304
3	3.79	6.5	21.07	243.7
4	3.82	5.89	20.13	289
5	3.82	6.7	21.48	166
6	3.78	7.0	21.25	177

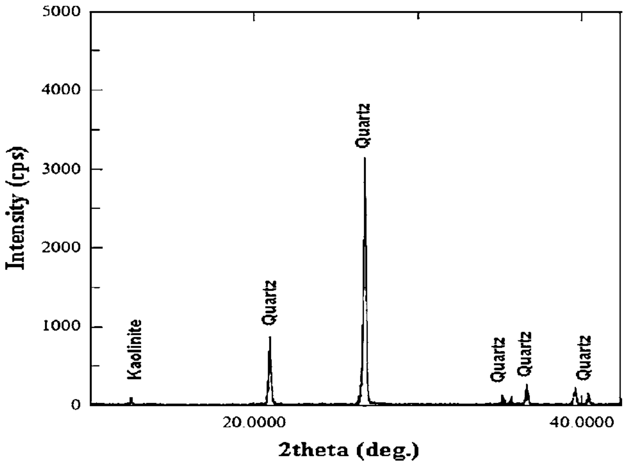


Fig. 1 XRD analysis of berea sandstone core sample

NaCl, 17 % $CaCl_2$) and brine III (83 % NaCl and 17 % $CaCl_2$). Brine III at 10 and 20 % (w/w) salinity was used as aqueous phase in further investigations such as CMC determination, adsorption and flooding process. Ionic solutions were prepared by diluting ILs with the brine composition and salinities indicated above.

Oleic phase was Saudi medium crude oil. Analysis of crude asphaltene content indicated the presence of aromatic hydrocarbon compounds (cyclic) with saturated carbon chains characterized with average length of six carbon atoms (five CH2 and one CH3). Small sample of asphaltene was tested with Carbon/Hydrogen/Nitrogen Analyzer implementing the ASTM D5291 method. The measured crude oil properties are listed in Table 2.

Table 2 Physical properties of crude oil

Physical property	Value
Gravity, API at ambient conditions	28.37
Density, gm/cm^3 at reservoir conditions	0.86
Viscosity, cp at reservoir conditions	5.6
Asphaltene content, %	9.6
Asphaltene Carbon content, %	81.29
Asphaltene Hydrogen content, %	9.13
Asphaltene Nitrogen content, %	0.7
Asphaltene other elements content %	8.88

Nine ionic liquids listed in Table 3 were screened. These ILs were prepared at different concentrations in different brine solutions of different compositions at 10 % (w/w) salinity. Screening process was based on ILs solubility in brine solutions and their surface activity, in addition to their thermal stability (no turbidity) at wide temperature ranges. The determined most effective ionic solution (tetra alkyl ammonium sulfate known as Ammoeng 102) was further investigated by testing its surface activity at various conditions of pressure, temperature and solution salinity. IFT investigation of crude oil-Ammoeng 102 solution was conducted at different concentrations ranging from 0 to 2,000 ppm. The Ammoeng 102 solutions were prepared in synthetic formation brine at 10 and 20 % (w/w) salinities at reservoir conditions of 60 °C and 2,000 psig.

IFT measurements

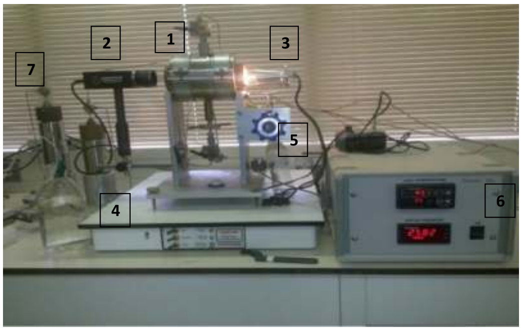
IFT measurements were conducted using high-pressure and high-temperature pendant drop tensiometer (Fig. 2). The tensiometer is composed of high-pressure cell, hand pump for fluids displacement, vibration-free table, needle, temperature controller, pressure transducer, back pressure regulator, lamb, digital camera supplied with video frame grabber for image display and analysis system using Young–Laplace equation. IFT is measured by upward injection of drop of oil to the tip of proper size needle immersed in brine or ionic solutions.

Table 3 Summary of ionic liquids screening results

Commercial name	Chemical name	Solubility	IFT trend with Temperature	Temperature Stability
Ammoeng 102	Tetra-alkyl ammonium sulfate	Soluble in distilled water, brine I, II, III	Decreasing	Stable until 90 °C in distillated water and all brines IFT is low
Ammoeng 110	Quaternary ammonium chloride	Soluble in distilled water, and brine III	Decreasing	Stable until 90 °C in brine (III) IFT is high
Ammoeng 111	Quaternary ammonium acetate (poly[oxy(methyl-1,2-ethandiyl)]- alpha-(diethyl-hydroxyethylammonio) ethyl]-acetate)	Not soluble	Unable to measure (not soluble)	Unable to measure (not soluble)
Ammoeng 112	(Poly[oxy(methyl-1,2-ethandiyl)]- alpha-(diethylhydroxyethylammonio) ethyl]-dihydrogenphosphate)	Soluble in distilled water, brine I, II	Increasing	Stable until 90 °C in brine (I) IFT is high
Ammoeng 120	Quaternary ammonium sulfate	Soluble in distilled water, and brine I	Increasing	Stable until 90 °C in distillated water and brine (I). IFT is high.
Ammoeng 130	1-Octadecanaminium,*N*,*N*-dimethyl- *N*-octadecyl-,chloride (1:1)	Not soluble	Unable to measure (not soluble)	Unable to measure (not soluble)
IL25	1-Ethyl-3-methylimidazolium dicyanamide	Soluble in distilled water	Increasing	Stable until 90 °C in brine (III) IFT is high
IL34	1-Ethyl-3-hydroxymethylpyridinium ethylsulfate	Soluble in distilled water, and brine III	Increasing	Stable until 90 °C in brine (III) IFT is high
IL37	Tri-*n*-butylmethylphosphonium methylsulfate	Soluble in Brine I	Increasing	Stable until 80 °C in brine (I) IFT is high.

Wettability measurements

Contact angle between crude oil and Ammoeng 102 solutions on rock surface was measured using pendant drop setup described above with some modification. The measurements were conducted at reservoir condition of 60 °C and 2,000 psig. Different concentrations (0, 250, 500 and 1,000 ppm) of Ammoeng 102 diluted in synthetic brine III solution at 20 % (w/w) salinity were tested. Thin smoothed surface sample of Berea sandstone rock was placed horizontally in the high-pressure cell and surrounded by ionic solution. Pressure and temperature were set and small oil drop was released using the needle to the bottom of the rock surface. Several pictures were captured and the contact angle was measured.



1. Cell 2. Camera 3. Light source 4. Vibration free table
5. Back pressure regulator 6. Back pressure controller 7. Fluids Accumulators

Fig. 2 Pendant drop tensiometer and contact angle setup

Adsorption measurements

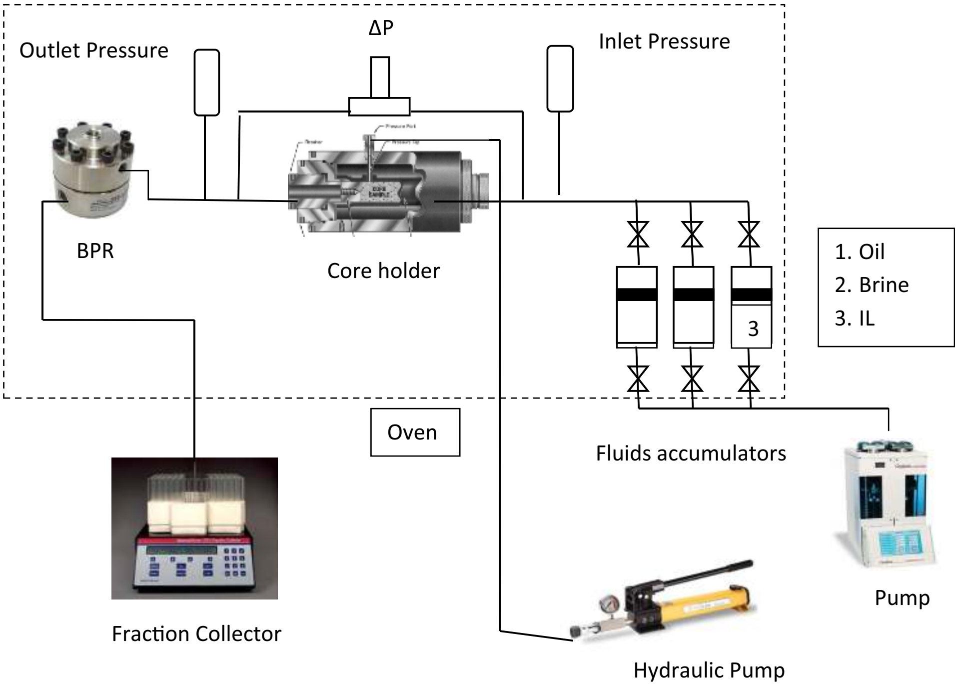
Adsorption is the adhesion of atoms, ions, or molecules on solid surfaces. Adsorption is affected by several factors and among these are the chemical structure of the liquid (i.e., ionic liquid), rock surface properties and mineralogical composition, composition of reservoir fluids, and solution conditions such as salinity, pH, pressure and temperature (Hurd and Research 1976; Bai et al. 2010). Adsorption mechanisms are classified into electrostatic attraction/repulsion, ion exchange, chemisorption, chain–chain interactions, hydrogen and hydrophobic bonding (Hurd and Research 1976).

Dynamic Adsorption of 500 ppm Ammoeng 102 solutions at 10 and 20 % (w/w) salinities was measured in two core samples representing the investigated porous medium. 100 cm^3 of ionic solution was continuously injected at 1 cm^3/min under reservoir conditions of 60 °C temperature and 5,000 and 2,000 psig confining and pore pressures, respectively. The effluent fractions were collected in 10 cm^3 tubes and analyzed using Ultra Violet Spectrophotometry to determine the IL adsorption.

Core flooding

Flooding was conducted using automated core flooding system (Fig. 3). It consists of a core holder capable of housing 1.5 in. diameter and up to 6 in. long sample. The setup is equipped with three transfer accumulators for crude oil, brine and ionic solution. Constant flow positive displacement pump is used to inject distilled water to the

Fig. 3 Schematic of core flooding setup



bottom of the three accumulators to transfer the content fluids as needed. Fluids are directed via a network of steel pipelines and air operated shut off valves. The overall components are incorporated in air-circulating oven for temperature control. Confining pressure is controlled by automated pressure intensifier while pore pressure is controlled via dome type backpressure regulator. Effluents produced are collected in graduated tubes placed in timely set fraction collector. Inlet, outlet pressures and pressure drop across the core are measured by high precision line and differential transducers. All components and measurements are controlled and collected continuously by data acquisition system.

The test started with core sample evacuated and pressure saturated with the desired brine solution. The fully brine saturated sample was then flooded with brine at different rates to record the corresponding pressure drops to determine rock absolute permeability utilizing Darcy law. Drainage cycle was started by oil displacement at 1 cm^3/min. Oil injection continued until water production ceases and irreducible water and initial oil saturations are determined using material balance. Brine and/or ionic solution flooding were conducted in secondary and/or tertiary modes and oil recovery and end point saturations were determined. Unsteady state method was used to calculate the imbibition relative permeability curves of the secondary flooding portion of the experiments implementing Jhonson–Bosler–Numan (JBN) method. Flooding process was conducted at reservoir conditions of 5,000 and 2,000 psig confining and pore pressures, respectively, and temperature of 60 °C. Rapoport and Leas (1953) indicated that Displacement is independent of length (L), displacing fluid viscosity (μ) and injection velocity (V) when laboratory scaling coefficient ($LV\mu$) is within the range of 0.4–5.0. The Rapoport and Leas scaling rule was used to ensure the displacement stability of conducted experiments and a value of 2.5 was found.

Results and discussion

Screening process

General screening of nine ionic liquids was conducted. The screening was conducted on ionic solutions of different ILs concentrations ranging from 100 to 1,000 ppm diluted in distilled water and different synthetic brines. The brines were of various salt (NaCl and $CaCl_2$) contents as indicated previously at 10 % (w/w) salinity. Tests were conducted at atmospheric pressure and different temperatures ranging from 22 to 90 °C. Screening criteria were based on ionic liquids solubility in distilled water and different brines, surface activity, and solutions thermal stability (no turbidity) at high temperatures. Table 3 lists the ionic liquids tested and summarizes the major outcomes of the screening process. Ammoeng 111 and Ammoeng 130 were excluded due to their insolubility in all aqueous solutions. Ammoeng 111 is characterized with very long cationic chain length, while Ammoeng 130 is characterized as nonpolar with long chain length of ethyl group and that may explain their insolubility. The rest of ionic liquids have different degree of solubility and they were screened based on their surface activity and IFT trend with temperature. Ammoeng 102 ionic solution provides the lowest IFT with decreasing IFT trend with temperature. Ammoeng 110 has a similar IFT trend with temperature but with less surface activity. Longer alkyl chain length of the Ammoeng 102 cation tends to increase its capability of reducing IFT and may explain its superior surface activity (Smit et al. 1990; Hezave et al. 2013c). Thermal stability of Ammoeng 102 maintains up to 81 °C above which, the ionic solution started to darken with full turbidity noticed at 86 °C and above. Figure 4 shows pictures taken for oil drop in 500 ppm ionic solution at temperatures ranging from 82 to 86 °C indicating the turbidity progress.

Accordingly, Ammoeng 102 was the ionic liquid of choice soluble in all aqueous phases tested with significant surface activity at increasing temperatures. Further investigation of Ammoeng 102 was conducted on Ammoeng 102 surface activity at reservoir conditions of pressure and temperature. The investigation was conducted on crude oil and ionic solutions prepared at 10 and 20 % (w/w) salinity. Figure 5 plots the IFT versus ionic liquid concentration at both solution salinities. The plots indicate IFT declines with the increasing IL concentration. In contrast to conventional organic surfactants, the decreases are more pronounced at higher solution salinity. This can be attributed to the role of negatively charged ions neutralizing the positive surface charges of the cationic ionic liquid leading to easier accumulation of IL molecules at the oil–brine interface, and hence more IFT reduction Hezave et al. (2013c). Critical Micelle concentration (CMC) was achieved at low concentration of 250 ppm for both salinities with IFT of 3.36 and 1.65 mN/m for 10 and 20 % (w/w) solutions salinity, respectively. A concentration of 500 ppm was decided to be the ionic liquid concentration used for flooding runs.

The effects of temperature and pressure on Ammoeng 102 solution-crude oil IFT at 10 % (w/w) solution salinity were investigated and Figs. 6, 7 are plots of IFT trends at different temperatures and pressures, respectively. The results indicate a decreasing trend of IFT with increasing temperature at constant pressure and a slight increase with increasing pressure at constant temperature. Effect of temperature on IFT can be described based on two competing factors. The first is the adsorption of IL into the

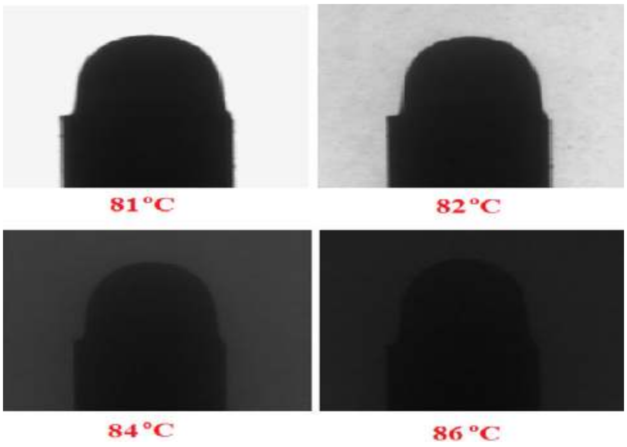


Fig. 4 Turbidity of 500 ppm Ammoeng 102 diluted in Brine III at 20 % (w/w) Salinity

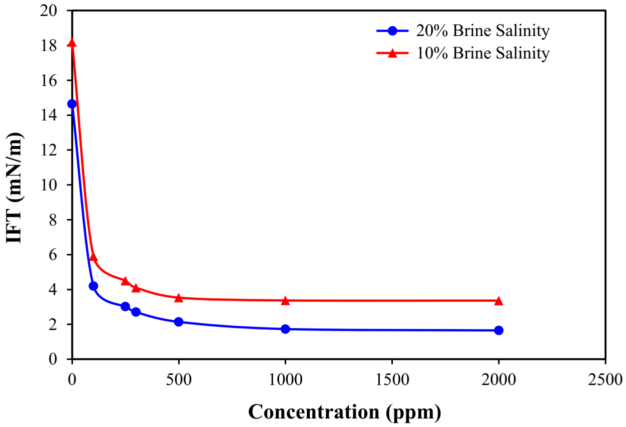


Fig. 5 IFT of Ammoeng 102 at different concentrations diluted in Brine III (83 % NaCl, 17 % $CaCl_2$) at 10 and 20 % (w/w) Salinities at 60 °C and 2,000 psig

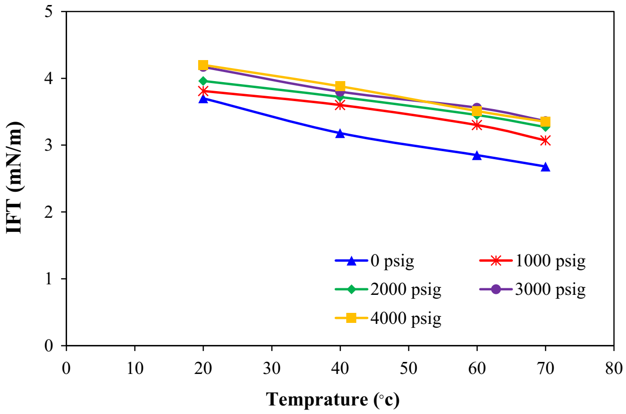


Fig. 6 Effect of Temperature on IFT of 500 ppm Ammoeng 102 Diluted in Brine III (83 % NaCl, 17 % $CaCl_2$) at 10 % (w/w) Salinity

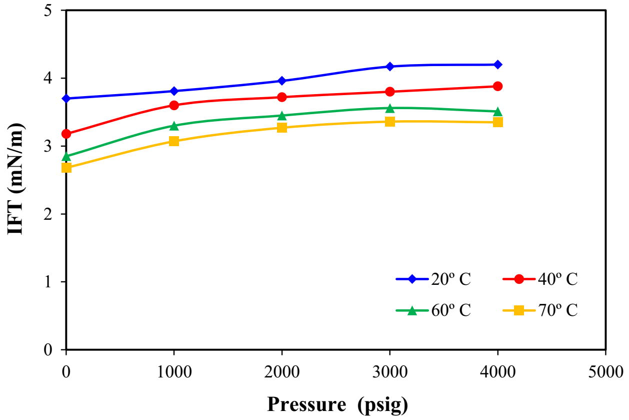


Fig. 7 Effect of Pressure on IFT of 500 ppm Ammoeng 102 Diluted in Brine III (83 % NaCl, 17 % $CaCl_2$) at 10 % (w/w) Salinity

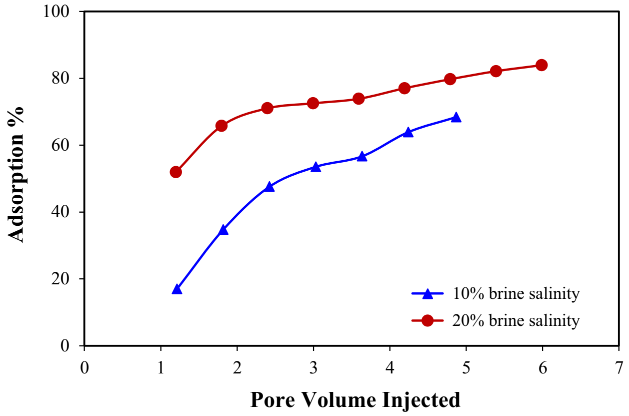


Fig. 8 Adsorption of 500 ppm Ammoeng 102 Diluted in Brine III (83 % NaCl, 17 % $CaCl_2$) at 10 and 20 % (w/w) Salinity

interface leading to lower IFT while the second is diffusion of the adsorbed IL into the oil phase leading to emulsion inversion and reverse effect of temperature on IFT. Similar trends are expected for Ammoeng 102 solution at 20 % (w/w) salinity but with lower IFT values. The ability of ionic liquid to tolerate high salinity, temperature and pressure in addition to its effectiveness in reducing interfacial tension at such conditions indicates the potential of these liquids over organic surfactants for EOR processes in harsh reservoir conditions.

Adsorption

Adsorption of 500 ppm Ammoeng 102 ionic solutions at 10 and 20 % (w/w) solution salinity was studied on two fresh Berea core plugs (plugs 5 and 6) with petrophysical properties listed in Table 1. Figure 8 plots the adsorption as a function of ionic solution pore volumes injected. The figure indicates high adsorption for both solutions with more adsorption for higher salinity one.

The high adsorption level can be attributed to the high specific surface area characterizing the Kaolinite clay in addition to the strong electrostatic interaction between the

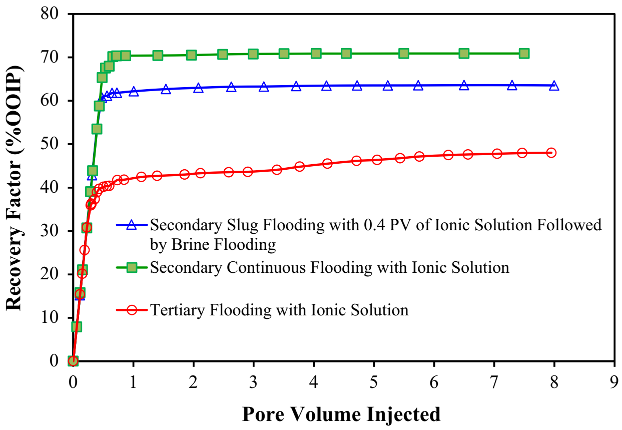


Fig. 9 Effect of injection mode on recovery curves

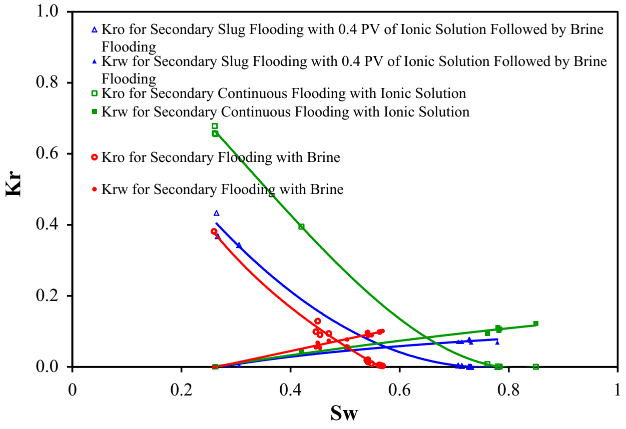


Fig. 10 Relative permeability curves of secondary flooding runs

negative charge at the kaolinite surface and the opposite cationic charge of the Ammonium cations (Song et al. 1994; Lv et al. 2011). Adsorption is expected to decrease in the presence of oil and formation brine which can limit the accessibility of ionic liquid molecules to rock grain surfaces Hezave et al. (2013b).

Flooding runs

A series of flooding runs on fresh cores were conducted at reservoir conditions. Figure 9 plots the recovery curves for three runs with irreducible water saturation (S_{wirr}) of 26 %. All runs were conducted with synthetic formation brine, injected brine and ionic solution all at 20 % (w/w) salinity. The first run was started with secondary brine flooding to residual oil saturation (S_{or}) followed by tertiary flooding of ionic solution. Second run was conducted in secondary mode where a slug of 0.4 pore volume of ionic solution was injected into core sample at initial oil saturation (S_{oi}) followed by continuous brine injection at the same salinity. Third run was conducted in secondary mode but with continuous ionic solution injection. The results indicate an incremental tertiary oil recovery of 5 % original oil in place (OOIP) over that obtained by secondary brine injection (43 % OOIP) corresponding to 8 % residual oil in place (ROIP). Secondary ionic solution flooding runs provided a much higher ultimate recovery of 63 and 70 % OOIP for slug and continuous ionic solution injection, respectively, indicating the efficiency of ionic solution injection in secondary mode at initial oil saturation. The higher ultimate recovery for the secondary ionic solution flooding can be attributed to the lower water content of the sample rocks and hence the less dilution of the ionic solution within the porous medium. At low water content, ionic solution is more effective in lowering the interfacial tension and altering rock wettability to more water wet characteristic.

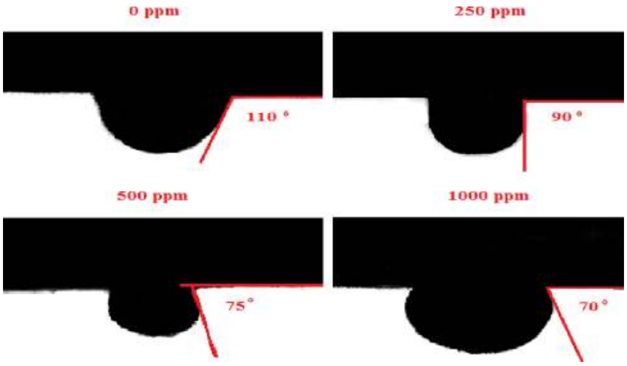


Fig. 11 Contact angle measurements at different Ammoeng 102 concentrations

Wettability alteration and IFT reduction are the main mechanisms in chemical EOR. IFT value as low as 0.01 mN/m is needed to mobilize significant residual oil indicating stronger role for wettability when IFT is not drastically low (Song et al. 1994). To investigate the wettability alteration, contact angel measurements were conducted at reservoir conditions in the presence of 20 % salinity ionic solutions at different concentrations (0, 250, 500 and 1,000 ppm). Figure 10 shows oil drops shapes in the presence of different ionic solution concentrations indicating the decrease of contact angle with the increasing ionic liquid concentration. The decreasing trend of contact angle indicates wettability alteration from slightly oil wet condition to medium water wet condition. Relative permeability curves constructed for the above runs (Fig. 11) indicate increasing rock water wetness, higher oil relative permeability (K_{ro}) and lower S_{or} as we proceed from secondary brine flooding to continuous secondary ionic solution flooding.

To further investigate the effect of rock water content on ionic solution recovery efficiency, one more run (run 4) was conducted in tertiary injection mode but at higher S_{wirr}

of 34 %. Figure 12 plots the recovery curve for this run in comparison to run 1 conducted at S_{wirr} of 26 %. Higher recovery was obtained in the secondary brine flooding stage for low S_{wirr} run with 44 % OOIP compared to 38 % OOIP for high S_{wirr} run. Tertiary recovery with ionic solution was slightly higher (6 % OOIP) for low S_{wirr} run compared to that of high S_{wirr} run (4 % OOIP). This corresponds to 8 and 9.4 % ROIP, respectively. The higher secondary recovery for low S_{wirr} run can be attributed to the presence of higher amount of recoverable oil and less water content compared to high S_{wirr} case. At the end of the secondary flooding, the water content for both rocks was very close and hence water content effect on tertiary cycle of both runs was minimized as indicated by the close tertiary recovery factors. Table 4 summarizes the outputs of the conducted runs listing the recoveries and the end point saturations and relative permeability's.

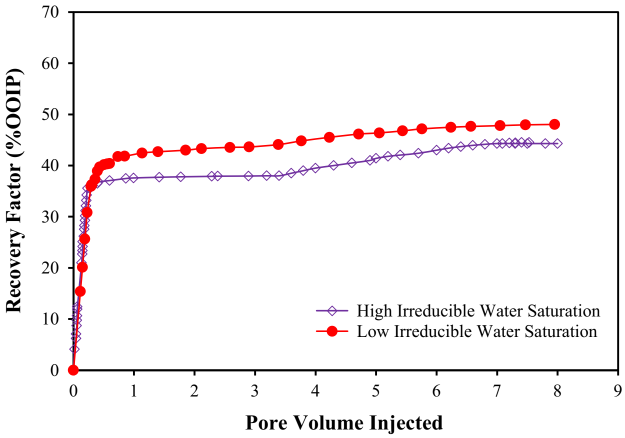


Fig. 12 Effect of irreducible water saturation on recovery curves

Conclusions

This study aimed at investigating the efficiency of ILs for chemical EOR. The work started by screening several ILs based on their solubility in brines, surface activity, and the solutions stability at high temperatures. Based on the screening process, Ammoeng 102 was the ionic liquid of choice. Reservoir condition measurements of Ammoeng 102 solutions-crude oil IFT at different IL concentrations and solutions salinities indicate significant IFT reduction with increasing concentration for both salinities with more IFT reduction at higher solution salinity. Low CMC values of 250 ppm were obtained for both solution salinities. Temperature and pressure have low effects on IFT measurements within the ranges investigated. Ammoeng 102 adsorption on rock surface at reservoir conditions indicates high tendency for adsorption with more adsorption noticed for higher salinity ionic solution.

A series of flooding runs on fresh Berea cores demonstrate the effectiveness of Ammoeng 102 ionic solution, especially when injected in secondary mode at S_{wirr} either as a slug followed with brine or continuous injection. Relative permeability curves indicate increasing rock water wetness, higher K_{ro} and lower S_{or} as we proceed from secondary brine flooding to secondary slug of ionic solution flooding to secondary continuous ionic solution flooding. Wettability alteration was confirmed by contact angel measurements demonstrating rock wettability shift from slightly oil wet to medium water wet condition as we increase the IL concentration in the aqueous phase. The effect of rock water content (S_{wirr}) on ionic solution recovery efficiency showed higher oil recovery for secondary brine and tertiary ionic solution flooding at low S_{wirr}

Table 4 Recovery factors and flooding parameters

Parameter	Run 1	Run 2	Run 3	Run 4
S_{wirr} (fraction)	0.261	0.264	0.263	0.340
Displacing phase for secondary flooding	Brine	0.4 PV of ionic solution followed by brine	Ionic solution	Brine
Displacing phase for tertiary flooding	Ionic solution		No tertiary flooding	Ionic solution
Secondary recovery (% OOIP)	44	63.55	70.87	38
Tertiary recovery (% OOIP)	4	No tertiary flooding	No tertiary flooding	6.5
Tertiary recovery (% ROIP)	8	No tertiary flooding	No tertiary flooding	9.4
S_{or} (fraction)	0.354	0.314	0.291	0.4269
K_{ro} at S_{wirr} (fraction)	0.429	0.433	0.678	0.126
K_{rw} at S_{or} (fraction)	0.109	0.069	0.122	0.0276

OOIP original oil in place
S_{wirr} irreducible water saturation
K_{ro} and K_{rw} oil and water relative permeability, respectively
ROIP residual oil in place
S_{or} residual oil saturation
PV pore volume

indicating the role of formation and rock water content in ionic solution effectiveness. It is worth mentioning that wettability is very much affected by rock mineralogy and rock type, hence the results obtained and presented are limited to the rock type investigated. Currently, we are investigating different sandstone and carbonate samples and so far promising preliminary results were obtained and more work is undergoing.

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References

Bai JM, Fan WY, Nan GZ, Li SP, Yu BS (2010) Influence of interaction between heavy oil components and petroleum sulfonate on the oil-water interfacial tension. J Dispers Sci Technol 31:551–556

Bermudez MD, Jimenez AE, Sanes J, Carrion FJ (2009) Ionic liquids as advanced lubricant fluids. Molecules 14:2888–2908

Dharaskar SA (2012) Ionic liquids (a review): the green solvents for petroleum and hydrocarbon industries. Res J Chem Sci 2:80–85

Domanska U (2005) Solubilities and thermophysical properties of ionic liquids. Pure Appl Chem 77:543–557

Fan H, Li Z, Liang T (2007) Experimental study on using ionic liquids to upgrade heavy oil. Fuel Chem Technol 35:32–35

Fan Z, Wang T, He Y (2009) Upgrading and viscosity reducing of heavy oils by [BMIM][AlCl$_4$] ionic liquid. Fuel Chem Technol 37:690–693

Hernandez JA, Cruz IG, Ramirez SL, Valencia CD, Dominguez JM, Aburto J (2009) Aggregation behavior of heavy crude oil—ionic liquids solutions by fluorescence spectroscopy. Energy Fuels 23:4584–4592

Hernández M, Alberto J, Jorge A (2011) Current knowledge and potential applications of ionic liquids in the petroleum industry. Ion Liq Appl Perspect 18:439–458

Hezave AZ, Dorostkar S, Ayatollahi S, Nabipour M, Hemmateenejad B (2013a) 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. Colloids Surf A Physicochem Eng Asp 421:63–71

Hezave AZ, Dorostkar S, Ayatollahi S, Nabipour M, Hemmateenejad B (2013b) Dynamic interfacial tension behavior between heavy crude oil and ionic liquid solution (1-dodecyl-3-methylimidazolium chloride ([C12 mim][Cl]$^+$ distilled or saline water/heavy crude oil)) as a new surfactant. J Mol Liq 187:83–89

Hezave AZ, Dorostkar S, Ayatollahi S, Nabipour M, Hemmateenejad B (2013c) Effect of different families (imidazolium and pyridinium) of ionic liquids-based surfactants on interfacial tension of water/crude oil system. Fluids Ph Equilib 360:139–145

Hu YF, Li S, Chu YP, Guo TM (2004) Wax precipitation in three Chinese reservoir oils under carbon dioxide (CO$_2$) injection. Energy Fuels 18:1183–1186

Hurd BG, Research M (1976) Adsorption and transport of chemical species in laboratory surfactant water-flooding experiments, in SPE Improved Oil Recovery Symposium. Tulsa, Oklahoma, pp 22–24

Keith E (2007) Johnson, What's an ionic liquid? Interface Electrochem Soc 16:38–41

Lemos RC, Silva EB, Santos AD, Guimaraes RC, Ferreira BM, Guarnieri RA, Dariva C, Franceschi E, Santos AF, Fortuny M (2010) Demulsification of water-in-crude oil emulsions using ionic liquids and microwave irradiation. Energy Fuels 24:4439–4444

Lucero DG, Flores P, Rojo T, Palou RM (2010) Ionic liquids as demulsifiers of water-in-crude oil emulsions: study of the microwave effect. Energy Fuels 24:3610–3615

Lv W, Bazin B, Ma D, Liu Q, Han D, Wu K (2011) Static and dynamic adsorption of anionic and amphoteric surfactants with and without the presence of alkali. J Petrol Sci Eng 77:209–218

Painter P, Williams P, Mannebach E (2009) Recovery of bitumen from oil or tar sands using ionic liquids. Energy Fuels 24:1094–1098

Painter P, Williams P, Lupinsky A (2010) Recovery of bitumen from Utah tar sands using ionic liquids. Energy Fuels 24:5081–5088

Rapoport LA, Leas WJ (1953) Properties of linear waterfloods. J Petrol Technol Trans AIME 198:139–148

Siedlecka EM, Czerwicka M, Neumann J, Stepnowski P, Fernández JF, Thöming J (2011) Ionic liquids: methods of degradation and recovery. In: Kokorin A (ed) Ionic liquids: theory, properties, new approaches. InTech. ISBN 978-953-307-349-1. doi:10.5772/15463

Simoni LD, Lin Y, Brennecke JF, Stadtherr MA (2008) Modeling liquid–liquid equilibrium of ionic liquid systems with NRTL, electrolyte-NRTL, and UNIQUAC. Ind Eng Chem Res 47 (256–272)

Smit B, Schlijper AG, Rupert LAM, Van OS (1990) Effects of chain length of surfactants on the interfacial tension: molecular dynamics simulations and experiments. J Phy Chem 94:6933–6935

Somasundaran P, Zhang L (2006) Adsorption of surfactants on minerals for wettability control in improved oil recovery processes. J Petrol Sci Eng 52:198–212

Song, Fu Y, Islam MR (1994) A new mathematical model and experimental validation of multi-component adsorption, in SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma pp 17–20

Xiao Y, Malhotra SV (2005) Friedel-Crafts Acylation reactions in pyridinium based ionic liquids. Org Chem 690:3609–3613