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The novel use of Deep Eutectic Solvents for enhancing heavy oil recovery

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ABSTRACT

Increasing demand and dwindling supply of crude oil have spurred efforts towards enhancing heavy oil recovery. Recently, applications of ionic liquids (ILs) for heavy oil recovery and catalytic upgrading have been reported. However, ILs are generally considered too expensive for industrial applications. Moreover, certain types of ILs are non-biodegradable and toxic. An alternative class of ILs called Deep Eutectic Solvents (DESs) have recently been discovered and investigated upon. A DES generally composed of two or more components that are capable of self-association, to form eutectic mixture with a melting point lower than that of each individual component. DESs are non-toxic, biodegradable, recyclable, non-flammable, environmentally friendly and cheap. Therefore, DESs have found application in fields like extraction/separation, solvent development/reaction medium, hydrometallurgy, etc. In this study, and for the first time to our knowledge, the effectiveness of two different types of DESs, Choline Chloride: Glycerol (1:2) and Choline Chloride:Urea (1:2), in enhancing heavy oil recovery was thoroughly investigated. Effect of the two DESs diluted with formation brine on emulsification, altering wettability, spontaneous imbibitions, surface and interfacial tensions and tertiary residual heavy oil saturation reduction are studied experimentally at different temperatures. Heavy oil with 16 °API and formation brine from one of the Omani heavy oil field were utilized. The core flood experiments were conducted at reservoir condition and using Berea sandstone core plugs.

The results showed that the two DESs did not make emulsion with the heavy oil. They increased the IFT of oil-brine system. Moreover, the two DESs altered the wettability of the sandstone rock surfaces from liquid-wetting towards intermediately air-wetting conditions at oil-air-rock system. The core flooding runs at different temperatures showed high potential of using these DESs for enhancing heavy oil recovery; where 14–30% of water flooded residual heavy oil was recovered after injecting the DES solvents as tertiary recovery stage. Wettability alteration phenomenon and viscose forces were known as the main mechanisms of enhancing the heavy oil recovery by DESs injection.

1. Introduction

In recent years, global demands of energy have been increased due to industrial growth while the worldwide production of conventional crude oil has almost reached to its peak. Recent statistics show that there is a decline in light oil production and composition of produced oil is getting heavier (Shah et al., 2010). Therefore, heavy oil production would play an important role in the future of the ever-growing world's energy consumption (Mohsenzadeh et al., 2012).

Unlike conventional light oil, the heavy oil production is much more difficult. Due to its high viscosity, oil-wet and low permeable matrices at reservoir conditions yield low recovery, around 5% to 10% by primary production (Xia and Graves, 2002). Thermal methods such as continuous steam injection, cyclic steam stimulation (CSS), steam assisted gravity drainage (SAGD) and in-situ combustion have been recommended as the most important techniques for enhancing heavy oil recovery based on mobility ratio improvement by oil viscosity reduction via effective heating, and by producing the oil through gravity and viscous displacements. However, for deep or low thickness heavy oil reservoirs, steam injection methods can be economically unfeasible due to extreme heat losses to the overburden, under burden and aquifer (Wu et al., 2012). Moreover, high-energy consumption, CO_2 emissions and fresh water source requirements for thermal methods

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especially for steam generation, have caused more attention for the use of non-thermal methods such as chemical injection (solvents, Alkalines, surfactants and polymers injection) to enhance the recovery of heavy oil.

Many attempts have been made to investigate the efficiency of chemical injection in enhancing the heavy oil recovery in both laboratory and field scale. Almost all the researchers have shown that oil-water IFT reduction (by surfactant flooding), emulsification (by alkaline flooding), increasing sweep efficiency (by polymer injection) and wettability alteration are the main mechanisms of oil recovery enhancement via the chemical injection methods (Nagarajan and Harold, 1982; Han et al., 1999; Liu et al., 2006; Wang and Dong, 2010; Wang et al., 2012; Kianinejad et al., 2013, 2015). Recently, new chemicals such as ionic liquids (ILs) have been reported in the literature for residual oil saturation reduction. Ionic liquids are liquids at or close to room temperature. They are organic salts that are composed of organic cations with organic or inorganic anions. ILs are considered as potential alternate to surfactants (Krystyna and Katarzyna, 2005; Zeinolabedini Hezavea et al., 2013). It is expected that ionic liquids, as a diluted salt solution, could be injected through the reservoir without causing any mechanical plugging of the porous medium. The polar compounds of heavy oil such as asphaltene and resins would diffuse in the ILs resulting in a reduction in heavy oil viscosity, a decrease in the asphaltene and sulfur contents and therefore an increase in the crude heavy oil °API gravity. Furthermore, the catalytic properties of ILs in crude oil oxidation, cracking and hydrocracking reactions that are partly responsible for heavy oil upgrading, have been reported recently (Nares et al., 2007).

Although ILs are, due to their unique properties, regarded as green replacements to volatile solvents in many electrochemical, synthetic, analytical, and engineering processes, they are generally considered too expensive for industrial applications. Moreover, certain types of ILs (i.e. imidazolium-based) are non-biodegradable and toxic Therefore, researchers continue to search for new and even greener alternatives to ILs that may overcome the said limitations(Nares et al., 2007). An alternative class of ILs called Deep Eutectic Solvents (DESs) have been discovered and investigated upon. A DES is a fluid generally composed of two or more mixtures of cheap and safe components that are capable of self-association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component. DESs are generally synthesized by the combination of various quaternary ammonium/phosphonium salts such as Choline Chloride (2-hydroxyethyl-trimethylammonium chloride, (ChCl)) with different Hydrogen Bond Donors (HBD) such as amines and carboxylic acids at a suitable temperature that would give a eutectic mixture. Based on this principle, DESs, like ILs, are tailorable solvents that could be designed for specific targets. Consequently, task-specific DESs, like ILs, with different physicochemical properties such as freezing point, viscosity, conductivity and pH among others can be prepared. Owing to these remarkable advantages, DESs have found application in fields like extraction/separation, catalytic processes, electrochemistry, CO_2 absorption and pharmaceutical, solvent development/reaction medium, hydrometallurgy etc. (Abbott et al., 2007).

DESs compared to ILs have many advantages such as biodegradability and biocompatibility as a green solvents, chemical compatibility with water, easy preparation, non- toxicity and very low prices (Abbott et al., 2007). In addition to the aforementioned properties, high viscosity, existing polar components and surface active agents in DESs give them high potential for application in heavy oil recovery.

In this work, we experimentally investigate the potential effects of two DESs on the main possible mechanisms of heavy oil recovery including viscose forces, emulsification, IFT reduction, wettability alteration, spontaneous imbibition and core flooding under reservoir condition. The effect of temperature on IFT, wettability and core flooding is also studied. To our knowledge, these set of experiments are the first of their kind as the use of DESs in EOR application has not been tested before.

2. Materials and methods

2.1. Rock and fluid samples

Heavy dead crude oil with 16 °API gravity and viscosity of 4200 cp at 25 °C and formation brine from an Omani heavy oil field were used in this study. Properties of the oil and formation brine are listed in Tables 1 and 2, respectively. The heavy oil density and viscosity were measured at different temperatures by Anton Paar viscometer model C-LTD80QC and density meter model DMA 4500M, respectively. The dependence of heavy oil density, specific gravity, API gravity and viscosity on temperature is shown in Table 1.

Two different DESs - choline chloride:Glycerol (molar ratio 1:2; molecular weight: 107.93 g/mol) and choline chloride:Urea (molar ratio 1:2; molecular weight: 86.56 g/mol)—were synthesized and used for the study. In the subsequent discussion, these are referred to as DES1 and DES2, respectively. A sample of DES was synthesized with choline chloride and Glycerol or Urea (molar ratio of 1:2). The choline chloride powder (a hygroscopic substance) was vacuum-dried at 80 °C for 6 h to minimize its water content. Then, measured quantities of choline chloride with Glycerol (liquid) or with Urea (powder) were mixed together. The mixture was put in an incubator shaker at 80 °C and allowed to completely melt to a homogeneous colorless liquid. The liquid DES was allowed to cool down to ambient temperature and it remained a colorless high viscose liquid (Abbott et al., 2007; Shuwa et al., 2014). The 50 vol%

Table 1
Heavy oil properties.

Chemical properties		Physical properties				
Molecular weight M_W	519	Temperature (°C)	Viscosity (cP)	Density (g/cm^3)	Specific gravity (SG)	°API
Total acid no. (mgKOH/mg)	5.11	25	4095.1	0.965	0.968	14.68
Sulphur content (wt %)	3.58	30	3050.3	0.961	0.965	15.13
Asphaltene content (wt %)	1.6	45	1211.0	0.951	0.960	15.90
Total nitrogen (mg/kg)	1948	60	426.2	0.941	0.957	16.36
Total salt (Lbs/1000 bbls)	11.0	70	246.1	0.934	0.956	16.51
Characterization factor UOP375		75	198.1	–	–	–
		80	158.6	–	–	–

Table 2
Brine properties.

Density @ 25 °C	1.05 g/cm^3
Total salinity	9 wt%
Sodium	25.083 kg/m^3
Calcium	3.672 kg/m^3
Magnesium	0.878 kg/m^3
Iron	0.045 kg/m^3
Chloride	47.722 kg/m^3
Sulphate	0.247 kg/m^3
Bicarbonate	0.079 kg/m^3
Filteration unit	0.45 μm