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Sequential deep eutectic solvent and steam injection for enhanced heavy oil recovery and in-situ upgrading

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HIGHLIGHTS

- Deep eutectic solvents followed by steam injection is tested for heavy oil recovery.
- High thermal stability of DESs makes them suitable for steam recovery methods.
- Sequential DES/steam flooding improves the pure steam recovery by 12%.
- Sequential DES/steam flooding is beneficial in terms of in-situ heavy oil upgrading.
- Produced oil has higher API gravity, lower sulphur and more saturate hydrocarbons.

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ABSTRACT

Recently, Deep Eutectic Solvents (DESs) have been introduced and investigated as new EOR agents for heavy oil recovery enhancement. In this study, sequential DES and steam flooding was proposed and experimentally investigated as a new scenario for heavy oil recovery enhancement and having potentials for in-situ heavy oil upgrading. DESs used in this study are Choline Chloride:Glycerol (DES1) and Choline Chloride:Urea (DES2). Primary and secondary DES flooding at different concentration followed by high-temperature steam flooding were conducted using 16.5 °API heavy oil and Berea sandstone core plugs. DES thermogravimetric analysis (TGA) performed and results verified the relatively high thermal stability of the selected DESs. Maximum decomposition temperature was found to be 320 and 370 °C for DES1 and DES2, respectively. This improves their potential for use as chemical additives or pre-flooding agents in thermal EOR methods. Sequential steam flooding after undiluted and 2-fold diluted DES injection recovered an additional heavy oil of 12% IOIP compared to steam flooding alone. However, using more diluted solutions (i.e., 20-fold diluted DESs) caused the same and in some cases lower total recovery factor by secondary steam flooding. When followed by steam flooding, DES2 exhibited superior heavy oil recovery enhancement (8–12%) compared with DES1 (1.5–6%) at the same concentrations. Analysis of physicochemical properties of produced oil for different cases revealed the favorable role of DES in upgrading the in-situ heavy oil. Heavy oil upgrading were quantified through various measurements including increase in API gravity up to 3.5 °API, 16.6% reduction in sulphur content or desulphurization and increase in the yields of saturate hydrocarbons. Comparatively, DES1 exhibited better overall performance than DES2 in terms of in-situ heavy oil upgrading.

1. Introduction

While non-thermal EOR methods such as CO_2-based techniques are commonly considered for lighter oil systems [1,2], thermal EOR methodologies are predominantly designed for improving the recovery from heavier oil resources. Numerous studies have been conducted on laboratory and field applications of thermal methods such as steam injection and in-situ combustion, demonstrating their effectiveness in enhancing heavy oil recovery. These thermal methods take advantage of transferring thermal energy to the reservoir and heating the heavy oil. As a result, heavy oil viscosity reduces drastically and the mobility ratio improves [3,4].

Although thermal recovery methods have shown promising performance, they have few drawbacks. For example, in steam

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injection method, large volumes of high quality steam are required which consume great sources of energy (natural gas) and cause CO_2 emission. In addition, the conventional steam flooding has some technical limitations such as steam condensation, heat loss to the over-burden and under-burden, and more importantly steam channelling and overriding. These challenges reduce sweep efficiency and increase steam to oil ratio (SOR). To overcome the challenges many laboratory studies and field trials were carried out to investigate different approaches and devise an optimise steam flooding with proficient heavy oil production. One of the approaches is to commence thermal methods as secondary or tertiary stages after primary or secondary non-thermal recovery stages such as water, gas or chemical injection. Another methodology is to co-inject steam with additives such as hydrocarbon and non-hydrocarbon gases, foam, solvents, surfactant and caustic steam [5,6].

Among those additives, chemicals have been very popular. Different types of Caustic soda and alkaline additives such as sodium hydroxide, sodium silicate, sodium carbonate and potassium hydroxide [7]; Surfactants like Triton-X100 [8,9]; biodiesels such as fatty acids methyl esters [10]; de-emulsifiers [11] and urea [12] have been investigated as steam additives. Results of previous laboratory works and field reports showed that combination of steam and these chemicals results in greater IFT reduction, more favorable wettability alteration, higher viscosity reduction, lower steam temperature and better displacement which all yield to improvements in recovery factor compared to conventional steam flooding.

One of the important concerns in application of chemical additives in steam flooding is thermal decomposition of the chemicals at high temperature which significantly reduces the effectiveness of these chemicals. Chemicals used in conventional enhanced oil recovery (EOR) have been shown to have low thermal stability. Amaefule et al. (1979), tested thermal stability of different anionic and non-anionic surfactants considered as steam flood additives. Their results showed that none of the evaluated surfactants had the required stability for use in steam floods. The most stable petroleum sulfonate they investigated had a half-life of 11 days at 180 °C [13]. Tongwa et al. (2013) reported the thermogravimetric analysis (TGA) of HPAM polymer. They observed that the HPAM starts to decompose at around 100 °C and the first main decomposition peak appears at 211 °C [14]. Ramimoghadam et al. (2012) performed TGA analysis of cetyltrimethylammonium bromide (C-TAB) and Sodium dodecyl sulphate (SDS). Results showed that thermal degradation of undiluted SDS and C-TAB commenced at 160 and 180 °C, respectively [15].

In-situ upgrading of heavy oil during thermal methods improves quality of produced oil which leads to increase in well production, enhance heavy oil recovery, lower lifting and transportation costs. The upgraded heavy oil has higher API, lower viscosity, higher amounts of saturates, lower resin and asphaltene content and less amount of heteroamtoms such as sulphur, nitrogen, oxygen, iron, nickel and vanadium [16,17]. Several reports have shown the synergic effects of chemical additives to steam on in-situ upgrading of heavy oil and bitumen. Hydrogen donor additives such as tetralin and/or catalysts were shown to be essential for upgrading process to take place such as hydrocracking, hydro-conversion, visbreaking and hydro-desulphurization [18].

Recently, a new class of Ionic Liquids (ILs)-analogue called Deep Eutectic Solvents (DESs) has been introduced to industries. A DES is a fluid generally composed of two or more 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. Generally, DESs are categories into four groups consisting: (1) metal salts + organic salts, (2) metal salt hydrate + organic salt, (3) organic salts + hydrogen bond donor, and (4) metal salts (hydrate) + hydrogen bond donor [19,20]. 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. In addition to the aforementioned properties, high viscosity, containing polar components and surface active agents (surfactants) in DESs, make them suitable for oil industry particularly in EOR applications. Recently, DESs from group 4 have been investigated as new EOR agents for potential heavy oil recovery enhancement from sandstone cores at reservoir conditions. These are Choline Chloride:Glycerol, Choline Chloride:Urea by Mohsenzadeh et al. (2015a–c) [21–23]; Choline Chloride:Malonic Acid by Al-Weheibi et al. (2015) [24] and Choline Chloride:Ethylene Glycol by Shuwa et al. (2014) [25]. In these cases, the DES flooding showed promising results in term of recovery enhancement through improvement in viscosity ratio and favorable wettability alteration of rock surface as the main mechanisms.

DESs due to their high thermal stability, high solvability and hydrogen donating [26,27], have been used in high temperature applications such as catalyst in catalytic processes, extraction-separation and hydrometallurgy [28–30]. Previous studies on the DESs reactions illustrate the role of DESs in various hydrogen donation reactions during organic synthesis such as alkylation, reduction, elimination, carbon rejection, hydrogenation, and desulfurization [30]. Shuwa et al. (2015) used Molybdenum oxide catalyst dissolved in DES (Choline Chloride/Urea) in the catalytic upgrading reaction of heavy crude oil. Results indicated encouraging performance of the DESs at high pressure and high temperature for upgrading reactions [27].

In this study, effect of steam flooding after DES flooding on heavy oil recovery enhancement and in-situ upgrading were investigated through core flooding experiments. The same DESs - Choline Chloride:Glycerol and Choline Chloride:Urea - introduced in our previous studies, were utilized for further investigations. Primary and secondary DES flooding at different concentrations at reservoir conditions followed by steam flooding experiments at high pressure and high temperature were conducted. Physicochemical properties of produced oil were analyzed to investigate the extent of oil upgrading or quality improvements during the proposed process.

2. Material and methods

2.1. Materials

Homogenized consolidated Berea sandstone core plug of 1.5″ diameter and about 4″ length was utilized for the core flooding experiments. Heavy crude oil and formation brine from an Omani oilfield were used for the experimental work. The heavy oil and brine properties are shown in Table 1. As it is shown, the heavy crude oil contains 1.6 wt.% of asphaltene which is considered as low-asphaltene heavy oil compared to other cases [31]. Two different DESs were synthesized and tested (details are published earlier by Mohsenzadeh et al., 2015a and b). They are namely Choline Chloride/Glycerol (DES1: molar ratio 1:2; molecular weight: 107.93 g/mol) and Choline Chloride/Urea (DES2: molar ratio 1:2; molecular weight: 86.56 g/mol). Different DES solutions were prepared at different dilution levels using the formation brine: (I) undiluted DES, (II) 2-fold diluted DES (50 vol.% DES in formation brine) and (III) 20-fold diluted DES (5 vol.% DES in formation brine). Equivalent mole fractions of different dilution levels along with physicochemical properties of DESs are presented in Table 2. Molecular structures of the raw material for both DESs are depicted in Fig. 1. As it is illustrated, both DESs contain the hydrogen bond