Journal of Molecular Liquids 269 (2018) 23–28

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Effects of non-ionic surfactants on the material exchange between crude oil and $scCO_2$

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ARTICLE INFO

Article history:
Received 14 May 2018
Received in revised form 3 August 2018
Accepted 4 August 2018
Available online 06 August 2018

Keywords:
CO_2
Non-ionic surfactant
Extraction
Material exchange

ABSTRACT

The effects of some designed non-ionic surfactants (Guerbet alkyl polyoxyethylene ethers and linear alkyl polyoxyethylene ethers) on the exchange of materials between crude oil and $scCO_2$ were investigated at 359 K. The efficiency of the surfactants was demonstrated by extraction tests, volume change rate tests and compositional analysis of the produced oil. Firstly, extraction tests have shown that the addition of these surfactants can help $scCO_2$ extract more crude oil. Secondly, adding these surfactants significantly increased the volume change rate of the oil droplets. At 15 MPa, the addition of C16(3) increased the volume change rate from 15.862% to 20.165%, indicating more materials were extracted from the oil drop. Finally, by analyzing the recovered oil content, we found that surfactants can promote the exploitation of crude oil. C16(3) + CO_2 can recover more short-chain alkanes (C5–C20) than CO_2.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is chemically inert [1], nontoxic, nonflammable [2], and it is well-known for its application in supercritical fluid extraction (SFE) processes, where it is commonly used to extract small and/or non-polar molecules from natural materials under very mild conditions [3–6]. Besides the extraction of essential oils from herbs and spices [7,8], the most prominent application of SFE is the removal of caffeine form coffee beans [9,10]. The process has also been employed for the extraction of antioxidants, preservations and sunscreen agents in cosmetics and for the extraction of functional compounds from Spirulina [11–13]. Beyond that, SFE is an important part in the process of CO_2 enhanced oil recovery (CO_2-EOR). Extensive surveys published have shown that the oil recovery rate could be enhanced 8–16% through CO_2-EOR [14–16]. CO_2-EOR is not only a promising oil recovery process, but also an environmentally friendly process that reduces greenhouse gas emissions [17–20].

The recovery rate of CO_2-EOR is highly dependent on the material exchange between crude oil and CO_2 [21–23]. Generally, at the first time, CO_2 cannot be miscible with the crude oil. However, under higher pressure, they can achieve the so-called dynamic miscibility through multiple mass exchanges. Initially, light compounds of the crude oil are extracted into the CO_2 phase, and some CO_2 also enter the crude oil phase. Next, the extraction process enriches the CO_2 phase, bringing density of the two phases closer, thereby improving the recovery of crude oil. In addition, the more carbon dioxide entering the oil phase, the more swelling of the oil phase, which will also help reduce the viscosity of the crude oil and improve oil recovery [24–27]. Nevertheless, the recovery rate of CO_2-EOR is limited because the exchange of material between crude oil and CO_2 is significantly confined by low solvation of CO_2 and the differences in density, polarity, and viscosity between oil and CO_2.

In water flooding, the most common way to increase oil recovery is to add additives such as water-oil surfactants, polymers and crosslinkers, which help to increase the interfacial interaction between water and crude oil [28,29]. Surfactants which have polar (hydrophilic) and non-polar parts (lipophilic), can steadily stay in the interface between water and oil, and reduce the interfacial tension and enhance the contact of the oil and water phases [30]. Moreover, since the surfactant can self-assemble in water to form various morphologies of micelles, this helps the non-polar oil molecules to be stably dissolved in the aqueous phase. Similarly, it has been found through research that changing the oil-CO_2 interface condition can help change the material exchange efficiency, the more oil could be extracted into the CO_2 phase, the more CO_2 enter the oil phase, which benefits the CO_2-EOR. Therefore, in the CO_2 flooding process, the addition of an auxiliary agent that facilitates the exchange of substances between the oil phase and the CO_2 phase is a reasonable method for improving oil recovery. [31,32]

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https://doi.org/10.1016/j.molliq.2018.08.018
0167-7322/

The objective of this study is to investigate the effects of some nonionic surfactants on the crude oil-CO_2 phases. These nonionic surfactants have oil-philic long-chain alkyl tails, and polar polyethylene glycol tails to improve the solvent power of CO_2. Based on our previous study, these compounds are capable of improving the solubility of heavy hydrocarbons in CO_2 [33]. We anticipate that these compounds would have a positive impact on enhancing the interfacial mass transfer behavior between crude oil and CO_2.

2. Materials and methods

2.1. Materials

Carbon dioxide with a mass purity >99.5% was purchased from Dalian Gas Co. Ltd. China. Guerbet alkyl polyoxyethylene ethers (mass fraction purity > 99%) and linear alkyl polyoxyethylene ethers (mass fraction purity > 99%) were prepared from Guerbet alkyl alcohol (Jarchem Industries, Inc., Newark, NJ, USA) at Liaoning Oxiranchem Co., Ltd., Liaoyang, China. Mass spectra of them were presented in our previous work [34]. Cm(n) denotes the linear alkyl polyoxyethylene ethers, Guerbet alkyl polyoxyethylene ether use the abbreviation GCm (n), wherein Scheme 1, the subscript n represents the average number of the repeating units (EO) per molecule and m represents the hydrocarbon chain length. All compounds, C14(5), C16(3), C16(5) and GC16 (3), were dried by a vacuum oven at 333 K for 24 h to remove moisture prior to tests.

Density of the crude oil provided by Daqing NO.8 reservoir oil field is 0.869 g/cm^3.The compositional analysis results of the crude oil are given in Table 1.

Table 1
Compositional analysis result of the crude oil.

Content	wt%	Content	wt%
N_2	0.081	C6	1.143
CO_2	0.001	C7	3.592
C1	1.693	C8	3.593
C2	0.624	C9	3.194
C3	0.198	C10	1.045
C4	2.842	C11	0.175
C5	2.652	C12+	79.168

2.2. Methods

2.2.1. Extraction tests

The supercritical CO_2 extraction tests were performed in a 1000 mL high-pressure stainless-steel kettle (273 K–473 K, 0 MPa–30 MPa) [35]. Fig. 1 shows the schematic diagram of the experimental set-up used for the extraction tests. Major component of this experimental set-up is a specially designed vessel with an electric heater (heating jacket). In the vessel, there are two sample disks, the additives disk (1), and the crude oil disk (2). In addition, two separators were installed at the end of the vessel to separate the extract and recycle the CO_2.

Firstly, the vessel was heated to 359 K (reservoir temperature) before each experiment. After temperature reached the stable value, the additive (surfactant) and crude oil (0.2800 g) were separately added onto disk(1) and disk(2). Then closed the vessel, vacuumed the air and pressurized with CO_2. Repeated three times to ensure air was completely out of the vessel. Finally, CO_2 was pumped into the kettle to the pre-specified pressure. After 2 h (refer to the supporting information for the selection of the extraction time and concentrations of the additives), CO_2 was slowly released, until the inside pressure reached the atmospheric pressure. Then the residual oil and the additive were weighed. The extraction rates were calculated by the percentage of the extracted oil in the original crude oil. The extraction tests were conducted at four different injection pressures of 15 MPa, 20 MPa, 25 MPa and 28 MPa for each surfactant.

2.2.2. Volume change rates

When a crude oil drop is surrounded by CO_2, there are two opposite effects on the pendant oil drop. After the pendant oil drop was formed in the CO_2 phase, its volume and shape were changed continuously (Fig. 2). The oil drop swelled initially, due to the dissolution of some CO_2 into the oil phase, then the oil drop began to shrink because components in the crude oil drop were extracted into the CO_2 phase.

The rate of volume change was calculated by the equation below,

$$\Delta V = (V_0 - V_1)/V_0 * 100\%$$

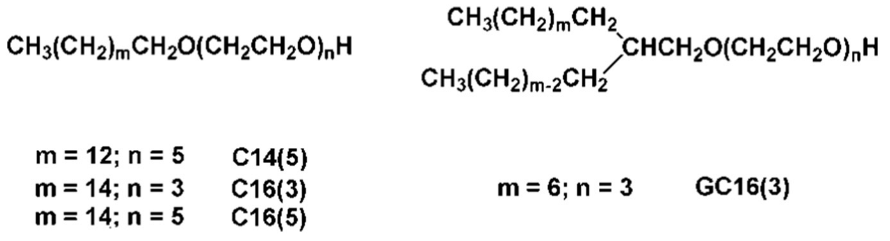
where, V_0 is the volume of the original crude oil drop; V_1 is its final volume (10 min later). The experiment setup was the same as that described in Ref. [24] for IFT tests. Firstly, the desired amount of surfactant was added to a high-pressure intermediate container and dissolved well in CO_2, then the surfactant/CO_2 solution was pumped into the see-through cell. The next step is to open the oil storage tank slowly until a large enough oil drop was formed in the cell. Volume of the oil drop was calculated by computer pictures taken at 10 min. The volumes were tested at four different injection pressures of 15 MPa, 20 MPa, 25 MPa, and 28 MPa.

2.2.3. Slim-tube tests

Table 2 lists the characteristics of the slim tube. The instrument used is similar to that described elsewhere [36].

Prior to each experiment, the apparatus was carefully cleaned with light petroleum and chloroform, then dried with nitrogen. After the slim tube was heated up to 359 K, the crude oil sample was pumped into the slim tube at the pre-specified pressure. After the tube was saturated with the crude oil, CO_2 was injected into the slim tube to displace the crude oil by a positive displacement pump at a rate of 12.0 cm^3/h, 359 K and 28 MPa. The experiment ended after 1.2 pore volumes (PV) of gas was injected.

The recovered oil samples were collected for each 0.1PV (after the CO_2 breakthrough) during the slim-tube test, then GC–MS chromatograph (Agilent, 7000B) was used to analyze the collected samples. Starting temperature in the GC oven was 323 K for 2 min, then followed by an increasing temperature to 573 K, the total time was 45 min. GC–MS data were collected using a selected ion recording and the oil fractions were characterized based on a calibration performed by using stock standard [37].



Scheme 1. Structures and abbreviations of the non-ionic surfactants.