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Enhanced oil recovery in high temperature carbonates using microemulsions formulated with a new hydrophobic component

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ABSTRACT

The positive feedback from previous studies has confirmed the high performance of microemulsion flooding. However, there are few researches assessing this efficient method in carbonates reservoirs, particularly at high temperature. This paper attempts to fill the gap. Furthermore, biodiesel is introduced and evaluated as a new hydrocarbon source of mixture. For this purpose, phase behavior of surfactant/brine/biodiesel/co-solvent was systematically studied using response surface methodology to find the optimum formulation. Thereafter, optimized microemulsion was characterized in terms of particle size distribution, zeta potential, electrical conductivity, polarized light microscopy, surface tension, interfacial tension, and viscosity. Finally, oil recovery tests comprising spontaneous imbibition, contact angle, core-flood and microvisual experiments were conducted to examine the potential of optimum formulation for chemical enhanced oil recovery (CEOR) purpose in carbonates. Experiments of different stages were carried out at elevated temperature (75 °C). Employing optimal microemulsion, 20.0% original oil in place (OOIP) in spontaneous imbibition and 6.4% OOIP in core-flood tests were tertiary added to oil recovery. The results of this study illustrate the efficacy of proposed formulation to increase oil recovery factor of carbonate formations.

Introduction

Microemulsions are thermodynamically stable isotropic phases formed almost spontaneously when thermodynamic equilibrium is established between all the components of a system comprising a mixture of oil, water, and nonionic or ionic amphiphile molecules, with the voluntary addition of a co-solvent [1,2]. Thermodynamic stability of a colloidal dispersion (e.g. oil-in-water microemulsion) means that its free energy is lower than the free energy of corresponding separate phases (oil and water). The change in free energy (ΔG_F) associated with the formation of dispersion from separate phases is expressed as:

$$\Delta G_F = \sigma \Delta A - T\Delta S \quad (1)$$

where σ is interfacial tension (IFT), ΔA is the change in interfacial area A, T is temperature, and ΔS is configurational entropy change. Gibbs free energy contains another term which is enthalpy change (ΔH) but it is negligible in the mixing process of two immiscible liquids.

The interfacial free energy term ($\sigma\Delta A$) always opposes the formation of microemulsions because it is always positive while the configuration entropy term ($-T\Delta S$) is always negative as the droplet number increases continuously and therefore it always favors the formation of microemulsions. To form a dispersion spontaneously, it is required that ΔG_F becomes negative ($\sigma\Delta A < -T\Delta S$). To fulfill the condition, the interfacial tension should reduce severely using a surface active agent [3].

Along with the complex nature of microemulsions and some limitations in their preparation, they are of increasing significance for scientific and industrial purposes because of their ultra-low interfacial tension, large interfacial area, thermodynamic stability, and high solubilization capacity of otherwise immiscible liquids. They span various areas including alternative fuels, remediation of contaminated soils, drug delivery, nanoparticle synthesis, agro-chemicals, food, cosmetics, and chemical enhanced oil recovery (CEOR) [4].

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The application of microemulsions is of great interest in CEOR methods [5]. The technique of microemulsion flooding is referred to as the injection of a mixture of water (brine), hydrocarbon, and surfactant with/without the addition of co-solvent in which the composition is thermodynamically stable. It has been variously called micellar flooding [6], miscible-type water flooding [7], Maraflood [8], and high-concentration surfactant flooding [9]. Apparently, it was conceived by Gogarty and Olson [10] in 1966 and from then on different studies were done to evaluate its performance from different standpoints: adsorption [11,12], chemical screening and additives [13,14], economic evaluation [15,16], flow in porous media [17–20], CEOR efficiency [6,21–26], mobility control and rheology [27,28], effect of reservoir parameters [29–33], physicochemical and phase behavior studies [34–37], scale-up [38,39], sensitivity analysis [30,40], simulation and numerical modeling [41–44], and wettability [45]. The promising results of micellar/microemulsion flooding have led to the application of this method for the tertiary recovery in the pilot and field scales [46]; such as Robinson Sand in Crawford County [47], Bradford [48], El Dorado [49], Bell Creek [50], and Torchlight [51] fields in the USA.

One of the main challenges of emulsion/microemulsion flooding is the selection of hydrocarbon source. Different alternatives have been proposed in the literature, e.g. CO_2 [52], supercritical CO_2 [53], diesel [54], gear oil [55], used engine oil [56], and palm kernel oil [36]. In this research, for the first time, biodiesel is used as the main source of hydrocarbon in microemulsion system. It is a renewable fuel composed of fatty acid methyl esters (FAME), mainly produced via transesterification of vegetable oils, animal fats and micro-algal oil. Not only does it have the advantage of renewability but it is also an eco-friendly component [57,58].

There are only a limited number of researches in the literature which employed biodiesel in oil industry; such as surface active component of heavy oil recovery methods [59,60] and hydrocarbon source of water-based drilling fluids [61]. However, the application of biodiesel in the formulation of microemulsions for CEOR purposes has not been reported yet. To expand the performance of biodiesel microemulsion for real reservoir conditions, the experiments are done at high temperature while most of the previous studies on microemulsion flooding have been reported at ambient temperature. Furthermore, the oil recovery tests were performed on aged carbonate samples as the representative of carbonate reservoirs. Carbonate formations contain more than half the world's hydrocarbon reservoirs [62]. Most carbonate reservoirs have a dual character of matrix and fracture with high temperature and/or high salinity [63]. On the other hand, their wettability status is typically intermediate to oil-wet. Therefore, they are mostly categorized in complex and unconventional reservoirs where the primary and secondary mechanisms of oil production are insufficient and tertiary oil recovery approaches should be applied [64]. In such harsh conditions, the potential of microemulsion flooding can be useful, which is neglected in previous studies. This work concerns the evaluation of the performance of microemulsion flooding formulated with biodiesel in carbonate reservoirs at high temperature.

The paper is commenced with the phase behavior of microemulsion system including brine/surfactant/biodiesel/co-solvent using response surface methodology to find optimum formulation of microemulsion. Then, it goes through the characterization of the optimum formulation in terms of particle size distribution, zeta potential, electrical conductivity, polarized light microscopy, surface tension, IFT and viscosity. Finally, the efficacy of optimum formulation for the improvement of oil recovery is examined using spontaneous imbibition, contact angle, core-flood, and micro-visual experiments.

Experimental

Phase behavior tests

Samples of aqueous (continuous) and oily (dispersed) phases were separately prepared. Aqueous phase consisted of surfactant (polysorbate 80, Fig. 1) and salt (NaCl, Merck). Biodiesel as the hydrocarbon component of the formulation and co-solvent (ethanol, Merck) formed the oleic phase. Biodiesel was prepared using transesterification method whose procedure for production and purification to meet ASTM D6751 [65] specifications has been thoroughly described elsewhere [57,66]. Table 1 shows the properties of biodiesel.

Samples were filled in glass pipettes. First, the 10 ml pipettes were sealed at the tip with an oxygen-acetylene torch. Next, individual aqueous phases were filled in the pipettes and their corresponding oily phases were carefully added so that unwanted mixing of separate phases could be prevented. Following this, the pipettes were sealed at the end using silicone glue and were then placed in a customized roto-spin apparatus by which two phases were mixed using end-over-end method for 24 h at reservoir temperature (75 °C) of Bibi Hakimeh oilfield located in the southwest of Iran [67]. It should be noted that different experiments of this study were performed at this temperature. Pipettes were finally transferred into an oven with the same temperature and stored to reach stability. The solubilization capacity (Eq. (2)) of dispersed phase was measured after about four weeks (26 days):

$$S_o = \frac{V_o}{V_a} \times 100 \tag{2}$$

where S_o is oil solubilization parameter (%), V_o and V_a are the volume of oleic and aqueous phases (cc), respectively [68].

Table 1
The properties and GC analysis of biodiesel.

Parameter	Value
Viscosity (cp) @ 40 °C	4.0733
Density (g/cm^3) @ 40 °C	0.8601
Flash point (°C)	171
C16:0 (%)	34.84
C16:1 (%)	0.22
C18:0 (%)	3.66
C18:1 (%)	40.55
C18:2 (%)	13.23
C18:3 (%)	0.51
C18:3c (%)	0.04
C19 (%)	5.81
Other components (%)	1.15

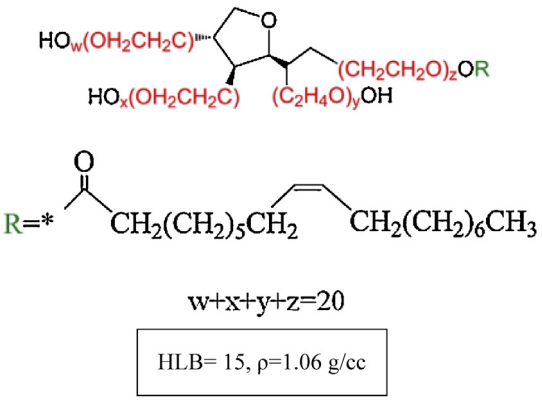

Fig. 1. Molecular structure of polysorbate 80.