Journal of Unconventional Oil and Gas Resources 15 (2016) 11–21

Contents lists available at ScienceDirect

Journal of Unconventional Oil and Gas Resources

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

Experimental study on adsorption and wettability alteration aspects of a new chemical using for enhanced oil recovery in carbonate oil reservoirs

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ARTICLE INFO

Article history:
Received 8 August 2015
Revised 7 May 2016
Accepted 9 May 2016
Available online 11 May 2016

Keywords:
Interfacial tension
Enhanced heavy oil recovery
Wettability
Free imbibition process
Core flooding
Ionic liquid compound

ABSTRACT

There is increasing interest in new multi-purpose chemicals for EOR in carbonate reservoirs, because of their oil wet nature that prevents oil from being produced. A new chemical compound $[Et_3NH]Cl/1.5\ AlCl_3$ ($X = 0.6$) modified with CuCl, is developed for enhancing the recovery of the free imbibition and core flooding mechanisms for naturally fractured reservoirs. Laboratory experiments have been conducted to understand the injection of such chemical into oil-wet, fractured reservoirs. The compound is tested on Iranian heavy oil sample from the Bangestan reservoir, Marun oil field. Core plugs were prepared and aged in the crude to attain restored state samples. It is found that ionic liquid compound significantly reduces oil viscosity, molecular weight and also alters wettability to a more desirable state. This chemical compound has the capability of reducing IFT and contact angle. These combined effects result in noticeable free water imbibition recovery enhancement in Amott cell after oil has undergone a reaction with the compound. The potential of the new chemical compound for increasing oil recovery and in situ upgrading of heavy oil are also examined at reservoir condition by core flooding experiments. In addition, the adsorption behavior of the new proposed chemical is also studied.

1. Introduction

About 60% of the world's oil is found in carbonate reservoirs (Akbar et al., 2000, 1995; van Golf-Racht, 1982). By reduction of reserve oil in conventional oil reservoirs, more and more attention is being focused on producing from unconventional and heavy oil reservoirs. Under these conditions, it is very important to distinguish innovative methods for effective exploitation of the discovered heavy oil reserves. Recovery from hydrocarbon reservoirs extremely depends on reservoir heterogeneity, oil quality and properties, reservoir management and drive mechanisms (Green and Willhite, 1998). Many carbonate reservoirs are naturally fractured and their wettability is oil-wet/mixed-wet (Roehl and Choquette, 1985; Chilingar and Yen, 1983; Anderson, 1986). In these reservoirs, it is difficult to produce oil after primary production, especially if the fractures form a connected network (Allan and Sun, 2003; Ahmadi et al., 2012). One of the most important keys to many heavy oil production enhancement mechanisms is viscosity reduction (Taber et al., 1997; Pei et al., 2014). To reduce the viscosity of heavy oils, aquathermolysis is the most efficient method which can decrease asphaltene and resins in heavy oils (Clark and Hyne, 1984). However, aquathermolysis operates at relatively high temperatures which can be well accommodated by the high reservoir temperatures and it can be even faster during thermal EOR methods (Fan et al., 2001, 2006; Wu et al., 2010; Saaid et al., 2014; Xiang-hai et al., 2003).

After the primary production from oil reservoirs, waterflooding is usually used to recover more oil from those reservoirs (Willhite, 1986). However, waterflooding does not show an acceptable recovery in naturally fractured reservoirs, since in these reservoirs, wettability is mixed to oil wet (Anderson, 1987). In these unconventional reservoirs, only if the matrix blocks are water wet, the production depends on free imbibition of water to drive out the oil from the matrix into the fracture system (McCaffery, 1973). Wettability has a crucially important role in controlling the capillary pressure, which produces the driving force for the free imbibition process. Free imbibition process is affected by so many other parameters such as heterogeneity of the reservoirs, the matrix permeability, size and shape, and boundary conditions. The interfacial tensions and viscosities of the phases also play very important role, as fluid properties, in free imbibition process (Morrow and Mason, 2001).

Some successful outcomes have been obtained from the accomplishment of surfactant flooding for some conventional oil reservoirs (Allan and Sun, 2003; Boneau and Clampitt, 1977; Berger et al., 2002; Tabary et al., 2012; Moritis, 2004; Alvarado and

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http://dx.doi.org/10.1016/j.juogr.2016.05.001
2213-3976/

Nomenclature

q	surfactant adsorption on rock surface (mg/g_{rock})
$m_{tot.solution}$	total mass of solution in original bulk solution (g)
C^o	initial surfactant concentration (ppm)
C	final surfactant concentration in aqueous solution (ppm)
$m_{carbonate}$	total mass of crushed carbonate (g)
K_f	Freundlich constant
$1/n$	factor of heterogeneity
C_e	equilibrium concentration (mg/L)

Manrique, 2010). However, enormous surfactant loss through flowing in the porous medium and related problems of adsorption and reactions between the reservoir rocks and surfactant are some reasons to show greatly that mentioned technique is not producing the intended outcome (Ahmadi et al., 2012; Schramm, 2000; Curbelo et al., 2007; Lawson, 1978).

Roosta et al. (2009) measured contact angles to examine the effect of maturing time in crude oil as well as those of steam disclosure on the wettability of glass, mica, calcite and quartz surfaces. They demonstrated that the wettability changed toward water-wet during steam and hot water injection, they also denoted that further maturing in crude oil made the surface more oil wet by precipitation of asphaltenes. Aoudia et al. (2010) worked on the possibility of the surfactant injection as an enhanced oil recovery process in the Yibal field, they discovered that tertiary surfactant injection seems to be a fascinating option for enhanced oil recovery (EOR). Ahmadi and Shadizadeh (2013a,b) introduced a new natural surfactant, extracted from *Ziziphus spina* christi leaves, with EOR application in carbonate reservoirs. They investigated its adsorption on carbonate rocks and approved its effectiveness by conducting core flooding experiments. Kianinejad et al. (2013) have conducted glass micro model tests to investigate the effect of fracture properties on efficiency of surfactant flooding in fractured reservoirs in a five spot pattern, they draw the conclusion that perpendicularity of fracture to pressure drop direction increases surfactant flooding efficiency in recovering oil from matrix blocks.

Surfactants can act in several ways to enhance oil recovery such as reducing the interfacial tension between oil and injected water (Fini et al., 2012), formation of emulsion (Zargartalebi et al., 2015; Jamaloei et al., 2010), altering the wettability of the reservoir rocks (Standnes and Austad, 2000), etc. Nowadays many different varieties of surfactants are used in chemical flooding for enhanced oil recovery in the world. All these surfactants have high cost, which makes chemical flooding so expensive and worthless in some circumstances (Barua et al., 1986; Vaskas, 1996; Smith, 2013).

Nowadays, some ionic compounds have been announced and employed for upgrading and viscosity reduction of the heavy crude oils (Fan et al., 2007; Maity et al., 2010; Fu et al., 2001). The common ionic compounds which are used for heavy oil recovery, are ionic liquids with $(PF6)^-$ and $(BF4)^-$ that would produce an HF gas when they are employed for this process. Moreover, they are not inert towards different organic compounds in heavy oil that may limit their applications. Hence, these ionic liquids were used in an inert atmosphere and they are not appropriate to be used according to the reservoir conditions where the controlling of moisture in the reservoir is so difficult. In addition, the preparation costs and the antecedents of these ionic liquids are uneconomic.

This study introduces a new ionic compound with a cheap synthesis cost which is used in the current work for enhancing heavy oil recovery in naturally fractured reservoirs. This chemical compound can improve oil recovery from oil-wet/mixed-wet fractured carbonate formations, while it is environmental friendly. This new chemical compound is harmful if swallowed, and it also causes skin irritation and eye irritation if any direct connection established in high concentrations. It may cause respiratory irritation. However this compound contains no components considered to be either persistent, bio accumulative and toxic (PBT), or very persistent and very bio accumulative (vPvB) at levels of 0.1% or higher. It is completely biodegradable. Based on these investigations, it can safely be concluded that this new chemical compound is an environmental friendly compound which can be used appropriately in the oil industry.

Also the capability of this new surfactant to enhance the spontaneous imbibition process in crude oil-aged cores is demonstrated. Changes of composition, viscosity and average molecular weight of oil after treatment with the chemical compound are also discussed. In addition to discussed aspects of this new proposed chemical, this paper presents its adsorption behavior on carbonate rock surface in the manner of batch experiments. Batch experiments were done to investigate the impact of adsorbent portion on adsorption density. Also, adsorption kinetic was experimentally demonstrated at 30 °C with monitoring the uptake of the new chemical as a function of time. The adsorption isotherm data was also checked out with Freundlich isotherm and the adsorption parameters were concluded. This paper also investigates the effect of the new surfactant on contact angle to investigate probable rock wettability alteration due to its adsorption. Results that are gained from this research can be useful in choosing of proper surfactant for chemical EOR and a reservoir stimulation agent in carbonate reservoirs.

2. Experimental procedure

2.1. Preparation of the chemical additive

The surfactant was synthesized at a 500 mL rounded bottom flask. 190 g (1.42 mol) of $AlCl_3$ was slowly added to 131.2 g (0.954 mol) of $[Et_3N]HCl$. This process was stirred slowly and the reaction container was put in an ice bath to be cooled. By adding the half amount of $AlCl_3$ to the flask, the ice bath was removed and the mixture was stirred at room temperature for 10 min and then at 85 °C for 8 h. Then a light yellow compound was monitored. After that 7.19 g (0.0723 mol) of CuCl was added and the reaction mixture was stirred further for 2.5 h. At the end of the process a light green product can be observed. This compound was our desired newly proposed chemical.

2.2. Reaction of the additive with heavy oil

130 g of heavy oil sample from Marun oil field (Bangestan reservoir) and 2 g of $[Et3NH]Cl/1.5\ AlCl_3$ ($X = 0.6$) modified with CuCl are put into an oven, where the system is kept at 95 °C for approximately 36 h. The system is permitted to cool down after the reaction is completed. The viscosity and average molecular weights of the oil samples are measured afterwards, as explained in the following procedures. And also the following experiments were conducted for investigation of the chemical compound in enhancing