Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Synthesis of branched geminal zwitterionic liquids as wettability modifiers in enhanced oil recovery processes

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ARTICLE INFO

Article history:
Received 28 June 2016
Received in revised form 18 August 2016
Accepted 27 August 2016
Available online xxx

Keywords:
Branched geminal zwitterionic liquids
Enhanced oil recovery
Rock wettability modifier
Oil viscosity reducers
Molecular design

ABSTRACT

A new class of branched geminal zwitterionic liquids (**BGZLs**) betaine base with a long alkyl chains with either 8 (**BGZL-ZW8**) or 12 (**BGZL-ZW12**) carbons was synthesized and characterized by nuclear magnetic resonance (**NMR**) and Fourier transform infrared (**FTIR**) spectroscopic techniques. The **BGZLs** molecules presents functionality as viscosity reducer and wettability modifier with application in enhanced oil recovery (**EOR**) processes with good oil recovery factors (**ORF**). The above is demonstrated by performing spontaneous imbibition tests on embedded limestone cores with light and heavy crude oils in Amott cells at high temperature (90 °C) and different concentrations of **BGZLs** in presence of connate water with high salinity and hardness (36,275 ppm as NaCl and 6700 ppm hardness as $CaCO_3$). The rheological behavior of **BGZLs** was also determined as viscosity reducers in heavy crude oil at concentrations of 2000, 1000 and 500 ppm at temperatures of 25 and 40 °C, in the range of 36.11% to 25 °C and 43.31% to 40 °C. To explain the mechanism through **BGZLs** act as viscosity reducers, we realized theoretical studies using the density functional theory (**DFT**), also as wettability modifiers taking **BGZL-ZW8** and **BGZL-ZW12** behavior, observed in the experimental part. The interaction energies show that **BGZLs** can disaggregate asphaltene (**Asph**) dimmer (**Asph:Asph**) by the formation of supramolecular sandwich complex (**Asph:BGZL:Asph**) among **BGZLs** and **Asph:Asph**, modifying the properties of crude oil such as viscosity, is possible to support the fact of the **BGZLs** can desorbs **Asph** molecules of the rock surface, modifying the calcite surface (**Cs**) wettability of oil-wet to water-wet. The results of this research show that it is feasible the use of zwitterionic liquids as viscosity and wettability modifier in **EOR** process.

Introduction

The decline of oil reservoirs discoveries and the diminished of the oil production; generate the need to increase the production of the operative wells. Much of the oil remain trapped at the reservoir, to promote the mobility of the oil, an alternative is the use of chemical products as a part of an enhanced oil recovery (**EOR**) technologies, which has a key role to satisfy the energy demand in the upcoming years [1–4]. Recent studies emphasize the development of new surfactant agents with a specific chemical structure which is directly related to the performance and effectiveness of the agents in **EOR** processes [5–7]. However, the efficiency of the surfactants largely depends on the characteristic features of the crude oil involved in the **EOR** processes, and the properties of the rock, usually carbonate reservoirs with low permeability [8–10], this implies that the surfactant should have an effect onto the wettability of the rock changing from oil-wet to water-wet. It have been reported important advances that contribute to the understanding of the supramolecular interactions, highlighting ion-dipole pair formations, between cationic surfactants and asphaltene molecules (**Asph**) [11–15]. The performance of ionic liquids used in the process of changing

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http://dx.doi.org/10.1016/j.jiec.2016.08.031
1226-086X/

wettability is based on the characteristics of both the rock and the ionic nature of the surfactant agent. Other studies have been published indicating the formation of ion pairs between cationic surfactants and anionic acidic oil components adsorbed on a surface of limestone or calcite, that is more effective and stress the importance of those charges and properties of the rock, crude oil and surfactant chemical characteristics [16–18]. The use of branched geminal zwitterionic liquids (**BGZLs**) which unlike cationic or anionic surfactants contain positive and negative charges on different atoms on the same molecule, *i.e.*, although they are electrically neutral and gives them the ability to behave as acids or bases (donor or acceptor, respectively) according to the environmental characteristics in which they are [19–24], *i.e.* are able to respond efficiently according to the characteristics of one or more means by which enables its application as wettability modifier on limestone surfaces without affecting their lithology. By the other hand, the **BGZLs** have the ability to reduce the viscosity of heavy crude oil increasing the oil recovery factor (**ORF**) [11]. To explain the viscosity reduction effect of heavy crude oil by **BGZLs,** is necessary to explain the disaggregation phenomena. Firstly, the formation of **Asph:BGZL:Asph** forming by **BGZLs** and **Asph:Asph** dimmer is proposed. This supramolecular complex lead to viscosity reduction by zwitterion-dipole pair **Asph:BGZL** formation process. The resultant complex is less viscous than the original crude oil adsorbed on the surface of the rock and the interfacial tension decreases, which is an important advantage that impact in the **ORF**, subsequently water imbibition occurs by capillary forces in the rock surface with this raising the recovery mechanism of crude oil by use of **BGZLs** [11,25–27]. We have previously performed the design of geminal zwitterionic liquids by molecular modeling, where several mechanisms proposed through the geminal zwitterionic liquids act as wettability modifiers [23,28,29], likewise synthesis of geminal zwitterionic liquids for application in **EOR** where the synthesis route presented the use of primary amines [30]. In this research, we innovated the synthesis route where secondary amines with different length in alkyl chains is used [25], spectroscopic characterization, the use of **BGZLs** as wettability modifiers in limestone lithology, also we made the determination of the viscosity reduction with heavy crude oil. The experimental evidence and the theoretical studies presented in this work present enough evidence to support the hypothesis that the **BGZLs** agents have the capability to change the rock wettability and reduce the oil viscosity by two mechanism that occur in parallel in the hole system.

Methodology

Molecular modeling

BGZLs have been modeled through a central curved alkyl chain containing 13 ether groups and one zwitterionic moiety (formed by a quaternary-amine and carboxylate group) bridging each of the curved alkyl chain ends with a pair of straight alkyl branches having 8 (**BGZL-ZW8**, Fig. 1c) or 12 (**BGZL-ZW12**, Fig. 1d) carbons in length. The **Asph** molecule (Fig. 1a) has been modeled following the literature, i.e., through fused aromatic and heteroaromatic rings such as phenolic (**OH**), thiophene (**S**) and pyridinic (**N**) groups [31,32]. The **Asph** model represents the average characteristics of heavy oil from the Marine Region in México.

We have chosen the (104) calcite surface as the model for a fractured oil reservoir rock since it is known that this surface is the most probable exposed one[33]. From the computational bulk structure included at the database of the Materials Studio (**MS**) software[34], we built a molecular model for the **Cs** in a cell; this results in an unit cell possessing dimensions of **a** = 8.10, **b** = 4.99, and **c** = 32.00 Å. In order to calculate the interaction energy of single molecules with the **Cs**, we have built simulation cells (**SC**) with extended dimensions of **5** × **5** relative to the above unit surface cell along **a** and **b** axis, which were sufficient to fully allocate the large **Asph** molecules; thus, the simulation cell dimensions are $\mathbf{a_{sc}}$ = 40.47, $\mathbf{b_{sc}}$ = 24.95, and $\mathbf{c_{sc}}$ = 32.00 Å. After a molecular or crystal structure is built, it usually needs to be refined to bring it to a stable geometry. The refinement process is known as optimization, and is an iterative procedure in which the

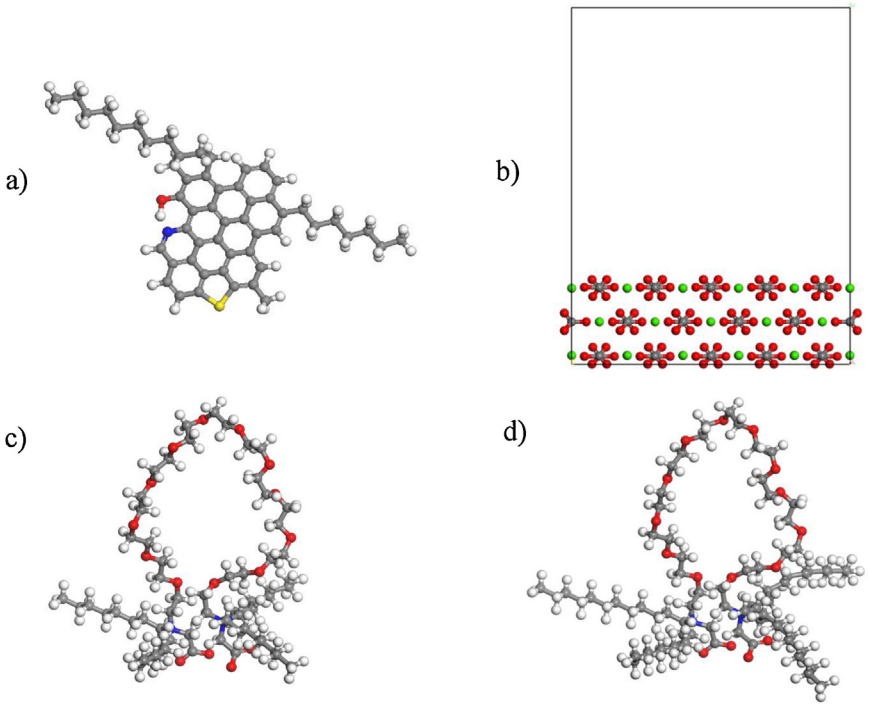

Fig. 1. Optimized geometries for: (a) **Asph**, (b) calcite surface, (c) **BGZL-ZW8** and (d) **BGZL-ZW12**. Organic molecules were led to minimal energies inside empty **SC**s (not shown in the sake of clarity) having the same dimensions of the calcite-surface-containing cell.

Please cite this article in press as: J.F. Ramírez-Pérez, et al., J. Ind. Eng. Chem. (2016), http://dx.doi.org/10.1016/j.jiec.2016.08.031