



ORIGINAL ARTICLE

# Molecular modeling, synthesis and characterization of branched geminal zwitterionic liquids for enhanced oil recovery



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**Abstract** A Sulfobetaine-based Branched Geminal Zwitterionic Liquid (SBGZL) and another one based on hydroxysultaine (HBGZL), were synthesized and their performance was evaluated in the enhancement of the oil recovery (EOR) when they are injected through flooding water into carbonate reservoirs. SBGZL obtained 39.4% and 215.5% more recovery factor for light- and heavy-oil, respectively, than obtained by a synthetic brine used as a reference; conversely, HBGZL obtained 37.5% and 44.7%, respectively. Density-Functional-Theory calculations of interaction energies reveal that both the SBGZL and HBGZL molecules adsorb on the carbonate surfaces stronger than an asphaltene molecule, implying that the good EOR performance of the zwitterionic liquids is due to the induced wettability change of the firstly-oil-wet carbonate surfaces.

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## 1. Introduction

Despite there exist in the world very-important and significant advances within the development of wettability-modifier chemicals to be applied onto hydrocarbon extraction, currently in Mexico there exist remaining oil deposits difficult to treat due to they are naturally fractured, exhibit low permeability, present heterogeneous lithologies, have high temperatures (greater than 90 °C), have high salinity (generally higher than 60,000 ppm as sodium chloride) and, especially, exhibit high content of divalent ions such as calcium and magnesium (more than 5000 ppm) (Hernandez-Altamirano et al., 2014 and references contained there).

In the field of Enhanced Oil Recovery (EOR) processes, chemicals have been designed to achieve wettability alteration to a more water-wet state in oil carbonate reservoirs by means of spontaneous imbibition (Pons-Jiménez et al., 2015). Nowadays, the design of novel and new Branched Geminal Zwitterionic Liquids (BGZL) structures has been addressed to be applied in EOR since they are tolerant to extreme conditions of high-temperatures, high-pressures, high-water salinities and high-hardnesses (Lopez-Chavez et al., 2012a,b; Lopez-Chavez et al., 2014). In particular, the Branched Geminal Zwitterionic Liquids based either in sulfobetaine (SBGZL) or in hydroxysultaine (HBGZL) are characterized to be electrically neutral, possess hydrophobic chains and zwitterionic polar groups and exhibit chirality.

As far as we know, there are not in the literature any references about SBGZL and HBGZL suggesting their applications to production processes nor their use as modifiers of wettability and corrosion inhibitors, although these chemicals can be exposed to brines with high content of divalent ions such as calcium, magnesium, barium and strontium (150,000 ppm), temperatures up to 220 °C and pressures up to 300 kg/cm<sup>2</sup>. At present paper, through experimental and theoretical approaches, we investigate the promising application of them to alter the rock wettability and then to favorably enhance the recovery of crude oil embedded in rocks such as calcite (Cal) and dolomite (Dol). Also, we briefly describe a possible chemical mechanism explaining the increase in oil recovery factor (ORF) found in this study.

## 2. Experimental

### 2.1. Materials and methods

All salts for brine, reagents, and solvents were acquired from Aldrich Chemical Co. (reagent grade) and used without additional purification. All Nuclear Magnetic Resonance (NMR) spectra <sup>1</sup>H and <sup>13</sup>C were recorded on a VARIAN Mercury 200-BB spectrometer in CDCl<sub>3</sub>. The chemical shifts ( $\delta$ ) are measured in ppm and referenced to the internal SiMe<sub>4</sub> (TMS) peak. Coupling constants (*J*) are measured in Hz. IR Spectra were recorded on a Bruker-Tensor 27 FT-IR using ATR mode. The heavy crude oil (HCO) utilized in this study was provided by the Mexican state-owned petroleum company PEMEX from a marine well drilled in the south of the Gulf of Mexico. The samples were characterized by the following standard procedure: Saturated, Aromatics, Resins and Asphaltenes ASTM D-2007-03 content (ASTM, 2011), whereas the Stiff and Davis Stability Index was calculated for the brines.

### 2.2. Synthesis of zwitterionic liquids

The general supramolecular synthesis of SBGZL and HBGZL is shown in Scheme 1.

#### 2.2.1. Synthesis of SBGZL

**2.2.1.1. First stage.** In a 50 mL round bottom flask containing 5.0 g of an aqueous 17% w/w solution of sodium hydroxide

(0.85 g, 21.25 mmol), it is added 4.24 g (7.75 mmol) of polyethylene glycol, whose number average molecular weight is 600 g/mol. The mixture was stirred for 20 min. After this time it is slowly added, at room temperature (20 °C) and atmospheric pressure, 7.37 g of a 40% w/w solution of tosyl chloride (2.95 g, 15.47 mmol) in tetrahydrofuran. Then, the reaction mixture was stirred for one hour at room temperature and subsequently the reaction mixture was placed in a separation funnel to recover the organic phase. The solvent was removed under reduced pressure, obtaining 6.27 g (7.47 mmol, yield 96%) of the product ditosylate polyether (TS-PE, **I**) as a clear yellow viscous liquid.

**2.2.1.2. Second stage.** In a 50 mL two neck round-bottom flask provided with a condenser, magnetic stirrer and thermometer, it is added dioctylamine (1.97 g, 8.16 mmol), TS-PE (6.27 g, mmol), potassium carbonate (4.77 g, 34.51 mmol) and 23 mL of acetonitrile. The reaction mixture was heated to reflux vigorously stirred for 8 h.

Once the reaction time was completed, the mixture was washed with water and carried out an extraction of the organic phase, which was evaporated under reduced pressure to obtain 6.18 g (6.12 mmol, yield 82%) of the product bis-N,N-dioctyl-N-polyether as a viscous amber liquid (**II**).

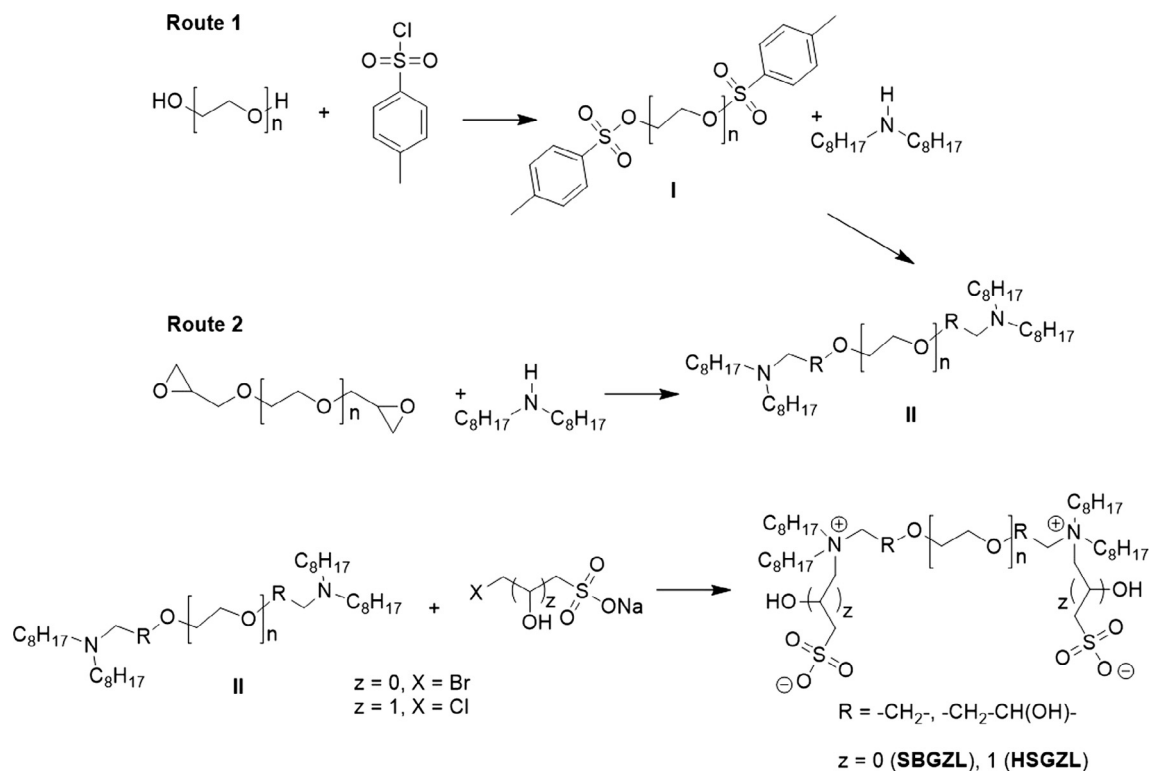
**2.2.1.3. Third stage.** In a 100 mL round-bottom flask provided with condenser, magnetic stirrer and thermometer, it is placed bis-N,N-dioctyl-N-polyether (6.18 g) and a solution of sodium 2-bromo ethane sulfonate (2.77 g, 13.13 mmol) in 50 g of water was added. The reaction mixture was placed under reflux and stirred vigorously for 48 h. Once the reaction time was completed, the aqueous phase was separated and evaporated under reduced pressure. The residue was washed with chloroform to remove the salts by filtration. The organic fraction was evaporated under reduced pressure to obtain 6.84 g (5.58 mmol, yield 91%) of a viscous and amber-in-color zwitterionic liquid, labeled as bis-N,N-dioctyl-N-sulfobetaine polyether (SBGZL).

#### 2.2.2. Synthesis of HBGZL

**2.2.2.1. First stage.** In a 50 mL round-bottom flask, 10 g (19 mmol) of polyethylene glycol diglycidyl ether (526 g/mol of average molecular weight) and 3.5 g (14.5 mmol) of dioctylamine were stirred for 1 h at 95 °C to obtain 13.5 g (13.37 mmol, yield 92%) of the bis-N,N-dioctyl-N-hydroxy polyether as a transparent yellow viscous liquid.

**2.2.2.2. Second stage.** In a 100 mL round-bottom flask, provided with a condenser, magnetic stirrer and a thermometer, it was placed 2 g (1.98 mmol) of bis-N,N-dioctyl-N-hydroxy polyether and a solution of 0.86 g (4.38 mmol) of sodium 3-chloro-2-hydroxypropane sulfonate in 15 g of water. The reaction mixture was placed under reflux conditions and stirred vigorously for 72 h.

Once the reaction time was completed, the aqueous phase was separated and evaporated under reduced pressure. The dry product was washed with chloroform to remove the salts by filtration. The solvent was removed to obtain 1.4 g (1.01 mmol, yield 51%) of the zwitterionic geminal liquid as a viscous and amber labeled bis-N,N-dioctyl-N-polyether hydroxysultaine (HBGZL).



**Scheme 1** Synthetic route for prepare zwitterionic liquids base sulfobetaine (SBGZL) and hydroxysultaine (HBGZL).

### 2.3. Computational construction of molecular structures

Theoretical studies on supramolecular interactions between BGZLs, asphaltene (Asph) and reservoir rocks in a water environment, were performed via Density Functional Theory (DFT). The water environment is taken into account since SBGZL and HBGZL are injected into oil reservoir through an aqueous solution, and it was simulated through its dielectric continuum (permeability constant: 78.54), as treated in the Conductor-like Screening Model (COSMO) approach (Klamt and Schüürmann, 1993).

It was used the Materials Studio (MS) interface (Version 7.0, 2012) to build molecular models of Asph, SBGZL, HBGZL, as well as Cal and Dol surfaces. SBGZL has been modeled consisting of a central curved alkyl chain, which contains 12 ether groups, at whose each of the two ends was attached one zwitterionic moiety (formed by a sulfobetaine group) bridging the curved alkyl chain ends with a pair of straight alkyl tail branches having 8 carbons in length (Fig. 1A). HBGZL has been modeled in a similar manner as SBGZL but includes a hydroxyl group at each zwitterionic head. Asph molecule has been modeled following the literature (Fig. 1B) (Buenrostro-Gonzalez et al., 2004), *i.e.*, through fused aromatic and heteroaromatic rings such as phenolic (OH), thiophene and pyridine groups. This asphaltene molecule represents the average characteristics of a HCO from the Marina District in Mexico (Hernandez-Altamirano et al., 2014).

In order to investigate adsorption of BGZLs and Asph on carbonate rocks of oil reservoirs, (104) surfaces of Cal and Dol were modeled (Pons-Jiménez et al., 2014).

To obtain the optimized molecular geometries for all complexes, DFT computations through MS DMol3 application

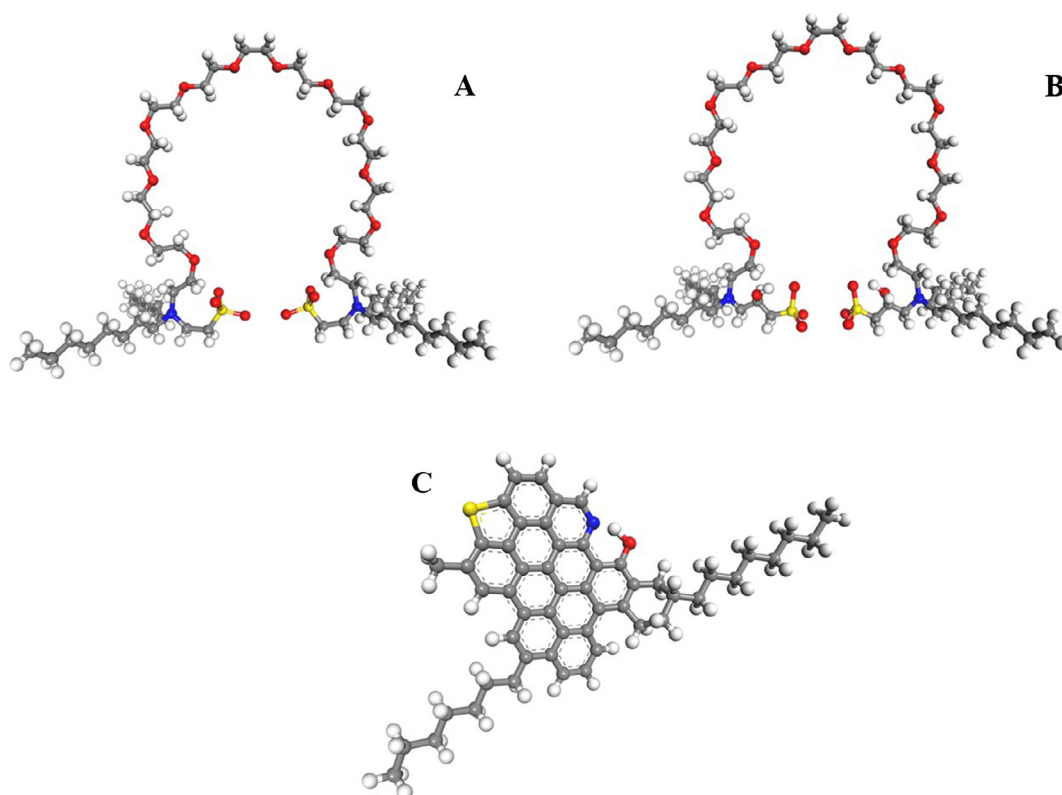
were executed in water environment. The molecular model of SBGZL, HBGZL or Asph was put over Cal and Dol surfaces in an orthorhombic simulation cell in such a manner that the adjacent molecule images, which appear due to the periodic boundaries, were separated by around 10 Å; so, the chosen cell dimensions were  $a = 32.38$ ,  $b = 24.95$  and  $c = 41.00$  Å for Cal, and  $a = 30.79$ ,  $b = 24.03$  and  $c = 41.00$  Å for Dol. The cells having these dimensions are denoted herein as Cal cell and Dol cell, respectively.

DMol3 runs were performed within the Local-Density Approximation (LDA), using the functional by Vosko S.H., Wilk L. and Nusair M. (VWN) (Vosko et al., 1980), the Double Numerical (DN) basis set, the Ortman, Bechstedt and Schmidt method for the DFT-Dispersion correction (Ortman et al., 2006), the Effective Core Potentials for core treatment (Dolg et al., 1987; Bergner et al., 1993), spin-polarized electrons, and water as the solvent. All run parameters were set at the coarse accuracy option.

Interaction energy  $\Delta E$  calculations for SBGZL, HBGZL and Asph molecules on carbonate surfaces in water environment can give insights into the performance of SBGZL and HBGZL in an oil field, and they were quantified for the pairs SBGZL/Cal, SBGZL/Dol, HBGZL/Cal, HBGZL/Dol, Asph/Cal and Asph/Dol through  $\Delta E = E_{M/S} - (E_M + E_S)$ , where  $E_M$ ,  $E_S$  and  $E_{M/S}$  are the total energies of individual molecules, pristine surfaces, and interacting molecule/surface system, respectively.

### 2.4. Spontaneous imbibition tests to determine ORF

The effects on the ORF by addition of SBGZL and HBGZL to brines were determined through tests of spontaneous



**Figure 1** Perspective view of molecular models of branched geminal zwitterionic liquid based on sulfobetaine (A), hydroxysultaine (B) and asphaltene (C). Atom colors stand for the following: gray, carbon; white, hydrogen; red, oxygen; blue, nitrogen; and yellow, sulfur.

imbibition over oil-containing Bedford Cal limestone cores in contact with the brine (Hernandez-Altamirano et al., 2014). Spontaneous imbibition tests using brine with added 0.03 wt% (300 ppm) of SBGZL and HBGZL were performed, and the results were compared with those of a reference consisting in brine without BGZL.

All tests were performed in a standard Amott cell (Hernandez-Altamirano et al., 2014). The Cal cores were impregnated separately with light and heavy oils at 120 °C under atmospheric pressure. After cooling to room temperature, the cores were placed into Amott cells at 90 °C, and then poured into either the pure brine or the surfactant-added brine. All systems were maintained at 90 °C temperature during 15 days and the oil recovery was monitored all of the time.

At the end of the experiment, the oil produced was gravimetrically determined using the equation:

$$F_r = \frac{A_r}{A_o} \times 100, \quad (1)$$

**Table 1** SARA analysis (in wt%) as well as acid and basic numbers (in mg KOH(g oil)<sup>-1</sup>) for Mexican oils.

Properties	Oil	
	Light	Heavy
Saturated	30.68	13.40
Aromatics	28.62	24.76
Resins	39.35	51.01
Asphaltenes	1.32	10.44
Acid number	0.21	1.83
Basic number	1.70	2.12

**Table 2** Composition and properties of brines at 20 °C temperature.

	Brine 1	Brine 2
Density (g/cm <sup>3</sup> )	1.0043	1.0216
pH	7.65	6.68
Turbidity (FTU)	4	15
<i>Cations (mg/L)</i>		
Na <sup>+</sup>	1703.66	11,630.06
Ca <sup>2+</sup>	416.00	1976.00
Mg <sup>2+</sup>	106.95	427.86
Fe <sup>2+</sup>	0.06	0.25
Ba <sup>2+</sup>	35	–
<i>Anions (mg/L)</i>		
Cl <sup>-</sup>	3200.00	22,000.00
SO <sub>4</sub> <sup>2-</sup>	350.00	825.00
HCO <sub>3</sub> <sup>-</sup>	405.04	122.00
Hardness as CaCO <sub>3</sub>	1480.00	6700.00
Salinity as NaCl	5275.00	36,265.59

where  $F_r$  is the recovery factor,  $A_r$  is the mass amount of recovered oil and  $A_o$  is the one of the original oil adsorbed in porous media.

### 3. Results and discussion

#### 3.1. Spectroscopic characterization of SBGZL and HBGZL

All compounds were obtained in high yields through two synthetic routes and were characterized by NMR and infrared

spectroscopies. The corresponding signals were observed for each intermediate involved in the reactions step. For SBGZL, there were observed  $^1\text{H}$  NMR signals around 3.94 ppm corresponding to the ether groups, as well as from 1.28 to 0.86 ppm due to the alkyl chains. Also, the  $^{13}\text{C}$  NMR signal at 70.4 ppm reveals the presence of carbon linked to sulfonate group, and peaks at 65.4 and 53.3 ppm mean there are C–N bonds. Infrared spectra show a band in  $1221\text{ cm}^{-1}$  corresponding to sulfonate group. Besides,  $1641\text{ cm}^{-1}$  confirms again C–N bonds.

On the other hand, infrared spectrum for HBGZL shows a peak at  $3423\text{ cm}^{-1}$  evidencing the OH group, whereas peaks at  $1647$  and  $1222\text{ cm}^{-1}$  reveal ammonium and sulfonate groups, respectively. The HBGZL NMR spectrum is analogous to the SBGZL one. The experimental confirmation on the presence of the above functional groups gives confidence on the molecular structures modeled at present paper. Below are the details of the NMR spectra:

### 3.1.1. SBGZL

$^1\text{H}$  NMR: 3.94 (m,  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n-$ ), 3.61 (m,  $-\text{NCH}_2\text{CH}_2\text{O}-$ ), 3.27 (m,  $-\text{NCH}_2\text{CH}_2\text{O}-$ ), 3.05 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.75 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.28 (m, alkyl chain), 0.86 (m, Me).  $^{13}\text{C}$  NMR: 70.4 ( $\text{C}\text{SO}_3^-$ ), 65.4, 53.3 (C–N), 52.1 (C–N), 31.1, 22.3 ( $\text{RCH}_2\text{Me}$ ), 13.9 (Me). IR, ATR ( $\text{cm}^{-1}$ ): 2922 ( $\nu_{\text{asymm CH}}$ ), 2853 ( $\nu_{\text{symm CH}}$ ), 1641 ( $\nu_{\text{C-N}}$ ), 1464 ( $\delta_{\text{CH}_2}$ ), 1221 ( $\nu_{\text{SO}_3}$ ), 1098 ( $\nu_{\text{symm ether linkage}}$ ).

### 3.1.2. HBGZL

$^1\text{H}$  NMR: 3.85 (m,  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n-$ ), 3.58 (m,  $-\text{NCH}_2\text{CH}_2\text{O}-$ ), 3.25 (m,  $-\text{NCH}_2\text{CH}_2\text{O}-$ ), 3.20 (m), 3.03 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 2.99 (m), 1.26 (m,  $-\text{NCH}_2\text{CH}_2-$ ), 1.24 (m, alkyl chain), 0.83 (m, Me).  $^{13}\text{C}$  NMR: 70.3 ( $\text{C}\text{SO}_3^-$ ), 65.5, 53.2 (C–N), 52.1 (C–N), 31.0, 22.3 ( $\text{RCH}_2\text{Me}$ ), 13.8 (Me). IR, ATR ( $\text{cm}^{-1}$ ): 3423 ( $\nu_{\text{O-H}}$ ) 2922 ( $\nu_{\text{asymm CH}}$ ), 2853 ( $\nu_{\text{symm CH}}$ ), 1647 ( $\nu_{\text{C-N}}$ ), 1465 ( $\delta_{\text{CH}_2}$ ), 1222 ( $\nu_{\text{SO}_3}$ ), 1098 ( $\nu_{\text{symm ether linkage}}$ ).

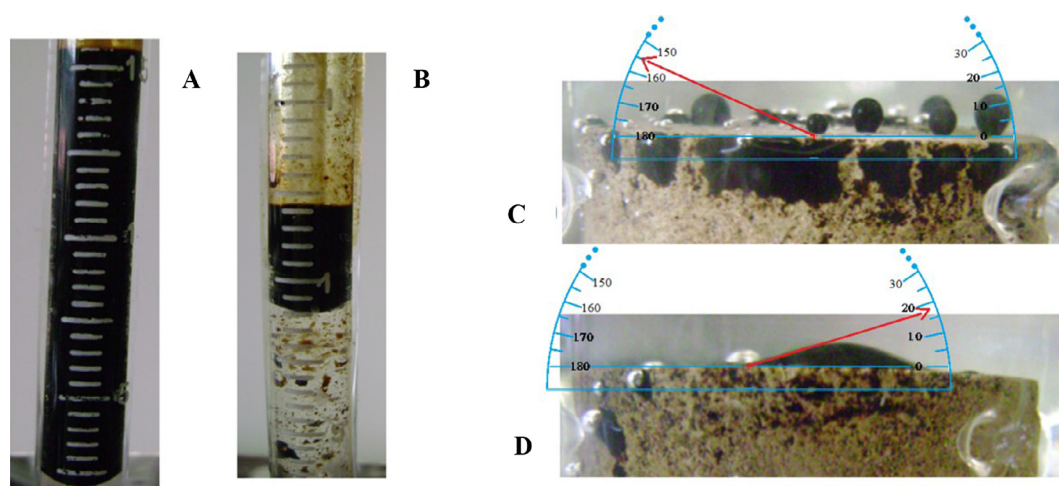
### 3.2. Oil and carbonate cores properties

Spontaneous imbibition tests used real light and heavy oils extracted from Mexican southeastern fields, whose saturated, aromatic, resin and asphaltene (SARA) analyses are shown in Table 1.

Two natural brines contained also at Mexican reservoirs, possessing high salinity and high content of calcium (Table 2) were used in all experiments to resemble conveniently the conditions of the oil fields. They are labeled as Brine 1 and Brine 2, and are used to recover light and heavy oils, respectively.

A number of cylindrical carbonate cores were employed to perform imbibition tests simulating the matrix rock of real reservoirs. Their permeabilities to helium are around 66 mD, the average porosity to water is 20%, and the diameter and height dimensions are around 3.8 and 7.0 cm, respectively.

Experimental results show that BGZL performs better than the reference brine since former recovers more oil

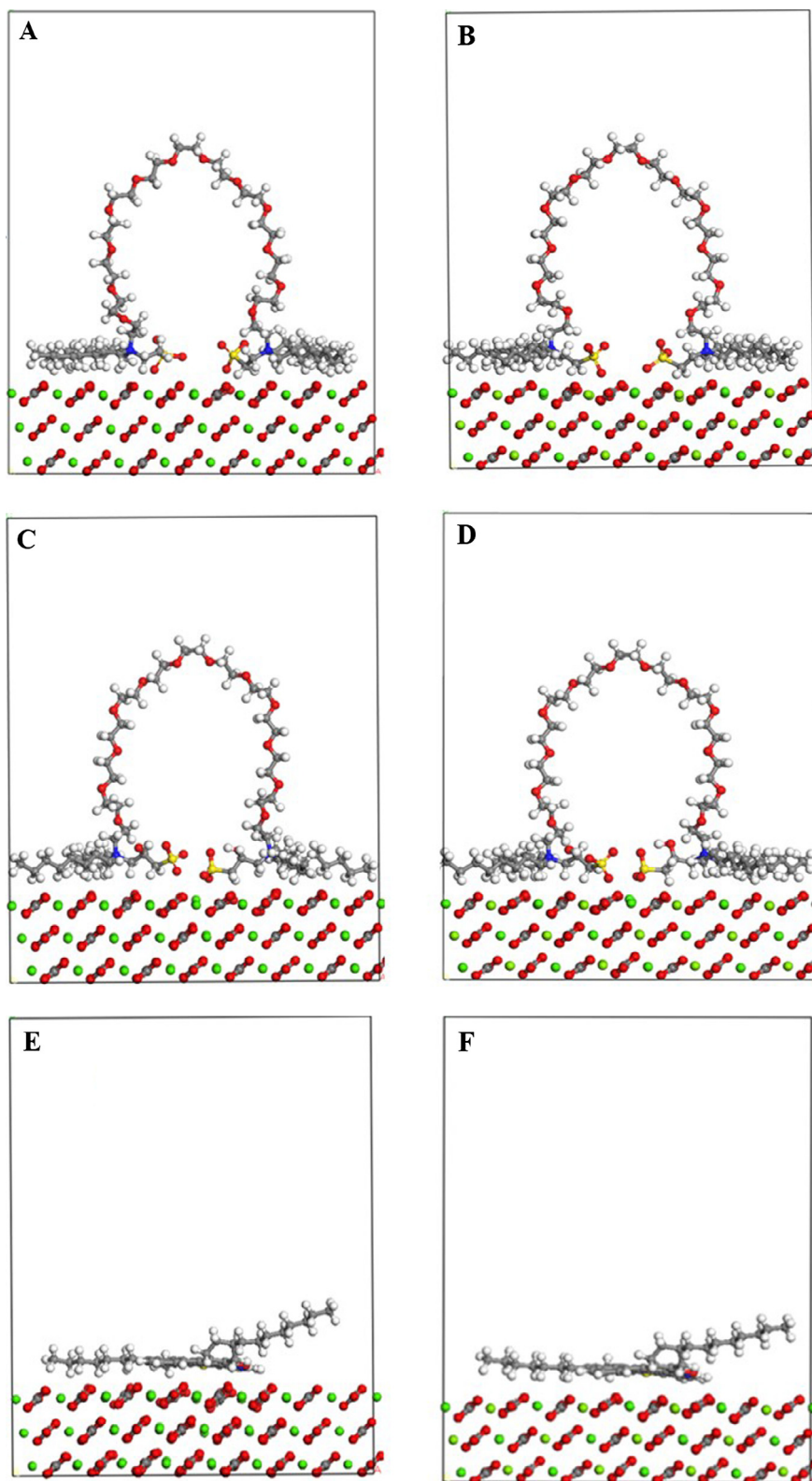


**Figure 2** Recovered heavy oil using (A) a GZL-containing brine and (B) the reference brine. Contact angles produced by using (C) a GZL-containing brine and (D) the reference brine.

**Table 3** Light and heavy oil recoveries using Brine 1 and Brine 2, respectively.

Chemical dissolved in brines	Light oil			Heavy oil		
	Impregnated (g)	Recovered (g)	$F_r$ (%)	Impregnated (g)	Recovered (g)	$F_r$ (%)
None	12.2874	4.5796	37.3	6.8124	0.8364	12.3
SBGZL	12.1547	6.3253	52.0	6.2834	2.4394	38.8
HBGZL	11.8760	6.0987	51.3	6.3646	1.1320	17.8

15-day duration of the imbibition tests.



**Figure 3** DFT optimized molecular models for SBGZL and HBGZL over A, C Cal and B, D Dol surfaces respectively, and for Asph over E Cal and F Dol surfaces. Atom colors are as in Fig. 1; additionally, dark and light green colors stand for Ca and Mg atoms, respectively.

**Table 4** Total energy of individual molecules and pristine carbonate surfaces, and interaction energy for the adsorption of SBGZL, HBGZL and Asph molecules on the pristine carbonate surfaces.

Individual or interacting systems	Carbonate-surface simulation cell	
	Cal cell	Dol cell
	Total energy (kcal/mol)	
SBGZL	-2,926,840.81	-2,926,839.73
HBGZL	-3,069,493.08	-3,069,494.20
Asph	-1,605,263.02	-1,605,263.16
Carbonate surface	-70,629,863.94	-52,685,361.02
SBGZL on the carbonate surface	-73,556,996.58	-55,612,462.60
HBGZL on the carbonate surface	-73,699,632.38	-55,755,154.16
Asph on the carbonate surface	-72,235,338.79	-54,290,818.26
Interacting systems	Interaction energy (kcal/mol)	
SBGZL on the carbonate surface	-291.83	-261.85
HBGZL on the carbonate surface	-275.36	-298.93
Asph on the carbonate surface	-211.83	-194.08

(Fig. 2A and B, and Table 3), *i.e.*, SBGZL and HBGZL recover about 1.3 times more light oil than the reference brine (Table 3). In the case of heavy oil, SBGZL recovers more than 3 times and HBGZL about 1.5 times the oil amount recovered by the reference brine.

Moreover, BGZL alters rock wettability but reference brine does not, from being oil-wet to water-wet (Fig. 2C and D). Latter fact reveals that BGZL molecules replace oil ones over the carbonate surfaces, it being their ether groups responsible for the induced affinity of carbonate surfaces to water.

### 3.3. Theoretical results

DFT results show that an Asph molecule approaches more closely onto Cal surface than onto Dol surface because the Asph OH-group interacts more intensively with  $\text{Ca}^{2+}$  than with  $\text{Mg}^{2+}$  atoms, as it is revealed by the OH- $\text{Ca}^{2+}$  distance (Fig. 3E) which is shorter than the OH- $\text{Mg}^{2+}$  distance (Fig. 3F). This suggests a more intense adsorption of Asph by Cal surface and it is confirmed through the interaction energies among Asph molecule and carbonate surfaces (Table 4) since Cal surface yields an interaction energy 9.15% more negative than Dol surface. Besides, bearing in mind the relative sizes among Asph (110 atoms) and water (3 atoms) molecules, it is expected that the interaction energy among Asph and carbonate surface is much more negative than that among water and the same carbonate surface, explaining the known tendency of the carbonate rock to be oil-wet (Pons-Jiménez et al., 2015; Lopez-Chavez et al., 2014).

However, interaction energies among SBGZL, HBGZL and the carbonate surfaces are more negative than those yielded by Asph (Fig. 3 and Table 4). In fact, SBGZL adsorbs more strongly to Cal surface than HBGZL, leading to the better EOR performance of SBGZL over HBGZL when they act on Cal cores. It is worthy to note that theoretical results

predict that on Dol cores HBGZL performs better than SBGZL instead. The theoretical result for Cal cores explains the above experimental result about the better EOR performance of SBGZL.

Following the molecular mechanism proposed by Mirna (Pons-Jiménez et al., 2014), there would exist supramolecular interactions among either SBGZL or HBGZL and the oil molecules to form zwitterion-dipole pairs. These pairs travel within the oil phase and arrive to the pore walls of cores, where BGZLs attractively interact with the carbonate surface more strongly than the adsorbed oil molecules and then latter are removed. Ether groups of BGZLs allow rock surface to become water-wet, emerging capillary forces that lead to water imbibition and thus the oil displacement. Details of this molecular mechanism explaining the enhancement of the oil recover will be given in a paper we are preparing.

## 4. Conclusions

Smart chemicals SBGZL and HBGZL were designed to have a greater adherence than oil to the oil reservoir rocks and then to change the rock wettability. The adsorption energies (*i.e.*, the negative of the interaction energies) of SBGZL molecules over carbonate rock surfaces, in comparison with the ones of the Asph molecule, are around 38% and 35% greater for Cal and Dol surfaces; in the case of the HBGZL, this tendency is reversed with around of 54% and 30% for Dol and Cal surface, respectively. Experimentally, SBGZL-containing flooding water injected within Cal cores obtained 39.4% and 215.5% more recovery factor for light- and heavy-oil, respectively. Conversely, HBGZL obtained an oil recovery factor greater than that of the reference by 37.5% and 44.7% for light- and heavy-oil, respectively. The above theoretical and experimental results suggest that both SBGZL and HBGZL increase the oil recovery factor, regardless of the light or heavy nature of the oil, by alteration of the wettability of the firstly-oil-wet carbonate rock, and that the *ab initio* adsorption-energies computations of BGZLs and Asph molecules over carbonate rock could be of vital importance to infer the technical feasibility and moneymaking of BGZLs as chemicals for application in the EOR.

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