



Quantum chemical characterization of zwitterionic structures: Supramolecular complexes for modifying the wettability of oil–water–limestone system

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ABSTRACT

In this work, we present a quantum chemical study pertaining to some supramolecular complexes acting as wettability modifiers of oil–water–limestone system. The complexes studied are derived from zwitterionic liquids of the types N⁺-alkyl-bis, N-alkenil, N-cycloalkyl, N-amylo-bis-beta amino acid or salts acting as sparkling agents. We studied two molecules of zwitterionic liquids (ZL10 and ZL13), HOMO and LUMO levels, and the energy gap between them, were calculated, as well as the electron affinity (EA) and ionization potential (IP), chemical potential, chemical hardness, chemical electrophilicity index and selectivity descriptors such Fukui indices. In this work, electrochemical comparison was realized with cocamidopropyl betaine (CPB), which is a structure zwitterionic liquid type, nowadays widely applied in enhanced recovery processes.

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1. Introduction

For over 30 years, chemically-based improved oil recovery methods have generated great interest among researchers and technologists [1,2]. Chemical methods focus mainly on alkaline–surfactant–polymer (ASP) processes that involve the injection of micellar-polymers into the reservoirs. Chemical flooding reduces the interfacial tension between in-place crude oil and injected water, allowing the oil to be extracted. Micellar fluids are composed largely of surfactants mixed with water. The twice-fold goal of polymer floods is to shut off excess water in the producing wells while improving the sweep efficiency in order to produce more oil. Chemical field trials by industry indicate that surfactants can recover up to an additional 28% of reservoir oil; however the economics have not been favorable when the price of oil is factored against the cost of surfactants and polymers [3]. A new chemical product, based on novel molecules of zwitterionic liquid (ZL), has

recently been proposed as an oil recovery enhancer. A great amount of studies on the structural, physical and chemical properties of zwitterionic liquids [3] have been carried out over the last two decades [4]. The results of these studies show the beginning of a new, improved, oil recovery method [5,6]. In the beginning of the year 2010, two new structures, based on zwitterionic liquids (ZL10 and ZL13), were proposed by Zamudio-Rivera et al. [7,8], based on the consideration that germinal zwitterionic molecules are characterized by having two hydrocarbon chains, one bridge, and two polar groups of zwitterionic class. Since then, as far as we know, no other authors have proposed similar models [9].

Although a large variety of new ZL forms structures have been proposed, many of their physical and chemical properties have not yet been reported or clearly understood, so that a deeper study is undoubtedly necessary [10].

Among the important physicochemical properties of ZL structures, the reactivity and selectivity descriptors play a key role. The knowledge of both global and local reactivity descriptors of ZL structures will allow us to predict the wettability-modifying ability of these molecules on oil–limestone and water–limestone systems. Presumably, even a quick analysis of these values can be used to understand the relationships between the structure, the

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stability and the electrochemistry of this molecule. In addition, the understanding of the chemical mechanisms of reaction between ZL and other molecules will allow us to visualize their potential technological applications in enhanced oil recovery (EOR) methods.

One of the most important questions connected with the problem of reactivity of molecules in different environmental conditions is the prediction and interpretation of the preferred direction of a reaction and the product formation [11]. The study of molecular interactions has been a great challenge from the experimental and theoretical point of view [12]. There have been a lot of attempts to explain the nature of bonding and reactivity of molecular systems based on some facts and intuitive ideas [13,14]. During quantum chemical methods development, many of the empirical chemical concepts were rigorously derived, thus providing a method for the calculation of chemical properties based on molecular structure and properties [15].

Within the context of density functional theory (DFT), rigorous theoretical basis for the descriptors of global and local reactivity indices have been provided. These reactivity indices are better appreciated in terms of the associated electronic structure principles such as electronegativity equalization principle, hard–soft acid–base (HSAB) principle [16], maximum hardness principle (MHP) [17], minimum polarizability principle (MPP) [18] and generalized philicity [19]. The global reactivity indices such as chemical hardness, chemical potential and electrophilicity are used to understand the chemical reactivity; whereas the local quantities such Fukui functions, local softness and local philicity indices have been employed to prove site selectivity and the reactivity of molecular systems of size ranging from small organic molecules to reasonably large drug molecules [20,21].

Furthermore, in Fukui's Frontier Orbital Theory [22], Fukui functions measure how sensitive a molecule's chemical potential is for external perturbations at a particular point, i.e., chemical reactivity toward nucleophiles or electrophiles is interpreted in terms of the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) electron density. For an electrophilic attack, the reaction will have effect where the HOMO electron density is the largest in the molecule. Similarly, for a nucleophilic reaction, the LUMO electron density indicates the chosen sites in the molecule. Fukui functions have been calculated for a large group of organic molecules, and it was thought that their values should always be positive, however, the occurrence of negative Fukui functions has been demonstrated by means of the electronegativity equalization method [23].

In this work, based on the above-mentioned issues, we have calculated chemical reactivity and selectivity indices of the most stable structures of ZL10 and ZL13 molecules with the aim of predicting the ability of molecules to undergo addition reactions and finding the preferred directions and sites of reaction on oil (asphaltene), rock (calcite or limestone) and water.

2. Methods

Since we treat the ZL10 and ZL13 as isolated molecules, the methodology used in this work is based on calculations performed with DMol3, a DFT computational code [24] of Materials Studio 6.0 specialized in quantum mechanical calculations on molecules.

The geometry of ZL10 and ZL13 are depicted in Figs. 1 and 2, respectively, along with atom numbering of both carbon and hydrogen atoms, which will be resumed in Tables 2 and 3 as charge distribution data on the respective structures. The geometries of these structures were optimized using the functional LDA-VWN [24] with a DN basis set. Previous studies on similar molecular systems show that LDA-VWN provides comparatively reliable results [25]. The calculations were carried out using DFT effective core potential as

approximation of treatment of core electrons, multipolar expansion hexadecapole, smearing 0.005 Ha, direct inversion in an iterative (DIIS size = 10) subspace was used to speed up SCF convergence.

To study reactivity and selectivity of ZL10 and ZL13 based on DFT, the following reactivity and selectivity descriptors were calculated for minimum energy structure: the ionization potential (IP) and electron affinity (EA) through [26]

$$IP = E(M^+) - E(M) \quad (1)$$

$$EA = E(M) - E(M^-) \quad (2)$$

where $E(M^+)$ and $E(M^-)$ are the total energies of the ionic state of each molecule M ; i.e., IP and EA are the vertical ionization potential and vertical well of the neutral, respectively.

The chemical potential μ and hardness η are used extensively to make predictions about chemical behavior. The chemical potential μ is defined as the first derivative of the total energy respect to the number of electrons. The hardness is defined as the second derivative of the total energy, together with the concept of electronegativity and the principle of equalization of electronegativities, has been used to develop the principle of hard and soft acids and bases. The finite difference approximation applied to the chemical potential μ and hardness η leads to

$$\mu = -\frac{IP + EA}{2} \quad (3)$$

and

$$\eta = \frac{IP - EA}{2} \quad (4)$$

electrophilicity index (ω) is obtained with next equation:

$$\omega = \frac{\mu^2}{2\eta} \quad (5)$$

From there, Mulliken [27] population scheme is used in order to provide Fukui function (FF) values, charge distribution on each atom [28] of ZL10 and ZL13. For a system of N electrons, independent calculations have been made using Mulliken scheme in $N - 1$, N and $N + 1$, electronic systems with the same molecular geometry to get the charges $q_k(N - 1)$, $q_k(N)$ and $q_k(N + 1)$ for all atoms k and these values were substituted in the next equations:

$$f_k^+ = q_k(N + 1) - q_k(N) \quad (6)$$

$$f_k^- = q_k(N) - q_k(N - 1) \quad (7)$$

$$f_k^0 = \frac{q_k(N + 1) - q_k(N - 1)}{2} \quad (8)$$

which represent nucleophilic, electrophilic and radical attack, respectively.

3. Results and discussion

3.1. Geometry and stability

The minimum energy of ZL10 and ZL13 structures, are shown in Figs. 1 and 2, respectively, and they are constituted by polyglycols derived from ethylene oxide and propylene oxide, in conjunction with two hydroxyl groups, alkyl amines, acrylic acid. ZL10 has each alkyl chain with just 10 carbon atoms, while the ZL13 has 13 carbon atoms in each alkyl chain. This result is consistent with the general structure of germinal zwitterionic liquid reported by Yoshizawa [29].

In this work, the total energy of ZL10 and ZL13 structures refers to the sum of energy components (atomic energies, kinetic energy, electrostatic energy, exchange-correlation energy, spin polarization energy, and DFT-D correction) of a specific arrangement of atoms corresponding to ground state molecule structure. The zero

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