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Structural, energetic and thermodynamic properties of some anionic surfactants performed by DFT calculations. Impact on their adsorption on clays.

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ABSTRACT/RESUME

Abstract: *Calculations by functional density theory (DFT) at the level B3LYP/6-311G (d,p) were performed, to optimize the geometry of Sodium Dodecyl Sulfonic Acid (DSA), Sodium Dodecyl Sulfonate (DSNS), Sodium Dodecyl Sulfate (SDS), Sodium Dodecyl Benzene Sulfonate (SDBS) and Dodecyl Benzene Sulfonic Acid (DBSA) to determine their structural, energetic and thermodynamics parameters. The results obtained provided a rich database for the surfactants studied. The second part of this work is to determine the pollutants sizes in order to explore the possibilities of their adsorption on natural and modified montmorillonite (Mt (natural), Mt (Na), Mt (Ca), Mt (K) and Mt (Mg)). The results showed that the above pollutants cannot be adsorbed in the interlayer space of Mt (K) and Mt (Na). However, DSA can fit in the interlayer spaces of Mt(natural, MT (Ca) and MT (Mg). SDS can fit in MT (Ca) and MT (Mg) interlayer spaces. While DSNS can be adsorbed only in MT (Ca) interlayer space. However SDBA and SDBS could not be adsorbed on any of the studied clays. Molecular orbital calculations, HOMO and LUMO showed that these surfactants have a high reactivity and promote electrophilic interaction with the adsorbent. Thermodynamics data confirm the high reactivity of the studied surfactants and provide an important database.*

I. Introduction

Pollution of water and soil, accidentally or intentionally, by certain chemicals of industrial origin (hydrocarbons, phenols, dyes, detergents ...) or agriculture is a source of environmental degradation and is currently of particular international interest. The increase in the use of synthetic detergents led to the presence of high concentrations of surfactants in wastewater [1]. Studies about surfactants' ecotoxicity have shown that these compounds are not very toxic at concentrations below 3 $mg.L^{-1}$ [2]. However, their accumulation involves significant toxicity, which therefore presents a real danger to the environment. Several techniques have been used for the elimination of these various pollutants from waterways [3-7]. Clay minerals are ubiquitous in natural media and are good adsorbents of different ions and molecules. Through adsorption-desorption reactions, clay minerals can participate in the control of the environmental mobility of many substances. In addition, and due to their adsorptive properties, clay minerals are widely used for the removal of dyes and coloring substances from wool, oils, wines, fruit juices, fats and waxes; as Ca^{2+} remover in water softening, and as adsorbent of many pollutants [8]. Treatment by the adsorption technique is used for its

effectiveness in the reduction of organic micro-pollutants by involving solid-liquid interactions. Several studies have shown that adsorption on activated carbon is easily achievable [9], but clays (montmorillonite) have also shown a capacity for adsorption of wastewater, degreasing and bleaching polluted by industrial discharges. Adsorption on a solid material remains the cheapest and most profitable way [10-14]. Indeed, the experimental study of the adsorption of anionic surfactant on montmorillonite has been the subject of several works [15-17]. To explain the mechanism of pollutants adsorption on clays, scientists moved towards theoretical study of adsorption on these types of materials. Indeed, Hakem and al [18] studied the adsorption mechanisms of aniline ($C_6H_5NH_2$), on montmorillonite (MMTs) using density functional theory (DFT).Their theoretical investigations showed that the sorption of aniline on (MMTs) is due to interactions between the amino group of aniline and the silicon atom of siloxane surface of (MMTs). The adsorption process of aniline on the (MMTs) is found to be an exothermic physisorption process. Also Bardzińsk [19] used molecular mechanics and ab-initio investigations to study the impact of intermolecular interactions between the quaternary ammonium ions on interlayer spacing of quat-intercalated montmorillonite. Molecular mechanics calculations were carried out to study some cationic surfactants adsorption on montmorillonite [20], Hallouch and al [21] used molecular mechanics to study the structures of triazine group and molecular dynamics using Chem 3D software, to determine the pollutants size and discuss their adsorption on clays. For this purpose, we have been interested by theoretical study of surfactant sorption on montmorillonite. The objective of this work is to study the structure of some anionic surfactants and their sorption on montmorillonite by theoretical methods. These calculations allowed us to determine the most stable structures of some anionic surfactants, their energetic, thermodynamic and structural parameters. The calculation of surfactants' sizes allows to study the possibility of their insertion into the interlayer space of natural montmorillonite Mt (natural)) and modified montmorillonite Mt (Na), Mt (Ca), Mt (K) and Mt (Mg)).

II. Materials and methods

The geometry optimization, frequency computation and measurement of the dimensions of anionics surfactants; Dodecyl Sulfonic Acid (DSA), Sodium Dodecyl Sulfonate (DSNS), Sodium Dodecyl Sulfate (SDS), Sodium Dodecyl Benzene Sulfonate (SDBS) and Dodecyl Benzene Sulfonic Acid (DBSA) were performed were performed with the Gaussian 09 package [22], using the density functional theory (DFT) computations with the three parameter compound function of Becke, B3LYP level [23,24] with basis set 6-311G (d,p). The optimization geometry and frequency parameters of anionic surfactants were predicted using Gaussian view 05 [25].

Thermodynamic parameters (total energy, heat capacity, dipole moment, enthalpy, entropy and vibratory energy at the zero point) of anionic surfactants were calculated in the ground state by DFT / B3LYP / 6-311G (d,p) at 298.15 K.

III. Results and discussion

III.1. Structural Study

The optimized geometries of the surfactants studied; (DSA), (DSNS), (SDS), SDBS and DBSA obtained by B3LYP / 6-311G (d,p) are shown in Figures (1-5).

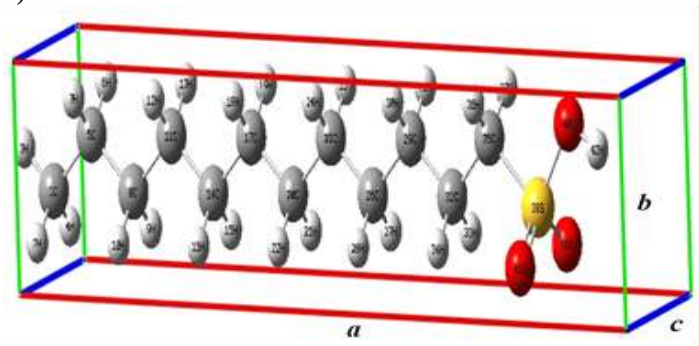

Figure 1. *Optimized Structure of DSA, using B3LYP / 6-311G (d,p)*

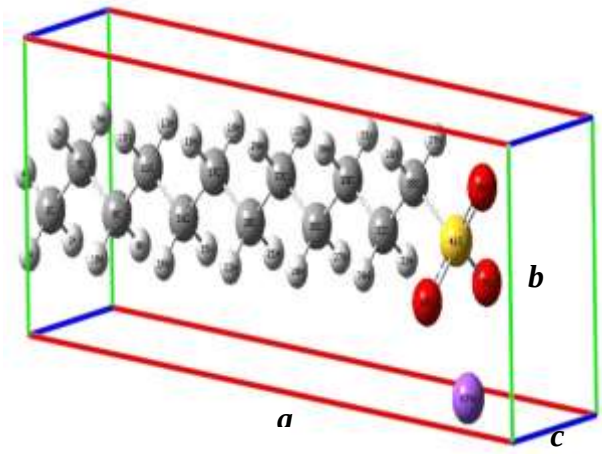

Figure 2. *Optimized Structure of DSNS, using B3LYP / 6-311G (d,p)*

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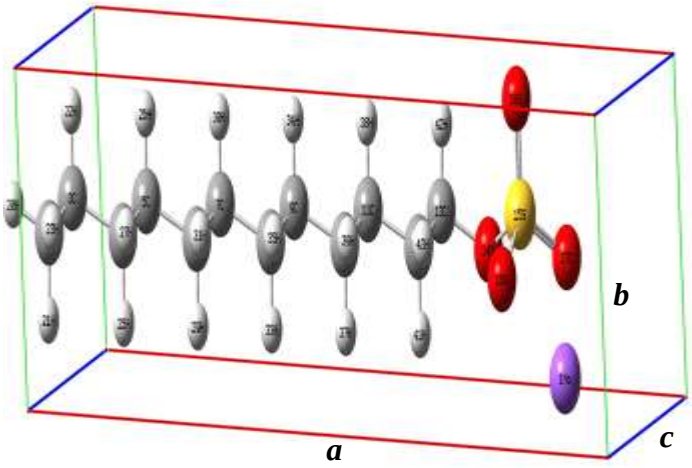

Figure 3. *Optimized Structure of SDS, using B3LYP / 6-311G (d,p)*

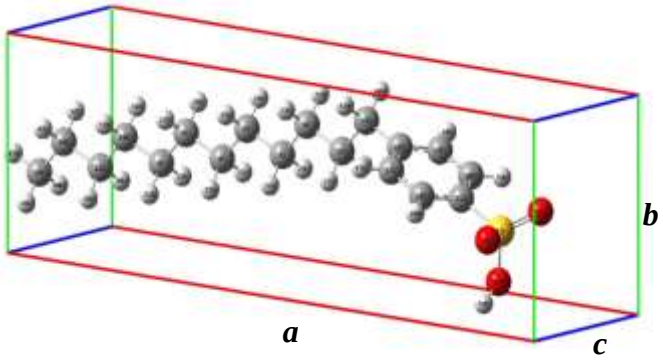

Figure 4. *Optimized structure of SDBA, using B3LYP / 6-311G (d,p)*

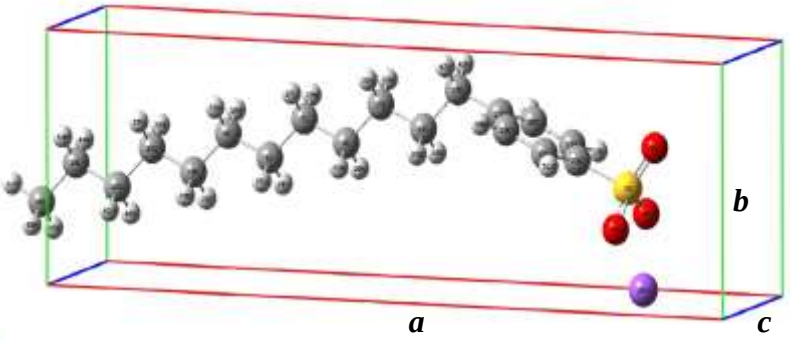

Figure 5. *Optimized structure of SDBS, using B3LYP / 6-311G (d,p)*

The values of bond length, bond angles and dihedral angles were calculated and assigned in table 1 and those of dimensions a, b and c were reported in table 2.

Table 1. *Structural parameters of DSA, DSNS, SDS, SDBA and SDBS*

bond length (Å)		Angle (°)		dihedral angle (°)	
Dodecylsulfonic Acid (DSA)6-311G (d,p)					
C_{32}-H_{35}	1.530	C_{35}-C_{32}-C_{29}	111.553	C_{35}-C_{32}-C_{29}-C_{26}	180.000
C_{35}-H_{36}	1.091	H_{36}-C_{35}-C_{32}	112.290	H_{36}-C_{35}-C_{32}-C_{29}	61.972
C_{35}-H_{37}	1.091	H_{37}-C_{35}-C_{32}	112.290	H_{37}-C_{35}-C_{32}-C_{29}	-61.972
C_{35}-S_{38}	1.803	S_{38}-C_{35}-C_{32}	110.840	S_{38}-C_{35}-C_{32}-C_{29}	180.000
S_{38}-O_{39}	1.456	O_{39}-S_{38}-C_{35}	110.438	O_{39}-S_{38}-C_{35}-C_{32}	67.290
S_{38}-O_{40}	1.650	O_{40}-S_{38}-C_{35}	96.517	O_{40}-S_{38}-C_{35}-C_{32}	180.000
S_{38}-O_{41}	1.456	O_{41}-S_{38}-C_{35}	110.438	O_{41}-S_{38}-C_{35}-C_{32}	-67.290
O_{40}-H_{42}	0.969	H_{42}-O_{40}-S_{38}	108.186	H_{42}-O_{40}-S_{38}-C_{35}	180.000
Sodium Dodecyl Sulfate (SDS) 6-311G (d,p)					
H_{19}-C_2	1.096	C_{13}-C_{12}-C_{11}	112.238	O_{14}-C_{13}-C_{12}-C_{11}	-179.094
C_3-C_2	1.531	O_{14}-C_{13}-C_{12}	107.263	S_{15}-O_{14}-C_{13}-C_{12}	179.960
C_{13}-C_{12}	1.519	S_{15}-O_{14}-C_{13}	116.110	O_{16}-S_{15}-O_{14}-C_{13}	71.138
O_{14}-C_{13}	1.449	O_{16}-S_{15}-O_{14}	105.456	O_{17}-S_{15}-O_{14}-C_{13}	-175.971
S_{15}-O_{14}	1.643	O_{17}-S_{15}-O_{14}	101.616	O_{18}-S_{15}-O_{14}-C_{13}	-52.366
O_{16}-S_{15}	1.505	O_{18}-S_{15}-O_{14}	107.994	C_9-C_8-C_7-C_6	179.982
O_{17}-S_{15}	1.493	H_{22}-C_3-C_2.	109.439	H_{42}-C_{13}-C_{12}-C_{11}	-60.010
O_{18}-S_{15}	1.454	C_{10}-C_9-C_8	113.612	H_{43}-C_{13}-C_{12}-C_{11}	61.781

Sodium Dodecyl Sulfonate (DSNS) 6-311G (d,p)					
C_{35}-C_{32}	1.526	C_{35}-C_{32}-C_{29}	112.443	C_{35}-C_{32}-C_{29}-C_{26}	179.994
H_{36}-C_{35}	1.092	H_{36}-C_{35}-C_{32}	112.065	H_{36}-C_{35}-C_{32}-C_{29}	61.131
H_{37}-C_3	1.092	H_{37}-C_{35}-C_{32}	112.062	H_{37}-C_{35}-C_{32}-C_{29}	-61.133
O_{38}-C_3	2.644	O_{38}-C_{35}-C_{32}	145.834	O_{38}-C_{35}-C_{32}-C_{29}	179.994
O_{39}-O_{38}	2.512	O_{39}-O_{38}-C_{35}	62.277	O_{39}-O_{38}-C_{35}-C_{32}	33.186
O_{40}-O_{39}	2.433	O_{40}-O_{39}-O_{38}	61.027	O_{40}-O_{39}-O_{38}-C_{35}	-73.086
S_{41}-O_{38}	1.463	S_{41}-O_{38}-C_{35}	41.013	S_{41}-O_{38}-C_{35}-C_{32}	0.010
Na_{42}-O_{40}	2.213	Na_{42}-O_{40}-O_{39}	56.657	Na_{42}-O_{40}-O_{39}-O_{38}	-140.206
Dodecylbenzenesulfonic acidDBSA 6-311G (d,p)					
O_2-S_1	1.447	O_3-S_1-O_2	122.504	C_4-S_1-O_2-O_3	150.875
O_3-S_1	1.456	C4-S_1-O_2	118.498	C_5-C_4-S_1-O_2	-70.991
C_4-S_1	11.713	C_5-C_4-S_1	46.019	C_6-C_4-S_1-O_2	-79.893
C_5-C_4	1.532	C_6-C_4-S_1	159.445	C_7-C_5-C_4-S_1	2.401
H_{49}-C_1	1.082	C_7-C_5-C_4	113.593	C_8-C_6-C_4-S_1	-172.951
H_{50}-C_{20}	1.082	H_{50}-C_{20}-C_{18}	121.078	C_9-C_7-C_5-C_4	-179.898
H_{51}-S_1	2.147	H_{51}-S_1-O_2	125.174	H_{51}-S1-O_2-O_3	-103.739
O_{52}-S_1	1.646	O_{52}-S_1-O_2	105.544	O_{52}-S_1-O_2-O_3	-121.829
Sodium dodecylbenzenesulfonate SDBS 6-311G (d,p)					
Na_2-S_1	2.738	O_3-S_1-Na_2	53.804	O_4-S_1-O_3-Na_2	123.515
O_3-S_1	1.512	O_4-S_1-O_3	114.843	O_5-S_1-O_4-O_3	125.043
O_4-S_1	1.461	O_5-S_1-O_4	114.678	C_6-S_1-O_4-O5	114.042
O_5-S_1	1.512	C_6-S_1-O_4	127.906	C_7-C_6-S_1-O_4	11.717
C_6-S_1	11.774	C_7-C_6-S_1	45.670	C_8-C_6-S_1-O_4	20.483
C_7-C_6	1.532	C_8-C_6-S_1	159.145	C_9-C_7-C_6-S_1	-2.314
H_{46}-C_1	1.094	C_9-C_7-C_6	113.610	C_{10}-C_8-C_6-S_1	173.336
H_{52}-C_{22}	1.082	C_{10}-C_8-C_6	113.640	C_{11}-C_9-C_7-C_6	-179.666

Table 2. *Dimensions of DSA, DSNS, SDS, SDBA and SDBS*

Surfactants size / Surfactants	a (Å)	b (Å)	c (Å)
DSA	19.42	3.45	3.51
SDS	20.31	4.48	4.02
DSNS	18.55	5.19	3.43
DBSA	21.99	6.39	5.31
SDBS	22.24	6.77	5.32

III.2. STUDY OF ENERGY

Calculation on the frontier orbitals, HOMO (the highest occupied molecular orbital) determining the electrons responsible for the nucleophilic attack and LUMO (The lowest vacant molecular orbital) which indicates electrophilic sites was made to determine the nature of the interactions between surfactant and adsorbent. The values found (Figures 6-10) are very close and show that the oxygen and sulfur atoms are electrophilic while sodium in DSNS and DSD and Hydrogen in DSA have nucleophilic sites. This suggests that all the studied surfactants will be able to fit into the interlayer spaces of the clays (in the case where there is a possibility of insertion), through side b (figures 1-5). The low values of the Gap (HOMO-LUMO), show that these surfactants are very reactive. However, Dodecylsulfonic acid (DSA) remains the most reactive surfactant due to its acidic character.

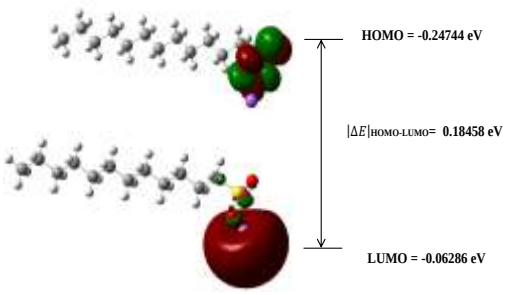

Figure 6. *Frontier molecular orbitals (HOMO and LUMO) of DSNS, at 6-311G (d,p) level*

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III.2. Study of energy

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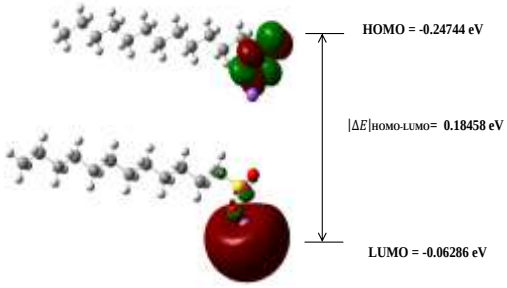

Figure 6. *Frontier molecular orbitals (HOMO and LUMO) of DSNS, at 6-311G (d,p) level*

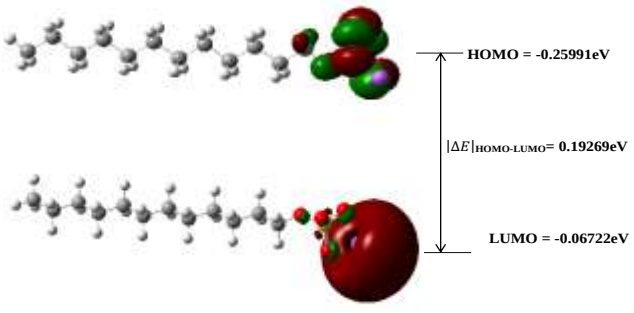

Figure 7. *Frontier molecular orbitals (HOMO and LUMO) of SDS, at 6-311G (d,p) level*

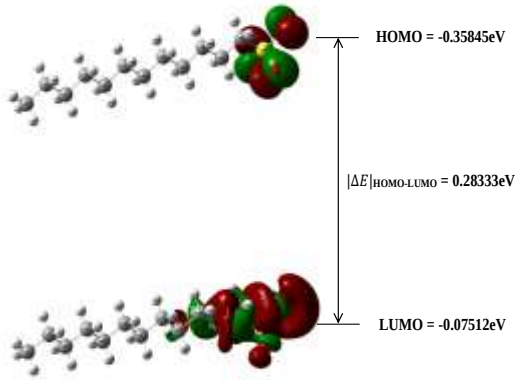

Figure 8. *Frontier molecular orbitals (HOMO and LUMO) of DSA, at 6-311G (d,p) level*

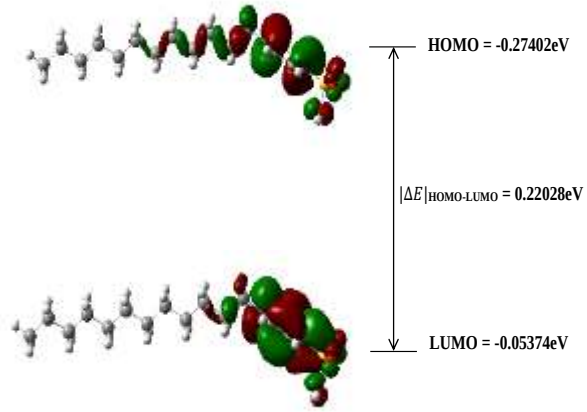

Figure 9. *Frontier molecular orbitals (HOMO and LUMO) of SDBA, at 6-311G (d,p) level*

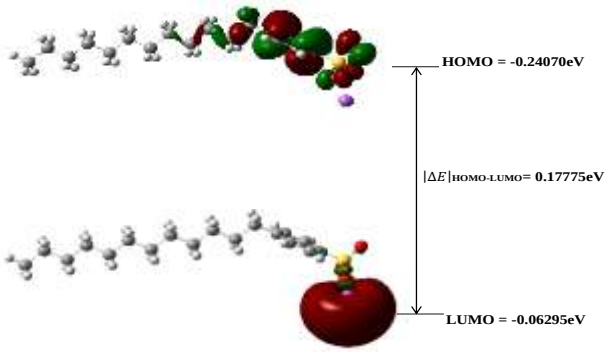

Figure 10. *Frontier molecular orbitals (HOMO and LUMO) of SDBS, at 6-311G (d,p) level*

III.3. Thermodynamic properties

Total energy, enthalpy, entropy were calculated in the ground state by DFT / B3LYP / 6-311G (d,p) at 298.15 K. Gibbs free energies were calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S, \text{ where T = 298.15 K}$$

The results of total energy, enthalpy, entropy and Gibbs free energy obtained are summarized in Table 3. The data show that the surfactants have very stable geometries, since the total energy values are negative (< 0). Positive data of entropy suggest that these surfactants are very active, while the positive values of enthalpy may suggest that at this temperature (T = 298.15 K), the micellization process is endothermic as mentioned by Kumar and al [26]. However, Gibbs free energy values are negative for all the surfactants studied, giving them a high reactivity.

Supplementary thermodynamic parameters (heat capacity, dipole moment and vibratory energy at the zero point) were calculated in the ground state by DFT / B3LYP / 6-311G (d,p) at 298.15 K and listed in table 6 and 7 as supplementary materials. These thermodynamic data contribute helpful information for the further applications of the surfactants studied in this work.

Table 3. *Thermochemical properties of DSA, SDS, DSNS, DBSA and SDBS at B3LYP /6-311G (d,p) level (Total Energy (au), Thermal energy (kcal mol^{-1})), Entropy (Cal mol^{-1}K^{-1}) and* Gibbs free energy G *(Cal.mol^{-1}. K^{-1}))*

Surfactants	***Total energy (a.u)***	***Enthalpy H (Kcal.mol^{-1})***	***Entropy S (Cal.mol^{-1}. K^{-1})***	*Gibbs free energy G* ***(Cal.mol^{-1}. K^{-1})***
DSA	-1096.9855	246.941	155.894	-46232.855
SDS	-1333.9992	245.504	170.932	-50717.872
DSNS	-1258.7667	242.011	162.784	-48292.038
DBSA	-1328.0866	300.842	184.937	-54838.124
SDBS	-1489.8664	295.250	191.414	-56774.834

III.4. Adsorption ON Montmorillonite

Montmorillonite is clay formed by an octahedral layer sandwiched between two tetrahedral layers (TOT). The thickness of these layers is 9.6 Å [27]. The d_{001} is the sum of the thickness of the layers and the interlayer space (Figure 11).

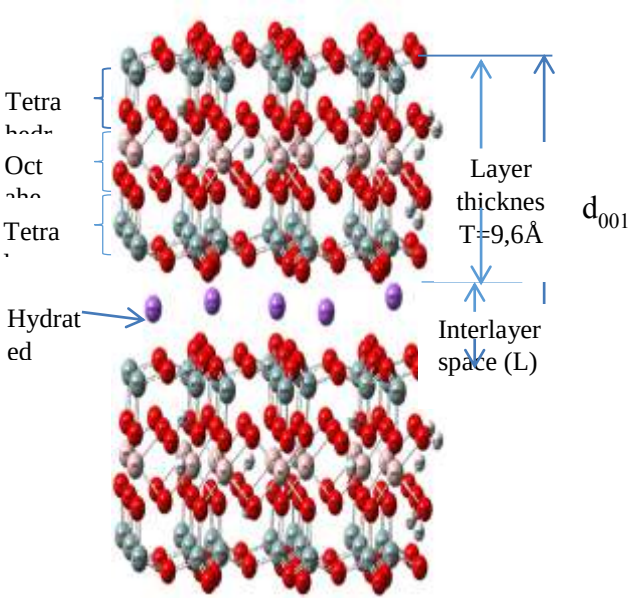

Figure 11. *Montmorillonite structure, by (Gauss View 5.0).*

Table 4 presents the d_{001} values of five types of montmorillonite provided from literature [28]. These values allowed us to calculate the distance of the interlayer space according to the following formula;

Interlayer space (L) = d_{001} - Layer thickness (as shown in figure 11)

Layer thickness = 9.6 **Å** [27].

Table 4 shows that d_{001} values vary according to the following order:

d_{001} (Mt (Ca)) > d_{001} Mt (naturelle) > d_{001} Mt (Mg)) > d_{001} Mt (K)) > d_{001} Mt (Na)

While the distances of the interlayer space vary as shown bellow

L(Mt(Ca)) > L(Mt(Naturel)) > L(Mt(Mg)) >L(Mt(K)) >(Mt(Na)).

Table 4. *d_{001} and interlayer space of (Mt (naturel), Mt (Na), Mt (K), Mt (Ca) et Mt (Mg))*

	Mt(Natural)	Mt(Na)	Mt(K)	Mt(Ca)	Mt(Mg)
d_{001} (Å)	14.26	10.06	10.47	15.08	13.68
L (Å)	4.66	0.46	0.87	5.48	4.08

Both of optimized geometries of surfactants (figures1-5) and their frontier molecular orbitals (figures 6-10), show that these anionic surfactant could fit into the interlayer space through side b. Thereby, to study the possibilities of surfactants insertion in Mt(naturel), Mt(Na), MMt(K), Mt(Ca) and/or Mt(Mg), we have to compare the dimensions b of these pollutants with the interlayer space (L) of the clays.as mentioned on table 5.

Table 5*. Sizes of DSA, DSNS, SDS, SDBA and SDBS*

	Mt(Natural)	Mt(Na)	Mt(K)	Mt(Ca)	Mt(Mg)
L (Å)	4.66	0.46	0.87	5.48	4.08
Surfactants	DSA	SDS	DSNS	DBSA	SDBS
b **(Å)**	3.45	4.48	5.19	6.39	6.77

A Comparison between b and L (***Table 5***); shows that these anionic surfactants cannot fit into the interlayer space of Mt (K) and Mt (Na). Indeed, the surfactants dimensions are much larger than the clays interlayer spaces. However, DSA (b = 3.45Å) can be adsorbed in the interlayer spaces of Mt(natural)(L= 4.66 Å), MT (Ca)(L = 5.48 Å) and MT (Mg)(L = 4.08 Å). SDS (b = 4.48 Å) can fit in MT (Ca)(L = 5.48 Å) and MT (Mg)(L = 4.08 Å) interlayer spaces. DSNS (b = 5.19 Å) can be adsorbed only in MT (Ca)(L = 5.48 Å) interlayer space. However SDBA (b = 6.39 Å) and SDBS (b = 6.77Å), which have dimensions larger than all the interlayer spaces could not be adsorbed on any of the studied clays. This is in good agreement with the data found by [27]

IV. Conclusion

Based on a theoretical approach, a molecular structural analysis DodecylSulfonic Acid (DSA), Sodium Dodecyl Sulfonate (DSNS), Sodium Dodecyl Sulfate (SDS), Sodium DodecylBenzene Sulfonate (SDBS) and DodecylBenzene Sulfonic Acid (DBSA) was performed by DFT at the B3LYP / 6-311G level (d,p). We optimized the geometries of these anionic surfactants and determined their sizes in order to study the possibility of their sorption on montmorillonite.

The data obtained show that these anionic surfactants cannot be adsorbed in the interlayer space of Mt (K) and Mt (Na). However, DSA can fit in the interlayer spaces of Mt(natural, MT (Ca) and MT (Mg). SDS can fit in MT (Ca) and MT (Mg) interlayer spaces. While DSNS can be adsorbed only in MT (Ca) interlayer space. However SDBA and SDBS could not be adsorbed on any of the studied clays. The calculations carried out on the molecular orbitals gave a very small gap for the five surfactants, thus suggesting for these anionic surfactants a high reactivity. The surfactant with an acidic character remains the most reactive surfactant. The energy calculation on the orbitals showed an electrophilic interaction between the surfactant and the material. Thermodynamics data show that all the surfactants studied have positive values of enthalpy and entropy and negative values of Gibbs free energy, suggesting for them a high reactivity and the micellization process will be endothermic. The negative data of total energies show that these surfactants have very stable geometries.

The present work also provided an important thermodynamics database, for the surfactants studied, helpful for experimental studies of the adsorption of these surfactants on clays.

V. Supplementary materials

Table 6. *Additional thermodynamic properties of DSA, SDS, DSNS, DBSA and SDBS at B3LYP /6-311G (d,p) level (Theoretically computed Dipole moment (Debye)), Zero point vibrational energy (kcal. mol^{-1}).*

Surfactants / Parameters	DSA	SDS	DSNS	DBSA	SDBS
Dipole moment (Debye)	3.2877	7.6177	7.5584	5.9707	7.8623
Zero point vibrational energy (Cal.mol^{-1}. K^{-1})	234.19491	231.15681	228.37891	284.7082	278.53713

Table 7. *Molar capacity at constant volume (Cal mol^{-1}K^{-1}) of DSA, SDS, DSNS, DBSA and SDBS at B3LYP /6-311G (d,p) level.*

Surfactants / Parameters	DSA	SDS	DSNS	DBSA	SDBS
Total	71.859	79.455	76.296	93.093	95.702
Translational	2.981	2.981	2.981	2.981	2.981
Rotational	2.981	2.981	2.981	2.981	2.981
Vibrational	65.897	73.494	70.335	87.131	89.740

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