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DFT calculations of Energies and thermodynamics parameters of Aniline sorption on Montmorillonite surface (MMTs)

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ABSTRACT/RESUME

Abstract:*The adsorption mechanisms of aniline ($C_6H_5NH_2$), on montmorillonite surface (MMTs) have been investigated using density functional theory (DFT) calculation with the three parameter compound function of Becke (B3LYP) level, in 6-31++G(d,p) basis sets. These theoretical investigations illustrate that the interactions between the amino group in aniline compound and the silicon atom of siloxane surface of (MMTs) play the key role in the sorption of aniline on (MMTs). Hydrogen bonds between the hydrogen atoms of the amino group and basal (O) oxygen atoms of silicate maintain the location of aniline. The sequences of computations explain that the adsorption process of aniline on the (MMTs) is exothermic. We have a physisorption process with an adsorption energy of -36.66 KJ mol^{-1} and an increasing in the randomness at the Aniline/MMTs interface during the adsorption.*

I. Introduction

The pollution of soils and water with an organic pollutant leads to significant environmental concerns. Aniline it is a compound also identified as phenylamine ($C_6H_5NH_2$), an archetypal aromatic amine in which the amino group is linked directly to a benzene ring. It is perceived to be one of the more toxic pollutants released as effluents of several industries. The presence of these contaminants is mainly due to industrial activities; the adsorption is a widely studied process used to remove contaminants from aqueous effluents. Anywhere montmorillonite (MMT) is a clay which has been extensively investigated as an adsorbent of several contaminants [1–2]. Montmorillonite is a 2:1 type hydrous aluminosilicate consists of two tetrahedral silica sheets with an octahedral alumina sheet sandwiched between the two silica sheets; tetravalent silicon (Si^{4+}) and especially trivalent aluminum (Al^{3+}) [3-4]. It is naturally able to adsorb efficiently organic molecules on its surface and interlayer space [5]. In the present work, we have studied the aniline adsorption on Montmorillonite surface (MMTs) using moléculaire modeling investigations.

II. Materials and methods

The geometry optimization, frequency computation and measurement of the distances of aniline molecule ($C_6H_5NH_2$), and montmorillonite surface, were performed with the Gaussian 09 package [6], using the density functional theory (DFT) computations with the three parameter compound function of Becke (B3LYP) level, in 6-31++G(d,p) basis sets.

The montmorillonite surface (MMTs), which is a type or clay, has the following chemical formula $[Si_8(Al_3Mg)O_{20}(OH)_4]$. The (MMTs) structure was built from an orthorhombic unit cell in Gaussian view according to the works of Katti and al [7].

The optimization geometry and frequency parameters of aniline-MMTs are predicted using

density functional B3LYP level with 6-31++G(d,p) basis sets in Gaussian 09 software package [6], using Gaussian view 05 [8].

III. Results and discussion

III.2. Geometric and energytic Study

The optimization of aniline geometry, pictured in figure 1, gives C–N, and N–H bond distances of 1.39 and 1.01 Å, sequentially, these values are in the same range of experimental results (1.402 and 1.001 Å) determined by Sinclair and al [9].

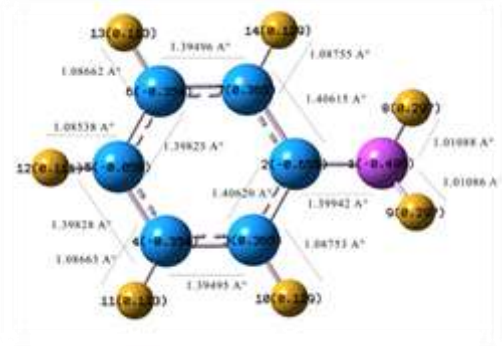

Figure 1. *Optimized and frequency structure of aniline by density functional (DFT) using the 6-31G++ (d,p) basis set and the three parameter compound function of Becke (B3LYP) level, (ε= 2.37°, ∠ $H_8N_1H_9$ =112.20°), (Blue = carbon, yellow = hydrogen, pink = nitrogen).*

Montmorillonite surface (MMTs) optimized by density functional (DFT) using the 6-31G++(d,p) basis set and the three parameter compound function of Becke (B3LYP) level is mentioned in Figure 2.

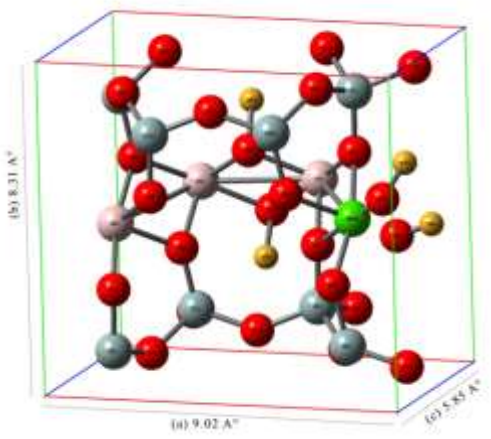

Figure 2. *orthorhombic primitive unit cell of montmorillonite surface (MMTs) optimized by density functional (DFT) using the 6-31G++(d,p) basis set and the three parameter compound function of Becke (B3LYP) level.(Silver =Silicon , red= Oxygen, pink= aluminum, green= magnesium).*

The values of ∠Si-O-Si, ∠H-N-H angles and length Si-O before and after adsorption reported on Tables 1 and 2**,** show that Si-O distance, ∠H-N-H and ∠Si-O-Si angles before and after adsorption are different, due to the destruction stretched of Si-O-Si, and the intramolecular steric repulsion, which reduces the angle of ∠H-N-H to 106.98° at the final step of adsorption.

Table 1. *Some of ∠Si-O-Si, ∠H-N-H angle and length Si-O before and after adsorption.*

Angles	***Before adsorption***	***After adsorption***
∠Si_{10}-O_{29}-Si_{11}	140.71°	109.47°
∠ Si_{10}-O_{18}-S_7	130.51°	87.60°
∠ Si_{11}-O_{19}-S_6	130.51°	87.60°
∠ H_9-N_1-H_8	112°.20°	106.98°

Table 2. *Some of length Si-O before and after adsorption.*

Length (A°)	***Before adsorption***	***After adsorption***
Si_{10}-O_{29}	1.63	1.90
Si_{10}-O_{18}	1.63	1.83
Si_{11}-O_{19}	1.63	1.83
Si_6-O_{19}	1.61	1.74

Si-doped can strongly adsorb aniline compound. Hydrogen H_8, H_9 of amine group react with the oxygen of the siloxane surface, and the nitrogen N1 atom attached and react with silicon atom surface.
The main interaction between aniline and the surface of montmorillonite (MMTs) takes place through the nitrogen of the amino group, which is the inhibitor center of adsorption system.
The Mulliken charges were calculated with same the functional and basic set B3LYP/6-31++G(d,p), in the way to make an accurate comparison shows in Table 3.

Table 3. *The Mulliken charge population of aniline and (MMTs-Aniline), calculated by B3LYP/6-31++G(d,p) method.*

Atom	**Mulliken charges**	
	Isolated	**Adsorbed**
N_1	-0.496055	-0.918886
C_2	-0.654760	-0.064065
C_3	0.364855	-0.241841
C_4	-0.353943	-0.230942
C_5	-0.058037	-0.122237
C_6	0.365321	-0.016454
C_7	-0.354015	-0.195024

H_8	0.296595	0.423853
H_9	0.296600	0.426920
H_{10}	0.128639	0.150397
H_{11}	0.112787	0.116401
H_{12}	0.110612	0.124199
H_{13}	0.112792	0.128729
H_{14}	0.128608	0.142269
O_{18}	-0.875655	-0.957576
O_{19}	-0.905014	-0.944004
O_{29}	-0.848243	-0.937796
Si_7	1.574431	1.743546
Si_{10}	1.627599	1.672489
Si_{11}	1.785154	1.395221

The computation of effective atomic charge plays a significant role [10.11], the Mulliken atomic charges measured by determining the electron population of atoms are defined in Table 3.
The atomic charge values of nitrogen and oxygen (N_1, $O_{18;}$ O_{19}, O_{29}) (Table 3), changes after adsorption, which had a significant negative charge and shows high polarization due to the high electronegativity of nitrogen N_1 and oxygen atoms that attract charges and behaved as electron donors.

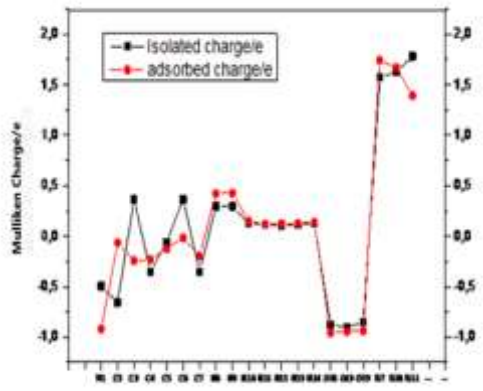

Figure 3. *Mulliken charge distribution of MMTs-Aniline*

The positive charge on hydrogen atoms and silicon Si_1, suggest the presence of intermolecular hydrogen bonding interactions (O---H) in Aniline/MMTs and this suggest that aniline is adsorbed on Montmorillonite surface (Fig.3).
Calculations were performed to determine the most stable configuration of aniline on montmorillonite surface (MMTs). Each configuration was performed by fixed calculation in the form of height optimization of aniline on MMT surface (MMTs) by moving away aniline position from the surface with interval between 3-4 A° in the z-axis directions until the convergences achieved. In every type of aniline configurations occur, some repulsions between aniline and montmorillonite surface (MMTs) at the range of 1 - 2.67 A° from the initial position which forming some spaces or distances between Aniline and montmorillonite surface (MMTs).
The interaction energies of MMTs / aniline were calculated to predict the adsorption ability on the clay surface of montmorillonite as following in Table 4.
The adsorption energy was calculated using:

$$\Delta Eads = E_{aniline/MMT} - (E_{aniline} + E_{MMTs}) \quad (1)$$

Where $E_{aniline/MMTs,}$ is the energy of aniline/MMTs system at its optimized geometry,
$E_{aniline}$, E_{MMTs} are , respectively, the total energy of isolated Aniline without MMT, and E_{MMTs} is the energy of MMTs alone.

Table 4. *Calculated energies of Aniline, MMTs and MMTs/Aniline*

Molecules	**Energy (Kcal mol^{-1}) B3LYP/631G++(dp)**
Aniline	-180467.55
MMTs	-971918.90
MMTs/Aniline	-1152420.95
ΔEads	-34.6 Kcal mol^{-1}

The negative values of ΔEads = -34.6 Kcal mol^{-1}, mean that aniline can be adsorbed on the surface of MMTs, and that the adsorption processes is exothermic, so we can say that this surfactant was significantly adsorbed on MMTs.
The DFT calculations of aniline adsorption on montmorillonite surfaces (MMTs) were performed to research the structures and energies of the two adsorption procedures; perpendicular approach (aniline^p) (Fig.4) and the parallel approcach (aniline^f) (Fig.5). The DFT results are shown in Table 5.

Table 5. *Calculated energy [kcal mol^{-1}] for some aniline arrangements on MMTs.*

Orientations	Energy (B3LYP/6-31G++ (dp))	Distance Aniline/MMTs (Å)
Perpendicular approach (Fig.4)	-55.42	1.69
Parallel approach (Fig.5)	-36.66	1.92

All E_{ads} values in Table 5 are negative. Various conclusions can be drawn from Table 5, first the lower aniline–MMTs interaction energy corresponds to closer approach of aniline to the surface; and preferential perpendicular conformation is predicted, which is energetically more favourable with the amino nitrogen of aniline pointing towards the siloxane surface Si-O-Si.

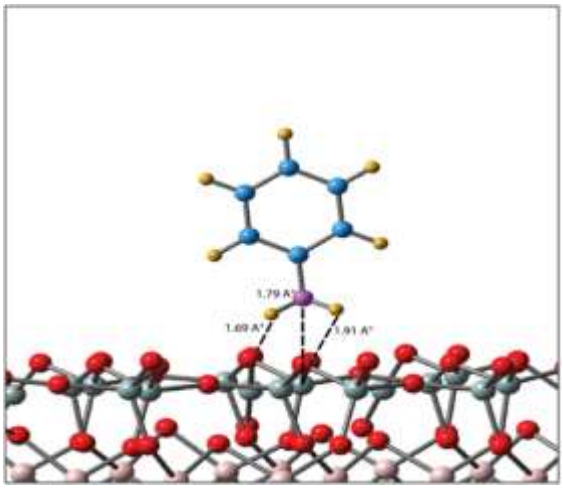

Figure 4. *MMTs intercalated with aniline (perpendicular approach to MMTs), view along the X- axis.*

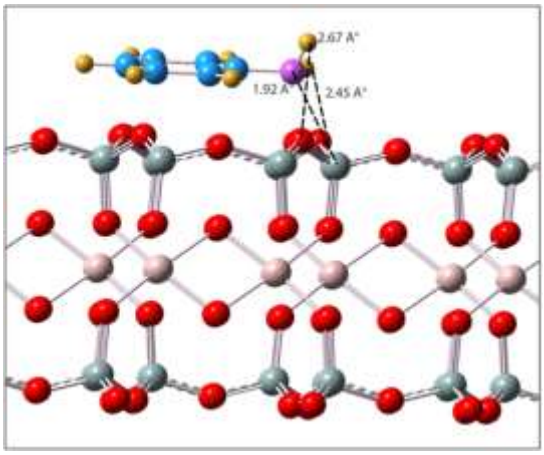

Figure 5. *MMTs intercalated with aniline (parallel approach to MMTs), view along the X- axis.*

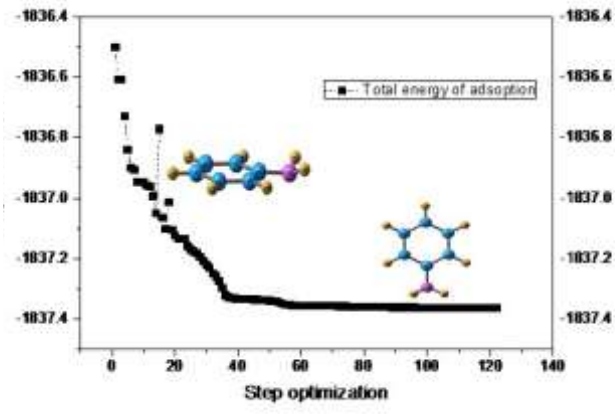

Figure 6. *Total energy of aniline sorption on MMTs.*

III.2. Thermodunamic Study

In order to understand, the adsorption process of aniline on montmorillonite, this section of work was performed to confirm the phenomena. The thermodynamic parameters such as standard Gibbs free energy ΔG°, standard enthalpy ΔH°, and standard entropy ΔS°, were computed by applying DFT level of calculation based on B3LYP level with 6-31++G(d,p), and these parameters are given in Table 6.

The variation in zero-point vibration energy and thermal corrections from zero degrees to 298 K° has been considered in the calculations. The calculations show that the adsorption center of inhibitor in our surfactant aniline is the NH_2 group, which is in a good agreement with the work of Samaraweera and al [12].

The values reported in Table 6 can allow to calculate the Gibbs free energy of adsorption (ΔG_{ads}) and the enthalpy of adsorption:

$$\Delta G_{ads} = G_{MMTs/anilne} - (G_{MMTS} - G_{aniline}) \qquad (2)$$

Where $G_{MMTs/anilne}$ is the Gibbs free energy of the complex MMTs/Aniline, G_{MMTS} is the Gibbs free energy of montmorillonite surface (MMTs) isolated, and $G_{aniline}$ is the Gibbs free energy of aniline isolated.

In addition, the enthalpy of adsorption was calculated as following in equation (3):

$$\Delta H_{ads} = H_{MMTs/anilne} - (H_{MMTs} - H_{aniline}) \qquad (3)$$

Where $H_{MMTs/anilne}$ is the enthalpy of the complex, H_{MMTS} and $H_{aniline}$ are the enthalpy of Montmorillonite surface and aniline isolated respectably.

Table 6. *Energy calculated using various theoretical models at 298 K°, KJ mol^{-1} at the B3LYP/6-31++G(dp) level.*

	Aniline	**MMTs**	**MMTs-Aniline**
ε_0	-755175.59	-3117571.45	-4823997.99
ε_{ZPE}	298.20	425.32	589.34
E_{total}	315.87	520.18	648.50
H_{corr}	267.53	423.78	650.97
G_{corr}	173.27	320.15	451.75
$\varepsilon_0+\varepsilon_{ZPE}$	-754877.39	-3117146,13	-4823408,65
$\varepsilon_{0\,+}\,E_{total}$	-754859.72	-3117051,27	-4823349,49
$\varepsilon_{0\,+}\,H_{corr}$	-754908.06	-3117147,67	-4823347,02
$\varepsilon_{0\,+}\,G_{corr}$	-755002.32	-3117251,30	-4823546,24

ε_0 : Total energy calculated using B3LYP/31++G(dp).
ε_{ZPE} : zero point energy of the molecule.

The negative value of the free Gibbs energy ΔG° (table 7), suggests that the adsorption of aniline on the steel surface is spontaneous; the ΔH° value could be used to distinguish chemical from physical adsorption. The negative values of ΔH° indicated that the attachment process was exothermic; ΔS° was found to be 4.46 KJ/mol K. The positive value of ΔS° indicates that there is an increase in the randomness at the Aniline/MMTs interface during the adsorption.

Table 7. *Thermodynamics parameters*

	MMTs/Aniline
ΔH_{ads}	-40,34 KJ/mol
ΔG_{ads}	-41,67 KJ/mol
ΔS_{ads}	4,46KJ/mol

IV. Conclusion

We investigated aniline ($C_6H_5NH_2$) adsorption on the surface of Montmorillonite (MMTs) by computer calculations by using density functional theory (DFT). First, the most stable geometries of aniline and the complex aniline/ MMTs were reached. The study of the charges on the complex aniline/ MMTs, suggests the presence of intermolecular hydrogen bonding interactions (O---H) in Aniline/MMTs and this confirms that the aniline is adsorbed on Montmorillonite surface. The negative values of adsorption energy suggest that aniline can be adsorbed on MMTs, and that the adsorption processes is exothermic.

We have shown through this theoretical calculation that the adsorption of aniline ($C_6H_5NH_2$) on Montmorillonite (MMTs) with the perpendicular approach is more favoured energetically than the parallel approach (face to face) configuration. The inhibitor adsorption center of aniline is the NH_2 group. The thermodynamic parameters were calculated. The negative value of the free Gibbs energy ΔG°, suggests that the adsorption of aniline on the steel surface is spontaneous, the negative values of ΔH° indicate that the attachment process was exothermic and the positive value of ΔS° indicates that there is an increase in the randomness at the Aniline/MMTs interface during the adsorption.

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