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Physical and chemical insights into molecular adsorption of copolymer's monomers on Rutile surface

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Physical and Chemical Insights into Molecular Adsorption of Copolymer's Monomers on Rutile Surface

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Abstract

The adsorption of triblock copolymer's moieties such as DME, 1,2-DME, and 1,2-DMP on a Rutile surface has been studied by DFT. The insights into their adsorption mechanism have been investigated by analyzing various physical and chemical properties such as the adsorption energies, the structural properties, difference of charge density, density of state, bond overlap population, and the atomic partial charge. Dispersion interaction plays a major role on the absorption energy in 1,2-DME, and the upward bridging oxygen configurations of DME and 1,2-DMP; whilst electrostatic and polarization energies are insignificant. A new O_b-Ti bond has been formed from the overlap of lone-pair electrons between orbital O 2p and Ti 3d in downward bridging oxygen configurations of DME and 1,2-DMP, which results in a significantly larger adsorption energies compared with other configurations. The molecular torsion is considered as a barrier that prevent O_b-down of 1,2-DME to create the bond with Ti.

1. Introduction

Aqueous Pluronic triblock copolymer lubricants have been introduced as potentially aqueous metalworking lubricants that will satisfy the surface quality and cleanliness that products require [1, 2]; they have also been used as detergents, stabilizers, foaming agents, emulsifiers, cosmetics, and drug adjuvants for industrial applications due to their environmental and economic advantages [3]. A triblock copolymer is a non-ionic surfactant that includes poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) blocks, but the differences in the chemical and structural properties of these constituent blocks means that the adsorption of an aqueous triblock copolymer to a metal surface is an interesting phenomenon. Although comprehensive investigations into the adsorption of normal and reverse Pluronics have been carried out experimentally [4-10], insights into their adsorption at atomic level have yet to be revealed due to its large molecular structure. Simulations of classical molecular dynamics (MD) have proven to be the best way to investigate the adsorption of copolymer onto a surface over the last two decades [11, 12]. In these MD simulations, dimethyl ether (DME), 1,2-dimethoxyethane (1,2-DME), and 1,2-dimethoxypropane (1,2-DMP) are commonly used to represent the copolymer's PEO and PPO blocks as their force field (FF) develops [1, 8, 11-29]. Unfortunately, they were represented by an empirical expression with a small number of parameters which could reproduce existing data on the material but could not provide the chemical adsorption mechanism of copolymers.

Previous experimental investigations into the adsorption of a reverse triblock copolymer on a TiO_2 surface in an aqueous solution have motivated us to investigate the mechanism by which each constituent block is adsorbed onto this surface [8, 15]. This study is therefore a theoretical investigation of the physical and chemical insights into how these copolymer moieties were adsorbed onto a Rutile surface in particular, and the mechanism by which copolymers are adsorbed onto metal or metal oxide surfaces in general. While previous investigations revealed that choosing a short training molecule could overestimate the real adsorption energy when applied to larger molecules [30], this work addressed a controversial assumption of using DME or 1,2-DME to represent a PEO block, and also investigated how the molecular chain length influenced its adsorption properties [11, 12].

Of the moieties of copolymers, DME is the most interesting molecule in catalytic analysis because it is a promising alternative fuel for internal combustion engines due to experiments which revealed that DME could be produced from methanol adsorption on a vacuum-annealed Rutile anatase $\text{TiO}_2(001)$ surface at 700K [31]. In fact a recent investigation using infrared Fourier transform spectroscopy (IFTS) indicated that the molecular interaction between DME and a steel surface was accompanied by the migration of a hydrogen atom to the metal surface to form metalhydride bonds [32]. This degradation of DME yielded a formation of formaldehyde and a methyl cation. Adsorption heat of 0.268 and 0.208 eV have been found for DME on molecular sieves 4 Å (Mol4A) and 5 Å (Mol5A) using the volumetric

adsorption method [33]; the adsorption of DME on Mol5A was controlled by an intra-crystalline diffusion resistance, whereas there was a surface layering resistance on Mol4A [33]. Investigations into the adsorption of DME onto silica gel indicated there is a hydrogen bonding between this molecule and the hydroxyl group on the silica surface [34]; this finding is similar to 1,2-DME [35]. Herron et al. investigated the mechanism whereby dimethyl ether electro-oxidation affects heavy transition metals (Au, Ag, Cu, Pt, Pd, Ni, Ir, Rh) using (111) and (100) fcc surfaces [36]. Their theoretical study disclosed that DME can be dehydrogenated to a greater extent on a (100) facet while the energy needed to break the C–O bond becomes more exergonic if the species is increasingly dehydrogenated. Moreover, Au, Ag, Cu, Pt, and Pd are more active on (100) facets than their respective (111) ones, whereas the trend for Ni, Ir, and Rh was opposite. In all these studies, contact between the molecules under consideration with the metal surface of a reactor is inevitable, but unfortunately there is the lack of data in the literature on how they behave on a Rutile surface.

Unlike DME, there are not many investigations into the way 1,2-DME and 1,2-DMP is adsorbed onto a metal or metal oxide surface. In an effort to derive an interfacial force field for interaction between copolymer and iron surface, Ta et al. reported adsorption energies of -0.742 and -0.855 eV for 1,2-DME and 1,2-DMP, respectively [12]; these adsorption energies are twice as large as those calculated for DME [12]. The dipole moment and polarisability calculated by Borodin et al. range between 1.37 to 2.67 D for 1,2-DME and 1.36 to 1.61 D for DME using different functions of the basis set, levels of quantum theory, and chosen configurations [21]. However, polarizability of DME (3.81 to $5.17 \text{ \AA}^3$) is much lower than 1,2-DME (9.14 to $10.4 \text{ \AA}^3$), whereas their calculated dipole moment for DME is higher than the experiment; they also found that the polarizability was only 7% of the total binding energies of these molecules [22].

Since triblock copolymers are widely used for lubrication, tribologists want to understand its adsorption mechanism. This is why a fundamental investigation has been now carried out to obtain insights into the physical and chemical properties of adsorption of copolymer's moieties. The adsorption structure and energies, charge transfer states, atomic electrostatic and polarizability of DME, 1,2-DME, and 1,2-DMP have also been studied using static density functional theory (DFT) calculations. The results obtained by this study will then be used to explain how PEO and PPO blocks are adsorbed onto a metal oxide surface.

2. Computational methodologies

The Vienna Ab Initio Simulation Package (VASP) simulation package has been used for this quantum chemistry calculation [37, 38]. The pseudopotential applied for each atomic species with electron-ion interactions is described by the projector augmented-wave (PAW) method [37]. The plane wave energy cutoff of 400 eV was set to truncate the plane-wave expansion of the electronic wave function, while the Brillouin zone was sampled using Monkhorst–Pack scheme with a k-point set of $3\times3\times1$. The generalized gradient approximation (GGA) exchange-correlation functional of Perdew-Burke-Ernzerh was applied in this calculation. The convergence criterion for total energy was 10^{-4} eV in electronic self-consistent loop with ionic relaxation. A dipole correction is included to eliminate any non-physical interactions by the image cell, and a large vacuum of 30 Å was applied onto the surface. Since conventional density functionals cannot describe the van der Waals (vdW) interactions correctly due to dynamic correlations between the fluctuating charge distributions; dispersion correction using the approximate method by Grimme are included to overcome this problem [39]. The dispersion correction included in this study to examine the adsorption of *n*-alkanes on Pd(111) and PdO(101) surface indicates that DFTD provides desorption energies that are closer to the experimental data than DFT [40]. Self-consistent calculations were also used to calculate the partial density of states (DOS), the charge transfer, and the bond overlap population (BOP). To calculate the net atomic charges and bond order (BO), the density derived electrostatic and chemical (DDEC6) approach was used [41, 42]. The BOP was computed by an integration of the crystal orbital overlap population (COOP) using the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) package [43].

For electronic structure calculations of DOS and charges transfer, a PBE + U with $U_{\text{eff}} = 3$ eV ($U = 4$ eV and $J = 1$ eV) was used because it gives good results for the oxidising energy of Ti_2O_3 and TiO_2 [44, 45]. The atomic partial charges obtained from the DDEC6 method, along with their relevant Cartesian coordinates are used to evaluate the electrostatic energy (Coulombic energy) between the adsorbed molecules and surface using LAMMPS code [46]. A cut-off distance of 12.5 Å and a particle–particle particle–mesh (PPPM) solver technique is also utilised to treat this Coulombic interactions [47].

Fig. 1 Adsorption configurations of DME on $\text{TiO}_2(001)$ surface using: (a) O_b -down in (110) direction; (b) O_b -down in (-110) direction; (c) O_b -up in (110) direction; and (d) O_b -up in (-110) direction. Cyan, red, grey, and white colors present Ti, O, C, and H, respectively.

A periodic $\text{TiO}_2(001)$ substrate of $p(2 \times 2)$ that includes three layers with 12 Ti and 24 O atoms is utilized because Bandura et al. found that the calculated structures of TiO_2 did not depend on the thickness of the slab, and therefore a slab with 3-layers is thick enough to carry out a chemical adsorption on the surface [48]. The two lower layers were fixed to represent a bulk crystalline structure, whilst the upper layer was relaxed during calculations. While facets of (001), (100), and (110) are commonly found on a TiO_2 surface [49], this work focuses on the molecular structure and chain length, so only the (001) facet is considered. Four different adsorption configurations where the back-bond atoms are in a plane normal to the surface, along the (110) and (-110) directions, and located on top and in between atomic rows are used for DME (Fig. 1). Ten adsorption configurations were applied for 1,2-DME (Fig. 2) and 1,2-DMP (Fig. 3) molecules. For 1,2-DME, molecular structures where the back-bond plane is parallel and normal to the surface were used. The adsorption sites where $-\text{CH}_2$ and O_b are on top and in between the Ti rows were also considered. Since the results indicated there was a very significant weak adsorption of 1,2-DME, as shown in the results section, additional adsorption configurations of trans-cis-trans (tct) (Fig. 2i,j) and other trans-trans-trans (ttt) (Fig. 2a-h) configurations were used to check whether the chosen configuration plays a vital role on the adsorption properties of this molecule. With the 1,2-DMP molecule, the molecular configurations with O_b downward and parallel to the surface were chosen, and the adsorption sites and directions are similar to those for 1,2-DME.

Fig. 2 Different adsorption configurations of 1,2-DME on $\text{TiO}_2(001)$ surface.

Fig. 3 Different adsorption configurations of 1,2-DMP on TiO₂(001) surface.

An additional hybrid functional of HSE06 is used to validate the results of standard PBE functional [50, 51]; the HSE06 and PBE0 hybrid functionals were the most accurate DFT calculations. Medvedev et al. [52] indicated that electron density tends to become more accurate as the density functional

approximation becomes more complex, in an order from LDA to GGA to meta-GGA to hybrids. However, since the HSE06 hybrid functional is very demanding computationally, only two configurations of each molecule were chosen for this validation. The configurations, k-points, and wavefunctions obtained from previous PBE-GGA optimization were been used for this extra calculation to save calculating time.

3. Results

3.1. Adsorption energies and structural properties

The adsorption energy was considered to be a physical component that reflects the adhesive strength of a molecule adsorbed onto a surface. This adsorption energy (E_{ads}) is defined as the difference between the total energy for individual organic molecule (E_{mol}) and a bare surface (E_{sur}) with that of a molecule adsorbed onto a surface system ($E_{mol+sur}$), as given in the following equation:

$$E_{ads} = E_{mol+sur} - (E_{mol} + E_{sur}) \quad (1)$$

The results of molecules considered are presented in Table 1. Note that the configurations where the O_b of DME and 1,2-DMP are located above Ti result in much stronger adhesion than those obtained from other configurations; in fact, this table shows that this difference is up to fourfold for DME and threefold for 1,2-DMP.

The long range dispersion interaction was evaluated to estimate its contribution to the total adsorption energy of the molecules, and a relaxation and single-point energy evaluation with and without dispersion correction have been carried out. This dispersion energy is given in the following equation:

$$E_{disp} = E_{DFTD} - E_{DFT} \quad (2)$$

In this work the dispersion energy was evaluated by first relaxing the chosen configuration and then evaluating its energy using standard DFT and DFTD calculations separately. There was a small difference in the adsorbed structure; in fact, there was an averaged distance of 0.03 Å closer to the surface when DFTD was used instead of DFT. In the second method, the configurations were relaxed using DTFD, and then the single-point energy was evaluated using DFT and DFTD approaches in similar relaxed configurations. The difference in energy between these methods was not significant. In Fig. 3f, there is a maximum tolerance of 0.093 eV, while the averaged tolerances of 0.007, 0.001, and 0.034 eV were measured respectively for DME, 1,2-DME, and 1,2-DMP molecules. Note that the adhesive strength in the case without dispersion correction (DFT) was almost 0.3, 0.2, and 0.6 eV lower than those with dispersion correction (DFTD). The averaged ratios of dispersion energy over the total one are 56, 81, and 85% for DME, 1,2-DME, and 1,2-DMP molecules, respectively. However, in

configurations where the $-\text{CH}_x$ groups adsorbed closer to the surface, these ratios could be up to 100% (Fig. 1c, Fig. 3a, Fig. 3d-h). These results reveal the major role that dispersion interaction played by molecules on the Rutile surface compared to other components such as electrostatic and polarization energies.

Table 1.

Adsorption energies (E_{ads}) and separations (ΔZ) of different configurations of DME, 1,2-DME, and 1,2-DMP molecules adsorbed on $\text{TiO}_2(001)$.

Fig.	E_{ads} (eV)					ΔZ (Å)
	DFT	DFTD				DFTD
		E_{total}	E_{disp}	E_{Coul}	E_{other}	
1a	-1.160	-1.493	-0.337	-0.930	-0.226	2.54 (1.75)
1b	-1.074	-1.406	-0.353	-0.895	-0.159	2.53 (1.72)
1c	-0.001	-0.290	-0.293	-0.052	0.055	3.39
1d	-0.097	-0.397	-0.300	-0.049	-0.048	3.38
2a	-0.032	-0.234	-0.202	0.003	-0.036	4.51
2b	-0.046	-0.250	-0.203	-0.003	-0.044	4.51
2c	-0.041	-0.245	-0.204	-0.008	-0.034	4.50
2d	-0.042	-0.246	-0.204	-0.008	-0.034	4.52
2e	-0.053	-0.251	-0.197	-0.010	-0.043	4.47
2f	-0.057	-0.255	-0.197	-0.011	-0.047	4.45
2g	-0.082	-0.293	-0.210	-0.033	-0.051	4.47
2h	-0.084	-0.294	-0.209	-0.032	-0.053	4.47
2i	-0.011	-0.174	-0.160	-0.000	-0.013	4.74
2j	-0.024	-0.197	-0.170	0.004	-0.031	4.98
3a	-0.024	-0.478	-0.519	-0.075	0.116	3.46
3b	-0.124	-0.828	-0.721	-0.097	-0.010	2.94
3c	-0.164	-0.713	-0.562	-0.243	0.092	3.40
3d	-0.110	-0.712	-0.666	-0.172	0.127	3.15
3e	-0.034	-0.622	-0.635	-0.203	0.216	3.17
3f	-0.013	-0.479	-0.559	-0.026	0.105	3.32
3g	-0.002	-0.570	-0.562	-0.092	0.084	3.35
3h	-0.040	-0.466	-0.430	-0.039	0.002	3.87
3i	-0.994	-1.644	-0.637	-0.799	-0.208	3.06 (2.14)
3j	-1.070	-1.801	-0.752	-0.740	-0.308	2.77 (2.16)

There was an exception has been found for some configurations of DME and 1,2-DMP where O_b were located above the Ti atom where a larger magnitude of adsorption energies of 1.406-1.493 eV, and

1.644-1.801 eV were measured for O_b-down configurations for DME (Fig. 1a,b) and 1,2-DMP (Fig. 3i,j), respectively. The energy disbursed by these molecules was only 25 and 40%, values which are much lower than the averaged values. A conventional DFT calculation in Table 1 provides a large magnitude of adsorption energies of 0.994-1.160 eV for these configurations. Interestingly, the adhesive strengths for 1,2-DME were low, despite a configuration where both bridging oxygens were located on top of the Ti atoms (Fig. 2i). The charge transfer states and electronic properties have been calculated and are presented in the following sections to explain these phenomena. Xiong et al. recently shown that a barrier energy of 1.77 eV was measured by DFT calculation to desorb the DME molecule into the gas phase [31]; this value is close to our current VASP evaluation. The current absolute adsorption energies of 1,2-DME on a TiO₂ surface are lower than those on pure Fe(100), whereas the result for 1,2-DMP [12] is lower.

The molecular structure of the considered molecules was investigated by measuring the distance from their centre of mass to the top surface atom. While the distances are different for different configurations, the results in Table 1 show the distances for 1,2-DME configurations are longer than with other molecules; in fact averaged values of 2.96, 3.25, and 4.56 Å were measured for DME, 1,2-DMP, and 1,2-DME molecules, respectively. This stronger adsorption of O_b-down configurations resulted in shorter distances than with other configurations. The bond lengths of 1.7 and 2.2 Å are shown in brackets in Table 1. The strongest adhesion and shortest bonding distance of O_b and Ti atoms occurred with O_b-down configurations of the DME molecule.

3.2. Electronic properties

3.2.1. Charge transfer states

The strength of the O_b-Ti interaction depends on an interaction that characterized by how the electronic structure between them is transformed. This electronic structure is analyzed by calculating the charge density difference (CDD, $\Delta\rho$), DOS, BOP of the system. This CDD was calculated to visualize the charge transfer between atoms, and it was obtained by subtracting the electron density of the absorbed systems ($\rho_{mol+sur}$) from the isolated surface and molecule (ρ_{sur} and ρ_{mol}), as shown in the following equation:

$$\Delta\rho = \rho_{mol+sur} - (\rho_{mol} + \rho_{sur}) \quad (3)$$

The quantitative values of charge transfer are evaluated using the LOBSTER and DDEC6 approaches [53].

Using an isosurface level of 0.0005 (e) in VESTA package, the CDD visualization of DME, 1,2-DME, and 1,2-DMP molecules are shown in Fig. 4-6. The CDD of 1,2-DME shown in Fig. 5 has much lower

CDD values than those observed from DME and 1,2-DMP. Note there is a ring-shaped electron depletion (negative) regime that surrounds the O_b -Ti bond of O_b -down configurations of DME (Fig. 4a,b), and there is another electron accumulation (positive) regime with a half-ring shape where both ends start from carbon atoms of $-CH_3$ groups and then go through the hole of the electron depletion ring to cover O_b . These observations disclose a charge transfer between O_b of DME with Ti atoms of the Rutile surface. For O_b -up configurations (Fig. 4c,d), there is a very small charge transfer between the hydrogen atoms of the molecules and oxygen located on top surface.

Fig. 4 CDD for different adsorption sites of DME on $TiO_2(001)$. Yellow and cyan colors represent the positive (electron accumulation) and negative (electron depletion) charge regimes, respectively, with isosurface level of $0.0005 \text{ e}/\text{\AA}^3$. These settings are applied throughout this work.

The 1,2-DME, CDD results shown in Fig. 5 are similar to the for O_b -up configurations of DME because there is almost no charge transfer between the molecule and the surface. While this is the same as the O_b -down configuration shown in Fig. 5i, there are larger regimes of electron accumulation and electron depletion for 1,2-DMP configurations, as shown in Fig. 6. This figure shows that major electron transfer occurs between hydrogens and oxygens at the surface. Interestingly, the O_b -down configurations of 1,2-DMP (Fig. 6i,j) has similar shapes of electron accumulation and electron depletion regimes as those for DME. The results of CDD reveal there was a possible bonding between the O_b and Ti atoms of the Rutile surface for O_b -down configurations.

Fig. 5 CDD for different adsorption sites of 1,2-DME on $\text{TiO}_2(001)$.

3.2.2. DOS and BOP

Oxygen has four covalent electrons at 2p orbital; the first two covalent electrons could be shared with adjacent carbons to form a covalent bond between them, while the remaining pair of electrons could be the cause of O_b–Ti bonding. The mechanism of this bonding was clarified and then the DOS of configurations (DME (Fig. 4a) and 1,2–DMP (Fig. 6i)) in which the new bonds were found was then evaluated. The DOS of an isolated DME molecule (Fig. 7a) has a strong overlap between 2p orbitals of C and O, which indicates their strong covalent bonds, but there is a peak of O below the Fermi level which does not overlap with C. The DOS of O_b shows that most of its peaks overlap with those of C, except those that are close to the Fermi level so this peak must belong to the lone pair orbital of oxygen. For the DOS of this O_b in adsorbed molecules at an energy level of -0.5 eV, the peak of this lone pair orbital disappeared for DME and 1,2–DMP but it shifted below the Fermi level and split into two lower peaks for 1,2–DME.

The electron overlap between a 2p orbital of O_b with a 3d orbital of Ti could explain the O_b–Ti bonds when the DME and 1,2–DMP are adsorbed onto the Rutile surface. In fact, Fig. 7 shows there are weak overlaps between the orbital O 2p and Ti 3d at an energy level of ~ -5 eV for DME and 1,2–DMP, whereas there is no overlap peak for the isolated DME or 1,2–DME. This means there is no O_b–Ti bond for 1,2–DME despite the fact that it has bridging oxygen on top of the Ti atom.

Fig. 6 CDD for different adsorption sites of 1,2-DMP on $\text{TiO}_2(001)$.

The covalent characteristic of bonds has been determined by analyzing BOP. The DDEC6 approach indicates there is a BOP of 0.209 and 0.198 e for the Ti–O bond in O_b -down configurations of DME in (110) and (-110) directions, respectively. The corresponding BOP values obtained by the LOBSTER

method were slightly lower with respective values of 0.159 and 0.147 e for these configurations. For 1,2-DMP, this method provided the BOP values of 0.147 e for both O_b -down configurations (Fig. 6i,j). These data reveal a significant charge transfer between O_b of DME and 1,2-DMP with Ti, which observation indicates there is an associated adsorption of these O_b -down configurations on the Rutile surface; other adsorption configurations are purely physisorption through dispersion interactions.

Fig. 7 DOS of: (a) 2p orbitals of O_b and C of isolated DME; and 2p orbital of O_b of (b) DME; (c) 1,2-DME; (d) 1,2-DMP and 3d orbitals of Ti on Rutile surface.

A question arises as to whether the new bonding between O_b and Ti atom affects the covalence bonds between adjacent carbons of $-CH_x$ and this O_b . A comparison of BOP in isolated molecules and in adsorption systems has been carried out using DME molecules. The LOBSTER package provided an averaged BOP value of 0.262 e between carbon and O_b in isolated molecules, this value is slightly higher than the 0.256 e obtained for adsorbed molecules. This result indicates that the new bonding does not affect the covalence bonds between carbon and O_b very much, and furthermore, the BOP of 0.159 e of O_b -Ti bond is lower than the 0.262 e value of O-C.

The atomic BO was evaluated to determine how the Rutile surface affected the BO of molecular elements. More emphasis was placed on O_b because it could form a new bond with Ti, and DME was chosen as a typical model for this BO comparison. Fig. 8a,b shows that the BOs of oxygen are ~3.00 O_b-down configurations of DME, whereas this value varied from 2.8 to 2.9 in isolated molecules and in other O_b-up configurations of DME (Fig. 8c,d), 1,2-DME (Fig. S1), as well as 1,2-DMP (Fig. S2). These results finally confirm that the O_b in O_b-down configurations have formed a completely coordinated covalent bond with Ti via the lone-pair of oxygen electrons.

Fig. 8 Effective bond order for different adsorption sites of DME on TiO₂(001).

3.2.3. Partial Charges

The charge evaluated for each atom in an isolated molecule using the DDEC6 method is shown in Fig. 9, and its average charge value is provided in Table 2. The results reveal a small difference in the partial charge of hydrogen, as well as the Ti and surface oxygen of surface between the current work and those used in previous references [17, 18, 21, 48]. However, the absolute values of charge for carbon and oxygen evaluated from the current DFT calculation are lower than the reference results. Deviations of

0.1-0.15 e have been found for oxygen in molecules and there is a larger difference of 0.232e for C(H) in 1,2-DMP.

Although the BOP of the O_b -Ti bond is smaller than O-C, there are not enough clues to conclude that the O-Ti bond is weaker than O-C because there is an additional attractive Coulombic interaction between a negatively charged atom (O) and a cation (Ti), however, there could be a weak Coulombic interaction between C and O due to the low atomic charge of C. In fact, Table 2 also shows there could be a repulsive Coulombic interaction between O_b with a negative atomic charge of -0.164 e with its neighboring carbons with an averaged negative atomic charge of -0.169 e. In contrast, there is an attractive Coulombic interaction between this oxygen and Ti with a positive partial atomic charge up to 2.6 e (Fig. 9d); this motif is similar for 1,2-DME and 1,2-DMP.

Fig. 9 Partial charge of each atom in: (a) DME; (b) 1,2-DME, (c) 1,2-DMP, and (d) $TiO_2(001)$.

These partial charge differences in molecules could be explained by using different levels of theory in quantum chemistry calculations; for instance, MP2 calculations were applied for molecules in these references, whereas ultra-soft pseudopotentials were applied in this work. In fact for the same level of theory, the results obtained for the TiO_2 surface agree closely with those obtained from the work by Bandura et al [48].

When adsorbed onto the surface the partial charge value of atoms close to the surface alters; the local atomic charge in each adsorption configuration of DME, 1,2-DME, and 1,2-DMP are presented in Fig. S3-S5 in Supporting Materials (SM), respectively, while Fig. S3 shows that when DME is adsorbed onto a Rutile surface, the partial charge of O_b is more negative than in isolated molecules and O_b -up configurations; in fact charges of -0.238 and +2.063 e have been found for O_b and Ti in O_b -down configurations. A reduced amount of -0.074 e has been found for O_b , while an increment of +0.063 e was evaluated for Ti. Similar observations were found for 1,2-DMP, but there was an insignificant change of atomic partial charges for 1,2-DME.

Table 2.

Comparison of averaged partial charges (e) of elements in DME, 1,2-DME, 1,2-DMP, and TiO₂ surface from the current DTFD calculation and those obtained from other references.

Element	DME		1,2-DME		1,2-DMP		TiO ₂	
	DFTD	Borodin ^a	DFTD	Smith ^b	DFTD	Smith ^c	DFTD	Bandura ^d
C(H ₃) _m	-0.169	-0.119	-0.167	-0.163	-0.168	-0.233		
C(H ₃)					-0.437	-0.529		
C(H ₂)			0.006	-0.066	-0.032	-0.162		
C(H)					0.194	0.426		
H	0.084	0.086	0.074	0.097	0.090	0.099		
O	-0.164	-0.279	-0.206	-0.256	-0.235	-0.330		
Ti							2.106	2.196
O(Ti)							-1.053	-1.098

Reference partial charge for: a DME obtained by Borodin et al. [21], b 1,2-DME obtained by Smith et al. [17], c 1,2-DMP obtained by Smith et al. [18], and d TiO₂ surface obtained by Bandura et al. [48]. C(H₃)_m denotes termination methyl group.

The electrostatic energy (E_{Coul}) of adsorbed molecules on a Rutile surface has been evaluated for each adsorption system. The results in Table 1 indicate there is a small amount of this energy component in the total interaction energy of systems without a O_b-Ti bond; in fact the absolute electrostatic energies less than 0.055, 0.033, and 0.203 eV have been evaluated for DME, 1,2-DME, and 1,2-DMP. Corresponding ratios that contribute to the total adsorption energy of 12, 19, and 3% have been found for these molecules, but their values are very low compared to the ratios evaluated for dispersion energies. Note that the electrostatic energies of configurations with the O_b-Ti bond are much larger than those without this bond. Values of -0.895 to -0.930 eV, and -0.740 to -0.799 eV have been evaluated for O_b-Ti bond configurations of DME and 1,2-DMP, respectively but these values are an order of magnitude larger than those calculated for other configurations. The electrostatic energies for O_b-down configurations of DME are three times larger than the dispersed ones, but they are almost equal for O_b-down configurations of DMP. The much larger electrostatic energies of these O_b-down configurations could be explained by an increase in the atomic partial charges of O_b (more negative) and Ti (more positive) atoms, as shown above; this is an attractive force at a very short distance of less than 2.0 Å, as shown in Table 1.

Finally, the remaining energy (E_{other}) was considered as a contribution from polarization [21, 22], the hydrogen bond, and the covalent bond. Table 1 shows that this energy contributes an average ratio of 14, 15, 16% for DME, 1,2-DME, and 1,2-DMP, respectively. These low ratios could be explained by the ttt and tttt configurations of 1,2-DME and 1,2-DMP which led to low dipole moments (nearly zero) [21]. These current results show an agreement with a previous observation by Borodin et al. who also reported that polarization energy (~7%) contributed almost nothing to the total amount of energy calculated [22].

4. Discussion

A comparison between a standard PBE and a HSE06 hybrid functional are presented in Table 3 to validate the current calculated results. According to this table, there are errors between 9% for adsorption energies and 2% for molecular separation, the adsorbed molecular structures reveal that the distances between the centroid of the molecules to the closest atom calculated from HSE06 are a slightly higher than those obtained from standard PBE, while the small errors in adsorption energy and molecular separation proves that the standard PBE functional is relevant to this current study.

Table 3.

Comparison of adsorption energies (E_{ads}) and separations (ΔZ) between a standard PBE functional and a HSE06 hybrid functional for different configurations of DME, 1,2-DME, and 1,2-DMP molecules adsorbed on $\text{TiO}_2(001)$.

Fig.	E_{ads} (eV)		Error %	ΔZ (Å)		Error %
	PBE	HSE06		PBE	HSE06	
1a	-1.493	-1.633	-8.55	2.54	2.57	-1.28
1d	-0.397	-0.394	0.81	3.38	3.41	-0.90
2a	-0.234	-0.221	6.09	4.51	4.55	-0.89
2b	-0.25	-0.236	5.87	4.51	4.54	-0.77
3b	-0.828	-0.857	-3.37	2.94	2.94	-0.06
3j	-1.801	-1.912	-5.82	2.77	2.80	-1.24

The charge transfer within the molecule itself is larger than between them and the surface for the configurations of physisorption; this is possibly because there is no covalent bond between the molecules and the surface in these configurations, so that the electron density of the molecules does not exchange to the surface, and there is a hydrogen bond characterized by a partially electrostatic attraction between the hydrogens, which are closer to the surface, and oxygen on the surface. For configurations without the $\text{O}_b\text{-Ti}$ bond such as paths 3 and 4 of DME (Fig. 4c, d), all the configurations of 1,2-DME (Fig. 5), and the first eight configurations of 1,2-DMP (Fig. 6a-h) have small amounts of accumulated electrons around the oxygen on top of the surface and depleted electrons around the nearby hydrogens. The depletion of hydrogen electrons results in an accumulation of electron around the neighboring carbons, and as mentioned in the introduction section, DME, 1,2-DME, and 1,2-DMP are polarizable molecules, so the electron density in these molecules could be changed due to the polarization induced by the oxide surface [21, 22].

For configurations with the chemical $\text{O}_b\text{-Ti}$ bond, the charge transfer between the molecules and the surface is mainly between O_b and Ti, and while the charge transfer between hydrogens and surface oxygens is still available, they contribute a much smaller amount. In fact when the isosurface level is increased to $\sim 0.009 \text{ e}/\text{\AA}^3$, the accumulation of electron around the oxygens and the depletion of nearby hydrogen electrons disappear. In contrast, the corresponding isosurface level for the charge transfer between the molecules and surface via $\text{O}_b\text{-Ti}$ bond is $\sim 0.02 \text{ e}/\text{\AA}^3$ is much larger than the aforementioned value.

The current theoretical system is calculated as an ideal condition in which adsorption is simulated at zero temperature and pressure. The practical Rutile surface could be altered due to the diffusivity of water molecules in the air onto the TiO_2 surface to form complex titanium hydroxide [48, 54], so to the best of our knowledge, current literature suggests there is no experimental study available for current systems. We have referred to close systems to assess the current adsorption results, so the absolute adsorption energies obtained for DME are higher than its heat of adsorption on a silica surface (0.166-0.207 eV) at boiling temperature of DME's (248.2 °K) [34]. This discrepancy in the adsorption energy could be explained by the difference in the adsorption mechanism because the adsorption of DME on the Rutile surface via oxygen lone-pair electrons with Ti is different with the bonds between methoxy ($-\text{O}-\text{CH}_3$)-silanol observed for silica. However, the $-\text{CH}_3$ down configurations of DME and all the adsorption configurations 1,2-DME in Table 1, produced results that are close to those measured for a silica surface [34].

The formation O_b -Ti bond when DME is adsorbed onto a Rutile surface agree well with recent investigation by Herron et al. who found that this O_b reacted with transition metals such as Au, Ag, Cu, Pt, Pd, Ni, Ir, Rh [36]. Table 1 reveals that the adsorption of 1,2-DME on $\text{TiO}_2(001)$ surface using a DFTD level are weaker than on a nascent Fe(100) surface (-0.742 eV) using a standard DFT calculation [12]. This could be because Fe has less electronegativity than Ti and the atomic density of a nascent Fe(100) surface is denser than $\text{TiO}_2(001)$, and therefore, there is a stronger adsorption of 1,2-DME on Fe(100) surface [30, 55]. Moreover, the chemisorption mechanism of DME on a Rutile surface is similar to the clean Pd surfaces studied experimentally by ultra-vacuum photoemission [56].

An interesting observation is that there is no bond between O_b of 1,2-DME with Ti despite the oxygen being positioned intentionally on top of the Ti atoms. The difference in charge density of the configuration shown in Fig. 5i and the full electron density shown in Fig. 10 reveal that the axis of lone-pair electron regime has changed and it can longer remain parallel in a Z direction on top of the Ti atoms. This could be due to the interaction of hydrogen at $-\text{CH}_3$ termination with terminating oxygen on the surface; in fact, a small BOP of 0.008 e has been evaluated for these interactions. Moreover, the O_b of 1,2-DME was positioned on the molecular back-bond plane to prevent the molecule distortion and help the lone-pair electron regime directly on top of the Ti atoms, in other words the attraction between this O_b with Ti was less than the necessary torsion energy barrier needed to adsorb directly onto the Ti atoms. In fact, compared to the initial configuration in which the $\text{CH}_3-\text{O}-\text{CH}_2$ was reduced while the $\text{O}-\text{CH}_2-\text{CH}_2$ was expanded to artificially position the bridging oxygen on top of Ti atoms (Fig. 2i), these relaxed molecules have resisted these artificial settings by an expanding the $\text{CH}_3-\text{O}-\text{CH}_2$ angle and reducing of $\text{O}-\text{CH}_2-\text{CH}_2$ angle.

Fig. 10 Total electron density of: (a) DME; (b) 1,2-DME adsorbed on TiO₂(001). Isosurface level of 0.02 e/Å³ was applied in this image.

This study aims to help tribologists and copolymer researchers to understand the interaction between PEO and PPO blocks of copolymers with metal oxide surfaces, and to propose a suitable representative model for a PEO block. DME has been partly successful as a model of PEO to develop its interaction force field with the TiO₂ surface by proposing a cluster of DME/TiO₅H₉ complex [11], but when a full surface of TiO₂ was used, the results revealed that DME is not a perfect choice due to its strong adsorption energy. The DME's BOP and adsorption energy (without correcting the dispersion) are larger than those obtained from 1,2-DMP, while 1,2-DME is a dimer of DME, but DME adsorbs onto the TiO₂(001) surface better than 1,2-DME. A molecule is considered to be a suitable model to represent a long chain copolymer if its adsorption energy is in direct proportion to the number of constituent monomers [30, 57]. Previous observations of the adsorption of reverse triblock copolymers on TiO₂ coated surfaces indicated that a weaker adsorption of PEO block than PPO occurred in an aqueous solution [1, 8, 13-15]. Therefore, 1,2-DME molecule has been proposed as a representative model for PEO block when simulating of the force field in molecular dynamics of these specific models.

The stronger adsorption of 1,2-DMP compared with 1,2-DME partly explains the adsorption structure of reverse copolymer's anchor-buoy-anchor (A-B-A) on TiO₂ coated surface [1, 8, 13, 15], while the physisorption nature of these molecules contributes more than 80% of the total adsorption energy. This explains why the PEO and PPO blocks were easily removed from the surface when they were dissolved in an aqueous solution and then subjected to shear in the experimental investigations. In an investigation using a similar method of simulation, Wang et al. analyzed the roles of the vdW and electrostatic interactions in the system energy [58]; they agreed with our work where the dispersion energy is the major contributor to the system energy. It could also be predicted that 1,2-DMP (or PPO block) could result in a higher friction force than 1,2-DME (or PEO block), due to the higher dispersion interaction of 1,2-DMP compared with 1,2-DME.

5. Conclusions

DFT calculations were used to investigate the adsorption of DME, 1,2-DME, and 1,2-DMP on a Rutile surface while various physical and chemical components were calculated to cover the adsorption energies, structural properties, difference in charge density, density of state, bond overlap population, and atomic charge. The major findings obtained are summarized as follows:

Dispersion interaction plays a major role in the adsorption energies of 1,2-DME, O_b -up configurations of DME and 1,2-DMP. The low partial atomic charge of these molecules results in a weak interaction energy between the molecules considered and the Rutile surface. The adsorption energies of these systems are much lower than those obtained from the O_b -down configurations.

For O_b -down configurations, a new coordinate covalent bond between the O_b and Ti atoms on the surface is formed by an overlap of orbital O 2p and Ti 3d. A higher BO, and BOP have been found for DME compared to 1,2-DMP, whereas DME has a stronger O_b -Ti bond than 1,2-DMP; while this bond is not formed for 1,2-DME.

1,2-DME has been recommended as a suitable representative model for PEO, while DME could result in an overestimation of adsorption energy of the PEO with the Rutile surface.

Supporting Information

Additional effective bond order and atomic partial charges for different adsorption sites of DME, 1,2-DME, and 1,2-DMP on TiO_2 have been presented in Supplementary Materials.

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