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Self-assembled monolayers of alkylphosphonic acids on aluminum oxide surfaces – A theoretical study

Regina Luschtinetz,^{*[a]} Augusto F. Oliveira,^[a, b] Hélio A. Duarte^[b] and Gotthard Seifert^[a]

Keywords: density functional calculations; adsorption; self-assembled monolayers; alkylphosphonic acids; aluminium surfaces.

Density-functional based calculations have been used to investigate self-assembled monolayers of different alkylphosphonic acids on corundum α -Al₂O₃ (0001), bayerite β -Al(OH)₃ (001) and boehmite γ -AlOOH (010) surface models. Mono-, bi-, and tridentate adsorption modes have been considered. In addition, the organization of single adsorbed molecules has been compared to the organization at full surface coverage. The height (thickness) of the self-assembled monolayers is always shorter than the length of the phosphonic acid molecules due to tilting of the alkyl chains. Tilt angles at full surface coverage are very similar to the tilt angle

of a single adsorbed molecule, indicating that the density of the self-assembled monolayers is limited by the density of adsorption sites. The lateral interactions between alkyl chains are evidenced by small torsions of the adsorbed molecules, which may serve to minimize the repulsion forces between interchain hydrogen atoms. Similar tilt angles have been obtained for mono-, bi-, and tridentate adsorptions. Hence, the coordination mode cannot be characterized by the molecule tilting.

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Introduction

The structure, formation and properties of self-assembled monolayers (SAMs) [1-4] have become the subject of much interest in recent years due to their potential application as protective coatings^[1], sensors^[2], electronic semiconductors^[3] and adhesive promoters^[1c, 4]. In order to create a SAM it is necessary to find a self-assembly capable molecule which can covalently bind to a specific surface. This molecule usually consists of three parts: an anchor group, a spacer group and a terminal functional group^[5].

The anchor group (*head group*) is responsible for the adsorption of the molecule by forming chemical bonds to the adsorbent surface. Thus, the choice of this group strongly depends on the nature of the adsorbent. The thiol group (–SH) is applicable to metals, especially gold surfaces, whereas phosphonic (–PO(OH)₂), sulfonic (–SO₂(OH)), silanol (–Si(OR)₃) and silyl (–SiR₃) groups are more suitable for adsorption on oxide materials such as Al/Al₂O₃, Ti/TiO₂, and mica^[5-6].

The terminal functional group (*tail group*) determines the properties of the SAM surface. Nonpolar groups such as methyl (–CH₃) give highly hydrophobic surfaces, being thus applicable in the field of corrosion protection^[1c, 6b]. Polar groups such as hydroxyl (–OH), carboxyl (–COOH) or amine (–NH₂) are able to react with an overlayer and are, therefore, good candidates to act as adhesion promoters on reactive metal surfaces or organic coatings^[1b, 6b]. For grafting polythiophene layers on metal oxide substrates,

ω -(thiophen-3-ylalkyl)phosphonic acids have been designed and characterized. Their structure allows surface polymerization as well as formation of polymers using additional monomers, resulting in densely packed films with long conjugated units. Thus, they are potentially applicable in the field of organic-based electronics^[4a, 4c].

The group between the anchor and terminal groups (*spacer group*) normally consists of a long alkyl chain with 10 to 18 methylene groups (–CH₂–). The spacer group determines the intermolecular interactions and promotes the ordering and orientation of the molecules within the monolayer^[5, 6b]. It might also influence the film formation and growth process^[6a, 7].

One important class of self-assembling molecules are alkylphosphonic acids (APAs), which produce robust, well-anchored SAMs on aluminum surfaces^[1a, 1b, 6a, 8]. Highly hydrophobic monolayers have been obtained and characterized by contact angle measurements^[1b, 6a, 8b-d, 8g]. It has also been shown by Fourier transform infrared (FTIR) spectroscopy that the CH₂ vibrational energy decreases with the adsorption time, indicating that the formed film is initially disordered, becoming gradually oriented as the adsorption takes place^[1a, 1b, 6a, 8d, 8e]. In addition, P=O and P–OH stretch bands are absent from the FTIR spectra of the adsorbed APAs. Instead, there are bands attributed to the symmetric and asymmetric stretches of the resonance stabilized RPO₃²⁻ group, which indicates that APAs bind to the aluminum surface via three symmetric P–O–Al bonds^[1b, 8c]. This has been also found by inelastic tunneling spectroscopy (IETS) on adsorbed phosphonic and vinylphosphonic acids^[9].

In a previous investigation, we studied the adsorption of phosphonic acid (H₃PO₃) and ethylphosphonic acid (H₅C₂–PO₃H₂) in order to find the most suitable adsorption sites on aluminum surface^[10]. Since natural aluminum

surfaces are covered by an oxide film, which is mostly amorphous^[4b, 11], we have used theoretical surface models based on corundum (α -Al₂O₃ (0001)), bayerite (β -Al(OH)₃ (001)), and boehmite (γ -AlOOH (010)).

In the present work, we complement our investigation by using density-functional based calculations to study SAMs of alkylphosphonic acids with longer carbon chains: pentylphosphonic acid (PPA), decylphosphonic acid (DPA), and octadecylphosphonic acid (ODPA), shown in Figure 1. The aim now is to find out whether the ordering of the molecules in the monolayer is related to the APA coordination mode to the surface, to the structure of the underlying surface and/or to the length (number of carbon atoms) of the alkyl chain of the adsorbed APA.

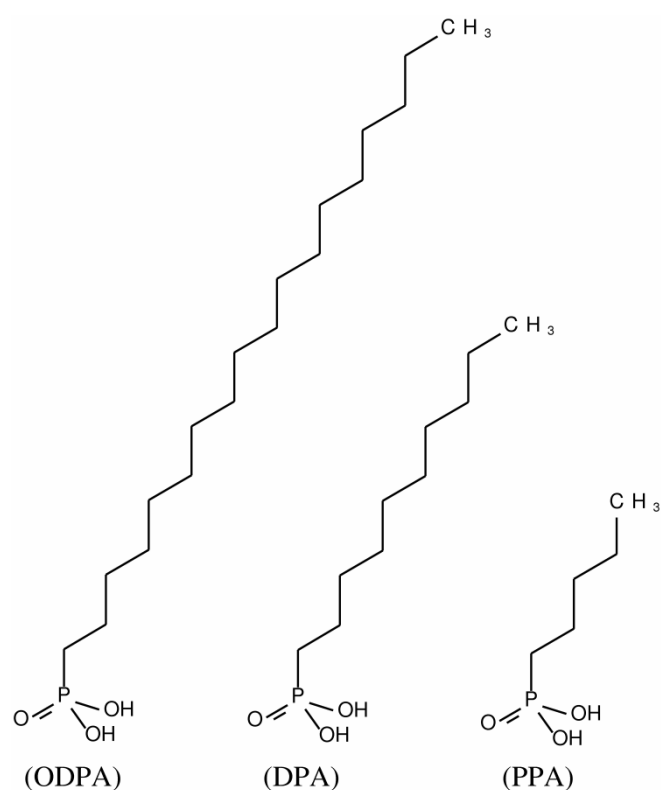


Figure 1. Chemical structure of the alkylphosphonic acids used in this work: octadecylphosphonic acid (ODPA), decylphosphonic acid (DPA), and pentylphosphonic acid (PPA).

We have considered mono-, bi- and tridentate adsorption complexes, where the anchoring phosphonic group binds to the surface via one, two or three P–O–Al bonds, respectively, corresponding to the stepwise condensation reaction (see Figure 2) between the phosphonic acids and the hydroxyl groups of the surface^[9c, 10, 12]. For each coordination mode we have used the energetically preferred sites of each surface, which we have determined in an earlier study^[10]. We have also studied the adsorption of single molecules in addition to SAMs formed when the maximum number of APA molecules is attached to the surfaces.

Computational Details

In this study we have used the self-consistent-charge density-functional based tight-binding (SCC-DFTB)

method^[13] with periodic boundary conditions, as implemented in the DFTB+ program^[14]. The SCC-DFTB method has been successfully applied in our group to study the adsorption of phosphonic and ethylphosphonic acids on aluminum and titanium oxides^[10, 15]. A recent review on the method and its approximations can be found elsewhere^[16].

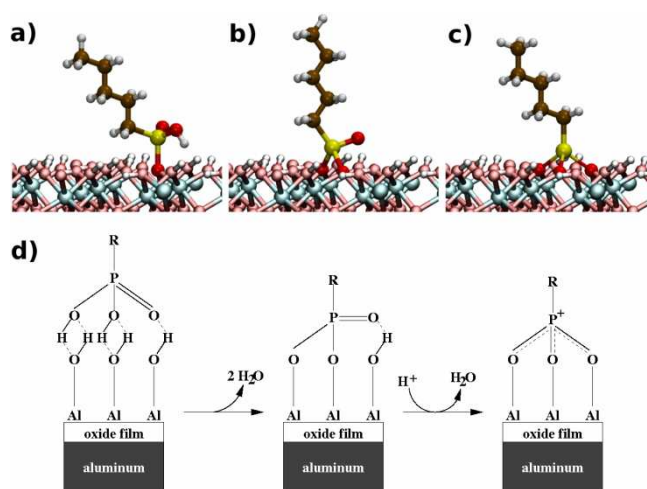


Figure 2. a) Monodentate, b) bidentate, and c) tridentate coordination of APAs on aluminum oxide surfaces. O atoms are red, Al atoms are blue, H atoms are white, C atoms are brown and P atoms are yellow. d) Schematic condensation mechanism for phosphonic acid chemisorption on aluminum oxide surface; formation of the bidentate complex is shown as a single step.

For the study of SAMs we used ideal α -Al₂O₃ (0001), β -Al(OH)₃ (001) and γ -AlOOH (010) surface models, terminated by hydroxyl groups. These models consist of periodic slabs derived from the optimized geometries of the respective bulk structures. A more detailed description of our surface models has been published in a previous paper^[10].

Mono-, bi- and tridentate adsorption complexes were constructed by adding the alkylphosphonic acids on the top and bottom of the slabs, in order to minimize artificial dipoles. The bonds between the APAs and the surface were assumed to follow the mechanism shown in Figure 2. In the present study we only considered the adsorption sites found to be the most favorable in our previous work^[10]. The adsorption sites for each surface model are shown in Figure 3.

In order to simulate the adsorption of single APA molecules, the periodic unit of each surface was replicated to ensure that the APA would not interact with its own periodic image. The lateral dimensions of the periodic cells are given in Table 1 as multiples of the respective bulk unit cells. A vacuum region of at least 50 Å was added in the direction perpendicular to the plane of the slabs in order to avoid self-interactions between the surface and its periodic images.

The number of APA molecules in each periodic unit, the surface coverage for each surface and the coordination mode are also listed in Table 1. The maximum adsorbate densities calculated for mono- and bidentate complexes on the different surfaces range from 4.3 to 4.7 molec. nm⁻². These values are in good agreement with the maximum packing

density of $\sigma^{-1} = 4.35 \text{ molec. nm}^{-2}$ for closely packed monolayers of APAs, which has been estimated by the cross-section area of the phosphonic acid head group ($\sigma = 0.23 \text{ nm}^2$)^[17]. This result also agrees with experimental surface coverages reported in the literature for ODPAs on mica^[18], TiO₂^[19], ZrO₂^[19] and Si/SiO₂^[20]. In the tridentate models we had to remove a proton from the adjacent adsorption site for each APA molecule in order to balance the positive charge which is implicated in this coordination mode (see Figure 2d)^[10]. Thus, the maximum coverage is always half of the values for mono- and bidentate adsorption.

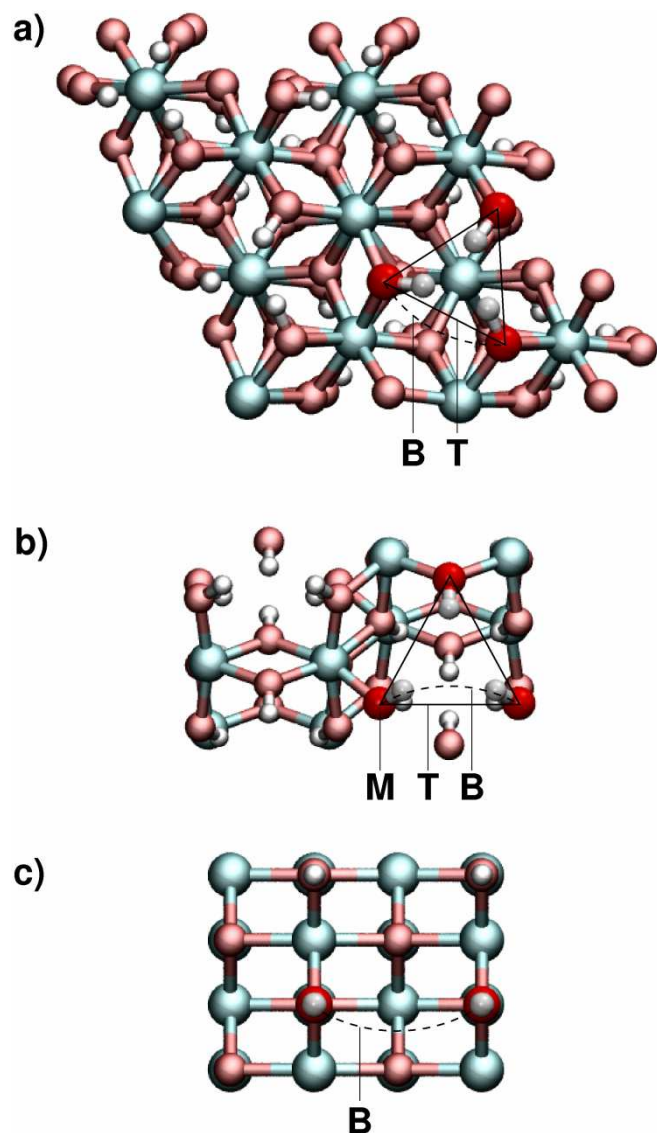


Figure 3. Surface structures and preferred adsorption sites for mono- (M), bi- (B) and tridentate (T) binding of the APAs: a) $\alpha\text{-Al}_2\text{O}_3$ (0001), b) $\beta\text{-Al(OH)}_3$ (001), c) $\gamma\text{-AlOOH}$ (010). Atoms are colored as in Figure 2.

All structures used in this work were fully relaxed using the conjugate gradient algorithm until the root mean square force was less than or equal to 3×10^{-4} a.u. The Γ -point approximation was used, as it has shown to be enough for producing accurate geometries while saving computational time.

Results and Discussion

The object of our work is to determine the orientation and torsional order of the APA molecules in the SAMs according to surface structure, surface coverage, coordination mode and length of the alkyl chain.

Table 1. Number of APA molecules per simulation cell and surface coverage for each coordination mode and surface structure. The size of the periodic surface cells is given in multiples of the unit cell of the corresponding bulk structures. I – $\alpha\text{-Al}_2\text{O}_3$ (0001), II – $\beta\text{-Al(OH)}_3$ (001), III – $\gamma\text{-AlOOH}$ (010).

	acid	cell size	# of molecules			Surf.cov. / nm^{-2}		
			mono	bi	tri	mono	bi	tri
I	PPA, DPA	3×3×1	1	1	1	0.49	0.49	0.49
II		3×2×1	1	1	1	0.36	0.36	0.36
III		5×1×4	1	1	1	0.47	0.47	0.47
I	ODPA	5×5×1	1	1	1	0.18	0.18	0.18
II		5×3×1	1	1	1	0.14	0.14	0.14
III		8×1×7	1	1	1	0.17	0.17	0.17
I	PPA,	2×2×1	4	4	2	4.38	4.38	2.19
II	DPA,	1×1×1	2	2	1	4.28	4.28	2.14
III	ODPA	2×1×2	2	2	1	4.65	4.65	2.33

Table 2. Average height of APA monolayers on each surface, at different coverages and coordination modes. I – $\alpha\text{-Al}_2\text{O}_3$ (0001), II – $\beta\text{-Al(OH)}_3$ (001), III – $\gamma\text{-AlOOH}$ (010). Heights are given in Å.

	Coord.	Single Molec.			Max. Coverage		
		I	II	III	I	II	III
PPA	mono	6.3	5.8	6.1	7.4	7.0	6.3
	bi	6.8	6.8	4.6	6.9	7.1	6.6
	tri	6.7	6.2	6.8	6.7	6.1	6.1
DPA	mono	12.0	11.0	8.7	12.4	11.1	12.0
	bi	12.7	13.1	8.4	12.3	13.0	12.6
	tri	11.5	11.4	12.7	11.6	9.9	9.2
ODPA	mono	20.6	20.3	20.4	20.7	18.1	19.7
	bi	23.6	22.7	23.0	20.8	21.5	20.0
	tri	19.7	21.0	21.0	19.4	18.5	20.1

Table 3. Experimental SAM heights and tilt angles of ODPAs on different substrate surfaces.

Surface	Height/Å	Tilt angle/°	Ref.
mica	18	40	[18]
	16.5	46	[21]
	17	45	[22]
TiO ₂	22	33	[23]
Si/SiO ₂	18	40	[20]
	24	–	[24]
Au/Cu(UPD)	20	30	[25]
Al/Al ₂ O ₃	–	31	[1a]

The height (or thickness) of the SAMs was taken as the distance between the average plane of superficial oxygen atoms and the farthest carbon atom of the alkyl chains of the adsorbed APA. As seen on Table 2, the height of SAMs ranges from 4.6 to 7.4 Å for PPA, 8.4 to 13.1 Å for DPA and 18.1 to 23.6 Å for ODPAs. Experimentally determined heights of ODPAs on different surface structures also vary about several angstroms, as shown in Table 3. Furthermore, except for the single bidentate ODPAs molecule on $\alpha\text{-Al}_2\text{O}_3$ (0001), the heights never reach the lengths of the fully extended, optimized, free molecules, which are about 7.5, 13.5, and 23.5 Å for PPA, DPA and ODPAs, respectively. The primary factor defining the SAM height is the tilting of the carbonic chains with respect to the

surface normal, although small variations have been observed in the length of the phosphonic acids after adsorption.

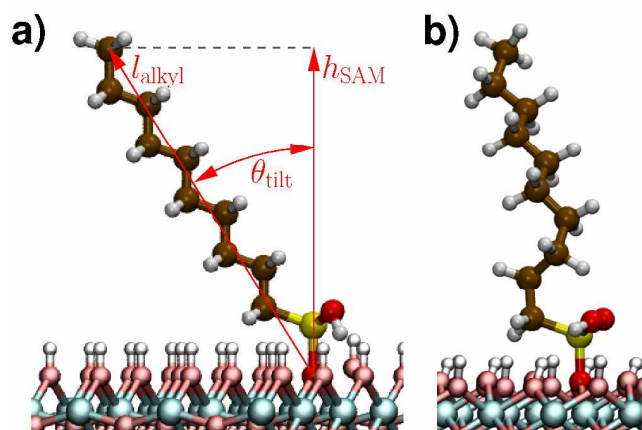


Figure 4. a) Chain tilting and b) chain distortion. Atoms are colored as in Figure 2.

The tilt angles (see Figure 4a) of the alkylphosphonic acids are calculated as

$$\theta_{\text{tilt}} = \cos^{-1} \left(\frac{h_{\text{SAM}}}{l_{\text{alkyl}}} \right)$$

where h_{SAM} is the SAM height and l_{alkyl} is the length of the alkyl chain. Experimentally, tilt angles (see Table 3) are estimated from the measured height of the SAMs, assuming the length of the adsorbed phosphonic acid to be the same as in the all-*trans* configuration of the free acid molecule. However, it is reasonable to assume the self-assembly process to result in some conformational change of the adsorbed molecules, induced by the chemical modification undergone by the head group in the adsorption and by the interactions between alkyl chains, which should lead to minimization of repulsive forces. In Table 4, we present the tilt angles calculated considering the length of the alkyl chain as the distance between the anchoring phosphonic oxygens and the farthest carbon atom. For comparison, the tilt angles calculated considering the fully extended alkyl chains are given in parentheses. The difference between the two calculated tilt angles is quite large for some cases, giving evidence of the chain distortions. However, it is important to notice that these differences may be caused by relatively small changes in l_{alkyl} . In average, the length of the adsorbed APAs is changed by less than $\pm 0.5 \text{ \AA}$.

Regarding the coordination modes, the alkyl chains are tilted in very similar angle ranges: from 10° to 52° for the monodentate, from 14° to 46° for bidentate and from 5° to 43° for tridentate adsorption complexes. Hence, it is evident that the tilt angle cannot be used to determine whether the phosphonic acid forms one, two or three bonds with the surface. Moreover, the tilt angles and SAM heights obtained in the case of single molecule adsorption are very similar to the case of full coverage, indicating that these properties are not significantly affected by the SAM density in the surfaces studied in this work. These results are in agreement with the findings of Liakos et al.^[8d]. Despite the authors'

expectations of observing the adsorbed phosphonic acids to be nearly perpendicular to the surface at maximum coverage, the adsorbed molecules were still tilted. Liakos et al. attributed this result to the density of adsorption sites on the surface, which would limit the number of adsorbed molecules to an amount where the alkyl chains are not maximally packed. This is consistent with our models, in which maximum coverage leads to about 4 molecules per nm^2 . However, our calculations resulted in very similar tilt angles for both the single adsorbed molecule and fully covered surface (in average, 29° and 30° , respectively), indicating that tilt angles are not significantly influenced by dispersion forces, as hypothesized by Liakos et al. Assuming that the tilt angle of a single molecule corresponds to the maximum tilting, if dispersion forces were significant in our models, the tilting observed in the case of full coverage should be lower, since the SCC-DFTB method employed in this work does not account for dispersion forces. Thus, it is likely that conformational organization in SAMs of alkylphosphonic acids on oxidized aluminum surfaces results from minimization of repulsion forces, rather than by maximization of dispersion interactions. This hypothesis is reinforced by the fact that the APAs in the present work only have sp^3 carbons, which present even weaker dispersion forces than the sp^2 carbons in graphite, where the cohesive energy between the sheets is less than 40 meV per atom^[26].

Table 4. Average tilt angles of the phosphonic acids with respect to the surface normal for different coverages and coordination modes. The values between parentheses were estimated considering the length of the free acid with fully extended carbonic chain. I – $\alpha\text{-Al}_2\text{O}_3$ (0001), II – $\beta\text{-Al}(\text{OH})_3$ (001), III – $\gamma\text{-AlOOH}$ (010). All angles are given in degrees.

		Single Molec.			Max. Coverage		
		I	II	III	I	II	III
mono	PPA	38 (33)	43 (39)	40 (36)	25 (9)	10 (20)	33 (33)
	DPA	33 (27)	40 (35)	52 (50)	31 (23)	33 (35)	27 (27)
	ODPA	33 (29)	35 (30)	34 (30)	32 (28)	34 (40)	31 (33)
bi	PPA	31 (25)	26 (26)	46 (51)	28 (23)	23 (19)	30 (29)
	DPA	27 (19)	18 (13)	14 (51)	25 (24)	22 (16)	25 (21)
	ODPA	0 (0)	11 (15)	5 (12)	28 (27)	26 (22)	30 (32)
tri	PPA	21 (27)	23 (34)	5 (32)	22 (27)	31 (35)	32 (35)
	DPA	31 (31)	29 (33)	22 (19)	30 (30)	42 (43)	43 (47)
	ODPA	33 (33)	31 (25)	0 (27)	35 (35)	38 (38)	32 (31)

For a more detailed analysis of the SAMs, the dihedral angles of the alkyl methylene groups in the adsorbates were also calculated. A dihedral angle of 180° means that the methylene units are in the staggered (all-*trans*) conformation, whereas a dihedral of 120° refers to the eclipsed configuration, as depicted in Figure 5. The average dihedral angles calculated in this work are shown in Table 5, where a value of 180° is indicative of perfectly ordered chains.

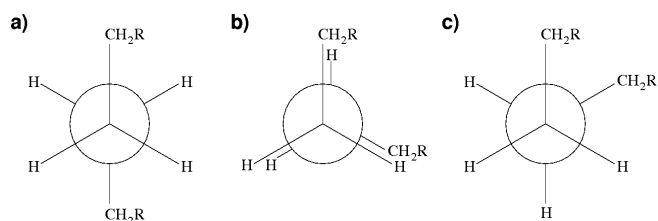


Figure 5. a) Staggered ($\varphi = 180^\circ$), b) eclipsed ($\varphi = 120^\circ$), and c) gauche ($\varphi = 60^\circ$) conformations of the methylene units.

Table 5. Average dihedral angles between methylene groups of the phosphonic acids adsorbed with different surface coverages and coordination modes. I – α - Al_2O_3 (0001), II – β - $\text{Al}(\text{OH})_3$ (001), III – γ - AlOOH (010). Angles are given in degrees.

		Single Molec.			Max. Coverage		
		I	II	III	I	II	III
mono	PPA	179	178	178	168	132	138
	DPA	177	175	177	169	144	163
	ODPA	179	179	179	171	156	157
bi	PPA	178	179	120	150	169	177
	DPA	177	179	134	164	173	175
	ODPA	170	177	172	165	174	170
tri	PPA	180	176	136	178	178	178
	DPA	180	178	179	179	179	167
	ODPA	179	179	163	179	179	178

For almost all cases, the average dihedral angle for the singly adsorbed phosphonic acid molecules differs from 180° by less than 5° . On the other hand, larger deviations can be observed for the fully covered surfaces. In these cases, it can be noticed that the order decreases with the coordination number, i.e., the monodentate complexes show more distorted carbon chains than bidentate ones, where the tridentate complexes are the least distorted. Nevertheless, it should be noted that the most distorted chain has an average dihedral angle of 132° (monodentate PPA on bayerite), as shown in Table 5. This is still a configuration between the fully staggered (all-*trans*) and the eclipsed conformations shown in Figure 5. Furthermore, the rotation energy barriers are known to be considerably small for alkyl chains. As a consequence, the dihedral angles are supposed to be capable of rotating at room temperature. Within SAMs, these rotations are likely inhibited by the lateral interactions. However, as pointed by Love et al.^[27], SAMs are dynamic systems which include a number of structural complexities. Thus, the alkyl chains are expected to have some mobility.

Conclusions

In this work we have investigated self-assembled monolayers of alkylphosphonic acids on the surface of corundum, bayerite and boehmite. The work has focused on the ordering of the SAMs regarding the phosphonic acid binding mode, the length of the alkyl chain and the structure of the surfaces.

Due to the tilting of the adsorbed alkylphosphonic acid molecules, the thickness (height) of the SAMs is always shorter than the length of the fully extended, all-*trans* APA molecules. Moreover, mono-, bi- and tridentate adsorption models have presented very similar tilt angles. Hence, the

tilting of the APA molecules does not reflect their coordination modes on the surface.

The tilt angles obtained for the single adsorbed APA molecules do not significantly differ from the angles observed in the fully covered surfaces. Since the tilt angle is expected to be reduced as the alkyl chains approach the maximum packing, it can be inferred that the density of adsorption sites (which is similar in all three surface models used in this work) limits the concentration of phosphonic acids in the SAMs to a situation in which the maximum packing of the alkyl chains is not reached.

On the other hand, we have found that the average dihedral angles of the alkyl chains are a little distorted in the full coverage situation. These conformational changes are likely to result from the rotation of the chains to minimize the repulsion forces between hydrogen atoms of neighboring alkyl chains. Nonetheless, the average dihedral angles are still consistent with staggered rather than gauche conformation.

It has also been noted that the ordering of the alkyl chains in the fully covered surfaces is influenced by the coordination number of the phosphonic acids. The average dihedral angles tend to be closer to 180° (all-*trans*) as the coordination number increases. This disorganization can be caused by the phosphonic group, which is free to rotate in the monodentate complexes and totally rigid in the tridentate ones, while assuming an intermediate rigidity in the bidentate adsorbates. The rotation of the phosphonic group can cause the alkyl chains to bounce off each other, thus causing higher disorder. Another possibility is that order in the tridentate complexes is higher due to the lower coverage used in our models, as explained in *Computational Details*, which leaves more space for the APA molecules.

It is important to mention that, although dispersion forces are not likely to significantly influence properties such as the tilt angle of alkylphosphonic acid molecules adsorbed on oxidized aluminum surfaces, this should not be generalized to all kinds of SAMs. Dispersion forces may become important contributions in SAMs where the hydrocarbon chains are formed by conjugated and aromatic system, where π -stacking can take place and where the anchoring bonds are not as strong as in the cases considered in this work.

In conclusion, in order to further investigate the influence of entropic factors, molecular dynamics simulations are being conducted in our group, exploring the influence of temperature on the organization of the molecules adsorbed at the surface.

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