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**Aqueous or solvent based surface modification: the influence of the combination solvent - organic functional group on the surface characteristics of titanium dioxide grafted with organophosphonic acids.**

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**KEYWORDS** Titanium dioxide, organophosphonic acid, surface modification, patchwise adsorption, random adsorption

To alter the versatility of interactions at its surface, TiO<sub>2</sub> is modified with organophosphonic acids (PA). A thorough understanding of the role of all synthesis conditions is necessary to achieve controlled functionalization. This study reports on the effect of using water, toluene and their mixtures when performing the modification of TiO<sub>2</sub> with PA. Sorption and calorimetry measurements of surface interactions with various probing species clearly indicate that, by grafting PA in water, clear differences appear in the distribution of organic groups on the surface. Also the functional group of the PA determines the impact of using water as solvent. Modification in toluene results in a higher modification degree for propylphosphonic acid (3PA), as the solvent–solute interaction may hinder the grafting with phenylphosphonic acid (PhPA) in toluene. Water is preferred as solvent for PhPA modification as stabilizing  $\pi$ –OH interactions enhance

Abbreviations: PA, organophosphonic acid; 3PA, propylphosphonic acid; PhPA, phenylphosphonic acid; TiP, titanium organophosphonate; TiPP, titanium propylphosphonate; ITO, Indium Tin Oxide; SAMs, self-assembled monolayers, CaHAP; Calcium Hydroxyapatite; DRIFT, diffuse reflectance infrared Fourier transform; TGA, thermogravimetric analysis; BET; Brunauer–Emmett–Teller; PBC, Periodic Boundary Conditions; QE, Quantum Espresso; WC, Wu and Cohen; PAW, projector augmented wave; DFT, density functional theory; TiPhP, titanium phenylphosphonate

surface grafting overcoming the competitive interaction of water at the surface as observed with 3PA. By using water in toluene mixtures for the functionalization of TiO<sub>2</sub> with 3PA, the degree of functionalization is higher than when only water or toluene is used. Furthermore, adding small amounts of water leads to the formation of titanium propylphosphonates, next to surface grafting.

## 1 Introduction

Through the grafting of organic groups on hydrophilic surfaces, the surface properties can be varied in a flexible way, changing its interactions and widening the area of applications. A considerable number of different applications exist for such surface-functionalized materials. They are applied in membranes[1], organic thin-film transistors[2], solar cells[3], chromatography[4,5], transparent nanocomposites[6], for the immobilization of bioactive molecules[7] and other technologies. A method for surface functionalization is modification with organophosphonic acids (PAs) or their derivatives[8–11]. Surface functionalised with a full monolayer of organophosphonic acids has a higher hydrolytic stability (pH 1-10) as for the functionalisation with organosilanes[12]. This is due to the strong specific interaction between the organophosphonic acid and the surface. For the reaction of PAs with the surface, the P-OH group will bind to and/or react with the surface hydroxyl groups, while the phosphoryl group can coordinate with Lewis acid sites on TiO<sub>2</sub>[13]. As a result, the PA can graft to the surface with different binding modes: mono-, bi- and tridentate. Alternatively, when it locally dissolves titania, titanium organophosphonates (TiP) can precipitate[14].

Powerful experimental techniques to investigate the binding between PAs and TiO<sub>2</sub> are <sup>31</sup>P MAS NMR and IR spectroscopy. The disappearance of the P-O-H and P=O bands and the presence of P-O-Ti bands in IR are used to distinguish the grafting of the PA to TiO<sub>2</sub>[9,15]. However, assignment of the binding modes is hampered due to the overlap of the P-O stretching region and the bands in the native TiO<sub>2</sub> spectrum. Via computational studies the adsorption energies of PA on TiO<sub>2</sub> are calculated, as well as the bond distances, <sup>31</sup>P chemical shifts and vibrational frequencies[16]. However, the binding mode is not the only parameter

influencing the  $^{31}\text{P}$  chemical shift, it is possible to determine the binding mode by the  $^{31}\text{P}$  chemical shift. While with IR the disappearance of the P=O stretching mode can only be used to distinguish physically adsorbed PA from covalently bonded PA.

It is possible to carry out surface modification with PAs in both aqueous[8,17–19] and organic environment (e.g. toluene[8,20], THF[11,19,21,22], methanol/water mixtures[14,23], butanol[24], ethanol[24], dichloromethane[25]). From an application point of view, the use of water based methods has an economical, health and ecological benefit. However, it is important to know its impact on structural control as the interaction of water with the surface is clearly different from that of any other solvent.

When grafting with PAs, it is important to create the desired surface properties and thus find the balance and interplay between surface, solute, and solvent. Ferreira *et al.*[21] used an equation describing the enthalpy change for self-assembly of aliphatic PAs on  $\text{TiO}_2/\text{ZrO}_2$  in THF to analyze the various contributions. The first contribution is related to the binding between self-assembled molecules and the surface. A second contribution is due to the solvent–solute interaction. The last contribution is related to the change in surface energy. They reported a changing reaction enthalpy from exothermic to endothermic by increasing the chain length (C1 to C18) of the PA. But, Ferreira *et al.* did not describe the influence of the type of organic group changing from aliphatic to aromatic, nor the influence of the use of aqueous versus organic solvents.

In our previous study, the impact of synthesis conditions on solute-surface interaction was investigated by altering the propylphosphonic acid (3PA) concentration, pH and reaction temperature in water and toluene[26]. It was concluded that the temperature and PA concentration in water have an influence on the modification type. In toluene, lower concentrations were needed to obtain high modification degrees. Due to these vast differences between both solvents, a clear interest in the interactions of the solvent with both solute and surface originated. Furthermore, the modified surfaces were studied with  $^{31}\text{P}$  MAS NMR, TGA and DRIFT, and a correlation between the characteristic signals is made.

The influence of solvents on the modification of Indium Tin Oxide (ITO) with PA (phenyl PA, n-octadecyl PA) has already been described[19]. Chen *et al.* observed that in polar solvents poorly packed self-assembled monolayers (SAMs) are formed, because the solvent adsorbs at the surface occupying binding sites for the PA. Displacement of solvent by PA gets harder for solvents with a higher polarity. However, although a thorough description of the solvent–surface interaction is made, the role of the interaction between solvent and solute has not been investigated yet. Moreover, the impact on the properties of the resulting monolayer formation and hence their sorption behavior, were not described. The effect of the solvent on the grafting of  $C_{18}H_{37}PO(OH)_2$  on Calcium Hydroxyapatite (CaHAP) was also discussed[24]. D’Andrea *et al.* modified CaHAP with aliphatic PAs in toluene, ethanol, *l*-butanol and THF at two temperatures. The grafting reaction is the fastest in toluene and ethanol. It was argued that the different interactions of the solvent (solvent–solute and solvent–surface) caused changes in the kinetics of the formation of the grafted layer. In a good solvent, there were strong solvent–solute interactions, which diminished the solute adsorption and the binding onto the surface. In a poor solvent, the solute–surface interactions were stronger. Nevertheless, as only one type of organic functional group was applied, the impact of the organic functional group on the surface-solvent-solute interactions could not be assessed. Furthermore, also in this case, the influence of the solvent on the final surface properties was not studied. Chen *et al.*[19] and D’Andrea *et al.*[24], both used PAs with long aliphatic chains to create hydrophobicity and assure self-assembly. However, many applications can also benefit from short alkyl groups, e.g. membranes functionalized with small organic groups show interesting properties for water filtration[27].

To study the benefit of replacing solvent based surface grafting by aqueous methods, a thorough analysis of solvent–solute–surface interactions is needed. These interactions may be  $\pi$ -bonding, hydrogen bonding or/and van der Waals forces. The present work investigates the influence of water versus solvent (toluene)

and its mixtures on the functionalization of TiO<sub>2</sub> with PAs possessing different functional groups (propyl- and phenylphosphonic acid). The impact of the combination of solvent and solute on the loading capacity, distribution of functional groups on the surface and its impact on sorption measurements and flow calorimetry (heat of interaction) is revealed.

## **2 Experimental section**

### **2.1 Materials**

Propylphosphonic acid (3PA) and phenylphosphonic acid (PhPA) were purchased from Sigma-Aldrich. To exclude difference between different batches of TiO<sub>2</sub>, commercial TiO<sub>2</sub> P25 is used. TiO<sub>2</sub> P25 is a powder consisting of a mixture of anatase ( $\pm$  80 %), rutile ( $\pm$  20 %) and small amounts of amorphous TiO<sub>2</sub>, was purchased from Degussa Hulls and was used without any pre-treatment[28]. It has a BET (Brunauer–Emmett–Teller) surface of 50 m<sup>2</sup>/g and average particle size of 21 nm.

### **2.2 Synthesis: surface modification**

1.0 g of TiO<sub>2</sub> P25 was stirred for 4 h in a heated solution of PA with a concentration between 0.003 and 0.150 M. Two oil bath temperatures were used: 90 and 130 °C. Water and toluene were used as solvent. The samples were washed on a filter with 3 \* 30 mL of the solvent used during the modification. For the samples made with PhPA in toluene an extra washing step was needed to remove physisorbed PhPA. Therefore, the samples were additionally washed with 3 \* 30 mL of water 60 °C. After the washing procedure, the samples were dried overnight in an oven at 60 °C. For the samples made in solvent mixtures, the same procedure (0.100 M and 130 °C) was applied as described above. The solvent mixtures contained 5 %, 10 %, 25 % or 50 % of water in toluene. After the modifications, the samples underwent a first washing step with toluene, followed by a drying step overnight at 60 °C. The next day, these samples underwent an additional washing step with water and were again dried overnight at 60 °C.

Each sample received a structural name, e.g. PhPA0.100M90W denotes TiO<sub>2</sub> modified with a 0.100 M solution of PhPA in water (W) at 90 °C, and 3PA0.100M130T refers to TiO<sub>2</sub> modified with a 0.100 M

solution of 3PA in toluene (T) at 130 °C. For the name of samples made in the solvent mixtures the percentage of water in toluene is given, e.g., “10 %” is TiO<sub>2</sub> modified in a mixture of 10 % water in toluene with 0.100 M 3PA at 130 °C. The synthesis and analysis of the samples were reproduced three times (table S1).

### 2.3 Instrumentation

The diffuse reflectance infrared Fourier transform (DRIFT) measurements were performed on a Nicolet 6700 Fourier Transform IR spectrometer, equipped with an electromagnetic source in the mid infrared region (4000-400 cm<sup>-1</sup>). The detector was a liquid N<sub>2</sub> cooled MCT-B detector. A resolution of 4 cm<sup>-1</sup> was used and for each spectrum 200 scans were accumulated. The sample holder contained a 2 wt% diluted sample in KBr and was measured under a flow of dry air. All samples were compared to a 2 wt% unmodified TiO<sub>2</sub> in KBr background. The titania support material is subtracted to clearly evidence the differences in the sample after the modification[26]. Newly formed bonds gave positive peaks, while negative peaks indicated that groups had reacted.

The thermogravimetric analysis (TGA) was recorded on a Mettler Toledo TGA/SDTA851<sup>e</sup>. The measurements were performed in an oxygen atmosphere and the samples were heated from 30-600 °C with a heating rate of 10 °C/min.

Nitrogen sorption measurements were recorded at -196 °C using a Quantachrome Quadrasorb SI automated gas sorption system. Before the measurements, the samples were degassed for 16 hours under high vacuum at a temperature of 60 °C. From the BET method, the BET area and C-constant were calculated in the P/P<sub>0</sub> region between 0.05 – 0.30.

Water sorption measurements were performed using a Quantachrome iQ-c automated volumetric gas sorption system. The samples were degassed under high vacuum conditions at 150 °C for 16 hours before measuring the water isotherm at 22 °C.

Flow adsorption microcalorimetry measurements were carried out with the aid of a Microscal flow microcalorimeter at room temperature. In a typical experiment, the cell was filled with 80 - 100 mg of powder and evacuated overnight down to a pressure lower than 0.1 mmHg without heating. Afterwards, the sample was flushed with *n*-heptane flowing through the cell at a constant flow of 4.2 mL/h in order to attain the thermal equilibrium. After 2 h, the flow of the solvent was replaced by the stream of a 2 g/L solution of *l*-butanol in *n*-heptane. The concentration of the stock solution had been chosen in such a way to prevent the formation of alcohol dimers and to ensure the displacement of *n*-heptane molecules from the hydrophilic surface domains by the adsorbing alcohol species building up a monolayer on the surface. The displacement phenomenon was monitored by the evolution of heat measured by thermistors. The so-obtained thermal peak was integrated to determine the integral enthalpy of displacement. Calibration was carried out by Joule heating using a calibration probe integrated in the calorimetric cell[29,30]. By using *n*-heptane as a solvent interacting with the surface sites only through van der Waals forces, the integral enthalpy of displacement could be attributed directly to the polar (Lewis acid-base) contribution to the surface enthalpy of the adsorbent. Therefore, the enthalpy value divided by the BET specific surface area was considered as an adequate measure of the polar character of the solid surface studied.

#### **2.4 Quantum chemical calculations**

Calculations were performed under Periodic Boundary Conditions (PBC) with the Quantum Espresso (QE) software package[31] using plane waves as basis sets and the Wu and Cohen (WC) modification of the PBE functional[32]. Treatment of the core electrons was based on the projector augmented wave (PAW) method[33] using the Troullier-Martins form[34]. The 1s electrons were treated as core electrons for C and O atoms, whereas P and Ti atoms were treated with the valence configurations  $3s^23p^3$  and  $3s^23p^64s^23d^2$ , respectively. A cutoff of 600 eV and a  $3 \times 3 \times 1$  k-grid were used.

The anatase (101) facet was selected in the model as it is the most exposed facet in P25. A 3-layer anatase (101) slab with a 15 Å vacuum width was constructed using the cif2cell program[35] and functionalized with

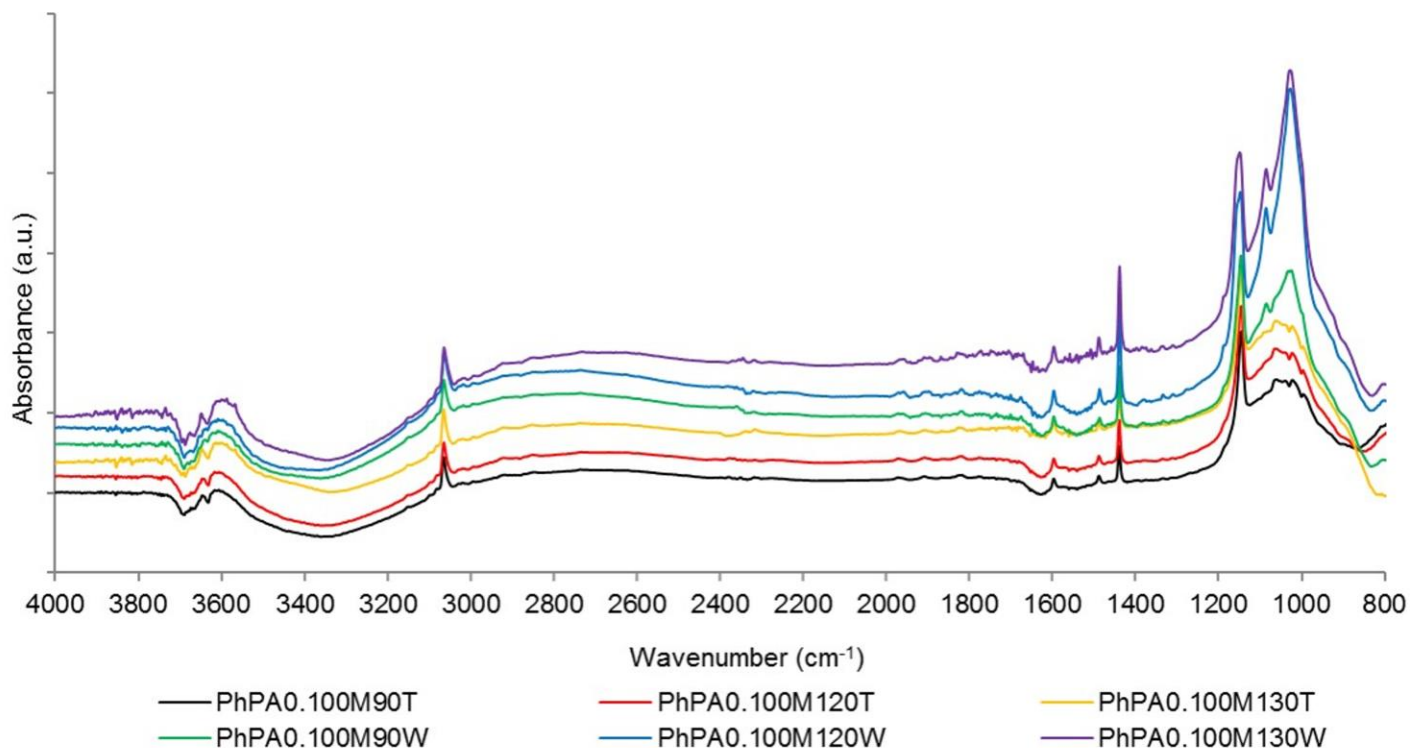


two benzylphosphonic acid molecules, both in monodentate binding modes. Geometries were optimized until the residual forces were below 0.001 Ry/au; the atoms in the lowest layer of the slab were constrained to their initial bulk positions, while all other layers were allowed to relax. This calculation method was validated in a previous study[16].

### **3 Results and discussion**

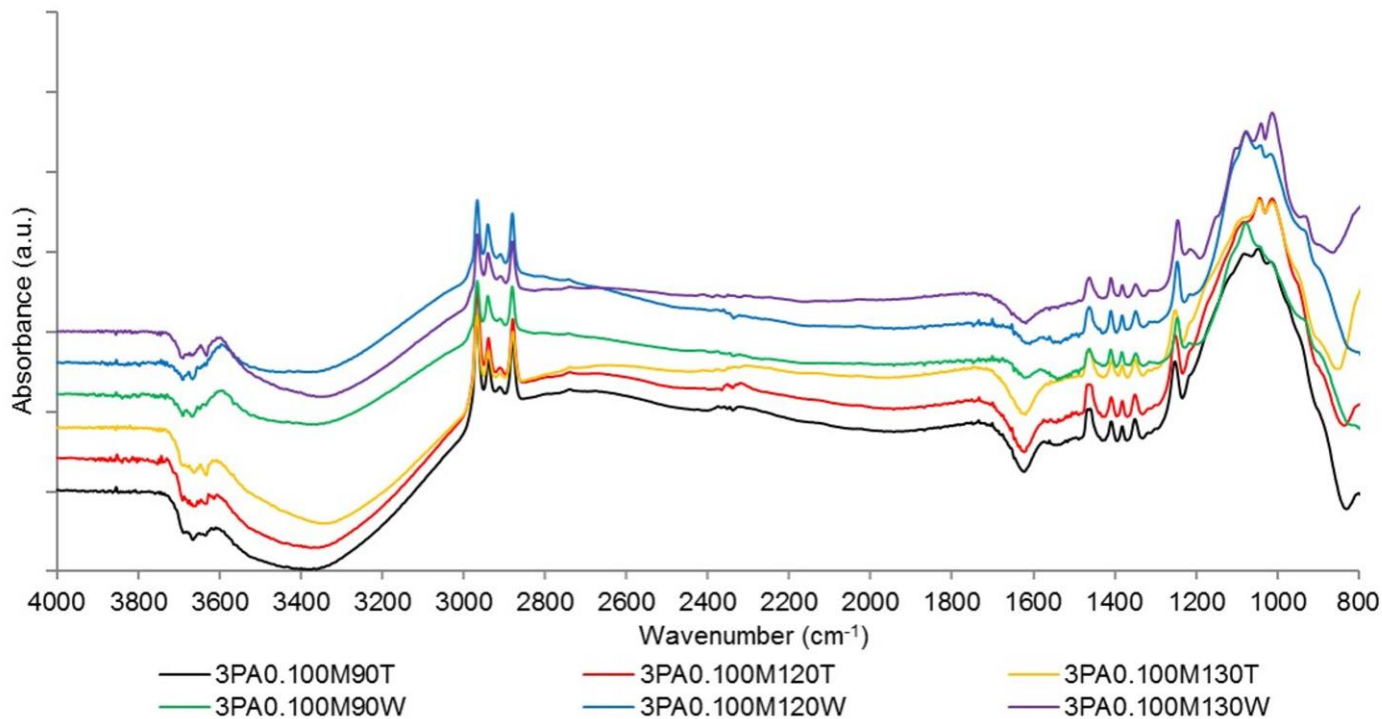
#### **3.1 Solute–solvent interaction: modification with 3PA and PhPA in toluene**

In the DRIFT spectra negative peaks between 3600 and 3100  $\text{cm}^{-1}$  and at 1630  $\text{cm}^{-1}$  appear, indicating a decrease of hydrogen bonding and the amount of adsorbed water for  $\text{TiO}_2$  modified with PhPA in toluene (T) (Figure 1). Furthermore, negative peaks are also observed between 3800 and 3600  $\text{cm}^{-1}$ , due to a decrease of free hydroxyl groups. This implies the binding between the PhPA and the  $\text{TiO}_2$ . Typical peaks for PhPA are present at 3064, 1597, 1486, 1438 and 1147  $\text{cm}^{-1}$ , and at 1060, 1040 and 1023  $\text{cm}^{-1}$  signals related to the stretching vibrations of P-OTi are visible.

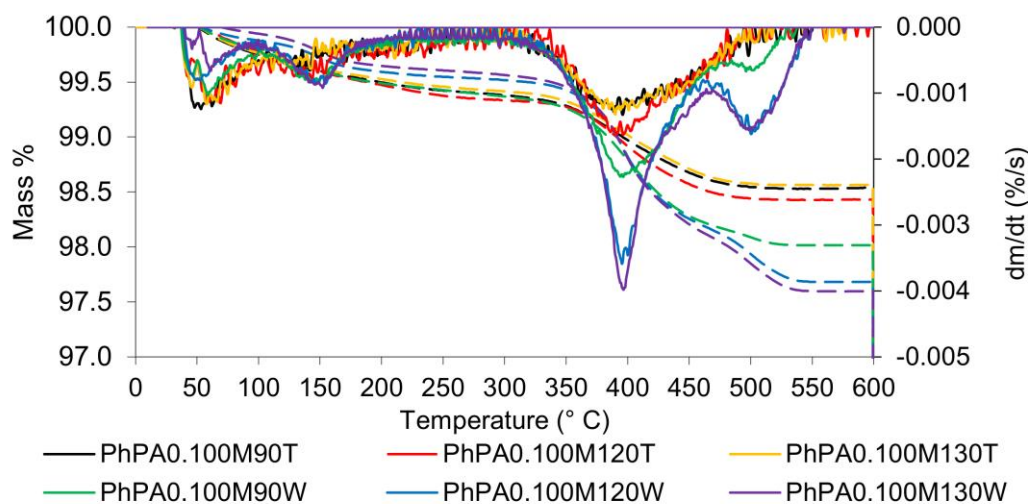


**Figure 1:** DRIFT spectra of  $\text{TiO}_2$  modified with 0.100 M PhPA in toluene (T) or water (W) measured with a 2 wt%  $\text{TiO}_2$  in KBr background. All spectra have an equal offset.

In analogy with the modification with PhPA,  $\text{TiO}_2$  was also grafted with 3PA in toluene. A similar decrease in the signals originating from OH-groups, hydrogen bonding interactions and water is visible. The typical alkyl stretching vibrations of 3PA are assigned in the DRIFT spectra (Figure 2) to the peaks at 2967, 2939, 2911, 2879  $\text{cm}^{-1}$  and the bending vibrations are found in the region between 1450 and 1340  $\text{cm}^{-1}$ . The P-C bending vibration is visible at 1461  $\text{cm}^{-1}$  and the P=O stretch vibration at 1246  $\text{cm}^{-1}$ . Moreover, in the P-OTi region a superposition of four peaks is observed: 1110, 1082, 1045 and 1012  $\text{cm}^{-1}$ . These indicate different binding types onto the surface[26]. By increasing the temperature from 90 to 120  $^\circ\text{C}$  the peak at 1012  $\text{cm}^{-1}$  becomes more intense, while the peak at 1082  $\text{cm}^{-1}$  diminishes.



**Figure 2:** DRIFT spectra of TiO<sub>2</sub> modified with 0.100 M 3PA in toluene (T) or water (W) measured with a 2 wt% TiO<sub>2</sub> in KBr background. All spectra have an equal offset.



**Figure 3:** TGA (dotted lines) and DTG (full lines) curve of TiO<sub>2</sub> modified with PhPA in water and toluene at different temperatures measured under an O<sub>2</sub>-flow and 10 °C/min heating rate.

In TGA/DTG a single, broad mass loss is visible between 250 and 450 °C for the modification of TiO<sub>2</sub> with 3PA and two not fully resolved mass losses between 300 and 500 °C when PhPA was used (Figure S1 and Figure 3). The modification degree was calculated from these mass losses (250-450 °C for 3PA and 300-500 °C for PhPA). This method was previously validated by comparing the modification degree calculated from the mass loss in TGA to the modification degree calculated from the detected amount of phosphorus by SEM EDX[26]. It is known that the hydrocarbon part of the PA will undergo a thermo-oxidation while the phosphorus atom remains bonded to the surface[20]. For both functional groups, no impact of temperature was observed. The loading of organic grafting is much higher for the modification of TiO<sub>2</sub> with 3PA (3.2 groups/nm<sup>2</sup>) than PhPA (1.3 groups/nm<sup>2</sup>) in toluene (Table 1).

**Table 1:** Overview of modification degrees for modification of TiO<sub>2</sub> with a 0.100M concentration of 3PA or PhPA at different temperatures in water or toluene (modification degree expressed in groups/nm<sup>2</sup>).

	PhPA			3PA		
Water	PhPA90W	PhPA120W	PhPA130W	3PA90W	3PA120W	3PA130W
	2.0	2.8	3.1	1.7	1.7	2.5
Toluene	PhPA90T	PhPA120T	PhPA130T	3PA90T	3PA120T	3PA130T
	1.3	1.4	1.3	3.2	3.3	3.3

This suggests an interaction between solute and solvent, as these are the only variables. PhPA and toluene contain both an aromatic ring, which may provide an additional  $\pi$ - $\pi$  type contribution to the solute-solvent interaction over the van der Waals one. This likely induces a competition between binding PhPA to the surface and their behavior in the solvent, thereby reducing their tendency to adsorb on the surface. On the contrary, 3PA contains an aliphatic chain and thus interacts less strongly with the solvent. Consequently, much less hindrance for the deposition of 3PA units in toluene is observed, which results in a modification degree being about 2.5 times higher. Important to note, the cross section of a PA group is 0.24 nm<sup>2</sup>, so a theoretical full monolayer has a modification degree of 4.2 groups/nm<sup>2</sup> [24]. However, also the number of hydroxyl groups is a determining factor for the grafting density. A PA can bind to multiple hydroxyl groups, depending on the binding modes of the PA (mono, bi and tridentate)[16]. Furthermore, not all hydroxyl groups are necessarily available due to steric effects. Therefore, it is very unlikely to achieve 4.2 groups/nm<sup>2</sup>. Even when longer reaction times (24 h) are used, no increase in modification degree has been observed[26]. In the case of a grafting density of 3.2 groups/nm<sup>2</sup>, the surface coverage does not exceed 75 % of that of a full monolayer.

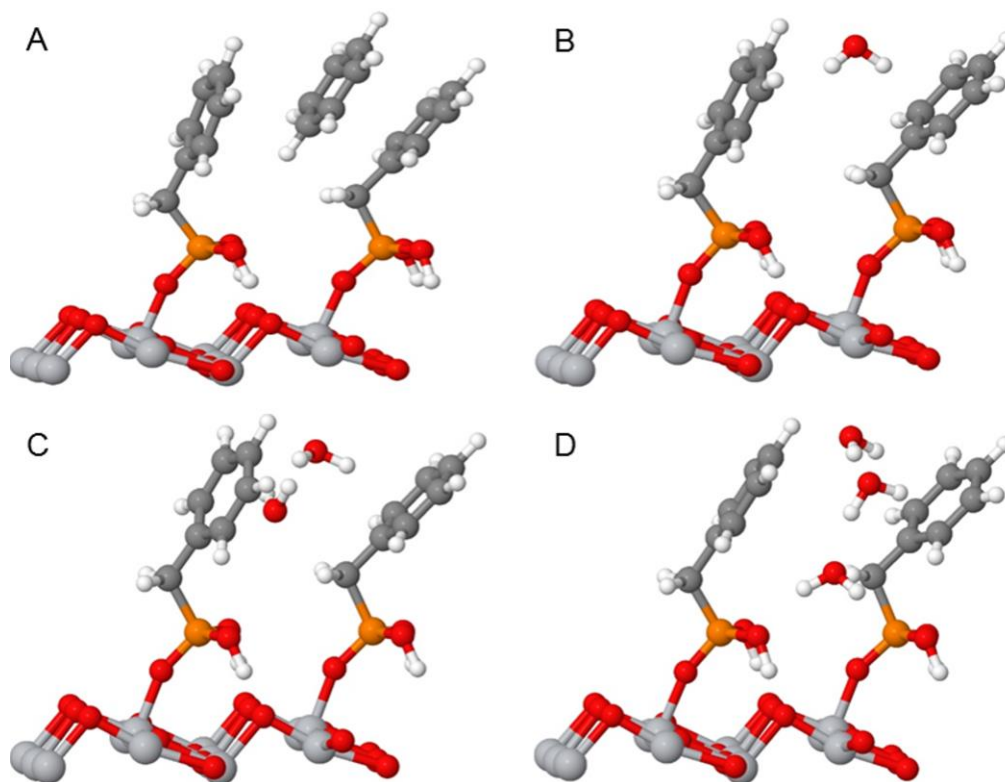
### 3.2 Solvent-surface interaction: modification with 3PA and PhPA in water

When the modification of TiO<sub>2</sub> with PhPA is performed in water, typical signals for PhPA appear in the DRIFT spectra (Figure 1)[14,36]. Each spectrum has clear peaks in the P-OTi stretch region as well as at 1085, 1030 cm<sup>-1</sup> and a small shoulder observed at 1045 cm<sup>-1</sup>. The presence of these bindings (1085 cm<sup>-1</sup> and

1030  $\text{cm}^{-1}$ ) indicates the presence of titanium phenylphosphonate (TiPhP), next to surface grafted groups. By elevating the reaction temperature in water, the TiPhP signal enhances further. These changes coincide with the appearance of an extra mass loss in DTG at 500 °C (Figure 3). This mass loss at 500 °C rises with increasing reaction temperature. When grafting  $\text{TiO}_2$  with 3PA in water, the typical vibrations of 3PA are present in DRIFT (Figure 2). Also here, differences in the P-OTi region are visible. The sample modified at 90 °C has only one broad peak at 1077  $\text{cm}^{-1}$  with small shoulders. By raising the temperature to 130 °C, these small peaks grow and the ratio between the peaks changes. In DTG, an extra mass loss is found between 400 and 520 °C next to the broad asymmetric mass loss with a maximum at 310 °C (Figure S1), indicating a titanium propyl phosphonate (TiPP) formation[26]. For this sample, a modification degree of 1.7 up to 2.5 groups/ $\text{nm}^2$  is calculated from the mass losses between 250-520 °C. The modification degree of the PhPA in water is calculated between 300-550 °C. The grafting density increases with the temperature for both PA modifications (Table 1), irrespective of the organic group present.

When comparing results in water versus toluene it is clear that the modification degree obtained for 3PA in toluene (3.2 groups/ $\text{nm}^2$ ) is higher than in water (1.7 groups/ $\text{nm}^2$ ) (Table 1). Due to the ability of water to form hydrogen bonds with the surface, PAs compete against water molecules to adsorb on the  $\text{TiO}_2$  surface. Before a PA can bind to the surface, it should first displace water and form hydrogen bonds with the surface hydroxyl groups. By elevating the reaction temperature, the solvent can desorb more easily from the surface, enhancing grafting. In toluene this competition at the surface is not present or not so strong and no such effects are observed. Moreover, in water the dissolution-precipitation mechanism can take place due to the presence of acidic protons of PA, which is much less likely in toluene (although an adsorbed layer of water might be present, but this seems insufficient). This dissolution of titania is enhanced at elevated temperatures, increasing the presence of the titanium phosphonate phases. Both effects can, therefore, influence surface grafted amounts.

In contrast to 3PA, modification with PhPA in water results in a higher surface loading of 2.0 up to 3.1 groups/nm<sup>2</sup>. The higher modification degree in water for PhPA may be caused by the interaction between toluene and PhPA. Furthermore, the phenyl-phenyl interactions between the phenyl groups adsorbed on the surface may induce a higher modification degree in water than in toluene. These interactions should be of the  $\pi - \text{H}_2\text{O} - \pi$  type[37] rather than direct  $\pi - \pi$  interactions considering the large inter-ring distances between the aromatic rings on the surface. To quantify these ideas DFT calculations were performed in which the stability of a pair of monodentate adsorbed PAs containing aromatic rings was evaluated when a single benzene ring or one or more water molecules was/were placed in between these rings. Figure 4a shows the resulting geometry in the former case: introduction of the benzene ring leads to a stabilization of 36.73 kJ/mol due to  $\pi$ - $\pi$  interactions. Figure 4b shows the resulting geometry when a single water molecule is placed between the rings: a stabilizing OH... $\pi$  interaction is formed with the benzene ring on the right with an associated stabilization of 22.88 kJ/mol. Even though the latter number is smaller than the one obtained with the benzene molecule, it is clear that more water molecules can be accommodated between the rings, leading to further stabilization. Indeed, as can be seen in Figure 4c, a second water molecule hydrogen bonds to the first one but does not break the existing OH... $\pi$  interaction; this second interaction raises the stabilization to 70.28 kJ/mol, which is considerably greater than the value obtained with benzene. A third water molecule (Figure 4d) hydrogen bonds to the second one and forms an OH...O interaction with one of the free hydroxyl groups of the acid; the total stabilization has now become 119.76 kJ/mol. A fourth and a fifth water molecules were added but since these position themselves outside of the space between the benzene rings, they were not considered. The van der Waals forces between the aliphatic chains of 3PA and the solvent are less strong than the OH... $\pi$  interaction; therefore, higher organic loadings are found for PhPA in water than for 3PA.



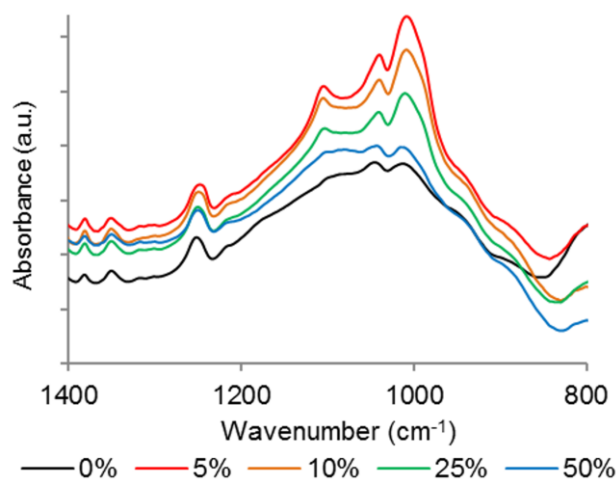
**Figure 2:** Optimized calculated geometries of the system with (a) one benzene ring, and (b) one, (c) two and (d) three water molecules.

### 3.3 Effect of water and toluene on the reaction mechanism

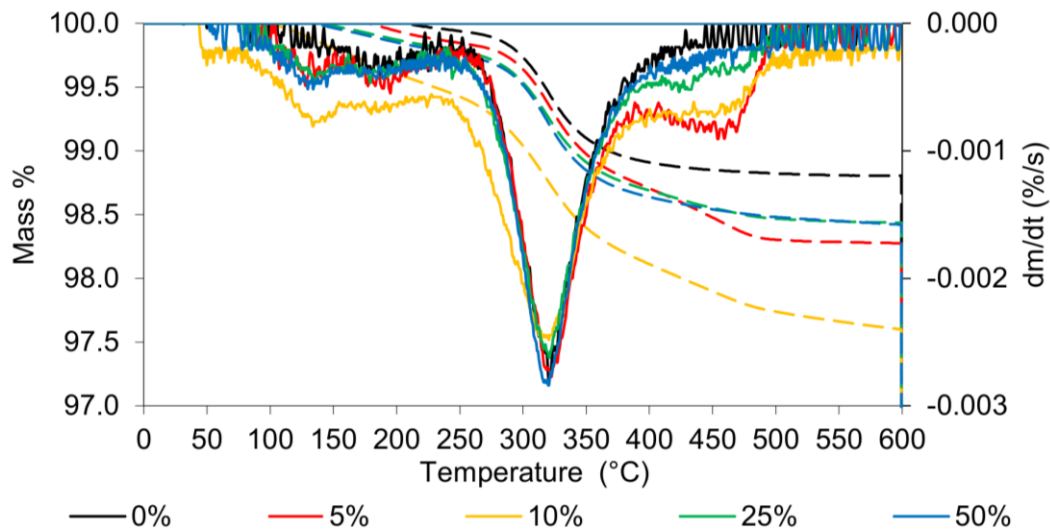
For the modification of 3PA, the formation of TiPP occurs by using water. But, the highest modification degree is reached when the reaction is performed in toluene. However, even when using toluene, a small amount of water will be present as water is set free by the condensation of the PA with the surface. Moreover, traces of adsorbed surface water might be present as well. Therefore, also the impact of mixtures of water in toluene were studied for the 3PA modification. When more than 25 % water is used, a two-layer system is formed and a similar DRIFT spectrum is found as when pure toluene is used (Figure 5). This is due to the low solubility of water in toluene causes a two-layer system even when the solution has been heated and stirred. When the solvent mixture contains less than 25 % water (homogeneous aqueous toluene mixture), the formation of TiPP is observed in DRIFT and DTG (Figure 5 and 6). As water is able to adsorb



at the  $\text{TiO}_2$  surface, local acid hydroxyl groups are present, leading to the dissolution-precipitation mechanism and the presence of phosphonate phases[26]. The grafting densities are calculated for both grafting (250-400 °C) and TiPP formation (400-520 °C) (Table 2). The amount of surface grafting is similar for most of the samples ( $\sim 3.2$  groups/ $\text{nm}^2$ ). Only in the sample made with 10 % of water the grafting density has increased ( $\sim 3.6$  groups/ $\text{nm}^2$ ). On the other hand, the amount of TiPP formation is clearly increasing with the addition of water. When a two-layer system is formed, the TiPP formation decreases as toluene seems to predominately interact with the surface[26]. Clearly, as the grafted amount does not change, the increasing loading capacities achieved, is caused by an additional dissolution-precipitation mechanism without affecting the grafting itself. Moreover, by working in a mixture of water and toluene, the organic loading exceeds those of modification in only water or toluene separately. Furthermore, the present water traces, when working in pure toluene (0 %), seem not high enough to initiate TiPP formation.



**Figure 5:** DRIFT spectra of  $\text{TiO}_2$  modified with 0.100 M 3PA in mixtures with different water percentages in toluene (measured with a 2 wt%  $\text{TiO}_2$  in KBr background). All spectra have an equal offset.



**Figure 6:** TGA (dotted lines) and DTG (full lines) curve of TiO<sub>2</sub> modified with 0.100 M 3PA in mixtures with different water percentages in toluene at 130 °C measured under an O<sub>2</sub>-flow and 10 °C/min heating rate.

**Table 2:** Modification degree (expressed in groups/nm<sup>2</sup>) calculated from TGA for modification in solvent mixtures of water/toluene of 3PA at 130 °C. The modification degree is calculated for grafting (250-400 °C) and TiPP formation (400-520 °C) separately, as well as their combined contribution (250-520 °C). The C value is calculated from N<sub>2</sub> sorption. In the table the % of water in toluene is given.

	0 %	5 %	10 %	25 %	50 %
250 – 520 °C	3.3	4.4	4.8	3.7	3.6
250 – 400 °C	3.2	3.2	3.6	3.1	3.1
400 – 520 °C	0.1	1.2	1.2	0.6	0.5
C value	23	22	21	23	23

### 3.4 The impact of solvent on the obtained surface properties

#### 3.4.1 Sorption based on nitrogen and water as probe molecules

N<sub>2</sub> sorption is used to calculate the C value from the BET equation[38]. This parameter is frequently viewed as a measure of the interaction energy between the solid surface and the probing molecules. It is important to note that one N<sub>2</sub> molecule possesses an electric quadrupole moment ( $-4.65 \times 10^{-40} \text{ C m}^2$ )[39] and may also act

as a borderline Lewis base. If one agrees that a polar contribution to the total adsorption energy is significantly lowered at -196 °C in comparison with the apolar one (due to dispersive forces), and when it is possible to neglect the confinement effects due to the adsorbent porosity (in our case: P25 is non porous), a downward trend in the C value observed for a series of materials exhibiting similar surface chemistry can be used to monitor increasing hydrophobicity of the surface. Although such an analysis has already been used to demonstrate the increased hydrophobic character of organic layers supported on mineral oxides[14,18], much attention should be paid when trying to go too far into the detailed interpretation of the results obtained. For example, there will be higher probability of multisite attachment of nitrogen molecules to downwardly oriented organic species grafted on the oxide surface, which is at variance with the basic assumption of the BET model. This procedure has been tested by determining the C values for all materials studied in the present paper.

**Table 3:** Modification degree calculated from TGA for modification at different concentrations of 3PA at 90 °C in toluene and water. The C value is calculated from N<sub>2</sub> sorption measurements. The heat of butanol adsorption is measured with flow calorimetry.

Toluene				Water			
material	Mod. deg. (#/nm <sup>2</sup> )	C value	Q (J/m <sup>2</sup> )	Material	Mod. deg. (#/nm <sup>2</sup> )	C value	Q (J/m <sup>2</sup> )
3PA0.003M90T	0.7	54	0.31	3PA0.025M90W	1.0	39	0.21
3PA0.005M90T	1.1	43	0.24	3PA0.050M90W	1.3	37	0.19
3PA0.013M90T	2.2	30	0.17	3PA0.075M90W	1.4	38	0.19
3PA0.026M90T	3.0	23	nd	3PA0.100M90W	1.7	37	0.20
3PA0.100M90T	3.2	24	0.07	3PA0.150M90W	2.1	39	0.20

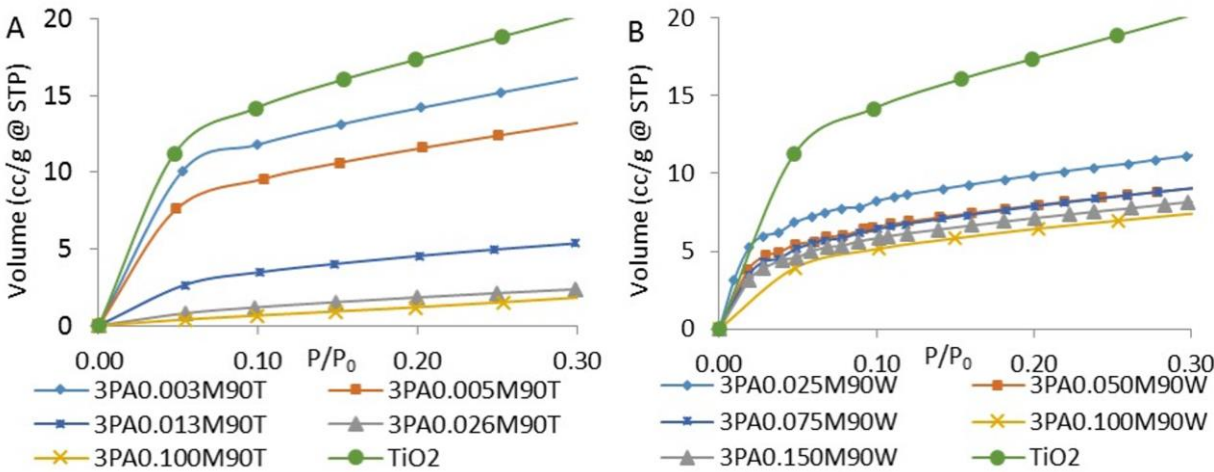
nd: not determined

The C constant of the pristine TiO<sub>2</sub> sample was determined to be equal to 108. For the 3PA modified TiO<sub>2</sub> in toluene with increasing concentrations, the surface loading increases and the C value decreases from 54 to

24 (Table 3). Since there are more groups attached to the surface, this likely means that the surface becomes more hydrophobic[14,18]. For the sample made in the solvent mixtures (Table 2) the C value is stable at around 22 and independent of the amount of water used during the reaction. This is similar to samples made in toluene with high modification degrees as no hydroxyl groups are attainable. In contrast, for the 3PA modification of TiO<sub>2</sub> in water, the C value remains constant (38) regardless of the modification degree (Table 3). Moreover, for the same modification degree the values are different in water compared to toluene. This difference can be obviously rationalized by referring to the binding mechanism and different topology of both types of modified surfaces. Water is competing with functionalization. But, once a PA is bound to the surface the water molecules will have fewer tendencies to adsorb among the hydrophobic propyl chains. In that case, those chains most likely interact between themselves to form patches of grafted PAs at the surface, causing local SAM formation at the surface next to patches of hydrophilic nests. In contrast to water, in literature, it is written that the modification of PA in toluene is driven by the strong covalent interaction between the PA and TiO<sub>2</sub>, leading to a random distribution of grafted PAs among the remaining hydroxyl groups[40]. With such random topography, the mean energy of adsorbate-adsorbent interactions will be much more sensitive to the energetic heterogeneity of surface sites and thus any increase in the surface hydrophobic character will show up clearly in the C constant. It should be mentioned that in the case of patchwise arrangement of homogeneous surface sites, the lateral interactions among the adsorbed nitrogen molecules can no longer be neglected even though the overall surface coverage remains relatively low. As a result, the differences in the interaction energy over the surface will be smoothed out by such a lateral contribution.

Further arguments were found by carrying out sorption measurements with water molecules probing more specifically for surface hydroxyl groups (Figure 7). For both types of systems, the surface coverage by water molecules at low P/P<sub>0</sub> values decreases constantly when more and more 3PA units are grafted on the TiO<sub>2</sub> surface. This is certainly a strong indication for the decreasing hydrophilic character of the modified surface.

The formation of a fully hydrophobic layer, covering the whole surface has been obtained neither in water nor in toluene, though the 3PA0.100M90T system characterized by the highest modification degree in toluene provides a surface adsorbing very low amounts of water vapor. The main difference between the two types of system lies in the trend observed for water sorption behavior with increasing modification degree. For similar values of the latter, a more pronounced decrease in the amount of water adsorbed is monitored for surfaces modified in water at low modification degrees (about 1 group/nm<sup>2</sup> (3PA0.005M90T and 3PA0.025M90W) in Figure 7), while at higher modification degrees (at ~2 groups/nm<sup>2</sup>) a more pronounced decrease is visible for modification in toluene. Since the linear isotherm portions at higher partial pressures (matching multilayer formation) have similar slopes, the differences seem to appear in the initial sorption mechanism. Here, the observed decrease in the amount of water vapor retained on surfaces previously grafted in water is to be attributed to repulsive forces operating among water molecules when they are adsorbed on the extended hydrophilic patches, namely for lower grafting degrees.



**Figure 7:** Adsorption isotherm of water vapour at 22°C on TiO<sub>2</sub> and TiO<sub>2</sub> modified with different concentration of 3PA (A) in toluene and (B) in water at 90 °C. Degassing was done at 150 °C for 16 h.

Water sorption is also performed for modification of TiO<sub>2</sub> with PhPA (Table S2 and Figure S2). For the samples made in water the monolayer formation is decreasing and is approximately constant for samples with

a higher modification degree as 1.3 groups/nm<sup>2</sup> (Figure S2). This is similar for the modification with 3PA. Therefore, it is derivative that also the modification of PhPA in water results in SAMs. However, the monolayer formation for the water probe molecule is always higher in the case of TiO<sub>2</sub> modified with PhPA than 3PA, which might coincide with the mechanism of  $\pi - \text{H}_2\text{O} - \pi$  interactions present during modification in water suggesting a more directed packing of the PhPA on the surface. For the modification in toluene, no modification degrees higher than 1.3 groups/nm<sup>2</sup> are achieved (Table S2). Therefore, no conclusions about random adsorption can be drawn from the water adsorption isotherms of PhPA in toluene.

### 3.4.2 Flow adsorption microcalorimetry

Liquid flow calorimetry allows the measurement of enthalpy of competitive adsorption between butanol and heptane. Taking into account the amphiphilic molecular structure of butanol molecules, this solute is capable of entering into competition with hydrophobic heptane to adsorb preferentially only on surface hydroxyl groups[29,30]. The enthalpy change measured upon this displacement process on a per sq. m basis is further regarded to monitor changes in the hydrophilic character of the modified surfaces. The resulting enthalpy values are given in Table 3.

For the samples modified by using toluene as a solvent, there is a nearly linear decrease of the heat effect with increasing modification degree. This indicates a steady decrease in the number of OH groups accessible to adsorbing butanol units. The nearly linear relationship between the integral heat of displacement and the modification degree points out that the affinity difference undergoes little change when passing from one hydroxyl group to another. Both observations again argue in favor of almost fully random distribution of the remaining OH groups on the modified surfaces. On the contrary, the heat effect for the samples made in water appears almost constant, irrespective of the PA grafting density. Two hypotheses may be advanced to explain this trend. The first hypothesis refers to the possibility for PA units in monodentate and bidentate binding modes to leave their free OH groups oriented outwards and thus capable of adsorbing additional

butanol molecules. The other hypothesis takes into account the lateral interaction among C<sub>4</sub>-chains of the neighboring alcohol species retained on hydrophilic OH patches. This additional contribution to the total interaction energy is negligible within the bulk solution where the solute molecules are dispersed at random. On a surface with a patchwise distribution of active sites, such a contribution cannot be neglected any longer and it is included in the total enthalpy change recorded upon adsorption from solution. Since both hypotheses may be validated by the previously discussed results, the overall thermal effect will be smoothed out by all such interaction modes involved in the displacement process.

#### **4 Conclusion**

In conclusion, the solute-solvent-surface interactions involved in the modification of TiO<sub>2</sub> with PA have been investigated. A clear impact of the solvent is visible and a number of aspects are dependent on the type of functional group, while others are only determined by the competing interaction of the solvent at the surface or the propensity to create acidity. In water, surface grafting and formation of TiPP (titanium phosphonate) occurs, while, in toluene, surface grafting is the most important result. By adding small amounts of H<sub>2</sub>O to the reaction, a high modification degree next to additional TiPP formation are found. Furthermore, the solvent has an influence on surface distribution of grafted groups and interacts with specific functional groups (solute) leading to a lower modification degree. From this work, clear differences in structural properties can be concluded and a vast impact on coverage are inherent to the applied solvent and solute.

This work has demonstrated the importance of the choice of solvent with respect to the organic functional group with the purpose of tuning the surface properties. It has a significant impact on applications involving surface interactions such as sorption, separation, catalysis, controlled release, immobilization etc. of which the performance is directly correlated to/influenced by surface properties. By this study, the different interactions of the solvent with the surface and solute are described, which makes it possible to choose the

reaction conditions that will result in a controlled surface with the appropriate characteristics for a specific application.

#### ASSOCIATED CONTENT

Additional figures are included in supporting information.

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