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Alkyl Phosphate Monolayers, Self-Assembled from Aqueous Solution onto Metal Oxide Surfaces

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Metal oxide surfaces have been coated by self-assembled monolayers (SAMs) of dodecyl phosphate (DDPO₄) and 12-hydroxy dodecyl phosphate (OH-DDPO₄), by means of a novel surface-modification protocol based on the adsorption of the alkyl phosphate ammonium salts from aqueous solution. Formation of DDPO₄ SAMs has been successfully demonstrated on anodized aluminum (Al₂O₃) as well as on smooth, thin films of tantalum oxide (Ta₂O₅), niobium oxide (Nb₂O₅), zirconium oxide (ZrO₂), and titanium oxide (TiO₂) deposited on glass substrates, resulting in highly hydrophobic surfaces with advancing water contact angles $\geq 110^\circ$. SAM formation does not occur on silica surfaces under the same conditions. The formation of SAMs based on hydroxy-terminated alkyl phosphates (OH-DDPO₄) onto Ta₂O₅ and Nb₂O₅ has also been observed. DDPO₄ and OH-DDPO₄ were codeposited onto Ta₂O₅ from aqueous solutions at different concentration ratios. It is shown that the water contact angle can be precisely controlled within the range of $110\text{--}50^\circ$ by adjusting the molar ratio of the two different molecules in the aqueous SAM forming solution. The SAMs were characterized by advancing water contact angle (wettability), microdroplet density measurements (condensation figures to judge homogeneity), and X-ray photoelectron spectroscopy (coverage and orientation of molecules).

1. Introduction

The formation of self-assembled monolayers (SAMs) on metal¹ or metal oxide surfaces² is widely employed for the fabrication of model surfaces with highly controlled chemical properties. SAMs can be used in the modification of metal oxide surfaces for the investigation of protein adsorption,^{3,4} for the study of cell behavior,⁵ or for the fabrication of tailored sensor surfaces.⁶ Passivation of metal surfaces, adhesion promotion, and interface corrosion protection in metal/lacquer systems are other examples of industrial applications of SAMs.⁷

To date, the best-studied SAM system has been that of self-assembled alkanethiolates on gold, where thiols adsorb onto the gold surface in an initial "lying-down" phase followed by rearrangement into a "standing-up" phase, which completes the monolayer and results in highly ordered, two-dimensional structures.^{1,8–12} Alkyl phosphates and phosphonates constitute two further systems that have been shown to form ordered SAMs on metal oxide surfaces.^{1,13–16} Transition metal oxides such

as tantalum oxide (Ta₂O₅), niobium oxide (Nb₂O₅), and titanium oxide (TiO₂), in particular, are known to interact strongly with phosph(on)ates and to form relatively stable interfacial bonds. Both systems, thiol–gold and phosph(on)ate–metal oxide, form monolayers with a "tail-up" orientation and a tilt angle of the hydrocarbon chains of about 30° with respect to the surface normal.^{17,18} Such amphiphile adlayers are generally produced from solutions in organic solvents.

The use of organic solvents in the deposition process has three main disadvantages: (1) In biomaterial applications, organic solvent molecules may be trapped within the adlayer and reduce the biocompatibility of the surface. (2) For the formation of mixed adlayer systems, it can be difficult to find an organic solvent that is suitable for both adlayer components. (3) On an industrial scale, organic solvents are increasingly falling into disfavor because of both air-pollution and water-pollution issues. We demonstrate in this paper that both pure and mixed alkyl phosphates with different terminal functionalities can be deposited from aqueous solution by converting the free (water-insoluble) alkyl phosphoric acids into the corresponding water-soluble salts. Mixed SAMs on metal oxide surfaces are of particular interest to the biosensor and biomaterial field, because they allow surface properties such as wettability, polarity, surface charge, and so forth to be tailored in a precise manner. Such surface tailoring may prove to be highly relevant for controlling the interaction between the SAM-modified surface and biological systems, such as proteins, antibodies, and cells.

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The present paper describes two novel approaches to modifying metal oxide surfaces: the use of aqueous solutions of alkane phosphates in the self-assembly process and the tailoring of surface wettability based on mixed alkane phosphate/hydroxy-terminated alkane phosphate SAMs.

2. Materials and Methods

2.1. Substrates. Samples with a Ta₂O₅ or Nb₂O₅ Surface. Glass slides (15 × 15 × 1 mm) were coated with 150 nm thick layers of Ta₂O₅ or Nb₂O₅ by physical vapor deposition (sputter coating) (Balzers AG, Balzers, Liechtenstein).

Samples with a ZrO₂ or SiO₂ Surface. Commercial optical waveguide substrates were used, consisting of AF45 glass slides (8 × 12 × 1 mm), which were coated by a 200 nm thick Ti_{0.4}Si_{0.6}O₂ sol-gel waveguiding layer, followed by a 14 nm thick top layer of ZrO₂ or SiO₂, using a magnetron sputtering unit (Microvacuum, Ltd., Budapest, Hungary).

TiO₂. Glass slides were sputter coated with a 100 nm thick layer of TiO₂ (Paul Scherrer Institut, Villigen, Switzerland).

Al₂O₃. Aluminum (Al 99.99) thin strip samples (1 mm in thickness) were electrolytically polished in phosphoric acid/sulfuric acid electrolyte and anodized in sulfuric acid electrolyte (200 g/L H₂SO₄, 20 °C, 4 min), producing an anodic oxide layer of about 2 μm thickness (Alusuisse, Neuhausen am Rheinfall, Switzerland).

The Nb₂O₅ and Ta₂O₅ surfaces are reported by the manufacturer to be nanocrystalline (crystallite size in low-nanometer range). The TiO₂ and Al₂O₃ are largely amorphous, as judged by X-ray diffraction. The cleanliness of the samples prior to functionalization was reported in a previous paper.¹⁷

2.2. Alkyl Phosphates. Precipitation of Ammonium Salt DDPO₄(NH₄)₂. A quantity (2.00 g) of dodecyl phosphate (DDPO₄) (technical grade, Aldrich) was dissolved in 200 mL of 2-propanol (UVASOL, Merck), heated to 82 °C, and refluxed. Subsequently, 6 mL of ammonia (25% aq. p.a., Merck) was added. After the reaction mixture was cooled with ice water, the precipitated ammonium salt of DDPO₄ was filtered. The product was washed with ice-cold 2-propanol and dried at 60 °C and 10 mbar in a vacuum oven for 20 h. A white powdery product (1.61 g; mp, 225 °C) could be isolated, corresponding to a yield of 71%. ¹H NMR (DMSO or CD₃OD): 0.88 ppm (t, 3H, -(CH₂)₁₀CH₃), 1.28 ppm (m, 18H, -CH₂CH₂(CH₂)₉CH₃), 1.54 ppm (m, 2H, -CH₂CH₂(CH₂)₉CH₃), 3.72 ppm (q, 2H, -OCH₂CH₂(CH₂)₉CH₃), 4.9 ppm (s, 8H, NH₄). The ³¹P NMR showing one single peak suggests that the product consists of a uniform alkyl phosphate species. Elemental analysis calculated: [C] 50.87%, [H] 10.67%, [N] 4.94%, [O] 22.59%, [P] 10.93%. Analysis: [C] 50.61%, [H] 10.94%, [N] 4.95%, [O] 22.75%, [P] 10.69%.

Precipitation of Ammonium Salt OH-DDPO₄(NH₄)₂. A quantity (500 mg) of hydroxy dodecyl phosphate (OH-DDPO₄) was dissolved in 20 mL of 2-propanol (UVASOL, Merck), and NH₃ was bubbled through the solution for 5 min. NH₃ was obtained from a hot 25% aqueous ammonia solution and transferred into the amphiphile solution via a glass pipet fixed onto a plastic tube. The precipitated ammonium salt of OH-DDPO₄ was separated from the solvent by centrifugation and removal of the solvent. The product was dried in a flow of dry nitrogen at room temperature using an evaporation system (EVAPOR) followed by drying at 10 mbar for 2 days. A white powdery product (515 mg; mp, 165 °C) could be isolated, corresponding to a yield of 91%. ¹H NMR (DMSO or CD₃OD): 1.24 ppm (m, 16H, -CH₂CH₂(CH₂)₈-CH₂CH₂OH), 1.38 ppm (m, 2H, -CH₂CH₂(CH₂)₈CH₂CH₂OH), 1.44 ppm (m, 2H, -CH₂CH₂(CH₂)₁₀OH), 3.35 ppm (t, 2H, -(CH₂)₇CH₂OH), 3.57 ppm (q, 2H, -OCH₂CH₂(CH₂)₁₀OH), 5.2 ppm (s, 8H, NH₄). Elemental analysis calculated as diammonium salt: [C] 45.6%, [H] 10.5%, [N] 8.9%. Analysis: [C] 44.1%, [H] 9.6%, [N] 5.7%.

The NMR results of the obtained product suggest that the substance is pure. The somewhat low nitrogen content found experimentally is likely to reflect a partial loss of ammonia and partial formation of the monoammonium salt. To be consistent with DDPO₄(NH₄)₂, we abbreviate the ammonium salt of hydroxy dodecyl phosphate with OH-DDPO₄(NH₄)₂.

Preparation of Amphiphile Solutions. (a) A quantity (15.0 mg) of DDPO₄(NH₄)₂ was dissolved in 5 mL of high-purity water by heating to ca. 50 °C, and the volume was subsequently adjusted to 100 mL with water. (b) A quantity (15.8 mg) of OH-DDPO₄(NH₄)₂ was dissolved in 5 mL of high-purity water by heating to ca. 80 °C. The solution was cooled to room temperature, filtered through a 0.22 μm filter (MILLEX-GV, MILLIPORE, Bedford, MA), and adjusted to a volume of 100 mL.

The alkyl phosphate and hydroxyalkyl phosphate solutions, (a) and (b), were mixed in different ratios from 0 to 100 vol % with respect to the amount of OH-DDPO₄(NH₄)₂, in steps of 10% resulting in 11 different solutions at constant total phosphate concentration of 0.5 mM.

2.3. Sample Preparation. The substrates were sonicated in high-purity water for 15 min, followed by a second sonication in 2-propanol (UVASOL, Fluka) for another 15 min. The slides were removed from the cleaning solvent, blow-dried with nitrogen, and transferred to an oxygen-plasma cleaner (Harrick Plasma Cleaner/Sterilizer PDC-32G, Ossining, NY). After 3 min of oxygen-plasma cleaning, the chips were transferred to 5 mL glass vials and amphiphile solution was subsequently added. The chips were immersed for 48 h in the solution for self-assembly and removed; each was rinsed with 10 mL of high-purity water and blow-dried with nitrogen.

2.4. Investigation of Surface Properties. The wettability of surfaces was investigated by measuring the advancing water contact angle (Contact-Angle Measuring System, with Kontaktwinkel Messsystem G2/G40 2.05-D software, Krüss GmbH, Hamburg, Germany).

Surface homogeneity was determined by means of microdroplet density, μdd, measurements.¹⁹ Microdroplet density data from condensation figures were obtained by means of an apparatus consisting of a metal table placed in a transparent humidity chamber and a CCD camera (Panasonic, model WV-BP 310/6, Matsushita Communication Deutschland GmbH, Germany) fixed on a microscope stage (Zeiss, Carl Zeiss AG, Switzerland). Images of the pattern of growing droplets on the surfaces were made after cooling the samples, which were placed on the metal table in the humidity chamber.^{18,19}

X-ray photoelectron spectroscopy (XPS) analyses were performed using a PHI 5700 spectrometer equipped with a standard Al Kα source (200 W) (Physical Electronics, Eden Prairie, MN). Photoelectron intensities were normalized using the standard sensitivity factors provided in the PHI quantification software. The details of the curve-fitting procedures and of the quantification of peak intensities have been published elsewhere.¹⁸

3. Results and Discussion

3.1. DDPO₄ on Different Metal Oxides. Self-assembled monolayers of dodecyl phosphate were produced on Al₂O₃, Ta₂O₅, Nb₂O₅, ZrO₂, TiO₂, and SiO₂ by immersion in 0.5 mM DDPO₄(NH₄)₂, as described in section 3.3.

Contact Angle. Advancing water contact angles (CA) were measured immediately following sample preparation (Table 1). The results show that highly hydrophobic SAMs form on all metal oxide surfaces investigated in this work, with the exception of silica. The contact angle values of ≥ 110° are typical for well-defined alkyl phosphate SAMs.¹⁴ The isoelectric points (IEP) of the different bare metal oxides, which vary from 2.7–3.0 for Ta₂O₅ to 7.5–8.0 for Al₂O₃, do not seem to be an important parameter for SAM formation with this system (Table 1). On SiO₂, the contact angle remains in the same range as it was prior to immersion in the amphiphile solution. This suggests that DDPO₄ does not adsorb on SiO₂ with this approach.

Microdroplet Density (Condensation Figures). To remove any particles that had adsorbed to the surfaces, the samples were rinsed with high-purity water just before measuring the microdroplet density (μdd). DDPO₄ SAMs on pure metal oxide surfaces show a low μdd value of 150–260 droplets/mm² (Table 1) and a homogeneous

Table 1. Literature Values of IEP^a of the Investigated Bare Oxides and Experimental Advancing Water Contact Angles, θ_a , (\pm Standard Deviation for 3 Probing Drops in Different Areas of the Sample, 10 Measurements per Drop) and Microdroplet Density, μdd , (\pm Standard Deviation for 4 Independent Measurements, Each on an Area of 0.25 mm²) Following Self-Assembly of DDPO₄ on the Oxide Surfaces^b

substrate	IEP	θ_a (\pm st dev)/deg	μdd (\pm st dev)/droplets mm ⁻²
Ta ₂ O ₅	2.7–3.0	114.6 \pm 0.5	129 \pm 19
Al ₂ O ₃	7.5–8.0	111.4 \pm 1.0	152 \pm 22
Nb ₂ O ₅	3.4–3.6	109.7 \pm 0.6	120 \pm 18
ZrO ₂	4.0	110.1 \pm 0.6	258 \pm 39
TiO ₂	4.7–6.2	111.4 \pm 1.2	221 \pm 33
SiO ₂	1.8–2.2	10.0 \pm 3.4	>3000

^a References 15–22. ^b References 20–27.

distribution of the growing droplets of condensed water (Figure 1). SiO₂ remains hydrophilic (as mentioned above), and microdroplets coalesce to a complete layer of condensed water before they can be detected as single droplets. The maximum value that can be detected with the used setup corresponds to about 3000 droplets/mm². The μdd value of >3000 droplets/mm² is consistent with the suggestion of the contact angle data, that DDPO₄ does not adsorb onto SiO₂ from aqueous amphiphile solution.

X-ray Photoelectron Spectroscopy. After immersion of the metal oxide and silica samples in a 0.5 mM DDPO₄-(NH₄)₂ solution for 48 h, the surfaces were investigated by XPS at two different takeoff angles Θ : at a takeoff angle of 15° (with respect to the surface plane), the analysis is highly surface sensitive, whereas a takeoff angle of 75° yields more information on the substrate.

Photoelectron intensities (peak areas) were normalized by dividing them by the standard sensitivity factors and converting them to a percent of the sum of all observed normalized intensity values (Table 2). We deliberately do not call these values “atomic concentrations” to take into account the fact that SAM surfaces are typically not homogeneous in the *z* direction (i.e., perpendicular to the surface). These normalized intensities are, however, useful for the comparison of coverages between different surfaces. The relative differences in the normalized intensities between the 15° (grazing angle) and the 75° electron takeoff angle provide qualitative information about the location of the hydrocarbon chain relative to the phosphate headgroup and the oxide substrate, respectively.

The comparison of the data at 15° and 75° electron takeoff angles supports our model of a surface architecture where the alkyl phosphates adsorb onto metal oxide substrate surfaces with the phosphate attached to the oxide surface and a hydrocarbon tail-up orientation. This can be deduced qualitatively from the fact that the carbon intensities are much higher and the metal intensities are much lower at 15° (i.e., in the more surface-sensitive mode) compared to 75° (i.e., in the higher sampling depth mode). This observation is true for all transition metal surfaces investigated as well as for aluminum oxide. Extensive quantitative evaluation of the XPS data using a multilayer model has been discussed in an earlier paper describing octadecyl phosphate self-assembled onto tantalum oxide surfaces from organic solvents. The results of these calculations were in excellent agreement with the assumption of a monolayer of ordered, oriented, and close-packed alkyl phosphate molecules.¹⁷

The amount of adsorbed amphiphile at the surfaces is in the same range for all investigated metal oxide substrates and points to a coverage close to one monolayer as discussed in an earlier publication.¹⁷ Consistent with

the CA and μdd results, no adsorbed alkyl phosphate could be detected on the SiO₂ substrate (no phosphorus and very low carbon concentration, typical of the clean substrate, Table 2). The absence of DDPO₄ SAM formation from aqueous solutions on silicon oxide surfaces is likely to be due to a much lower affinity of phosphate for Si(IV) in comparison to Al(III), Ti(IV), Nb(V), and Ta(V), which all form highly stable phosphate–metal cation coordination bonds, that is, a direct bond of the phosphate headgroup to the metal cation through either one oxygen atom (monodentate) or two oxygen atoms (bidentate).¹³

3.2. OH-DDPO₄ on Ta₂O₅ and Nb₂O₅. 12-Hydroxy dodecyl phosphate (OH-DDPO₄) was self-assembled on Ta₂O₅ and Nb₂O₅ slides by immersion in a 0.5 mM OH-DDPO₄-(NH₄)₂ aqueous solution for 48 h, as described in section 3.3.

Contact Angle and XPS. The advancing water contact angle was measured immediately after the self-assembly process. The contact angle was approximately 50°; that is, the surface is much more hydrophilic than in the case of the methyl-terminated DDPO₄ SAMs. This is evidence that the terminal hydroxy groups are indeed exposed at the SAM surface. However, in comparison to hydroxy-terminated alkane thiol SAMs (advancing water contact angle of typically 20°²⁸), the value of 50° of the OH-DDPO₄ SAMs seems high. This may indicate a comparatively higher degree of heterogeneity, a lower packing density, and/or a lesser degree of order in case of the alkane phosphates. A near-edge X-ray absorption fine structure (NEXAFS) study to determine orientation and order in a number of alkane phosphate SAMs is planned.

To prove this hypothesis, XPS spectra were recorded at different takeoff angles. The variation of the signal intensity as a function of the takeoff angle may give information about the vertical position of the corresponding element within the depth sampled by XPS. The O(1s) signals of the spectra at the two grazing angles 11.5° and 20.5° are shown in Figure 2. Compared to the nonfunctionalized, methyl-terminated SAM, the hydroxy-terminated SAM shows an additional shoulder at approximately 534 eV in the O(1s) XPS spectrum (Figure 2) with a relative intensity that is significantly higher at the electron takeoff angle of 11.5° compared to 20.5°. This is good evidence that the terminal hydroxy groups in the OH-DDPO₄ SAM are indeed exposed at the surface, because the O(1s) signal from such hydroxy groups is not affected by inelastic scattering within the alkyl monolayer, whereas the O(1s) signal intensities from the interfacial phosphate groups and from the metal oxide substrate are strongly reduced at the grazing takeoff angles because of inelastic scattering within the organic overlayer.

No nitrogen could be detected by XPS, demonstrating that the ammonium cations are not incorporated in the self-assembled adlayer.

It has been shown that water contact angle data of alkyl phosphate SAMs reflect the degree of coverage of SAMs of long-chain alkyl phosphates.¹⁴ Contact angle values of complete monolayers from various types of hydroxy-

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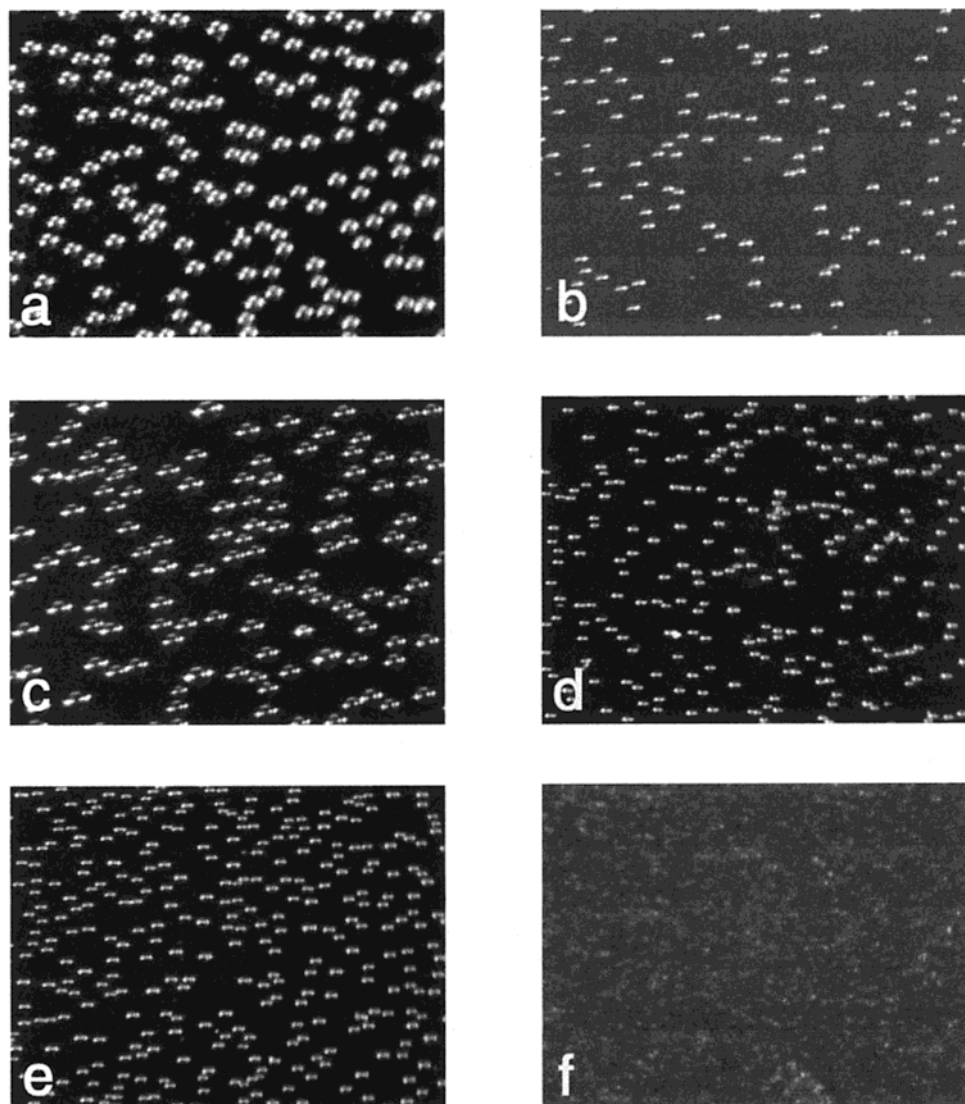


Figure 1. Microdroplet density images of DDPO₄ SAMs on different smooth metal oxide surfaces: (a) Al₂O₃, (b) Ta₂O₅, (c) Nb₂O₅, (d) ZrO₂, (e) TiO₂, and (f) SiO₂. The homogeneous distribution of growing water droplets reflects the homogeneity of the hydrophobic SAM surfaces on a microscopic scale. SiO₂ (f) does not adsorb DDP under the same self-assembly conditions; it remains hydrophilic and is completely covered by a layer of condensed water during the water condensation test. Image size: 1 mm².

Table 2. Normalized XPS Intensities (Intensities of C(1s), O(1s), Ta(4f), Al(2p), Nb(3d), Zr(4f), Ti(2p), (Si2p), and P(2p) Divided by the Corresponding Elemental Sensitivity Factors and Normalized to 100%) of DDPO₄ Self-Assembled onto Different Metal Oxide Substrates^a

substrate					substrate				
normalized intensity					normalized intensity				
MO _x	% C	% O	% M	% P	MO _x	% C	% O	% M	% P
15° Electron Takeoff Angle					75° Electron Takeoff Angle				
Ta ₂ O ₅	67.8	23.2	6.71	2.36	Ta ₂ O ₅	27.3	53.7	17.4	1.61
Al ₂ O ₃	67.6	21.1	8.85	2.53	Al ₂ O ₃	25.3	47.1	25.5	2.10
Nb ₂ O ₅	59.7	29.6	8.5	2.26	Nb ₂ O ₅	31.9	49.4	17.3	1.30
ZrO ₂	72.2	22.0	3.06	2.77	ZrO ₂	35.9	49.0	12.9	2.28
TiO ₂	68.6	23.0	6.13	2.23	TiO ₂	31.2	49.4	17.6	1.83
SiO ₂	6.2	70.8	22.9	0	SiO ₂	nd ^b	nd ^b	nd ^b	nd ^b

^a The measurements were performed at takeoff angles of 15° and 75°, with respect to the surface plane. ^b nd = not determined.

terminated amphiphiles have been reported to be 50–80°.¹ Although contact angles on hydrophobic, methyl-terminated SAMs provide a very sensitive indicator of complete coverage and order, no straightforward prediction can be made from contact angles of hydroxy (or other polar group) ω -functionalized alkyl phosphates. Therefore, to test whether OH-DDPO₄ forms densely packed SAMs,

we first compared the coverage-dependent XPS C(1s) signals from DDPO₄ SAMs with those of OH-DDPO₄ measured by XPS at different takeoff angles (Figure 3). The carbon concentration is plotted in Figure 3 as a function of the sine of the takeoff angle Θ , because the sampling depth scales linearly with the sine of the takeoff angle. The carbon signal intensities for both amphiphiles on Ta₂O₅ as well as on Nb₂O₅ are very similar, suggesting that hydroxy-terminated dodecyl phosphate and dodecyl phosphate indeed form SAMs with comparable molecular surface densities.

Normalized XPS intensities of OH-DDPO₄ self-assembled onto Ta₂O₅ and Nb₂O₅ are summarized in Table 3 as a function of the electron takeoff angle. The data are again qualitatively consistent with our model of a surface architecture where the alkyl phosphates adsorb onto metal oxide substrate surfaces with a tail-up orientation of the alkane chain.

The O(1s) signal was curve-fitted into three different O(1s) subpeaks representing five different oxygen species: (a) the metal oxide (530.2 eV), (b) the phosphate oxygen (531.4 eV for P–O–Metal and P=O and 532.6 eV for R–O–P and P–OH), and (c) the hydroxy group

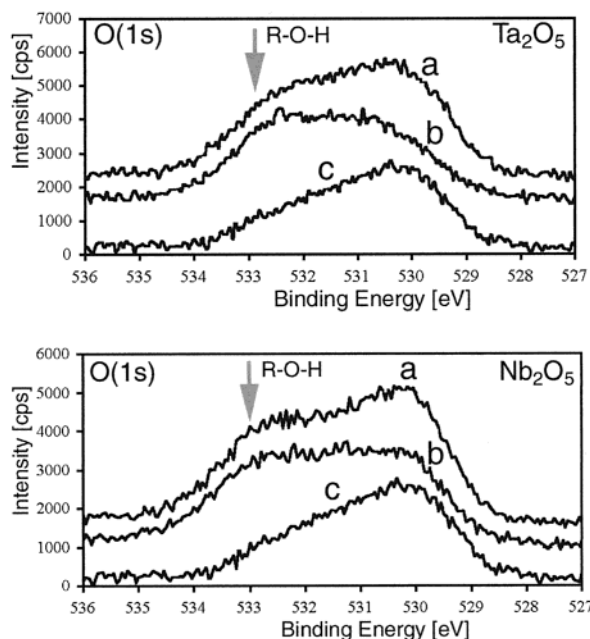


Figure 2. XPS O(1s) spectra of *hydroxy-terminated* dodecyl phosphate (OH-DDPO₄), self-assembled onto Ta₂O₅ and Nb₂O₅ (curves a and b). The spectra were recorded at two different electron takeoff angles Θ (curve a, 20.5°, and curve b, 11.5°, relative to the surface plane) and are compared to the O(1s) spectrum of a *methyl-terminated* dodecyl phosphate (DDPO₄) SAM on the corresponding substrate, measured at a takeoff angle Θ of 15° (curve c). The electron emission at a binding energy of approximately 534 eV is assigned to the terminal R-OH group in the OH-DDPO₄ SAM. The observed increase of the intensity with decreasing electron takeoff angle provides evidence for the location of the hydroxy group at the outermost surface.

(approximately 534 eV, position can only be approximately determined because of the comparatively weak signal). The details of the curve-fitting procedures have been published elsewhere.¹⁸ The assignment of different binding energies to the different species in the substrate and coordinated phosphate groups has been described in a previous paper.¹⁷ The angle-dependent intensity data (peak areas) for the Nb(3d), C(1s), and P(2p) photoelectrons and for the three deconvoluted contributions to the O(1s) signal are plotted in Figure 4 for the case of the OH-DDPO₄-coated niobium oxide surface.

The increase of the substrate *oxygen* signal as the takeoff angle approaches the surface normal is due to the increase of the sampling depth and the consequent increased detection of the metal oxide layer, which can be considered as semi-infinite for XPS measurements. The phosphate oxygen O(1s) signal decreases slightly upon increasing the takeoff angle. This can be explained by our model where the phosphate groups form an interfacial monolayer between the substrate and the alkane chain layer. The signal from the ω -terminal hydroxy group (ROH) decreases only slightly with increasing takeoff angle Θ .

The strong decrease of the *metal* (Ta, Nb) signal originating from the cations in the semi-infinite oxide substrate with decreasing takeoff angle Θ is again, as in the case of the oxygen substrate signal, clearly due to the corresponding decrease of the sampling depth, depending on the sine of the takeoff angle Θ . This is paralleled by a corresponding increase of the *carbons* signal of the organic adlayer.

All signals, on the other hand, that originate from a purely two-dimensional, roughly monatomic surface or interface layer (O(1s) and P(2p) of the PO₄ interface and

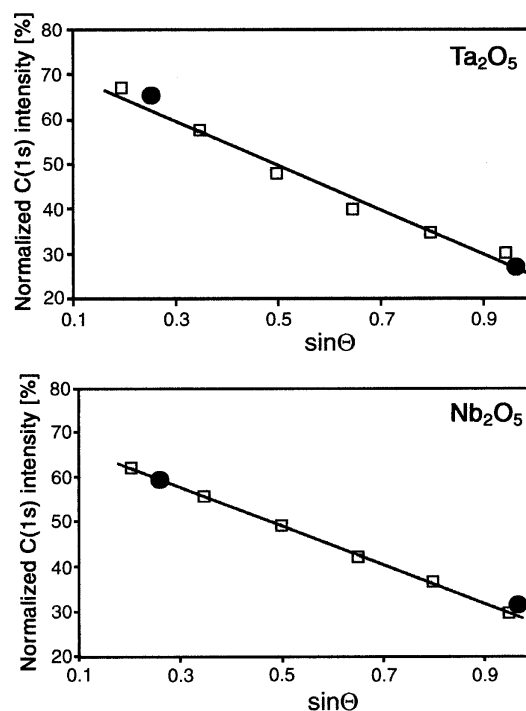


Figure 3. XPS C(1s) normalized intensities (in %) of OH-DDPO₄ and DDPO₄ SAMs on Ta₂O₅ (top) and Nb₂O₅ (bottom), measured at different electron takeoff angles Θ and plotted as a function of $\sin \Theta$. C(1s) intensity values of the OH-DDPO₄ SAM are represented by squares; those of the DDPO₄ SAM (only two measurements) are represented by circles. A linear trend line is added.

Table 3. Normalized XPS Intensities (Intensities of Ta(4f), Nb(3d), O(1s), P(2p), and C(1s) Divided by the Corresponding Elemental Sensitivity Factors and Normalized to 100%) of OH-DDPO₄ Self-Assembled onto Ta₂O₅ and Nb₂O₅^a

takeoff angle Θ	$\sin \Theta$	normalized XPS intensities OH-DDPO ₄ on Ta ₂ O ₅			
		% Ta	% O	% P	% C
11.5	0.20	3.05	26.6	3.69	66.72
20.5	0.35	6.27	33.0	3.91	56.79
30.0	0.50	9.21	39.8	3.12	47.78
40.5	0.65	11.9	45.8	2.83	39.46
53.1	0.80	13.42	50.3	2.00	34.29
71.8	0.95	14.88	53.3	2.12	29.65

takeoff angle Θ	$\sin \Theta$	normalized XPS intensities OH-DDPO ₄ on Nb ₂ O ₅			
		% Nb	% O	% P	% C
11.5	0.20	4.64	29.3	3.86	62.21
20.5	0.35	6.74	33.9	3.32	55.97
30.0	0.50	9.53	38.5	3.07	48.62
40.5	0.65	11.97	43.6	2.78	41.97
53.1	0.80	14.05	47.7	2.01	36.24
71.8	0.95	16.38	51.6	2.07	29.98

^a The measurements were performed at different electron takeoff angles Θ . The sine of the takeoff angle (Θ) was increased linearly corresponding to a linear increase in the effective sampling depth.

O(1s) of the terminal ROH group) give rise to intensities that show comparatively less dependence on the takeoff angle. The same observation has been reported for the interfacial phosphate in the closely related system of octadecyl phosphate, self-assembled on tantalum oxide and discussed in terms of a quantitative evaluation of the angle-dependent XPS intensities assuming a three-layer model.¹⁷

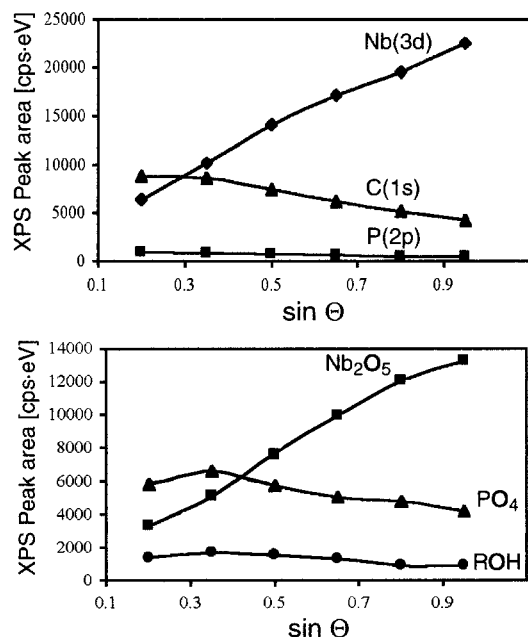


Figure 4. Angle-dependent XPS peak areas of Nb(3d), C(1s), and P(2p) (top) and of O(1s) of different oxygen types (bottom) for the OH-DDPO₄ SAM on Nb₂O₅. The O(1s) detail spectrum was deconvoluted in three different subpeaks representing three types of oxygen [O(Nb₂O₅), O(PO₄), and O(ROH)]. The peak areas are shown as a function of the sine of the electron takeoff angle Θ , basically reflecting the $\sin \Theta$ dependence of the effective sampling depth. The results of OH-DDPO₄ SAMs on Ta₂O₅ are very similar and not shown.

3.3. Mixed SAMs of OH-DDPO₄/DDPO₄ on Ta₂O₅ and TiO₂. Mixed solutions of 0.5 mM OH-DDPO₄(NH₄)₂ and 0.5 mM DDPO₄(NH₄)₂ were prepared according to section 2.2. Ta₂O₅ samples were cleaned and immersed in the mixed amphiphile solutions, as described in section 2.3.

Contact Angle and Microdroplet Density. The advancing water contact angle was measured immediately following sample preparation. The results show that the wettability of the resulting SAM correlates with the molar ratio OH-DDPO₄(NH₄)₂/DDPO₄(NH₄)₂ of the amphiphile solution and spans a range of approximately 110° (pure DDPO₄) to 50° (pure OH-DDPO₄) (Figure 5).

The relationship between amphiphile solution composition and molecular ratio of the two alkane phosphate molecules in the SAM based on XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements will be published in a separate paper.

The microdroplet density images appear homogeneous on the micrometer scale, suggesting that hydroxy-functionalized and nonfunctionalized alkyl phosphates in the monolayer are both equally homogeneously distributed at this scale. The large difference in wettability across the range of SAM composition ($\Delta = 50^\circ$) does not significantly affect the μ dd (Figure 5). In separate publications,^{18,19} we have shown that the microdroplet density value does not primarily depend on the wettability or water contact angle of a surface but on the concentration of condensation nucleation sites, believed to be induced by features such as surface roughness, molecular defects, and/or disorder in surfaces and adlayers. The experimental μ dd value of 90–230 droplets/mm² is low when compared to more disordered SAMs, for which this value is typically in the range of 1000–3000 droplets/mm².^{18,19} From the condensation figure evaluation, we deduce the presence of rather

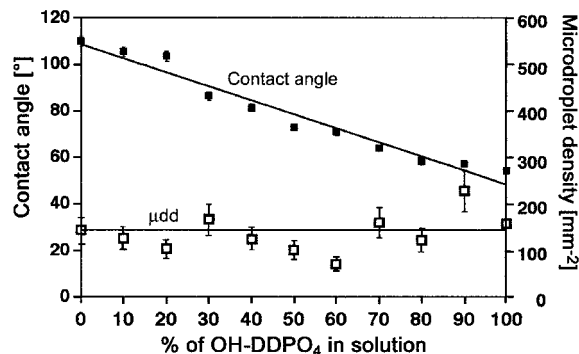


Figure 5. Advancing water contact angle θ_a (sessile drop) and microdroplet density (μ dd) data of mixed OH-DDPO₄/DDPO₄ SAMs on Ta₂O₅. The results are presented as a function of the mole percentage of OH-DDPO₄ in the amphiphile solutions, defined as $100\% \times [\text{OH-DDPO}_4]/([\text{OH-DDPO}_4] + [\text{DDPO}_4])$. The total alkyl phosphate concentration $[\text{OH-DDPO}_4] + [\text{DDPO}_4]$ is kept constant at 0.5 mM. 0% corresponds to the pure DDPO₄ SAM, and 100% to the pure OH-DDPO₄ SAM. Error bars correspond to \pm standard deviation (contact angle, θ_a : 3 probing drops in different areas of the sample, 10 measurements per drop; microdroplet density, μ dd: 4 independent measurements, each on an area of 0.25 mm²).

well-defined, smooth adlayers, independent of the composition of the SAM within the investigated OH-DDPO₄/DDPO₄ system.¹⁹ To what extent these SAM layers are ordered on a molecular level, however, cannot be concluded from the results of the experimental techniques used in this work. NEXAFS and atomic force microscopy (AFM) would be the methods of choice to unambiguously comment on structural order and molecular orientation, and such a study is currently underway.

4. Conclusion and Outlook

It has been shown that it is possible to self-assemble alkyl phosphates from aqueous solutions of their ammonium salts, on a wide range of different metal oxides. XPS analysis did not reveal the presence of nitrogen, suggesting that ammonium cations do not adsorb on the substrate surface but serve only to increase the solubility of the alkyl phosphates in water. Highly hydrophobic surfaces are readily formed by self-assembly from aqueous solutions of the ammonium salt of dodecyl phosphate. On all investigated transition metal oxides as well as on aluminum oxide, defined SAMs are formed with approximately the same molecular coverage and correspondingly similar properties (e.g., advancing contact angles in the range of 110–115°). Silicon dioxide, on the other hand, does not form adlayers from aqueous alkyl phosphate solutions, probably because of the far lower affinity of phosphate for Si(IV) compared to Al(III), Ti(IV), Nb(V), and Ta(V), which are known to form strong phosphate coordination complexes.

It is also possible to produce more hydrophilic SAMs using aqueous solutions of the ammonium salt of hydroxy-terminated dodecyl phosphate. Furthermore, the wettability (water contact angle) imposed onto a metal oxide surface can be varied in a controlled, predictable way by the formation of mixed methyl-/hydroxy-terminated dodecyl phosphate SAMs, self-assembled from aqueous solutions containing both molecules in an appropriate ratio. Investigations of the relationship between adsorbate composition and solution amphiphile concentration ratio for mixed SAM systems (by XPS and ToF-SIMS) as well as amphiphile orientation and order in the different SAMs (by NEXAFS and AFM) are currently under way.

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