The Role of Polarity in the Structure of Silanes Employed in Surface Modification

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Abstract
An overview is presented on the range of interactions between silane-treated surfaces and aqueous systems. In this context, new data for silanes in which both polar and non-polar functionalities together in a single organic substituent are presented. Significant differences in behavior are observed between silanes in which the polar substituent is proximal to the silicon atom and represents an “embedded” hydrophilicity compared to polar substituents distal to the silicon and represents a “tipped” hydrophilicity.

Keywords
Silanes, hydrophobic, hydrophilic, embedded hydrophilicity, alkylsilanes, polyethyleneoxysilanes

1. Introduction

Silanes that alter the chemical properties of surfaces have been studied intensively for over fifty years. In the context of coupling agents for polymer composites, biomolecule immobilization and adhesive technology, silanes have been both reviewed and have been the subject of many symposia. In contrast to silanes utilized as coupling agents in adhesive applications, silanes used to modify the surface energy or wettability of substrates under most conditions are not intended to impart chemical reactivity to the substrate. They are often referred to as non-functional silanes in order to indicate the absence of functional (reactive) groups on the organic substituent of the silane. Non-functional silanes are important since water adsorption at the interface is an important factor in coupling agent effectiveness. Although the use of non-functional silanes for surface modification is more pervasive than silanes used as coupling agents, they have been the subject of only a single review [1] which emphasizes hydrophobic surfaces. The full range of interactions of silane-treated surfaces with aqueous systems, from hydrophobic to hydrophilic, has not been reviewed. The objective of this overview is to demonstrate trends in behavior of substrates treated with non-functional silanes in aqueous environments by

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providing examples of data from the literature on polar and non-polar substituted silanes and new data in which polar groups and non-polar groups are both present together as a single substituent on the silane.

2. Background

2.1. Wettability and Contact Angle [2–8]

A surface is said to be wetted if a liquid spreads over the surface evenly without the formation of droplets. When the liquid is water and it spreads over the surface without the formation of droplets, the surface is said to be hydrophilic. In terms of energetics this implies that the forces associated with the interaction of water with the surface are greater than the cohesive forces associated with bulk liquid water. Water droplets form on hydrophobic surfaces, implying that cohesive forces associated with bulk water are greater than the forces associated with the interaction of water with the surface. Surface interactions with water must compete with a variety of internal interactions of liquid phase water: van der Waals forces, dipole interactions, hydrogen bonding and proton exchange.

Practically, hydrophobicity and hydrophilicity are relative terms. A simple quantitative method for defining the relative degree of interaction of a liquid with a solid surface is the contact angle of liquid droplet on the solid substrate. If the contact angle of water on a surface is less than 30°, a preponderance of literature refers to the surface as hydrophilic, presumably since the forces of interaction between water and the surface approach the cohesive forces of bulk water, i.e. the difference between the work of adhesion and the work of cohesion is less than 10 $\mathrm{mJ/m^2}$ and water does not cleanly drain from the surface. If water spreads over a surface and the contact angle at the spreading front edge of the water is less than 10°, the surface is often designated as superhydrophilic provided that the surface does not absorb the water, dissolve in the water or react with the water. On a hydrophobic surface water forms distinct droplets. The greater the hydrophobicity the greater the contact angle. Surfaces with contact angles greater than 90° are designated as hydrophobic. The upper limit of the contact angle for water on a smooth surface is 120° which is approached by closely packed trifluoromethyl groups. Micro-textured or micro-patterned surfaces with hydrophobic asperities can exhibit superhydrophobicity associated with the “Lotus Effect”. The data presented in Table 1 indicate that non-functional alkylsilanes and fluoroalkylsilanes provide hydrophobic surfaces while silanes with polyethyleneoxy (PEGylated) substitution are hydrophilic. The data in the table are gathered from a variety of sources for either equilibrium contact angle or an average of advancing and receding contact angles. It should be emphasized that the data provide only a first-order relative comparison of hydrophobicity. Recent advances in the understanding of contact angle hysteresis and kinetics provide a keener insight into the behavior of water on surfaces [9, 10].

Table 1.
Contact angles of water (degrees) on smooth surfaces

Heptadecafluorodecyltrimethoxysilane	113–115
Poly(tetrafluoroethylene)	108–112
Polypropylene	108
Octadecyldimethylchlorosilane	110
Octadecyltrichlorosilane	102–109
Tris(trimethylsiloxy)silylethyldimethylchlorosilane	103–104
Octyldimethylchlorosilane	104
Butyldimethylchlorosilane	100
Trimethylchlorosilane	90–100
Polyethylene	88–103
Polystyrene	94
Poly(chlorotrifluoroethylene)	90
Human skin	75–90
Diamond	87
Graphite	86
Silicon (etched)	86–88
Talc	82–90
Chitosan	80–81
Steel	70–75
Methoxyethoxyundecyltrichlorosilane	73–74
Methacryloxypropyltrimethoxysilane	70
Gold, typical (see gold, clean)	66
Intestinal mucosa	50–60
Kaolin	42–46
Platinum	40
Silicon nitride	28–30
Silver iodide	17
[Methoxy(polyethyleneoxy)propyl]trimethoxysilane	15–16
Sodalime glass	<15
Gold, clean	<10
Trimethoxysilylpropyl substituted poly(ethyleneimine), hydrochloride	<10

Note: Contact angles for silanes refer to hydrolytic deposition of the silane onto smooth surfaces. The data here are drawn from various literature sources and from the authors' work. Exact comparisons between substrates do not take into account differences in test methods or whether advancing, receding or equilibrium contact angles were reported.

2.2. Critical Surface Tension (γ_c)

The contact angle of water on a substrate is a good indicator of the relative hydrophobicity or hydrophilicity of a substrate. The contact angle of water on a substrate is not a good indicator for the wettability of the substrate by other liquids. Young's equation provides a method for considering interfacial energetics of a solid as a product of a liquid surface tension and the contact angle of the liquid on the solid:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos\theta_e,$$

where γ_{lv} is surface tension of liquid, γ_{sl} is interfacial tension, γ_{sv} is interfacial tension between the solid and vapor, θ_{e} is equilibrium contact angle. The critical surface tension is an operational parameter for any solid and is determined by plotting the cosine of the contact angles of liquids of different surface tensions and extrapolation to 1. Liquids with a surface tension below the critical surface tension of a solid substrate will wet the surface, i.e. show a contact angle of 0° ($\cos\theta = 1$). Critical surface tension is associated with the wettability or release properties of a solid. It serves as a better predictor than the contact angle of water for the behavior of a solid with liquids. γ_{c} values also mitigate or eliminate the effect of surface features, providing for water a metric of surface interaction that is less dependent on topographical effects.

Hydrophilic behavior of surfaces is generally considered to occur when critical surface tensions are greater than 45 mN/m. As the critical surface tension increases, the expected decrease in contact angle is accompanied with stronger adsorptive behavior.

Hydrophobic behavior of surfaces is generally considered to occur when critical surface tensions are less than 35 mN/m. At first, the decrease in critical surface tension is associated with oleophilic behavior, i.e. the wetting of the surfaces by hydrocarbon oils. As the critical surface tensions decrease below 20 mN/m, the surfaces resist wetting by hydrocarbon oils and are considered both oleophobic as well as hydrophobic. Silane surface modification can be used to generate a broad range of critical surface tensions. Table 2 compares the critical surface tensions of silane modified surfaces with unmodified surfaces.

3. Hydrophobic Silane Surface Treatments

Factors which contribute to the ability of an organosilane to generate a hydrophobic surface are its organic substituent, the extent of surface coverage, residual unreacted groups (both from the silane and the surface) and the distribution and orientation of the silane on the surface.

Aliphatic hydrocarbon substituents and fluorinated hydrocarbon substituents are the hydrophobic entities which enable silanes to induce surface hydrophobicity. Beyond the simple attribute that in order to generate a hydrophobic surface the organic substituent of the silane must be non-polar, more subtle distinctions can be made. The hydrophobic effect of the organic substituent can be related to the free energy of transfer of hydrocarbon molecules from an aqueous phase to a homogeneous hydrocarbon phase. For non-polar entities, van der Waals interactions are predominant interactions with water and such interactions compete with hydrogen bonding in ordering of water molecules. Van der Waals interactions for solid surfaces are primarily related to the instantaneous polarizability of the solid which is proportional to the dielectric constant or permittivity at the primary UV absorption frequency and the refractive index of the solid. Entities which present sterically closed structures

Table 2.
Critical surface tensions (mN/m)

Heptadecafluorodecyltrichlorosilane	12
Poly(tetrafluoroethylene)	18.5
Octadecyltrichlorosilane	20–24
Methyltrimethoxysilane	22.5
Nonafluorohexyltrimethoxysilane	23
Vinyltriethoxysilane	25
Paraffin wax	25.5
Ethyltrimethoxysilane	27.0
Propyltrimethoxysilane	28.5
Glass, sodalime (wet)	30.0
Poly(chlorotrifluoroethylene)	31.0
Polypropylene	31.0
Poly(propylene oxide)	32
Polyethylene	33.0
Trifluoropropyltrimethoxysilane	33.5
3-(2-Aminoethyl)aminopropyltrimethoxysilane	33.5
Polystyrene	34
p-Tolyltrimethoxysilane	34
Cyanoethyltrimethoxysilane	34
Aminopropyltriethoxysilane	35
Acetoxypropyltrimethoxysilane	37.5
Poly(methyl methacrylate)	39
Poly(vinyl chloride)	39
Phenyltrimethoxysilane	40.0
Chloropropyltrimethoxysilane	40.5
Mercaptopropyltrimethoxysilane	41
Glycidoxypropyltrimethoxysilane	42.5
Poly(ethylene terephthalate)	43
Copper (dry)	44
Poly(ethylene oxide)	43–45
Aluminum (dry)	45
Nylon 6/6	45–46
Iron (dry)	46
Glass, sodalime (dry)	47
Titanium oxide (anatase)	91
Ferric oxide	107
Tin oxide	111

Data compiled from Refs [11–14].

that minimize van der Waals contact are more hydrophobic than open structures that allow van der Waals contact. Thus, in comparison to polyethylene, polypropylene and poly(tetrafluoroethylene) are more hydrophobic. Similarly, when deposited as monolayers, methyl-substituted alkylsilanes and fluorinated alkylsilanes provide better hydrophobic surface treatments than linear alkylsilanes. Data are reported by

Fadeev and McCarthy [15] for the contact angles (advancing and receding) of water on silica substrates treated with alkylsilanes deposited from solution and from the vapor phase. They observed that the contact angle of water is relatively independent of alkylsilane length. It is flat especially on deposition from solution, presumably due to the fact that orientation of the alkylsilane occurs more readily. The similar values drive the conclusion that the contact interface mainly consists of methyl groups of the alkylsilane terminus with a lesser contribution from the methylene groups of the alkylsilane. Other investigators have speculated that the deviation from methyl terminal groups as the sole contribution to contact angle may be dependent on tilt angle of highly extended self-assembled monolayers, end-*gauche* defect content and imperfections in deposition engendered by the substrate, adsorbed water or hydrolytic condensation of the silane [16].

Fluoroalkylsilane contact angle data generated in the course of our investigations and presented in Table 3 show a dramatic trend especially when combined with other studies that considered smaller ranges of fluoroalkylsilanes [17, 18]. By way of background, the carbons alpha and beta to silicon are not fluorinated since substitution at alpha and beta positions results in compounds that are thermally unstable. The contact angle of water increases dramatically with the number of fluorinated carbons. The probable explanation is that at low numbers of fluorinated carbons, e.g. 1 in the trifluoropropyl silane, the electronegativity of the fluorines and the electropositivity of silicon create a strong dipole-induced dipole interaction with water. As the number of fluorinated carbons increases, the sterically closed, rigid, non-polar fluorinated segment dominates and presents a trifluoromethyl group for contact that has no electronic interaction with the silicon.

Surfaces to be rendered hydrophobic usually are polar with a distribution of hydrogen bonding sites. A successful hydrophobic coating must eliminate or mitigate hydrogen bonding and shield polar surfaces from interaction with water by creating a non-polar interface. Hydroxyl groups are the most common sites for hydrogen bonding. The hydrogens of hydroxyl groups can be eliminated by oxane bond formation with an organosilane. The effectiveness of a silane in reacting with

Table 3.
Fluoroalkylsilanes modified surfaces: water contact angles and critical surface tensions*

Silane	Contact angle of water (degree)	Critical surface tension (mN/m)
Trifluoropropyltrimethoxysilane	84	33.5
Nonafluorohexyltriethoxysilane	103	23.0
Tridecafluorooctyltriethoxysilane	110	14
Heptadecafluorodecyltrimethoxysilane	115	12 ± 0.7
Heneicosafluorododecyltrichlorosilane	118	6 ± 1

* Carbons alpha and beta to silicon are not fluorinated.
Data in this table are from the authors' work, Brzoska *et al.* [17] and Yoshino *et al.* [18].

hydroxyls impacts hydrophobic behavior not only by eliminating the hydroxyls as water adsorbing sites, but also by providing anchor points for the non-polar organic substituent of the silane which shields the polar substrates from interaction with water.

Strategies for silane surface treatment depend on the population of hydroxyl groups and their accessibility for bonding. A simple conceptual case is the reaction of organosilanes to form a monolayer. If all hydroxyl groups are capped by the silanes and the surface is effectively shielded, a hydrophobic surface is achieved. Practically, not all of the hydroxyl groups may react, leaving residual sites for hydrogen bonding. Further, there may not be enough anchor points on the surface to allow the organic substituents to effectively shield the substrate. Thus the substrate reactive groups on the silane, the conditions of deposition, the ability of the silane to form monomeric or polymeric layers and the nature of the organic substituent all play a role in rendering a surface hydrophobic.

Hydrophobicity is frequently associated with oleophilicity, the affinity of a substrate for oils, since non-polar organic substituent is often hydrocarbon in nature and shares structural similarities with many oils. The hydrophobic and oleophilic effects can be differentiated and controlled. At critical surface tensions of 20–30 mN/m, surfaces are wetted by hydrocarbon oils but are water repellent. At critical surface tensions below 20 mN/m, hydrocarbon oils no longer spread and the surfaces are both hydrophobic and oleophobic. The most oleophobic silane surface treatments have fluorinated long-chain alkylsilanes and methylated medium chain alkylsilanes.

Superhydrophobic surfaces are those surfaces that present apparent contact angles that exceed the theoretical limit (120°) for smooth surfaces. The most common examples of superhydrophobicity are associated with surfaces that are rough on a sub-micrometer scale and contact angle measurements are on composites of solid surfaces and air, designated as the Cassie state. The mechanism proposed by Cassie and Baxter [19] appears to have been successfully challenged by Gao and McCarthy [20], who argue that kinetics and contact line tortuosity as well as thermodynamics of wetting all must be considered. Perfectly hydrophobic structures (contact angles of 180°) consistent with this understanding have been prepared by hydrolytic deposition of methylchlorosilanes as microfibrillar structures [21].

4. Hydrophilic Silane Surface Treatments

The vast majority of surfaces are hydrophilic and water is ubiquitous in the environment, yet the precise nature of interaction of water with specific surfaces is largely unknown. Water adsorption may be uniform or in isolated patches. It may be driven by a number of different physical and chemical processes. The adsorption of water by a surface may be assisted or retarded by other adsorbates present in the environment. The purpose of applying a hydrophilic surface treatment is to control the nature and extent of interaction of water with the surface.

The controlled interaction of water with substrates can offer various degrees of hydrophilicity (ranging from physisorption to chemisorption and centers for ion-interaction). The utility of hydrophilic surfaces varies widely. Anti-fog coatings exploit high surface energies to flatten water droplets rather than allowing them to form light-scattering droplets. In biological systems they reduce non-specific bonding of proteins. Hydrophilic coatings with hydrogen bonding sites allow formation of tightly adherent layers of water with high lubricity in biological systems and the ability to resist oil adsorption in anti-graffiti coatings. They can also be used to disperse particles in aqueous coatings and oil-in-water emulsions. Hydrophilic coatings with ionic sites form antistatic coatings and dye receptive surfaces and can generate conductive and electrophoretic pathways. Thick films can behave as polymeric electrolytes in battery and ion conduction applications.

In general, surfaces become increasingly hydrophilic in the series: non-polar < polar, no hydrogen bonding < polar, hydrogen-bonding < hydroxylic < ionic.

Much of the discussion of hydrophobicity centers around high contact angles and their measurement. As a corollary, low or 0° contact angles of water are associated with hydrophilicity, but practically the collection of consistent data is more difficult. Further, discriminating between surfaces with a 0° contact angle is impossible. Computational methods based on contributions of both solvation energy and entropy of hydration spheres have been presented for single phase systems, but have not been developed for water interaction with solid substrates [22, 23]. The use of heat of immersion is a method that generates more consistent data for solid surfaces, provided they do not react with, dissolve or absorb the test liquid.

Another important consideration is whether once water is adsorbed it is "free" or "bound". Free water is water that is readily desorbed under conditions of less than 100% relative humidity. If water remains bound to a substrate under conditions of less than 100% relative humidity the surface is considered hygroscopic. Another description of hygroscopic water is a boundary layer of water adsorbed on a surface less than 200 nm thick that cannot be removed without heating. A measure of the relative hygroscopic nature of surfaces is given by the water activity, the ratio of the fugacity or escaping tendency of water from a surface compared to the fugacity of pure water.

The hydrophilicity of a surface as measured or determined by contact angle is subject to interference by loosely bound oils and other contaminants. Heats of immersion and water activity measurements are less subject to this interference. Heat of immersion data for silane-treated surfaces recalculated for unit surface area from literature data are provided in Table 4 [24, 25].

Measurements on silane modified surfaces demonstrate true modification of the intrinsic surface properties of substrates. If the immobilized hydrophilic layer is in fact a thin hydrogel film, then swelling ratios at equilibrium water absorption provide useful comparative data.

Table 4.
Heats of immersion in water (mJ/m^2)

Titanium dioxide	225–250
Talc	220–260
Aminopropyltriethoxysilane*	230–270
Silicon dioxide	210–225
Glass	200–205
Vinyltris(methoxyethoxy)silane*	110–190
Mercaptopropyltrimethoxysilane*	80–170
Graphite	32–35
Poly(tetrafluoroethylene)	24–25

*Data for silane-treated surfaces in this table are primarily from Marciniec [24] recalculated for unit surface area.

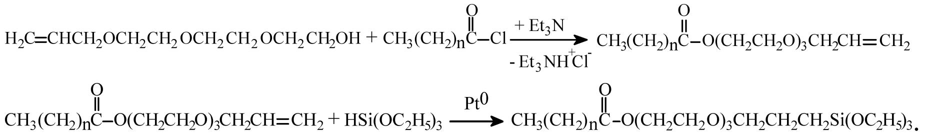
5. Combining Polarity and Non-polarity in Silane Surface Treatments

In the course of experimental work we synthesized various new silanes with polar substituent with and without opportunities for hydrogen bonding and in which the polar groups were either embedded below a hydrocarbon tail (i.e. proximal to the surface) or tipped at the end of the hydrocarbon (i.e. polar group proximal to the contacting phase) as shown below.

Tipped

$$CH_3OCH_2CH_2O(CH_2)_9CH{=}CH_2 + HSiCl_3 \longrightarrow CH_3OCH_2CH_2O(CH_2)_{11}SiCl_3.$$

Embedded



$$H_2C{=}CHCH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OH + CH_3(CH_2)_n\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow[-Et_3\overset{+}{N}H\overset{-}{Cl}]{+Et_3N} CH_3(CH_2)_n\overset{O}{\overset{\|}{C}}{-}O(CH_2CH_2O)_3CH_2CH{=}CH_2$$

$$CH_3(CH_2)_n\overset{O}{\overset{\|}{C}}{-}O(CH_2CH_2O)_3CH_2CH{=}CH_2 + HSi(OC_2H_5)_3 \xrightarrow{Pt^0} CH_3(CH_2)_n\overset{O}{\overset{\|}{C}}{-}O(CH_2CH_2O)_3CH_2CH_2CH_2Si(OC_2H_5)_3.$$

New data are presented in Table 5 which compares contact angle data of various silanes with polar substituent with and without opportunities for hydrogen bonding and in which the polar groups were either embedded below a hydrocarbon tail (i.e. adjacent to the surface) or tipped at the end of a hydrocarbon (i.e. polar group proximate to the contacting phase). Contact angles were gathered for both water and hexadecane. Control silylated surfaces were prepared with dodecylsilane as the hydrophobic control and methoxyPEG$_6$propyl as the hydrophilic control. The results were unexpected. Tipped polar silanes showed higher contact angles with water than the embedded polar silanes, regardless of opportunities for hydrogen-bonding. Further, the number of PEG units had relatively small impact on contact angle of the tipped silanes although an increase in number of PEG units did correlate to decreased water contact angle. PEG units embedded in silanes had a stronger effect on contact angle than PEG units in the tipped analogs. Hexadecane contact angle seems to be controlled by the number of carbon atoms in the

Table 5.
Contact angles of water and hexadecane on silane layers with tipped and embedded polar groups

Silane	Contact angle (degrees)	
	Water	Hexadecane
Hydrophobic control		
Dodecyltriethoxysilane	100	21
Hydrophilic tipped silanes		
(Methoxytriethyleneoxy)trimethoxysilylundecanoate	74	7
Methoxyethoxyundecyltrichlorosilane	73	5
Hydrophilic embedded silanes		
Triethoxysilylpropoxy(triethyleneoxy)octadecanoate	68	28
Triethoxysilylpropoxy(triethyleneoxy)dodecanoate	62	6
Triethoxysilylpropoxy(hexaethyleneoxy)octadecanoate	42	28
Triethoxysilylpropoxy(hexaethyleneoxy)dodecanoate	35	3
Hydrophilic control		
Methoxy(hexaethyleneoxy)propyltrimethoxysilane	16	17

carbon chain, although a step-change increase in contact angle is observed with C18-PEG silanes. Reconsideration of the anthropomorphic term *hydrophobic* or "water-hating" or "water-fearing" perhaps provides a too simplistic explanation. It appears not so much that hydrocarbons hate water, but that water hates hydrocarbons. Hydrocarbons appear indifferent to water. In the case of alkylsilanes tipped with polar groups, water molecular interaction proceeds until interaction with the hydrocarbon. In the cases of alkylsilanes in which polar groups are embedded near the surface, the hydrocarbon poses only a small barrier to the access of water to the polar groups.

6. Experimental

6.1. Silane Synthesis

6.1.1. Triethoxysilylpropyl(triethyleneoxy)dodecanoate

A 1 l 4-neck flask equipped with a cooling bath, a magnetic stirrer, a pot thermometer, an addition funnel and a nitrogen protected dry-ice condenser was charged with 131.3 g of lauroyl chloride, 15.0 g of triethylamine and 800 g of methylene chloride. The mixture was cooled to 5°C. Allyloxytriethylene oxide (114.1 g) (3 PEG units) was added through the addition funnel over a period of 15 minutes to the mixture maintaining pot temperature below 15°. The mixture was stirred for 60 minutes after the addition was completed. 300 ml of water was added to the mixture to give two layers. The aqueous top layer was discarded. The bottom organic layer was washed an additional time with 300 ml of water. The organic layer was dried over sodium sulfate, filtered and the methylene chloride removed by heating the pot to

80°C at atmospheric pressure and then at 5 mmHg for 60 minutes to give 201 g of a pale yellow liquid, allyloxytriethyleneoxydodecanoate.

A 1 l 4-neck flask equipped with a magnetic stirrer, a pot thermometer, an addition funnel and a nitrogen protected dry-ice condenser was charged with 100 g of allyloxytriethyleneoxydodecanoate and heated to 80°. Approximately 15 g of triethoxysilane was added to the flask followed by 0.25 ml of 2% Pt Karstedt catalyst. A slight rise in temperature was observed indicating initiation of the hydrosilylation reaction. The triethoxysilane addition was resumed maintaining pot temperature at 75–105° over 30 minutes until a total of 49.3 g was added. An additional 0.25 ml of Pt catalyst was added and the mixture was heated to 90° for 1.5 hours and then stripped under vacuum. The mixture was cooled to room temperature to give a clear yellow liquid, density, 20°C: 0.963, refractive index, 20°C: 1.4466, with IR and NMR results consistent with triethoxysilylpropyltriethyleneoxydodecanoate.

6.1.2. Triethoxysilylpropylpoly(ethyleneoxy)dodecanoate PEG-6

A 1 l 4-neck flask equipped with a cooling bath, a magnetic stirrer, a pot thermometer, an addition funnel and a nitrogen protected dry-ice condenser was charged with 109.4 g of lauroyl chloride, 12.5 g of triethylamine and 365 g of methylene chloride. The mixture was cooled to 5°C. Ethoxylated allyl alcohol (PEG 6) 161.2 g was added through the addition funnel over a period of 15 minutes to the mixture maintaining pot temperature below 15°C. The mixture was stirred and after 60 minutes the addition was completed. 300 ml of water was added to the mixture to give two layers. The aqueous top layer was discarded. The bottom organic layer was washed an additional time with 300 ml of water. The organic layer was dried over sodium sulfate, filtered and the methylene chloride removed by heating the pot to 80°C at atmospheric pressure and then at 5 mmHg for 60 minutes to give 210 g of a pale yellow liquid, allyloxyPEG$_6$dodecanoate.

A 1 l 4-neck flask equipped with a magnetic stirrer, a pot thermometer, an addition funnel and a nitrogen protected dry-ice condenser was charged with 100 g of allyloxyPEG6dodecanoate. and heated to 80°C. Approximately 25 g of triethoxysilane was added to the flask followed by 0.25 ml of 2% Pt Karstedt catalyst. A slight rise in temperature was observed indicating initiation of the hydrosilylation reaction. The triethoxysilane addition was resumed maintaining pot temperature at 75–105°C over 30 minutes until a total of 68.8 g was added. An additional 0.25 ml of Pt catalyst was added and the mixture was heated to 90°C for 1.5 hours and then stripped under vacuum. The mixture was cooled to room temperature to give a clear yellow liquid, density 0.976 g/cm^3, refractive index 1.4479 with IR and NMR results consistent with triethoxysilylpropylPEG$_6$dodecanoate.

6.1.3. Triethoxysilylpropyltriethyleneoxyoctadecanoate

A 1 l 4-neck flask equipped with a cooling bath, a magnetic stirrer, a pot thermometer, an addition funnel and a nitrogen protected dry-ice condenser was charged with 75.7 g of stearoyl chloride, 6.2 g of triethylamine and 174.2 g of methylene chloride. The mixture was cooled to 5°C. Allyloxytriethylene oxide (47.6 g) (3 PEG units) was added through the addition funnel over a period of 15 minutes to the mixture maintaining pot temperature below 15°C. The mixture was stirred for 60 minutes after the addition was completed. 300 ml of water was added to the mixture to give two layers. The aqueous top layer was discarded. The bottom organic layer was washed an additional time with 300 ml of water. The organic layer was dried over sodium sulfate, filtered and the methylene chloride removed by heating the pot to 80°C at atmospheric pressure and then at 5 mmHg for 60 minutes to give 74 g of a pale yellow liquid, allyloxytriethyleneoxyoctadecanoate.

A 1 l 4-neck flask equipped with a magnetic stirrer, a pot thermometer, an addition funnel and a nitrogen protected dry-ice condenser was charged with 65.2 g of allyloxytriethyleneoxyoctadecanoate and heated to 80°C. Approximately 5 g of triethoxysilane was added to the flask followed by 0.25 ml of 2% Pt Karstedt catalyst. A slight rise in temperature was observed indicating initiation of the hydrosilylation reaction. The triethoxysilane addition was resumed, maintaining pot temperature at 75–105°C, over 30 minutes until a total of 33.1 g was added. An additional 0.25 ml of Pt Karstedt catalyst was added and the mixture was heated to 90°C for 1.5 hours and then stripped under vacuum. The mixture was cooled to room temperature to give an amber solid, mp. 35–40°C, with IR and NMR results consistent with triethoxysilylpropyltriethyleneoxyoctadecanoate

6.1.4. Methoxyethoxyundecyltrichlorosilane

A 2 l 4-neck flask equipped a Hershberg stirrer, a pot thermometer, an addition funnel, a nitrogen protected dry-ice condenser and heating mantle was charged with 650 g of toluene and 57.5 g of sodium metal. The pot was heated to 100°C with stirring until the sodium metal had dispersed into small granules. The mixture was allowed to cool below 60° and 237.8 g of methoxyethanol was added dropwise. The reaction mixture was stirred for 4–5 hours until all sodium metal was consumed. A rapid addition of 583 g bromoundecene produced a mild exotherm and salt formation was observed. The mixture was heated at 60–80°C for 16 hours until no bromoundecene was observed by GC. Slow addition of 1000 ml of water to the reaction mixture followed by separation of the organic layer, a wash with an equal volume of water and drying over sodium sulfate produced a crude methoxyundecene solution. Volatile components were removed from the reaction mixture at 60°C at 5 mmHg to produce methoxyethoxyundecene.

A 1 l 3-neck flask equipped a magnetic stirrer, a pot thermometer, an addition funnel, a nitrogen protected dry-ice condenser and heating mantle was charged with 571.0 g of methoxethoxyundecene. The addition funnel was charged with 355.6 g of trichlorosilane. About 25 g of trichlorosilane was added to the methoxyethoxyundecene and the mixture was heated to 80–90°C. 1 ml of a 5% solution of chloroplatinic acid was added. Once reaction initiation was observed, the balance of the trichlorosilane was added at a rate to maintain temperature at 90–110°C. The mixture was heated for two hours after the addition. The product, methoxyethoxyundecyltrichlorosilane, was obtained in 72% yield (by distillation at 90–95°C/0.2 mmHg, density 1.07 g/cm^3).

6.2. Surface Modification

Clean borosilicate glass slides (Part No. PA 1615P, SPI Supplies, West Chester, PA) were the test substrates. Silane solutions were prepared at 2 wt% concentration in 95% ethanol–5% water (wt/wt) and adjusted to pH 4.5–4.9 with acetic acid if required. The solutions were used for surface treatment after a minimum hydrolysis time of 5 minutes and before a maximum of 5 hours. The glass slides were dipped into the hydrolyzed silane solution for 2 minutes. The treated glass slides were rinsed by dipping briefly in ethanol three times. Solvent was allowed to evaporate from the treated slides in an exhausted hood. Finally, the treated slides were heated at 110°C for 10 minutes.

6.3. Contact Angle Measurement

Water and hexadecane contact angles were measured with a Ramé-Hart Goniometer Model 100. All values reported are an average of all treatments with varied hydrolysis time.

7. Conclusion

Organosilanes with appropriate substituents can modify surfaces to encompass the full range of surface interaction with water, from hydrophobic to hydrophilic. In general, the polarity of substituent can be correlated to the relative hydrophobicity or hydrophilicity of the silane. The case of mixed polarity of substituent is less straightforward. Tipped polar silanes showed higher contact angles with water than the embedded polar silanes, regardless of opportunities for hydrogen-bonding. Further, the number of PEG units had relatively small impact on contact angle of the tipped silanes although an increase in number of PEG units did correlate to decreased water contact angle. PEG units embedded in silanes had a stronger effect on contact angle than PEG units in the tipped analogs.

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[*] References 2–8 provide a general overview of the concepts of contact angle and wettability.

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