Role of Solvent on the Silanization of Glass with Octadecyltrichlorosilane

Mark E. McGovern, Krishna M. R. Kallury, and Michael Thompson*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 1A1, Canada

Received December 21, 1993. In Final Form: June 30, 1994®

The relative surface concentrations of octadecyltrichlorosilane (OTS) deposited on glass substrates in the presence of 11 different solvents were evaluated by X-ray photoelectron spectroscopy, with supporting evidence from contact angle measurements. The density of the observed OTS films cannot be explained entirely on the geometrical similarities or differences between the solvent and the octadecyl moiety, as it was observed that *n*-pentane produces an OTS film much sparser than that of hexadecane or toluene. A new mechanism involving extraction of surface moisture into the bulk solvent, followed by OTS hydrolysis and subsequent deposition, is proposed. Aromatic solvents (benzene and toluene) which are capable of extracting significant amounts of water from the substrate surface yield the densest OTS films, indicating a preference for OTS hydrolysis in the bulk solvent phase rather than at the substrate surface. A novel protocol was developed to quantitate the surface water extracting capacities of pentane and toluene. Dehydrated silica powder was rehydrated with D_2O, followed by extraction with solvent, and the dissolved heavy water was trapped by treatment with phenyllithium to form deuterobenzene. The ratio of mass 79 (deuterobenzene) to mass 78 (benzene), determined by GC-MS, enables the quantitation of extracted D_2O. The results show that toluene can extract significant amounts of D_2O from the silica surface, whereas *n*-pentane is much less effective. OTS dissolved in anhydrous toluene only reacts with the surface silanol groups, producing a low density film. However, the same toluene, when spiked with a small quantity of D_2O, forms an OTS film nearly twice as dense as that obtained under anhydrous conditions. The optimum quantity of moisture for the formation of a closely-packed monolayer is about 0.15 mg/100 mL of solvent.

Introduction

Self-assembled monolayers made from molecules consisting of long aliphatic chains have attained considerable prominence in recent years as viable alternatives to Langmuir–Blodgett films, owing to their stability and resistance to various perturbing conditions.[1] The two major categories of organic compounds used for this purpose include alkanethiols[2] and alkyltrichloro/alkyltrialkoxysilanes,[3,4] the former with gold or silver substrates and the latter with hydroxylic materials such as silica-based substrates or metals with oxide coatings. Amongst the silanes, octadecyltrichlorosilane (OTS) is the most extensively used surface-active reagent for generating self-assembled monolayers on a variety of substrates. This silane finds extensive applicability in the preparation of reverse phase HPLC columns for the chromatographic separation/analysis of a range of organic/bio-organic molecules.[5] Emerging fields of research employing OTS-treated hydroxylic substrates include environmental analysis,[6] biomedical studies[7] (e.g. protein-surface interactions), formation of antithrombogenic biomaterials,[8] lubricants/water-repellant/antifouling coatings,[9] glass-reinforced composites,[10] studies on polymer interfacial properties,[11] chemical sensors/biosensors,[12] and electrochemical studies,[13] to name a few.

In spite of the extensive range of applications summarized above, the nature of the interaction of OTS with hydroxylic substrates remains unclear.[14] The commonly accepted mechanism is a three-step process, the first step being the hydrolysis of the chloro moieties of OTS at the hydroxylic substrate surface to generate a silanetriol, which then physisorbs onto the substrate via hydrogen bonding and ultimately forms both $Si_{substrate}$—O—Si_{silane} and Si_{silane}—O—Si_{silane} cross-linking types of covalent bonds.[15] There exists a subtle difference between this mechanism and that proposed by Angst and Simmons,[16] as well as by Britcher et al.,[17] in that the latter two groups postulate that the hydrolysis of the chloro entities of OTS occurs in the bulk solution phase instead of at the substrate surface as envisaged earlier. This proposal receives support from the observation of Kessel and Granick[18] that a closely-packed monolayer of octadecylsilyl moieties could be generated on a freshly cleaved muscovite mica surface by treatment with octadecylsilanetriol in cyclohexane solution. The silanetriol is prepared by the hydrolysis of octadecyltriethoxysilane in THF with dilute acid.

The surface coverage resulting from the silanization reactions involving OTS and hydroxylic substrates depends on several variables such as reaction time, temperature, degree of hydration of the substrates, nature of

® Abstract published in *Advance ACS Abstracts,* September 1, 1994.

(1) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 950.
(2) Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1987**, *3*, 932.
(3) Plueddemann, E. P. *Silane Coupling Agents*; Plenum: New York, 1982.
(4) Engelhardt, H.; Orth, P. *J. Liq. Chromatogr.* **1987**, *10*, 1999.
(5) (a) Regnier, F. E.; Unger, K. K.; Majors, R. E. *J. Chromatogr.* **1991**, *544*. (b) Nanrocki, J.; Buszewski, B. J. *Chromatogr. Rev.* **1988**, *449*, 1.
(6) Ballschmiter, K.; Bacher, R.; Mennel, A.; Fischer, R.; Riehle, U.; Swerev, M. *J. High Resolut. Chromatogr.* **1992**, *15*, 260.
(7) Zimmermann, R. M.; Schmidt, C. F.; Gaub, H. E. *J. Colloid Interface Sci.* **1990**, *139*, 268.
(8) Pitt, W. G.; Grasel, T. G.; Cooper, S. L. *Biomaterials* **1988**, *9*, 36.
(9) De Palma, V.; Tillman, N. *Langmuir* **1989**, *5*, 868.
(10) Cave, N. G.; Kinloch, A. J. *Polymer* **1992**, *33*, 1162.
(11) Migler, K. B.; Hervet, H.; Leger, L. *Phys. Rev. Lett.* **1993**, *70*, 287.
(12) (a) Andersson, L. G.; Mandenius, C. F.; Mosbach, K. *Tetrahedron Lett.* **1988**, *29*, 5437. (b) Kim, J. H.; Cotton, T. M.; Uphaus, R. A. *J. Phys. Chem.* **1988**, *92*, 5575. (c) Kallury, K. M. R.; Thompson, M.; Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, *8*, 1028.
(13) Charych, D. H.; Landau, E. M.; Majda, M. *J. Am. Chem. Soc.* **1991**, *113*, 3340.
(14) Tripp, C. P.; Hair, M. L. *Langmuir* **1992**, *8*, 1120.
(15) Sagiy, J. *J. Am. Chem. Soc.* **1980**, *102*, 92.
(16) Angst, D. L.; Simmons, G. W. *Langmuir* **1991**, *7*, 2236.
(17) Britcher, L. G.; Kehoe, D. C.; Matisons, J. G.; Smart, R. St. C.; Swincer, A. G. *Langmuir* **1993**, *9*, 1609.
(18) Kessel, C. R.; Granick, S. *Langmuir* **1991**, *7*, 532.

0743-7463/94/2410-3607$04.50/0

the solvent, the cleaning procedure utilized prior to silanization of substrates, and the nature/morphology of the oxide layer on the substrate. Silberzan et al.[19] as well as Angst and Simmons[16] have emphasized the importance of the water content on the substrate surface in determining whether a complete monolayer is formed or not. Angst and Simmons[16] obtained a tightly-packed monolayer of OTS on a fully hydrated oxidized silicon wafer surface, while with a dry silicon wafer a lower surface coverage results. Tripp and Hair,[14] through an IR spectroscopic study, showed that no direct reaction occurs between OTS and either the silica surface hydroxyl groups or even the first water layer bound to the fumed silica surface. However, the authors did observe that adsorption of OTS takes place on the subsequent layers of water, and this was confirmed by Silberzan et al.[19] On the other hand, Le Grange and co-workers[20] conclude that a fully hydrated surface is not essential for complete coverage by OTS, suggestive of the fact that not every silane group is bonded to the surface.

A different, albeit important, factor is the nature of the solvent employed for the silanization reactions with OTS. The pioneering work of Sagiv and co-workers[21] clearly demonstrates the fact that greater packing densities of OTS on silica-based substrates could be achieved with toluene or bicyclohexyl as solvent in comparison with hexadecane. Sagiv and co-workers[21] attribute this difference to geometrical matching between the hexadecane and the C18 chain of the OTS molecule which facilitates the incorporation of the solvent in a rodlike fashion. In fact, this property was favorably employed by several groups[12] to develop recognitive surfaces for organic molecules possessing long alkyl chains (e.g. cholesterol, Vitamin K1, stearic acid, etc.) on the basis of an insertion mechanism of the alkyl chains of the probe molecules into the vacant sites created by the removal of the intercalated hexadecane from the surface-anchored OTS layer by chloroform washing. Other solvents investigated include dichloromethane, carbontetrachloride, hexane, decane, dodecane, isooctane, cyclohexane, and a mixture of Isopar G and carbon tetrachloride.

The effect of alkyl chain length on the extent of silanization was also demonstrated by the Whitesides group,[22] making use of a homologous series of trichlorosilanes and bicyclohexyl as the solvent. This group found that, with the exception of very short chains, the wettability of the monolayers is approximately independent of the chain length. The presence of small amounts of water, again, was found to be necessary for effecting silanization. Brzoska et al.[23] have observed a temperature effect on the silanization of oxidized silicon wafers by alkyltrichlorosilanes but reported that the threshold temperature of *n*-decyltrichlorosilane in decane, dodecane, and isooctane is independent of the solvent nature. Silberzan et al.[19] have also demonstrated that approximately ambient temperatures produce the highest quality monolayers, the effect being attributed to solubility factors.

The current work has been undertaken with a view to investigating the effect of the nature/polarity of solvent on the silanization of glass substrates with OTS. To the best of our knowledge, no systematic investigation of the solvent polarity parameter on such silanizations has been reported to date. We used X-ray photoelectron spectroscopy and contact angle measurements to ascertain the solvent effect in the present work. Furthermore, a novel chemical probe technique was developed to quantify the amount of surface water extractable into the bulk solvent layer, and the influence of this extracted water on the reaction of OTS with glass substrates under anhydrous and hydrated conditions was examined. This protocol was expected to shed light on the effect of nonextractable and extractable surface water on the packing density of OTS on the glass substrates utilized.

Experimental Section

Materials and Reagents. Octadecyltrichlorosilane was purchased from Hüls America and was used as received. Toluene, benzene, carbon tetrachloride, and methylene chloride were obtained from BDH (ACS grade) and were either purified by distillation over molecular sieves or distilled over phosphorus pentoxide. *n*-Pentane and cyclohexane were obtained from Caledon and used as such. *n*-Hexane, *n*-octane, cyclooctane, and *n*-hexadecane were procured from Aldrich and used without further purification. All *n*-alkanes were claimed by the manufacturer to be virtually pure *n*-isomers, and in the case of the lower *n*-alkanes, ^{13}C NMR was used to verify that no isomeric fractions were present in the samples. 1,4-Dioxane was Baker, Analyzed Reagent grade, and was distilled over anhydrous calcium chloride (Fisher, 4−20 mesh). Glass microscopic coverslips (Trophy brand No. 2) were cut using a diamond-tipped pencil to approximately 12 mm × 10 mm × 0.2 mm. Silica powder (Aldrich catalog (1993) No. 28,851-9, average particle size 5−25 μm, neutral, BET surface area ~500 m^2/g), D_2O (99% atom), and 1.8 M phenyllithium in 70/30 cyclohexane/diethyl ether were purchased from Aldrich.

Apparatus. Silanization was carried out in a reactor which is referred to as the total immersion reactor (TIR). The reactor consists of a Schlenk tube 9.5 cm in height, with a 24/29 ground glass female joint, and a side arm fitted with a Teflon stopcock was located near the bottom of the ground glass joint. Four indentations protruding inside the tube located 3 cm above the bottom of the tube were used to support a glass bucket which can fit a substrate 1 cm in width. The glass bucket held the substrate in a vertical position by its edges only and prevented the substrate from falling through its open bottom by means of a small ledge on which the substrate rested. The bucket was submerged under 15 mL of solution, the height of which was marked on the side of the tube.

Instrumentation. Analysis of the OTS silanized surfaces was performed through contact angle measurement and XPS. A Ramé-Hart Model 100-00 contact angle goniometer was used to assess the hydrophobicity of the silanized surfaces. Both advancing and receding measurements were performed on 3 and 5 mm size water drops. All measurements were performed under similar conditions of humidity and temperature.

X-ray photoelectron spectra were recorded on a Leybold MAX-200 X-ray photoelectron spectrometer using either an unmonochromated Mg Kα source run at 15 kV and 20 mA or an unmonochromated Al Kα source run at 15 kV and 30 mA. The energy scale of the spectrometer was calibrated to the Ag $3d_{5/2}$ and Cu $2p_{3/2}$ peaks at 368.3 and 932.7 eV, respectively. The binding energy scale was calibrated to 285 eV for the main C(1s) feature. For all samples, a survey run (pass energy = 192 eV, and from 0 to 1000 eV on the binding energy scale) was performed, along with both low-resolution (pass energy = 192 eV) and high-resolution (pass energy = 48 eV) scans of the C(1s), O(1s), and Si(2p) regions. Each sample was analyzed at a 90° angle relative to the electron detector using an X-ray spot size of 4 × 7 mm, and the experiments took approximately 5 min each. For the spectra obtained with the magnesium anode, satellite subtraction and normalization were performed with software obtained from the manufacturer. Quantitation of the low-resolution spectra was performed using empirically derived sensitivity factors (obtained from the manufacturer). For the Mg anode, the sensitivity factors were C(1s) = 0.34, O(1s) = 0.78, and Si(2p) = 0.4, and the sensitivity factors for the Al anode were C(1s) = 0.319, O(1s) = 0.75, and Si(2p) = 0.36. High-resolution peak fitting was performed using the manufacturers' software.

(19) Silberzan, P.; Leger, L.; Ausserre, D.; Benattar, J. J. *Langmuir* **1991**, *7*, 1647.
(20) Le Grange, J. D.; Markham, J. L.; Kurkjian, C. R. *Langmuir* **1993**, *9*, 1749.
(21) Gun, J.; Sagiv, J. *J. Colloid Interface Sci.* **1986**, *112*, 457.
(22) Wasserman, S. R.; Tao, Y.; Whitesides, G. M. *Langmuir* **1989**, *5*, 1074.
(23) Brzoska, J. B.; Shahidzadeh, N.; Rondelez, F. *Nature* **1992**, *360*, 719.

The GC-MS analysis system consisted of an HP5890 gas chromatograph interfaced to a VG 70-250S (double focusing) mass spectrometer. The GC used a J&W Scientific DB-5, 30 m, 0.250 i.d. capillary column, with helium carrier gas at a volumetric flow rate of 1 mL/min and a linear flow velocity of 32 cm/s. The temperature program began at 50 °C for 2 min, after which the temperature increased by 20 °C per minute until a final value of 250 °C was reached. The sample was subjected to electron ionization at 70 eV and an accelerating voltage of 8 keV. The source was set at 250 °C and a pressure of 10^{-6} mbar. Masses 78.0470 and 79.0532 were observed by using the selected ion monitoring technique in which the indicated masses were scanned every 80 ms. The peak areas were integrated and were used to determine the total number of counts arising from the respective ions. Perfluorokerosene was introduced into the spectrometer via a separate, continuous introduction system, and the CF_3^+ ion (mass 68.9952) was used as a reference. Under these conditions, the mass spectrometer had a resolution of about 1200 ($m/\Delta m$) at 10% valley.

Procedures. The blanks were cleaned before silanization by sequential sonication in 5% NaOH (30 min), three rinses with aliquots of deionized water, a chromic acid cleaning solution wash (50 °C for 15 min), and sonication with three aliquots of deionized water. The blanks were then rinsed with acetone and dried under a stream of nitrogen.

Solvent-Mediated Silanization. Eleven solvents were used in the preparation of the OTS-coated surfaces, viz. *n*-pentane, *n*-hexane, *n*-octane, *n*-hexadecane, cyclohexane, cyclooctane, 1,4-dioxane, benzene, toluene, carbon tetrachloride, and methylene chloride. Eleven glass blanks were each coated under identical conditions using one of the solvents listed above for the silanization. The entire series of eleven solvent-mediated silanization reactions was repeated twice. All glassware was pre-silanized with OTS in toluene before any solvent-dependent work was carried out. A 1×10^{-3} M solution of OTS in the desired solvent was prepared under nitrogen in a separate vessel and mixed via magnetic stirring for 1 min, and 10 mL was transferred to the total immersion reactor (see Apparatus section) which contained the blank substrate. A nitrogen atmosphere filled the TIR during the silanization reaction. When the reaction was complete (1 h), the silanized substrate was transferred from the TIR to a small vial containing chloroform and agitated for 5 min before removal, followed by rinsing with fresh chloroform. The washed substrate was then dried with a stream of nitrogen gas and placed in a labeled glass thimble which was kept in a desiccator until analysis. Prior to XPS analysis, the prepared samples were washed in a Soxhlet extractor with ACS chloroform overnight and quickly transferred into sealed glass containers.

Deuterium Exchange Experiments. Two grams of silica powder was weighed quantitatively into a preweighed 100 mL round bottomed flask with a 24/29 female joint. A special filtering device was assembled which consisted of a porous coarse glass filter (3 cm diameter) sealed halfway into a 7 cm long glass tube fitted with male 24/29 ground glass male joints. These two items were placed in a heat treatment oven at 450 °C (±50 °C) for 1 h, after which they were removed to a desiccator for cooling. The cooled apparatus was then reweighed, and the quantity of H_2O lost was recorded. D_2O (5 mL) was added to the flask containing the dried silica powder, the special filter was then connected to the flask, and the contents were thoroughly shaken for 5 min. A vacuum line adapter was connected to the top end of the filter, and the excess D_2O was removed under a pressure of approximately 1 mmHg. A heat gun was used to warm the flask periodically. After about 90 min, the sample was removed from the vacuum and weighed. The process of drying and weighing was continued until the molar percentage of D_2O adsorbed to the silica surface was nearly identical to the molar percentage of H_2O removed during the initial drying. All efforts were made to prevent atmospheric H_2O from entering the apparatus during the weighing part of the experiment. The toluene utilized for the extraction experiments with D_2O/silica was refluxed for 1 h over sodium metal under dry nitrogen and distilled off into a receiving flask equipped with a side arm fitted with a septum. The filter assembly was separated from the flask, and 10 mL of the dried toluene was transferred using a glass syringe to the flask containing the D_2O-treated silica powder. The filter assembly was attached to the flask, and the apparatus was gently shaken for 5 min to ensure the toluene was in contact with all of the silica powder. A small receiving vessel was attached to the top end of the filter, and the whole device was inverted so that 5 mL of the toluene was separated from the powder and transferred into the receiver. A 1 mL aliquot of the filtered toluene was placed in a screw-capped vial and was saved for later use. The receiving vessel was disconnected, and 5 drops of 1.8 M phenyllithium in 70/30 cyclohexane/diethyl ether was added via syringe. The mixture was transferred to a separatory funnel and extracted with distilled and deionized H_2O. The toluene layer was dried over $CaCl_2$ and then transferred to a screw-capped vial for analysis by GC-MS. The experiment was repeated three times, and three additional trials were performed using *n*-pentane (previously dried over phosphorus pentoxide and distilled) as the extraction solvent.

Table 1. Solvent-Dependent Silanization of Glass Substrates with OTS

solvent	average XPS elemental ratios C(1s):O(1s)	C(1s):Si(2p)	Si(2p):O(1s)	dielectric constant
benzene	0.92	2.12	0.43	2.284
toluene	0.85	1.97	0.43	2.379
cyclooctane	0.85	0.87	0.45	2.116
hexadecane	0.76	1.80	0.42	2.015[a]
octane	0.72	1.60	0.45	1.948
CCl_4	0.69	1.64	0.42	2.238
cyclohexane	0.68	1.66	0.41	2.023
hexane	0.64	1.51	0.42	1.890
CH_2Cl_2	0.46	1.55	0.39	9.08
pentane	0.42	1.06	0.39	1.844
dioxane	0.25	0.66	0.37	2.209

[a] Equal for dodecane.

Silanization with Toluene Containing the Extracted D_2O. The silanization procedure described under the "Solvent-Mediated Silanization" section was modified to provide better control over surface hydration. A drybox filled with nitrogen gas was used to provide a low-moisture environment for the silanization reaction. In addition, toluene was distilled over sodium metal inside the drybox for use in the reaction. The substrates were cleaned as mentioned previously, except that three received heat treatment at 450 °C for 1 h. One substrate was silanized for 1 h under anhydrous conditions using a 1×10^{-3} M solution of OTS in dry toluene and a preheated substrate. The second substrate was silanized using a solution of dried toluene (30 mL) which had been spiked with 1 mL of the toluene from the D_2O/silica extraction experiments, to which 50 mg of OTS was added. The OTS mixture was allowed to stand for 5 min before 15 mL of this solution was added to the TIR containing the dehydrated substrate and was allowed to react for 1 h. The third substrate was allowed to soak in 1 mL of the toluene/D_2O extract overnight before silanization in anhydrous toluene. A fourth substrate was not subjected to heat treatment but instead was allowed to soak in 5 mL of D_2O overnight and, after being dried under a stream of nitrogen, was silanized in anhydrous toluene.

Results and Discussion

Solvent Dependence of the Silanization of Glass Substrates with OTS. As detailed in the Experimental Section, eight hydrocarbon solvents (six aliphatic and two aromatic) were utilized in the current study to ascertain the influence of chain length and polarity on the extent of OTS deposition on glass substrates. In addition, two chlorinated solvents (CCl_4 and CH_2Cl_2) and a cyclic ether (1,4-dioxane) were also included in the investigation with the same objective as for the hydrocarbon solvents. The X-ray photoelectron spectra of all of the silanized substrates as well as the corresponding cleaned blank surfaces were recorded, and the ratio between the C(1s) and O(1s) binding energy peaks were computed to evaluate the relative surface coverages. The C(1s):O(1s) ratios (Table 1) were considered to be more pertinent than the C(1s):Si(2p) binding energy peak ratios (Table 1), since the former include the water content of the silanized surfaces

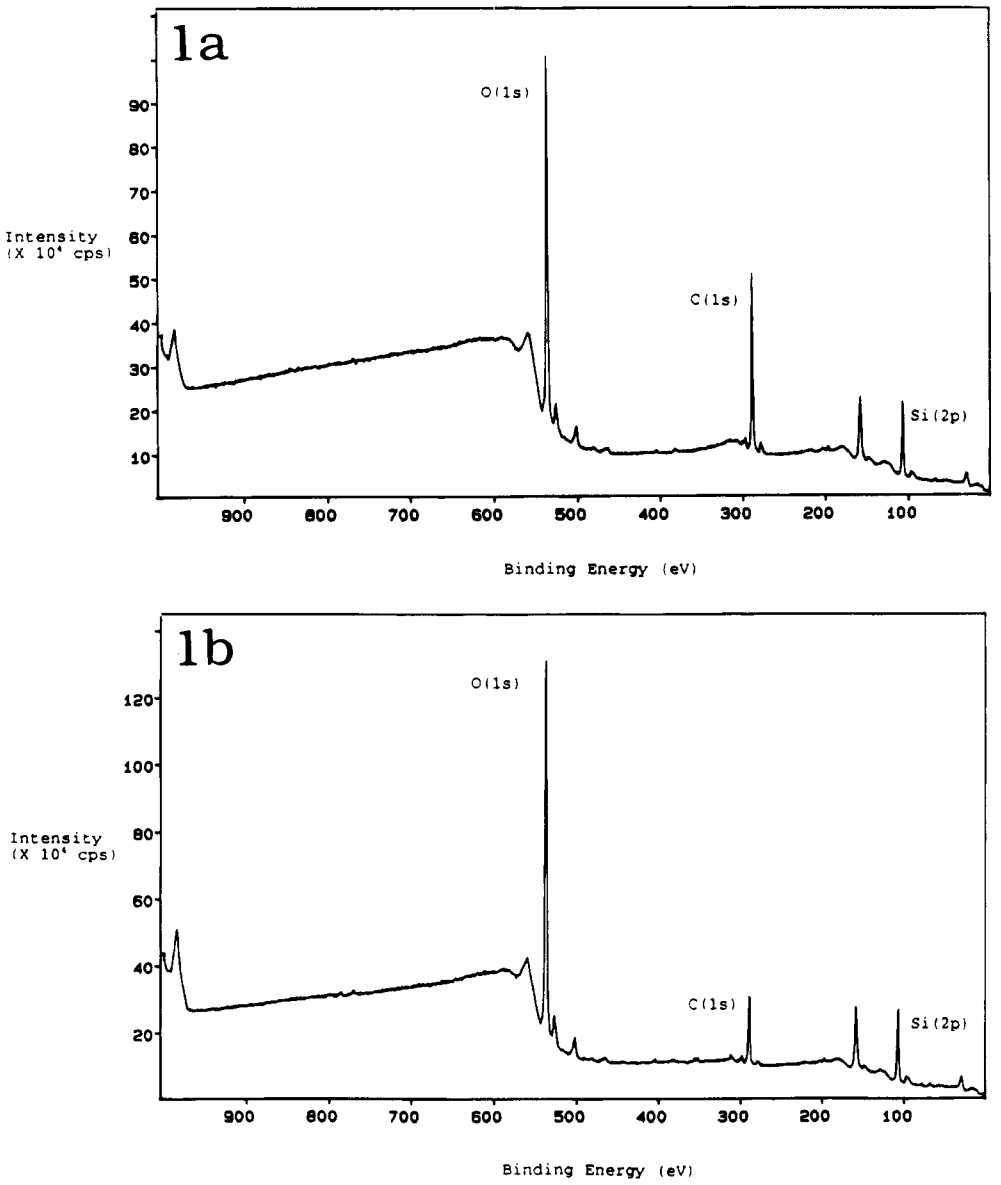

Figure 1. XPS surveys of OTS films prepared using (1a) toluene and (1b) pentane solvent. Analysis conditions: Unmonochromated Al anode (1486.6 eV), $\theta = 90°$; excitation voltage, 15.0 kV; pass energy, 192 eV; emission current, 30 mA; detector voltage, 2.20 kV; survey from 0–1000 eV; step time, 20 ms; step energy, 800 meV; spot size, 4 × 7 mm; 5 scans, data normalized.

as well. The latter ratios serve to verify that the C(1s):O(1s) ratios are indeed indicative of the relative quantities of OTS coverage and are not merely caused by varying amounts of water interposed between the OTS layer and the glass. Both the C(1s):O(1s) and the C(1s):Si(2p) ratios are comparable and have been included in Figure 2. The Si(2p):O(1s) ratios (Table 1) have also been included in Figure 2 to show that the O(1s) contribution due to surface moisture remaining after the silanization reaction is essentially constant for all the samples. About 5% carbon-containing contamination was observed on all samples, since compounds containing C—O and C=O moieties are known to adsorb onto surfaces exposed to the atmosphere. No attempt was made to subtract the contamination from the OTS C(1s) peak, because the contamination was of minor proportions; it was essentially consistent on all the samples, and the calculated ratios are intended to be compared on a relative basis. Two representative XPS survey spectras are shown in Figure 1.

The data in Table 1 and Figure 2 clearly demonstrate that significant differences exist in the amounts of OTS deposited on the glass substrates, depending upon the solvent used. The reaction time was maintained constant at 1 h for all the solvents, the concentration of OTS was 10^{-3} M in all the cases, and the same temperature of 20 °C was utilized throughout. Benzene shows a C(1s):O(1s) ratio of close to unity (Table 1), while toluene, cyclooctane, hexadecane, and octane all show a value of approximately 0.8 ± 0.05 for this ratio. Surprisingly, hexane and cyclohexane both show a figure of 0.66 ± 0.02 for this ratio, and pentane displays a low value of 0.42. Among the chlorinated solvents, CCl_4 exhibits more than a 25% increase in surface coverage relative to CH_2Cl_2. Of all the solvents studied, 1,4-dioxane shows the lowest surface coverage relative to benzene.

Among the open chain hydrocarbon solvents, the order is hexadecane = octane > hexane > pentane with respect to their abilities to form well-packed OTS monolayers. Clearly, these differences must arise from the dimensional variations due to differences in chain length among these solvents and not from other factors such as polarity or miscibility with water. For example, from the dielectric constants[24] of all the solvents used in the silanization

(24) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 54th ed.; CRC Press: Boca Raton, FL, 1974.

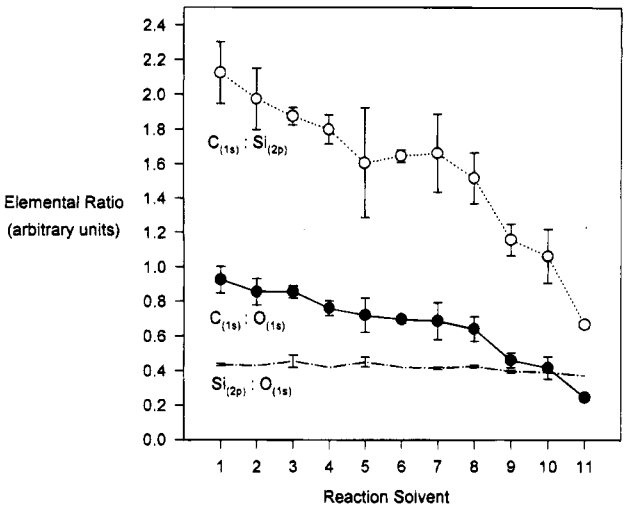

Figure 2. Effect of solvent on OTS silanization reaction vs XPS C(1s):O(1s) ratio. Key: Solvent 1 = benzene, 2 = toluene, 3 = cyclooctane, 4 = hexadecane, 5 = octane, 6 = carbontetrachloride, 7 = cyclohexane, 8 = hexane, 9 = methylene chloride, 10 = pentane, 11 = 1,4-dioxane.

experiments listed in Table 1, it can be readily seen that the *n*-alkanes have dielectric constants which average approximately 1.9 ± 0.1. Therefore, through polarity factors and by extension, water extractability of the *n*-alkane solvents seems to play only a minor role in influencing the outcome of the OTS silanization reaction. It seems that long chain hydrocarbons, which can intercalate into the octadecylsilyl chains in a rodlike fashion, can be more readily displaced by the octadecyl chains of the silane through competing hydrophobic interactions. On the other hand, aggregation of the hexane or pentane molecules in between the octadecylsilyl moieties could reduce the repulsive interactions between adjacent chains and/or pose steric problems for their removal by the rodlike octadecylsilyl molecules. This hypothesis is supported by Gangoda and Gilpin,[25] who observed that hexane had a very high motional averaging effect on silica modified with $Cl_3Si(CH_2)_{10}CD_2CH_3$ as probed by ^2H NMR, which indicates that intercalation of hexane into the silane film was thermodynamically favorable. In a similar manner, Zeigler and Maciel[26] observed that cyclohexane assisted the octadecyl moieties of the OTS film to find an energetically more favorable conformation.

There is no significant difference with respect to the OTS surface coverages between the open chain and cyclic hydrocarbons carrying the same number of carbon atoms (octane vs cyclooctane and hexane vs cyclohexane). Although the exact reason for this behavior is not clear, a plausible explanation is that these solvent pairs possess approximately the same polarity and the same capacity to extract the surface water (see subsequent discussion on this aspect).

The contact angle data measured for glass substrates silanized with different solvents are graphically shown in Figure 3 and reflect the same trend as observed by XPS measurements. The contact angle measurements show that the wettability of the OTS surface can be controlled by choosing an appropriate solvent for the silanization reaction.

The large variations in the surface coverages of OTS on the glass substrates when the reaction solvents are pentane, cyclohexane, benzene, and 1,4-dioxane, respectively, are related to the difference in water extractability of these solvents. If the mechanism of OTS deposition proceeds through the initial step of physisorption of the unhydrolyzed silane at the substrate surface, no such solvent-based differences should be expected, since the same amount of surface water is available in all instances. On the other hand, if hydrolysis of OTS occurs in the bulk solvent phase, the amount of water available in this phase will become an important factor. It is conceivable that the observed differences are caused by the relative capacities of the solvents to extract water from the surface of the glass substrates into the bulk phase. This in turn causes different concentrations of octadecylsilanetriol produced, resulting in the variation of surface coverages. It has been noted by several authors that trace amounts of water are necessary for effecting silanizations with OTS in a variety of solvents, although the exact requirement has never been defined in any of these earlier studies. It is interesting to note that the percentage compositions of the solvent and water in the respective azeotropes for the four solvents under discussion are 98.6/1.4 for pentane/water, 91.5/8.5 for cyclohexane/water, 91.1/8.9 for benzene/water, and 81.6/18.4 for 1,4-dioxane/water.[24] From these values, it can be visualized that the surface water extracting capabilities of the solvents are in the order 1,4-dioxane > benzene > cyclohexane > pentane. With the exception of 1,4-dioxane, the observed surface coverages of OTS on glass are in accord with this order. A graphic comparison between the computed XPS C(1s):O(1s) ratios and the composition of the azeotropes for these four solvents is presented in Figure 4. The anamolous

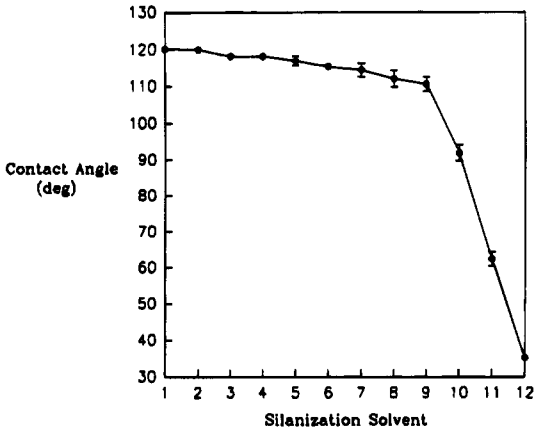

Figure 3. Effect of solvent on OTS silanization reaction vs water contact angle. Key: Solvent 1 = benzene, 2 = toluene, 3 = cyclooctane, 4 = hexadecane, 5 = octane, 6 = carbontetrachloride, 7 = cyclohexane, 8 = hexane, 9 = methylene chloride, 10 = pentane, 11 = 1,4-dioxane, 12 = uncoated glass blank.

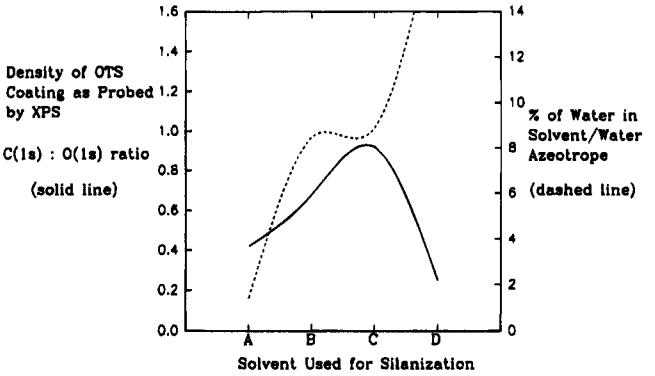

Figure 4. Comparison of the percentage of water in four solvent–water binary azeotropes (dashed line) and the XPS C(1s):O(1s) ratio (solid line). Key: A = pentane, B = cyclohexane, C = benzene, D = 1,4-dioxane.

(25) Gangoda, M. E.; Gipin, R. K. *Langmuir* **1990**, *6*, 941.
(26) Zeigler, R. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1991**, *113*, 6349.
(27) Kallury, K. M. R.; Macdonald, P. M.; Thompson, M. *Langmuir*, **1994**, *10*, 492.

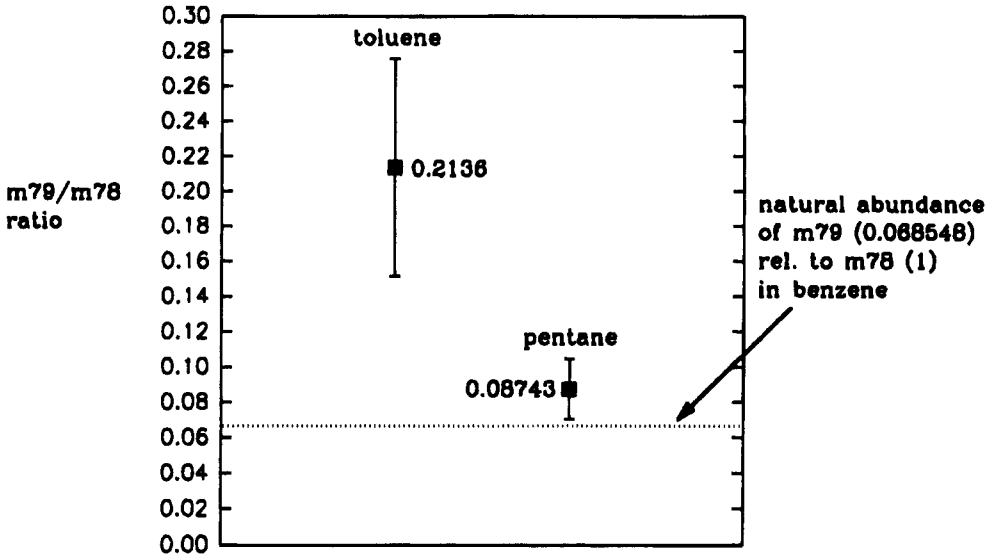

Figure 5. Average values of $m79/m78$ enrichment for toluene and pentane extraction experiments.

behavior of 1,4-dioxane is attributed to its ability to draw an excess of water from the surface into the bulk solvent phase so that extensive hydrolysis of OTS occurs, which facilitates excessive polymerization of the intermediate silanetriol in competition with the surface adsorption of this triol. Alternately, the silanetriol could H-bond to the oxygens of the dioxane, and hence physisorption at the substrate surface is retarded.

Quantitation of the Extractable Water from the Substrate by Toluene and Pentane. The relationship between the OTS surface coverage and the quantity of surface water extractable by a solvent, as proposed in the previous section, needs experimental verification. Toluene and pentane are two hydrocarbon solvents which exhibit widely differing behavior, and they were selected to evaluate their surface water-extracting capacities.

The existence of molecular water on glass was established only recently. Although conventionally melted commercial glasses based on silica contain less than 0.1% water by weight, borate and phosphate glasses carry water concentrations as high as 1%. The presence of even minute amounts of water on glass has a significant effect on its key physical, thermal, electrical, and optical properties. Dunken[28] summarizes the desorption of water from glasses to occur in three stages. The water skin of variable thickness on the outer surface can be removed at room temperature in vacuum; the permanently adsorbed water molecules can be desorbed at different temperatures, depending upon their binding energies, viz. between 393–493 K (hydrogen-bonded water) and 493–593 K (coordinately adsorbed water); above 595 K, the desorption of water from the condensation of surface hydroxyls begins. The three steps are analogous to the removal of water from high surface area silicas.

Several methods are documented in the literature for estimating the water content of different varieties of glasses, which consist of both spectroscopic and nonspectroscopic techniques.[27-29] The most widely applicable of these are the FTIR and solid-state ^1H NMR procedures. Each of these have their own advantages and disadvantages, as outlined by Knickerbocker and co-workers.[30] In order to facilitate isotopic exchange (which is the procedure followed in the deuterium/tritium exchange-based NMR and radiolabeling analyses reported earlier),[30,31] the glass samples have to be heated to temperatures above 1100 °C for long durations with high pressures of D_2O or ^3H_2O. Such isotopic exchange reactions on glass substrates are tedious to carry out, and hence in the current work, silica was utilized for investigating the water-extracting capacities of toluene and pentane.

Griffith and Callis[32] reported a thermogravimetric method for evaluating the water content in glass by estimating the weight loss upon ignition of alkali phosphate glasses with ZnO. In the current investigation, the microscopic cover slips utilized for the solvent-dependent silanization studies were also found to exhibit around 10% weight loss upon heating to 400 °C for 2 h. However, it is known[33] that borosilicate glasses undergo leaching of a certain percentage of their constituent elements upon thermal treatment. Therefore, gravimetric estimates of the water content of glass samples are not quantitative.

In an earlier study,[34] the behaviors of low water content synthetic silicate glasses and dried silica gel were found to be similar. Furthermore, amorphous silica (with a surface area of 230 m^2/g) prepared by the combustion of $SiCl_4$ in oxygen showed no difference compared to fused silica glass in studies reported by Maniar and Navrotsky.[35] Hence, the utilization of dehydrated/dehydroxylated silica in place of microscopic cover slips in the current deuterium exchange reactions was considered to be practicable.

Since moisture is ubiquitously found on surfaces of analytical instruments (e.g. the source of a mass spectrometer), on glassware, and in solvents, it is difficult to judge the authenticity of any "surface water" which is measured. It was decided to use D_2O as a way of labeling the water adsorbed to the silica, since Chuang et al. showed that 97% of the silanols on high surface area silica can be deuterated in a deuterium exchange experiment.[36] Gilpin

(28) Dunken, H. H. In *Treatise on Materials Science and Technology*; Tomozawa, M., Doremus, R., Ed.; Academic Press: New York, 1982; Vol. 22, pp 1–74.
(29) Abe, Y.; Clark, D. E. *J. Mater. Sci. Lett.* **1990**, *9*, 244.
(30) Knickerbocker, S. H.; Joshi, S. B.; Brown, S. D. In *Materials Science Research—Advances in Materials Characterization*; Rossington, D. R., Condrate, R. A., Snyder, R. L., Eds.; Plenum Press: New York, 1983; Vol. 15, pp 571–589.
(31) Eckert, H.; Yesinowski, J. P.; Stolper, E. M.; Stanton, T. R.; Holloway, J. *J. Non-Cryst. Solids* **1987**, *93*, 93.
(32) Griffith, E. J.; Callis, C. F. *J. Am. Chem. Soc.* **1959**, *81*, 833.
(33) Mitra, N. K.; Vasistha, S. R.; Das, A. C.; Basumajumdar, A. *J. Indian Chem. Soc.* **1988**, *65*, 617.
(34) Rosenberger, H.; Scheler, G.; Burger, H.; Jakob, M. *Colloids Surf.* **1984**, *12*, 53.
(35) Maniar, P. D.; Navrotsky, A. *J. Non-Cryst. Solids* **1990**, *120*, 20.
(36) Chuang, I-S.; Kinney, D. R.; Maciel, G. E. *J. Am. Chem. Soc.* **1993**, *115*, 8695.

Table 2. Quantitation of the Extractable Water from the Substrate by Toluene and Pentane

mass of silica *m*79/*m*78 powder (g)	mass of silica after heat treatment (g)	moles of H_2O lost	mass of silica after D_2O treatment (g)	moles of D_2O adsorbed	extraction solvent	ratio
2.0182	1.8663	8.4295×10^{-3}	2.0340	8.3724×10^{-3}	toluene	0.2489
2.0188	1.8715	8.1742×10^{-3}	2.0568	9.2511×10^{-3}	toluene	0.1420
1.9833	1.8447	7.6914×10^{-3}	2.0033	7.9181×19^{-3}	toluene	0.2498
1.9694	1.8198	8.3019×10^{-3}	2.0293	10.459×10^{-3}	pentane	0.0770
2.0073	1.8529	8.5682×10^{-3}	2.0896	11.817×10^{-3}	pentane	0.1071
2.0017	1.8536	8.2183×10^{-3}	2.0012	7.3689×10^{-3}	pentane	0.0782

Table 3. Average Values of the Data Presented in Table 2

solvent	average *m*79/*m*78	S.D.	ratio of *m*79/78
toluene	0.2136	0.062	1:5
pentane	0.08743	0.017	1:11

Table 4. Drybox Method XPS C(1s):O(1s) Data

experimental conditions					
heat 400 °C	anhyd toluene	anhyd toluene spiked with D_2O	substrate soaked in D_2O extract	substrate soaked in 99% D_2O	analysis XPS C(1s):O(1s) (trial 1, trial 2)
yes	yes	no	no	no	0.60, 0.65 ("A")
yes	yes	yes	no	no	1.37, 1.30 ("B")
yes	yes	no	yes	no	0.81, 1.00 ("C")
no	yes	no	no	yes	1.25, 0.92 ("D")

and Wu used deuterium exchange combined with mass spectrometry to quantitate the amount of surface water on silica;[37] however, the D_2O extraction experiments in our current work required two main modifications to their proceedure in order to quantitate the very small quantities of D_2O expected to be present in the extraction solvent. The first modification was to transform the readily exchangable deuterium label into a nonexchangable derivative which could be unequivocally identified by mass spectrometry. Phenyllithium reacts quantitatively with any labile proton source to form benzene, and it is well-known that benzene furnishes a high percentage of its molecular ion coupled with a low percentage of fragment ions upon electron impact ionization. The second modification to the method was the use of GC prior to MS to effectively separate the benzene formed from the solvent (toluene or pentane). Two grams of silica were heated to 450 °C to effect the removal of the surface water and then rehydrated with deuterium oxide. Earlier literature reports[20] indicate that silica could be reversibly hydrated up to 450 °C. By repeated thermal dehydration (as well as dehydroxylation) and rehydration with deuterium oxide, the same level of hydration (about 7.5%) of the silica with D_2O as was originally present with water could be achieved (see Table 2). This deuterated silica was extracted with 10 mL of either toluene or pentane, and 5 mL of this extract was filtered out for treatment with a known amount of phenyllithium reagent. The D_2O in the organic solvent quantitatively reacts with PhLi to form C_6H_5D and LiOD. The excess PhLi was converted into undeuterated benzene by shaking with water. Thus, a mixture of mono- and undeuterated benzene is formed in the toluene or pentane extracts, the proportion of which could be assessed by GC-MS separation from the extracting solvents and analysis of the two peaks at *m/z* 79 and 78 representing the deuterated and undeuterated benzene, respectively. The experimental results are then compared to the natural abundance of *m/z* 79 to *m/z* 78 in benzene, which is 0.068 548 to 1, respectively. If the experimentally measured *m*79/*m*78 ratio is significantly higher than the natural abundance ratio, then it could be said, at least qualitatively, that significant quantities of D_2O must have been extracted from the silica surface in order to furnish the high abundance of *m*79. It is to be noted that the natural isotopic abundances of ^{13}C and ^{2}D in the phenyllithium reagent or in the H_2O used in the wash step do not affect the manner in which the data are interpreted. The intensity of the *m/z* 79 peak is proportional to the amount of D_2O extracted into the solvent and that of *m/z* 78 represents the excess PhLi left over subsequent to the reaction of D_2O in the organic solvent with this reagent. The results of the solvent extraction experiments for both toluene and pentane are shown numerically in Tables 2 and 3 and graphically in Figure 5.

The measured ratio of *m/z* 79:*m/z* 78 for toluene was 1:5, which represents a factor of 0.2 for the extent of D_2O extracted. Since the amount of PhLi employed was about 1×10^{-4} mol, the extracted D_2O translates into 2×10^{-5} mol in the 5 mL of toluene collected from the extraction. Since a total of 10 mL of toluene was utilized in the extraction, the total amount of D_2O is 4×10^{-5} mol, which is equivalent to 8 mg per 100 mL of toluene, or roughly 0.1% concentration. The gravimetric data in Table 2 indicate that around 160 mg of D_2O is originally present on the silica surface before solvent extraction and hence the amount of D_2O extracted is 5% of the maximum possible amount.

In the case of pentane, the *m/z* 79:*m/z* 78 ratio computed by mass spectrometry is about 1:11. By a similar calculation as above, it can be shown that this represents about 3.6 mg of D_2O per 100 mL of pentane, or roughly 0.05% concentration. The quantity of D_2O extracted from the silica surface into the pentane is about 2%, which is about half of the amount extracted by toluene.

These experiments clearly demonstrate that much more water is extracted by toluene from the surface of silica or by analogy, glass, compared to pentane. In the next section, it will be shown that a small fraction of 0.1% moisture in the toluene solvent is more than sufficient to cause excess hydrolysis of OTS and subsequent surface deposition on the glass.

Drybox Experiments with Toluene/deuterium Oxide Extract. These experiments were designed to evaluate the effect of the water extracted by toluene from silica/D_2O on the silanization of glass substrates. Four sets of conditions were utilized for this purpose, as detailed in Table 4. Under totally anhydrous conditions (experiment A in Table 4), an XPS C(1s):O(1s) ratio of 0.6 was obtained. When the anhydrous toluene was spiked with 1 mL of the toluene/D_2O extract (experiment B in Table 4), this ratio is dramatically increased to around 1.35. The effective concentration of D_2O in experiment B was about 0.3 mg/100 mL of toluene. Therefore, it is now clear that the optimal moisture content of the solvent must be less than 0.3 mg/100 mL of solvent; otherwise excessive polymerization will occur in the bulk solution. On the other hand, when the dry glass substrate was soaked in the toluene/D_2O extract and then silanized with OTS in dry toluene (experiment C in Table 4), the ratio was 0.9, which compares well with the first silanization experiments using toluene (Table 1). Finally, with a fully

(37) Gilpin, R. K.; Wu, L. *J. Chromatogr.* **1991**, *556*, 415.

hydrated glass substrate, obtained by soaking the dry substrate in D_2O (experiment D in Table 4), the C(1s):O(1s) ratio increases to 1.25 upon silanization with OTS, which indicates a greater degree of coverage than expected when compared to the data in Table 1. This sample was not oven-dried to remove excess water, and thus the sample may have been overhydrated. It therefore seems that the optimum quantity of water needed to produce a tightly packed monolayer is between that of the spiked solvent (0.3 mg/100 mL) and that of the anhydrous substrate (around 0 mg/100 mL). Thus it seems likely that about 0.15 mg of moisture/100 mL of solvent are needed to form a tightly packed monolayer.

Conclusions

Our D_2O extraction experiments indicate that a closely packed octadecylsiloxane layer could be formed on glass substrates when about 0.15 mg of moisture/100 mL of solvent is present in the silanization system. Less water content leads to incomplete monolayer formation, and overdoses of water result in overpolymerization in the bulk solvent phase. The mechanism of silanization of glass with OTS, in particular, involves extraction of a small percentage of surface moisture into the bulk solution, which leads to hydrolysis of the chloro moieties of the silane in the bulk solvent phase. The trisilanol species then polymerize onto the surface, perhaps with steric assistance or hinderance due to solvent geometry.

Solvents with a high capacity for dissolving water such as 1,4-dioxane are not preferable for generating self-assembled monolayers of OTS, as they may oversolubilize the alkyltrisilanol species and prevent polymerization onto the substrate surface. Conversely, solvents with a very low capacity for dissolving water such as *n*-pentane cannot supply enough moisture to the bulk phase, and little alkyltrisilanol is produced. The best quality monolayers are produced when toluene or benzene is used as the solvent because they can solubilize the optimum quantity of water necessary for the formation of alkyltrisilanol species and allow the alkyltrisilanol species to polymerize onto the substrate surface without providing undue hinderance. The nature of the solvent also plays an important role in determining the surface concentrations of OTS. Thus, long-chain hydrocarbon solvents have a positive effect, while shorter chain alkane solvents retard the surface deposition. The density of the OTS film cannot be solely controlled by the geometric shape of the solvent, as pentane produces a film much less dense than that produced by hexadecane or toluene. As well, 1,4-dioxane produces a sparser film than that produced by cyclohexane.

Acknowledgment. We are greatly indebted to the Natural Sciences and Engineering Research Council of Canada for support of this work. Also, we wish to thank Dr. R. Sohdi of The Center for Biomaterials, University of Toronto, for assistance with the acquisition of the XPS data, Prof. G. Nairn for kind use of the goniometer, Dr. A. Young for assistance with the GC-MS, and Prof. A. G. Harrison for kind use of his laboratory and equipment.