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Interaction of Water with Silane Modified Aerosil Samples

Misael Silas Nadiye-Tabbiruka

Department of Chemistry, University of Botswana, Gaborone, Botswana

Email address:
nadiyemst@yahoo.com, nadiyem@mopipi.ub.bw

Abstract: The interaction of water with pre-heat treated silylated aerosil samples was investigated by adsorption of water and by contact angle measurements at 293 K. Type II adsorption isotherms were obtained. The resulting BET specific surface areas were found to depend on pre-treatment. Contact angles were measured by the captive bubble method at the three phase contact line in water, on glass slides similarly modified. Silylation was found to decrease water adsorption on aerosil and increase the contact angles on the glass slides to extents that depend on the silane used as well as the concentration of residual silanols and on concentration and size of surface silyl groups.

Keywords: Modified Aerosil, Characterisation, Water Adsorption, Contact Angle

1. Introduction

Numerous studies have found the interaction of various adsorbates with silica to be influenced by concentration and environment of surface siloxanes and silanols. The properties of these surface groups have been investigated and characterised using a variety of techniques [1, 2, 3].

Removal of surface silanols by heating or by irradiation with ultra violet light modifies the silica surfaces [2]. Surface silanols' protons may also be replaced with bulky organic groups producing a modified hydrophobic and non-polar surface [4 – 7]. In this case, the extent of hydrophobicity will depend on the size and surface density of the added organic groups. Consequently, designed intermediate properties can be achieved by fractional hydrophobisation [5] or by using organic molecules of varying sizes that leave varying densities of surface silanols. Increased hydrophobicity by such surface treatment is used in preservation of masonry and sculptures or statues from corrosion by acid rain. Similar modification also finds use in chromatography where designed fractional hydrophobisation can achieve required polarity of stationary phases. It is also used in improving mechanical properties especially brittleness of optical fibres that are now used in telecommunications as well as in surgical and diagnostic tools in hospitals. In the nanotechnology world, surface modification is used in biomedical applications including tissue engineering, chemical and drug delivery, chemical and biochemical

diagnostics, nano and micro encapsulation for stabilisation, modification, and controlled release, thin and nano-structured film formation, and advanced material fabrication [8-13]. Surface chemical modification has also been used in tuning holes of colloidal masks used for nanolithography [11] and for modification of silica and cellulose based micro-filtration membranes with functional poly amino acids for sorption of heavy metals such as copper and selective rejection of chromium VI [14-15].

The changes that occur during modification and how these changes affect the surface properties of the particles and particularly their interaction with water are not quite clear. In view of the fact that silicate materials are often used as adsorbents and stationary phase carriers in chromatography where water is a solvent or a bye product of combustion, we need to obtain the necessary information to elucidate their interaction with water. Currently, most of the literature on the interaction of water with siliceous materials has been from spectroscopic studies under varying conditions [16-20]. This paper describes water-silica interaction studies through water adsorption on a non-porous silica aerosil to minimise complications that may arise from pores. Aerosil, normally used in research as a non-porous standard, was modified using various halogenated silanes. These included trimethylchlorosilane (TMCS) and dimethyl dichlorosilane, (DMDCS), which generate surfaces with compact organic groups. A more open surface is obtained from treatment with triethylchlorosilane, TECS, and triphenylchloro silane, TPCS.

Partial treatment to ¼ TMCS silylation was also used to vary the density of surface organic groups. The BET water specific surface areas were determined as a function of these pre-treatments. Contact angles on similarly modified glass slides were also determined using the captive bubble method [21-22]. The values obtained from the modified samples were compared with those from the unmodified sample. It is believed that a better understanding of the surface properties of these modified adsorbents will lead to many more applications.

2. Experimental

Contact angles were measured at the three phase contact line in water on glass slides by the captive bubble method using equipment described in detail elsewhere [21-22]. The glass slides had previously been cleaned by immersion in fresh, hot chromic acid, rinsed copiously in double distilled water, and then silylated as described in earlier work [23, 24].

Adsorption of water is obtained by measuring the change in mass at equilibrium of a pre-treated hand compacted sample of aerosil of known initial weight using a vacuum microbalance, after each successive dose of the adsorbate until saturation is achieved. The isotherm is scanned up and down the pressure several times, repeating the measurements for two or three other samples to ensure reproducibility. The apparatus used in this work has been described in detail in an earlier paper [25].

The possible sources of error in the determination of the weight adsorbed (adsorption of the microbalance assembly, buoyancy and Knudsen flow effects [23 - 25] have been considered previously and found to be negligible. Similar conditions were used in the work reported here consequently errors will also be minimal.

2.1. Materials

2.1.1. Aerosil and Glass Plates
The samples of aerosil and modified aerosil used as adsorbents and the modified glass plates used in the measurements of contact angles in this work were those produced in earlier silylation kinetics' studies [23, 24].

2.1.2. Water
Double distilled and de-ionised water was transferred directly to a reservoir bulb. It was out-gassed immediately using the freeze – thaw cycles [25, 26] and then redistilled into a second reservoir bulb. It was frozen using liquid nitrogen and out-gassed with the rest of the apparatus to a pressure of 10^{-5} torr or lower for several days.

2.2. Procedure

Aerosil samples were hand compacted and 200 mg of the appropriate sample was loaded in a small glass vessel of known weight and then suspended on one arm of an electronic vacuum microbalance. Details of the electronic microbalance have been given elsewhere [23-27]. A counterweight made from a solid glass rod, equal in weight to the combined weight of the vessel and the sample, was suspended on the other arm. Details of the evacuation of the sample, the dosing with adsorbate vapour and the measurement of adsorption have been given in detail elsewhere [23-26].
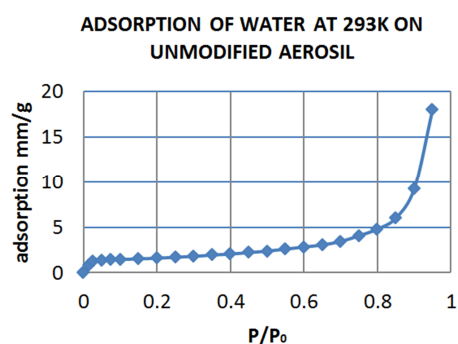
3. Results and Discussion

At the start of each adsorption experiment, the water reservoir was left open to the adsorbent for at least 6 hours to allow the adsorbent to come to equilibrium with the saturated vapour. Measurements were then started on the desorption process, in most cases, rather than the usual adsorption. This procedure also avoided unnecessary adsorption measurements which are usually obtained as the adsorbent recovers from effects of heating used during pre-treatment.

3.1. Shapes of the Isotherms

The adsorption isotherms for water on aerosil are given in the figures given in table 1.
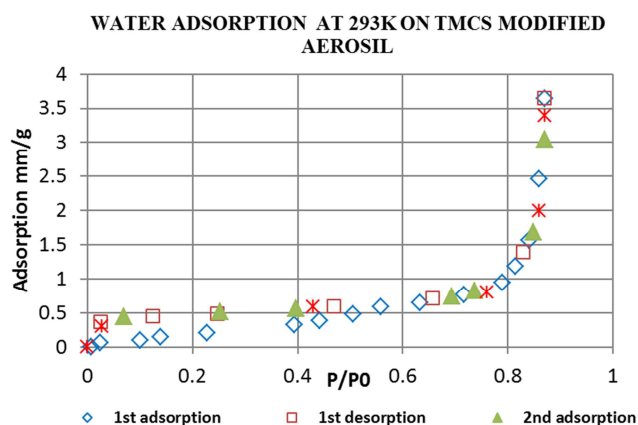
Table 1. List of temperatures of evacuation, silylation and the figures of their corresponding adsorption isotherms.

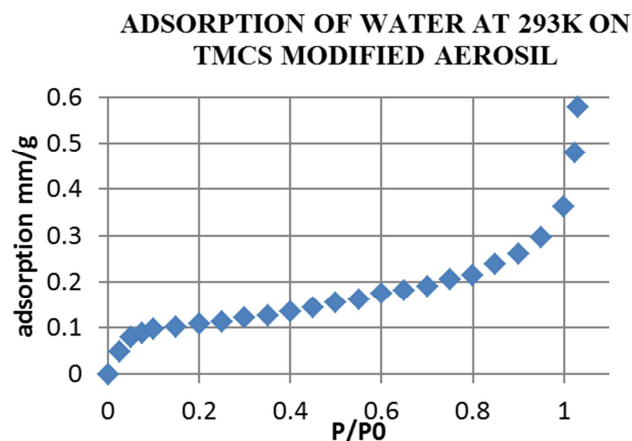| Modifier	Evacuation Temp K	silylation Temp K	Figure
NIL	673	653	1
TMCS	598	598	2
TMCS	673	653	3
TECS	673	653	4
TPCS	673	653	5
DMDCS	673	653	6
Multiplots for comparison			7
Isotherms' Cross-plots			8

Figure 1. Adsorption of water at 293K on unmodified aerosil evacuated at 673K. The sharp point B and the high adsorption capacity are clearly portrayed.

The aerosil-water isotherms are all of type II in the revised classification [28]. Some of the isotherms, just like those of benzene and ethanol, exhibit sharp knees and hence easily accessible monolayer capacities; (see figs 1-6). In some, for the modified surface in particular, knees are not sharp as the isotherms tend towards type III (figs 2-6. This is also evident in the lower BET C values in the range 10 - 20 than the value of C=97 for the unmodified sample (table 2).
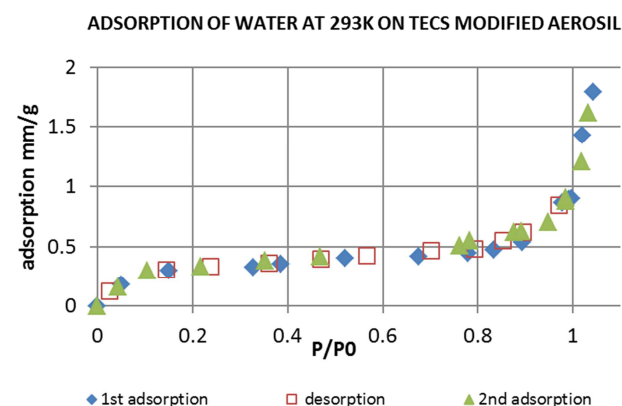
Figure 2. *Scanned data for the adsorption of water at 293K on aerosil evacuated at 598K and modified using TMCS at 598K. 1st adsorption isotherm shows the recovery of the solid from heat effect. The reduced adsorption capacity is clearly portrayed.*
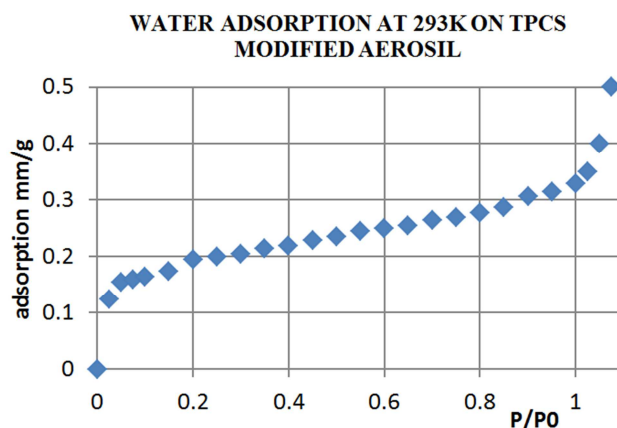
Notable examples of this adsorption reduction are those of TMCS and TECS-treated aerosil evacuated at 673K and then silylated at 653K (figure 3 and 4).
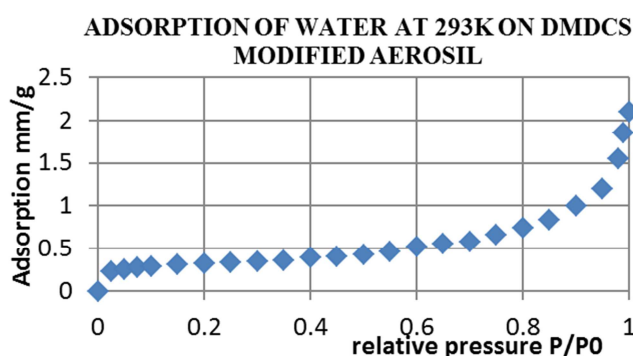

Figure 3. *Water adsorption at 293K on TMCS modified aerosil evacuated at 673K and silylated at 653K. The low adsorption capacity and the blunt point B are very clear.*

Figure 4. *Scanned adsorption of water at 293K on TECS modified aerosil evacuated at 673K and silylated at 653K. The low adsorption capacity and the blunt point B are very clear here as well.*

Figure 5. *Adsorption of water at 293K on TPCS modified aerosil evacuated at 673K silylated at 653K. The low adsorption capacity and the sharp point B are very clear in this case.*

Figure 6. *Adsorption of water at 293K on DMDCS modified aerosil evacuated at 673K and silylated at 653K. The slightly higher adsorption capacity and the reasonably sharp point B are very clear.*

Adsorption-desorption cycles should normally give reversible isotherms. In the present system this is not realised in a number of cases (not shown here as these are averaged plots obtained by flex curve fitting) particularly at or near saturation. Condensation at points of contact of the adsorbent particles and in some cases in the spaces between particles cannot alone account for the present anomaly. It is thought that during the first cycles, adsorption of water alters the properties of the surface. This could be either by chemisorption of water across the strained siloxane bonds to reconstitute the surface silanols, or by the hydrolysis of the halogen (chlorine) chemisorbed across the siloxane bonds during silylation. The scatter of adsorption points may also be attributed to experimental errors particularly as the masses involved are very small.

3.2. BET Surface Area

The BET surface areas and C constants are shown in table 2. The water BET surface areas were calculated using a value of 0.108 nm^2 for the cross-sectional area of the adsorbed water molecule. This value is close to the value of 0.06 nm^2 calculated using the liquid density of water. Avery, Wade, and Hackerman [29] calculated values ranging from 0.103 nm^2 to 0.204 nm^2 by comparison of water adsorption on silica with krypton adsorption. Emmett and Cines [30]

used a value of 0.195 nm^2 for water adsorption on glass whilst McClellan and Hansberger recommended a value of 0.202 nm^2. In a situation such as the present one, no single value can be claimed to be correct because the values depend on the interactions between the adsorptive and the surface and also on the environments. In the present work, the value of 0.108 nm^2 was chosen on the grounds that it
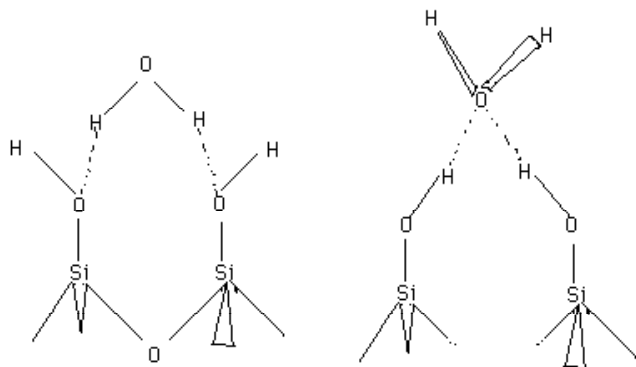
was derived using an adsorbent similar to the one under investigation [29] and the value is very close to that calculated using water liquid density.

For the untreated aerosil, the BET surface area values are consistently lower than the values obtained using ethanol and benzene (see tables 2).

Table 2. *BET specific surface areas S in m^{2}g^{-1}, BET C constant from water adsorption on aerosil of various evacuation/silylation temperatures together with corresponding contact angles (surface areas from ethanol and benzene adsorption are also shown in brackets, for comparison).*

Silane: evacuation TK/. Silylation TK	BETA/m^2/g: S Water; (S etOH) (S benzene)	BETC const (water)	Contact. θ_a In water
NIL- 673K	67.2, (104.5) (199.3)	96.8	0
TPCS 673K 653K	4.5, (29.2) (111.2)	11.5	
TECS 673K 653K	7.1, (42.2) (54.9)	8.6	76°
DMDCS 673K 653K	10.1, (85.2)	16.7	81°
TMCS 673K 653K	7.1, (37.5) (61.8)	9.9	79
TMCS 598K 598K	10.6, (39.0)	33.5	70°

Similar results were found by Emmett and Cines [30], despite using 0.195 nm^2 as the cross-sectional area for the water molecule. Water is the most polar of the three adsorptives used in this study, and hence adsorbs on silica by specific interaction, due to the hydrogen bonding with surface silanols [31], in the same way that ethanol does. Unlike ethanol, however, one water molecule is capable of two hydrogen bonds. Therefore, the first few water molecules to adsorb might do so through two hydrogen bonds with close neighbouring surface silanols. These include geminal silanols, vicinal silanols, and those between crevices, between crystal steps and in pores. Such adsorption gives rise to the structures such as the ones below:

Hydrogen bonding between adsorbed water molecules and silica surface silanols.

The number of water molecules adsorbing by these modes is restricted by the population of these very conveniently spaced, but non- interacting, neighbouring silanols. Once these uniquely situated silanols are used up, water molecules adsorb to the remaining silanols by a one-to-one interaction only. Lange has found desorption of water from silica to have two activation energies. One has a low value of about 29 kJmol-1, and the other has a higher value of 42 kJmol-1. He associates the latter value with adsorption through double hydrogen bonding of the type described above, and the former is associated with physical adsorption [31].
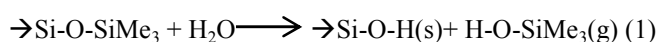
In the above mechanisms, one molecule of water covers two adsorption sites and thus reduces the potential for further

adsorption. This will give rise to very low values of BET specific surface area.

If the validity of the application of the BET theory, for the determination of the surface areas of silica samples, was questionable in the case of benzene and ethanol, it is more so in the case of water. This is because water is more polar and hence its adsorption is more highly specific and localised than that of benzene and ethanol. Just like ethanol, water molecules can interact with silanols and amongst themselves through hydrogen bonding and, furthermore, each molecule can form two hydrogen bonds. This leads to adsorption of water in clusters. Therefore, the BET areas obtained from water adsorption will be in error for the same reasons as those discussed in the case of ethanol, and can, in the same way, only be used for comparative purposes.

3.3. Effects of Modification on the Adsorption of Water

Modification of silica surfaces with silanes reduces the adsorption of water in a way similar to that found for ethanol, by a factor which depends on the type of silane used, and the concentration of the silyl groups at the surface. Figures 7 show the superimposed water adsorption isotherms for aerosil samples treated with various silanes. Figures 8 show some of the isotherms cross-plotted with the isotherm of the untreated sample. The effect of pre-treatment is clearly portrayed for all the partial pressures covered by the adsorption experiment. Possibilities available include the hydrolysis of the chemisorbed silanes and chlorine or the hydrolysis of the siloxane bond. The option of hydrolysis of the added organic groups to reform silanols is highly unlikely. If it does occur, the monolayer and multilayer region should show some apparent loss in adsorption because in the reaction scheme at the silica surface,

$$\rightarrow Si\text{-}O\text{-}SiMe_3 + H_2O \longrightarrow \rightarrow Si\text{-}O\text{-}H(s) + H\text{-}O\text{-}SiMe_3(g) \quad (1)$$

(72g) (for -SiMe$_3$) changes to (-72+1) that is for every one group hydrolysed, 72 gm of the SiMe$_3$ are lost in return for the one gm of hydrogen which reforms the silanol. Even if this hydrolysis led to further adsorption of 2 or even 3

molecules of water at the surface at the relevant partial pressure, there would still be a net loss in weight. In the extreme case, this hydrolysis would produce a desorption branch which would lie below the adsorption branch! In the present work, adsorption and desorption were reversible, and quite reproducible within experimental error. Gavrilynk and his co-workers found water and methanol desorption from TMCS-treated silica between 420K and 570K not to affect the silyl coating [32]. It is therefore unlikely that any quantitatively substantial hydrolysis occurs at the adsorption temperature. However, rehydration of the surface which results from the hydrolysis of siloxane bonds and the chlorine chemisorbed during silylation could occur. This surface hydration leads to increased interaction with the adsorptive which results in the observed decrease of contact angle (see table 3) compared to those in the literature [33-35].

The results of both receding and advancing contact angles on glass slides similarly modified after similar heat treatments are given in table 3. The trend in the contact angle for these modified glass slide samples is:
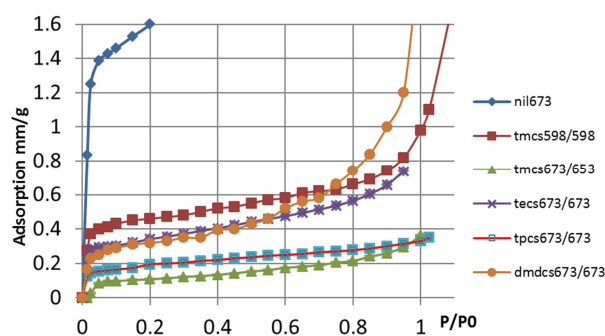
DMDCS673/653>TMCS673/653>TMCS653/653>TECS673/653>TMCS598/598

Table 3. *Contact angles in water on a nitrogen gas bubble for treated and untreated glass slides.*

silane	T pretr/	advancing	receding
	T reactoK	angle	angle
NIL	673/653	0	0
TMCS	598/598	70	51
TMCS	653/653	77	70
TMCS	673/653	79	65
TECS	673/653	76	60
DMDCS	673/653	81	71

The position of DMDCS is not surprising as this is the most efficient in removing silanols. The residual silanols will be fewer and hence the contact angle will be larger as the surface will be more hydrophobic. TMCS598/598 gives the smallest contact angle because dehydroxylation at 598K will leave more silanols at the surface rendering the surface more hydrophilic compared to those hydroxylated at higher temperatures. The surface concentration of the organic groups will also be higher in this case; however, water molecules can sneak through the gaps between the organic groups to hydrogen bond the silanols under the organic umbrellas. The differences in contact angle size between the remaining three in between the two extremes are within experimental error hence not much can be read into their relative magnitudes.

Figure 7 shows the effect of modification with the various silanes on water adsorption. The large decrease in adsorption of water onto the various modified samples compared to the unmodified aerosol sample is clearly portrayed. The most hydrophobic to the least at various relative pressures is clearly shown. Similar findings are reported elsewhere [36-39]
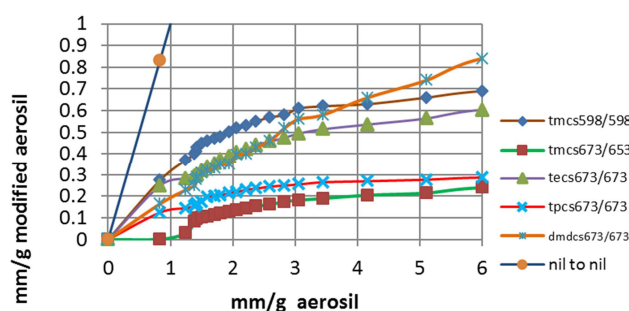

Figure 7. *A multiple plot of adsorption of water on the various silane modified aerosil samples to compare the effect of modification by the different silanes at various relative pressures.*

The trend in water adsorption up to a relative pressure of 0.6 is

nil673>>TMCS598/598>TECS673/673≈DMDCS673/673>TPCS673/673>TMCS673/653.

While most isotherms retain their position in the above trend at higher relative pressures, that of DMDCS673/673 crosses those above it to become number two. This is probably caused by the hydrolysis of the residual chlorine atoms on the DMDCS molecules resulting from attachment of the organic group to the surface through one chlorine atom. Hydrolysis of these residual chlorine atoms provides free silanols that can then adsorb additional water through hydrogen bonding.

Figure 8 is a cross-plot of the adsorption on various modified samples against that on the unmodified sample to reveal the relative adsorption trends as a function of pressure during the process. A similar trend is shown here too. A line to show water adsorption on unmodified sample against itself (nil against nil) is given for comparison. The weak jump at 1.3 mg per gram on aerosil is not so clear on some of the lines and its interpretation is not apparent yet. However, the drastic reduction in adsorption due to modification is very clear here as well. The line for DMDCS after the kink, crosses all the others implying that water adsorption continues to occur whereas the lines for the other samples are developing into a plateau. This is probably due to the continued adsorption onto silanols resulting from the hydrolysis of residual chlorine. This chlorine originated from chemisorption of the silane (DMDCS) through one chlorine atom rather than two during silylation.

Figure 8. *Cross-plots of adsorption of water on the various modified aerosil samples at 293K against that on the unmodified sample to show the relative changes occurring at the various stages of the process.*

Further work should involve water adsorption onto modified porous silica to reveal the effect of the presence of pores on water adsorption. The use of these modified samples in removal of inorganic and organic pollutants in water should also be investigated.

4. Conclusions

The investigations on the interaction of water with modified non-porous silica aerosil revealed a drastic decrease in uptake of water caused by surface modification. The decrease depends on the type and surface concentration of modifier, as well as the concentration of residual silanols. Type two adsorption isotherms with relatively sharp knees were observed. Modification reduced drastically the BET C constant and the water specific surface areas to varying extents depending on the modifier and the area values were consistently lower than those obtained using less polar molecules ethanol and benzene.

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