

## Interaction of Ethanol with Modified Aerosil Samples

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The interaction of ethanol with heat treated aerosil samples; silylated with various silanes at various temperatures has been investigated by ethanol adsorption at 293 K. Type II adsorption isotherms were retained in all cases except for dimethyldichlorosilane modified sample which changed to type I. The values of the BET constants and specific surface areas were found to depend on the concentration and type of modifier silane as well as the concentration and accessibility of residual silanols. The initial ethanol molecules adsorbed are believed to react with silanols, the next lot to hydrogen bond with the less accessible silanols to form and develop clusters. The final molecules physisorb laterally through hydrophobic interactions, as well as on top of the organic layer by dispersion forces.

**Key Words: Modified aerosil, Characterization, Ethanol adsorption.**

### INTRODUCTION

Numerous studies have found the surface properties of silica to be influenced by concentration and environment of surface siloxanes and silanols. The surface silanols have been investigated using a variety of techniques including infrared<sup>1,2</sup>, NMR<sup>3</sup>, adsorption using various adsorptive<sup>2,4</sup>, deuterium hydrogen exchange<sup>6</sup>, thermal gravimetric and time of flight secondary ion mass spectroscopy (TOF-Sims)<sup>7</sup>, and identified those originating from physically adsorbed water<sup>1,3,5</sup>, free isolated silanols<sup>6-8</sup> and hydrogen bonded *geminal* and *vicinal* silanols<sup>5,7-9</sup>.

Silica surfaces may be modified by removing surface silanol by heating or by irradiation with ultraviolet light<sup>7</sup>. Alternatively, the surface silanols protons may be replaced with bulky organic groups producing a hydrophobic and non-polar surface<sup>10-13</sup>. The extent of hydrophobicity depends on the surface density and size of the added organic groups. Consequently, designed intermediate properties can be achieved by fractional hydrophobisation<sup>11</sup> or by using larger organic molecules that leave a higher density of surface silanols. Increased hydrophobicity by such surface treatment is used in preservation of masonry and sculptures or statues from corrosion by acid rain. 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 stabilization, modification and controlled release, thin and nano-structured film formation and advanced material fabrication<sup>14-16</sup>. Surface chemical modification has also been used in tuning holes of colloidal masks used for nanolithography<sup>17</sup> and for modification of silica and cellulose based microfiltration membranes with functional poly amino acids for sorption of heavy metals such as copper<sup>18</sup> and selective rejection of chromium(VI)<sup>19</sup>.

The questions that need to be answered are “What changes occur during modification and how do these changes affect the surface properties of the particles and hence their interaction with other materials such as alcohols?” How much of this information can we obtain from ethanol adsorption?

Interaction of alcohols on siliceous materials has been investigated using spectroscopic methods under varying conditions<sup>20-22</sup>. At lower temperatures, physisorption mechanisms dominate. However, residual alkoxide groups have been detected at the surface<sup>20,21</sup> indicating that chemisorption does occur as well. At higher temperatures chemisorption occurs with the formation of alkoxides and the release of water indicating the occurrence of a reaction between alcohols and surface silanols<sup>21</sup>. Thus, surface silanols are directly involved in both mechanisms. Consequently, a change in their surface concentration and accessibility will directly affect ethanol adsorption.

This paper describes investigations of the interaction of ethanol with samples of non-porous silica aerosil, often used as a non-porous standard, modified using a variety of halogenated silanes including trimethylchlorosilane (TMCS) and dimethyl dichlorosilane, (DMDCS), which generate surfaces with compact organic groups. A more open surface is expected 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 specific surface areas were determined as a function of these pre-treatments. A better understanding of surface properties of these modified adsorbents will lead to many more applications.

## EXPERIMENTAL

Adsorption of ethanol 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<sup>23</sup>.

The possible sources of error in the determination of the weight adsorbed (adsorption of the microbalance assembly, buoyancy and Knudsen flow effects<sup>24,25</sup>) have been considered previously and found to be negligible. Similar conditions were used in the work reported here consequently errors will also be minimal.

**Aerosil:** The samples of aerosil and modified aerosil used as adsorbents in this work were those produced in earlier silylation kinetics' studies<sup>26</sup>.

**Ethanol:** Ethanol 99.95 % (BDH chemicals Ltd.) was transferred directly to a reservoir bulb without further purification. It was out-gassed immediately using the freeze-thaw cycles<sup>23</sup> and then redistilled in a 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.

**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<sup>23</sup>. 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<sup>26</sup>.

## RESULTS AND DISCUSSION

The reaction scheme for the modification of aerosil with TMCS is given in Fig. 1. Adsorption isotherms for the various systems are given in Fig. 2, as a multiplot for comparative purposes. Fig. 3 is a collection of isotherm cross-plots between ethanol adsorption on unmodified aerosil and that on modified samples at the same pressure to reveal in a simple way the changes in interaction at the surface resulting from the modification of aerosil. Adsorbed group parameters are given in Table-1. Fig. 4 is a sample BET plot for ethanol adsorption on aerosil at 293 K. The surface area and C constant values obtained for the various systems are given in Table-2.

TABLE-1  
ADSORBED GROUP PARAMETERS

Silyl group / evacuation (T/K)	Concentration $\pm$ 0.01 (mm <sup>3</sup> )	Groups $\pm$ 0.01 (mmm <sup>2</sup> )	Area/group (nm <sup>2</sup> )	X-sectional area from other sources
TMS 598 K	3.1	1.9	0.53	
TMS 673 K	2.4	1.4	0.71	0.35 <sup>26</sup>
DMS 673 K	3.2	1.9	0.52	
<sup>b</sup> TMS 673 K	1.1	0.7	1.46	0.374 <sup>a</sup>
TES 673 K	2.6	1.6	0.64	0.465 <sup>a</sup>
TPS 673 K	0.7	0.4	2.53	0.87 <sup>43</sup>

<sup>a</sup>Values calculated from liquid densities of the chlorinated silane.

<sup>b</sup>Chemisorption to a quarter of the total adsorption.

**Physico-sorption experiments:** Fig. 2 shows ethanol adsorption isotherms on aerosil plotted before and after treatment with TMCS, 1/4TMCS, TECS, DMDCS and TPCS. Ethanol was chosen as an adsorptive because of its polar and at the same time, organic nature to monitor the varying specific interactions with varying silanol concentration. As a result, information about the corresponding variation of monolayer and multilayer adsorption can be obtained.

TABLE-2  
SUMMARY OF THE RESULTS OF BET SURFACE AREAS, IN  $\text{m}^2 \text{g}^{-1}$   
AND BET CONSTANTS OF AEROSIL, FOR THE SURFACE  
TREATMENTS USED IN THIS STUDY

Evacuation/silylation temp.	Area ( $\text{m}^2 \text{g}^{-1}$ )	BET C constant
NIL-673	104.5	23.7
1/4TMCS-673/673	76.9	24.5
TPCS 673/653	29.2*	29.7
TECS 673/653	42.2	25.8
DMDCS 673/653	85.2*	109.9
TMCS 673/653	37.5	30.0
TMCS 598/598	39.0	9.6

\*Values obtained by using the original data points.

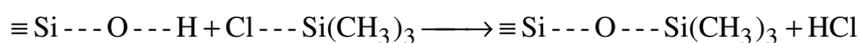


Fig. 1. Process of surface grafting of groups by silylation

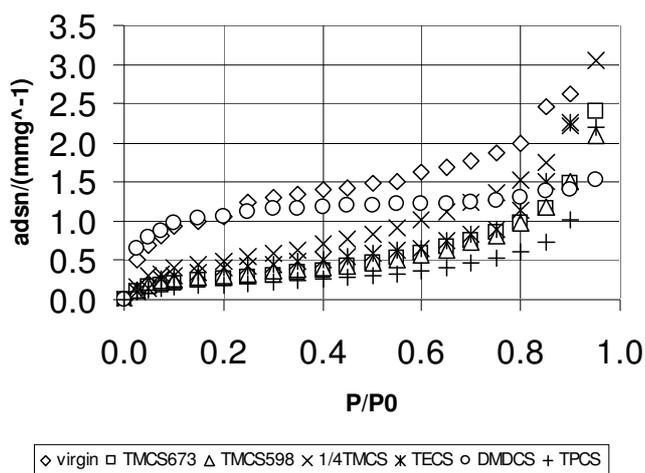


Fig. 2. Collected smooth isotherms: Adsorption of ethanol at 293 K on aerosil modified using various silanes. Samples were evacuated at 673K, or as shown in the list, then silylated.

**Surface modification by various silanes:** Modification of the surface with various silane modifiers produces surfaces with silyl group coverages which depend on the cross-sectional area of each group. Table-1 shows the various group concentrations at the surface obtained in this work and Fig. 1a, shows the silylation process. The group surface concentrations were calculated from the final masses of the silanes adsorbed at the end of the chemisorption experiments on aerosil, which has a specific surface area of  $170 \text{ m}^2 \text{g}^{-1}$ . The evacuation temperature before the chemisorption experiments was 673 K on most of the samples. In other cases they are shown in the Table-1 together with the modifier.

The maximum silanol concentration at the surface under these conditions<sup>26</sup> is around  $8 \text{ mmm}^{-2}$ . This is equivalent to  $4.816 \text{ groups per nm}^2$ ; each silanol therefore occupies a minimum area of  $0.21 \text{ nm}^2$ . Therefore, using even TMCS, the silylating agent with the smallest cross-sectional area, only a fraction of the silanol population can be silylated. The maximum coverage achieved<sup>27</sup> is in the range<sup>28</sup>  $3.7 \text{ to } 4.5 \text{ mmm}^{-2}$  or around  $2.4 \text{ groups per nm}^2$ . Thus, at most 50 % of the silanols can be replaced by TMS groups<sup>23</sup>. The presence and concentration of residual silanols has been detected and estimated by isotopic exchange and infrared spectroscopy<sup>29,30</sup>. Coverage by various silane molecules on a variety of silica samples, under specific conditions, has been discussed by Unger<sup>31</sup>.

**Ethanol adsorption isotherms:** Type II ethanol adsorption isotherms were obtained for aerosil samples with various pre-treatments<sup>32</sup>. They exhibit detectable knees and hence reasonably clear points B which provide quick estimates of the monolayer coverages. Fig. 2 is a collection of the isotherms for the various systems showing the various monolayers and multilayers regions. The isotherms were obtained by scanning up and down the relative pressure range several times to ensure reproducibility of results. A smooth curve was then fitted by hand to provide averaged data for further work.

Ethanol has easier access to hidden silanols under the umbrellas of the surface silyl groups in the modified silica samples than benzene<sup>23</sup>. Furthermore, it has stronger specific interactions with the silanols, (sometimes resulting in the formation of ethoxides), through hydrogen bonding. This is intermediate between physico-sorption and chemico-sorption. Consequently, the monolayer coverage will represent adsorption on these specific sites. At multilayer level, the weaker of these sites are involved together with adsorption on top of the surface groups which uses the weaker van-der Waal's forces. Condensation of ethanol occurs at a relative pressure higher than around 0.8 with the exact starting pressure depending on the system (Fig. 2).

Thus, monolayer development is steepest for DMDCS- treated aerosil showing the clearest knee and the highest point B probably because of the combined interaction of ethanol with residual silanols and with residual chlorine left by chemisorption of one DMDCS molecule to one silanol rather than to two. This is also clear on the cross-plot on Fig. 3. However, the multilayer plateau has the smallest slope, indicating a change to type I isotherm probably because DMDCS leaves fewer easily accessible residual silanols as the rigidly fixed DMS surface groups do not screen them well.

Therefore, silylation of the aerosil surface reduces its ethanol adsorption with an effectiveness trend of  $673/653 \text{ TPCS} > 673/653 \text{ TMCS} > 598/598 \text{ TMCS} > 673/653 \text{ TECS} > 673/598 > 1/4\text{TMCS}$ . With the exception of TPCS, which actually leaves the largest quantity of residual silanols at the surface, the rest of the trend represents the increasing concentration of the residual silanols.

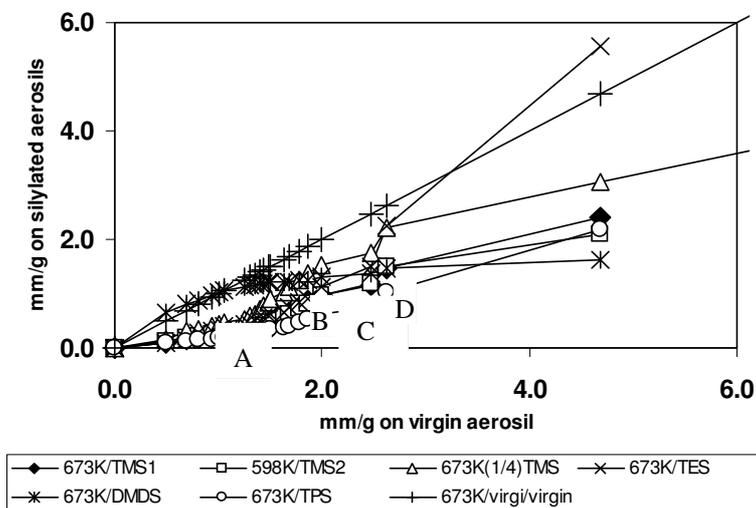


Fig. 3. Isotherm cross plots: obtained by plotting the adsorption isotherm of a sample-against the isotherm of unmodified sample at the same relative pressures; equal adsorption (a line of slope = 1) for two systems with equivalent adsorption is shown for comparison.

**Cross-plots of adsorption isotherms:** Collected isotherm cross-plots showing the relative effect of modification on adsorption are given in Fig. 3. They were obtained by plotting the quantity adsorbed by the unmodified adsorbent sample at a given pressure against the quantity adsorbed by the modified sample at the same pressure. The figure also shows the expected cross-plot (a line of slope = 1) for two systems with equivalent adsorption. If we consider samples modified by TMCS, TECS and TPCS, after a short initial proportionate adsorption, with the modified samples adsorbing a lot less, a break at A leads to an increase in adsorption on the modified samples. This is followed by a second break at B at higher relative pressure which is followed by increasing adsorption at higher pressure with a smaller slope. There is a common upward slip from C, corresponding to  $P/P_0$  0.85, to D in all the systems, followed by a segment with lower slope beyond D.

It is believed by the author that the initial proportionate adsorption up to A is on the remaining specific sites (the easily accessible silanols) in the modifier defects and gaps to form clusters as a result of the higher adsorption potential at the sites enhanced by the hydrogen bonding interaction. Increasing pressure causes clusters to grow bigger by increasing adsorption through lateral interaction again enhanced by ethanol to ethanol hydrogen bonding; augmented with the formation of more new clusters on remaining silanols and siloxanes under the silyl umbrellas up to B (shown by the increased slope). The lower slope for segment B to C is because adsorption is by piling up only (no more new clusters are forming), on the small clusters which are few after modification and have a positive curvature. At C, the

growing clusters reach a critical size with less positive curvature. At the same time, neighbouring clusters coalesce to form bigger clusters also with less positive curvature due to increased width and due to distortion from adsorption potential effects from the solid, which is still quite close. This results in fast adsorption shown by the increased slope of segment C to D. However, after modification, the clusters are sparsely distributed on the surface. Therefore, coalescence to form multilayers cannot occur; instead, the increased hydrostatic pressure in the clusters overcomes the surface tension forces resulting in the break up of the clusters to give small droplets with more positive curvature and hence lower adsorption. This is demonstrated by the reduced adsorption (lower slope) beyond D. This slope is higher for the TECS modified sample because of the larger number of clusters resulting from the easier accessibility of silanols and siloxanes under the silyl umbrella due to the large but light and flexible nature of the ethyl groups on the silyl unit. However, the slope of this segment is higher than that of the equivalent adsorption indicating that the adsorption potential at this point is higher than that on the unmodified sample. It is presumed that since there are more clusters and droplets on this sample, this is due to the increased lateral hydrogen bonding between adsorbed ethanol molecules augmented by hydrophobic interactions between the hydrocarbon chains of the ethanol molecules and those of the silyl groups together with dispersion forces. However, in the present cases the reduction in adsorption potential was not large enough to transform the type II isotherms to type III as in the cases with benzene<sup>23</sup>.

**BET surface areas:** The requirements for the suitability of a molecule in surface area determination by the BET method have already been discussed<sup>23</sup>. They include the variation of molecular shape and hence cross-sectional area, molecular polarity and hence specific interactions with polar surfaces. Ethanol molecules have hydrogen bonding among themselves and with surface silanols and are not spherically shaped. Consequently, several values of cross-sectional area are possible. The value used in this work was derived from similar adsorbents to aerosil. However, results obtained in this work will be used for comparative purposes only.

A BET plot  $\{P/P_0/(X_a(1 - P/P_0))\}$  against  $P/P_0$ , where  $X_a$  represent moles of ethanol adsorbed per gram of TMCS silylated aerosil, is given in Fig. 4 and the results for various samples are given in Table-2. The BET surface areas were determined in the same way as for the adsorption of benzene<sup>23</sup>, by choosing points in the partial pressure range  $0.05 < P/P_0 < 0.35$  and fitting them on the BET function using a fortran program based on least squares' analysis. The BET surface areas were determined<sup>33</sup> using a value of  $0.28 \text{ nm}^2$  for the cross-sectional area of an adsorbed ethanol molecule. This is much smaller than the  $199.3 \text{ m}^2\text{g}^{-1}$ , obtained for adsorption of benzene<sup>23</sup> and smaller than the value of  $170 \text{ m}^2\text{g}^{-1}$  obtained<sup>34</sup> for the adsorption of nitrogen at 77 K. For the BET ethanol surface area to agree with that for nitrogen, the cross-sectional area of the ethanol molecule would have to be adjusted to a value of  $0.46 \text{ nm}^2$ . This value is twice the value of  $0.23 \text{ nm}^2$  obtained from calculations using the liquid density of ethanol. Ethanol adsorbs on silica

through hydrogen bonding between the ethanol molecules and the surface silanols. The number of surface silanols imposes a restriction on the number of ethanol molecules in the monolayer and therefore determines the specific surface area. Benzene is adsorbed on silica through conjugation with the oxygen of the silanols and that of the surface siloxane bonds, whereas nitrogen adsorbs by quadrupole interaction. Although these interactions are less specific than hydrogen bonding, more benzene (or nitrogen) molecules will be adsorbed at the surface than ethanol molecules, particularly on a non-porous adsorbent such as aerosil. Furthermore, benzene can adsorb by several orientations, each of which has a different cross-sectional area; varying from  $0.25 \text{ nm}^2$  for end on orientation to  $0.57 \text{ nm}^2$  for a flat lying molecule<sup>33,35</sup>.

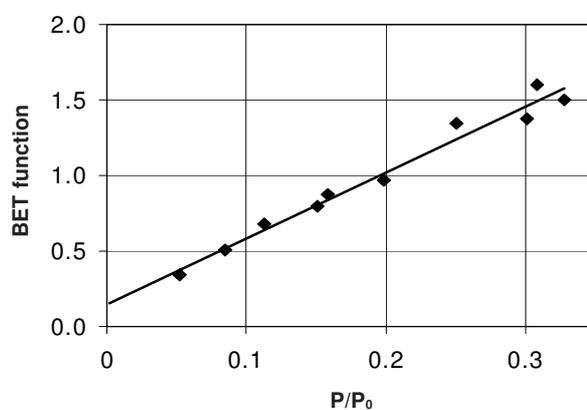


Fig. 4. BET plot for ethanol adsorption at 293 K on aerosil evacuated at 673 K and TMCS-silylated

The strong specific and localized adsorption through hydrogen bonding between the surface silanols and ethanol<sup>36,37</sup> is reflected in the higher isosteric heat of adsorption of  $51.8 \text{ kJmol}^{-1}$  compared to  $28.3 \text{ kJmol}^{-1}$  for benzene at half coverage<sup>37</sup>. Babkin *et al.*<sup>37</sup> found that the isosteric enthalpies of adsorption for methanol on silica to vary with coverage. At the start, a large value of  $52 \text{ kJ mol}^{-1}$  was observed. This value is in reasonable agreement with the value for hydrogen bonding. At coverage of 0.3, however, the enthalpy of adsorption had dropped to  $39 \text{ kJ mol}^{-1}$ , which is the heat of condensation for methanol. Furthermore, negative entropy of adsorption was also initially observed. This entropy gradually increased with increasing coverage and after a monolayer or so, became positive. Apparently, the mode of adsorption of alcohols on silica and the orientation of the alcohol molecules, change with coverage, resulting in a variation in the value for the cross-sectional area and hence the BET specific surface area. The cross-sectional area of the ethanol molecules, in this case, would be smaller if the molecule were standing upright, (which is likely to occur when the molecule is chemico-sorbed or adsorbed by hydrogen bonding through the hydroxyl group) than the value when the molecules

were either standing at an angle or lying flat (which will occur when the molecule is physically adsorbed). In the former case more molecules would fit on the surface; if a larger cross-sectional area is used, the specific surface area would be over estimated, as in the case with benzene<sup>23</sup>.

**Effects of modification on BET surface area and 'C' constant:** The surface concentrations of the various silyl groups on aerosil are given in Table-1. Modification of silica reduces ethanol adsorption by a factor depending on the type of modifier, its concentration at the surface and the relative vapour pressure of ethanol. Isotherms in Fig. 2 show the effect of modification by the various silanes on the monolayer and multilayer adsorption region on aerosil, the corresponding surface areas are given in Table-2. The BET surface areas have been reduced by factors that depend on the concentration of the modifier group. The trend of the surface area of aerosil samples is as follows: untreated > DMCS > TECS > (598/598) TMCS - > (673/653) TMCS > TPCS. With the exception of TPCS-treated aerosil and (673/653) TMCS-treated aerosil, this trend is the reverse of that of the concentration of the modifier groups. It can be concluded that the trend of the surface area is identical to the trend of the concentration of the residual surface silanols. This confirms the belief outlined earlier<sup>38</sup> that the first alcohol molecules adsorb by hydrogen bonding through the defects of the layer of modifier groups. In this way, these defects are patched up, leaving a more uniform layer of methyl groups exposed at the surface. This first adsorption on the high energy sites is reflected in the very high BET constant values given in Table-2 and in the trend of isosteric enthalpy of adsorption obtained by various workers<sup>29</sup>. Specific orientation of the initial molecules adsorbed at the surface has also been used in explaining the behaviour of polar molecules adsorbed on alumina<sup>39,42</sup>.

The trend for the BET constant, given in Table-2, for ethanol adsorption on modified aerosil samples is: DMDCS > TMCS > TPCS > TECS > unsilylated. The position of DMDCS-treated aerosil sample is not surprising, because the effect of the residual silanols is boosted by the presence of residual halogens on the DMS group at the surface from DMDCS molecules which chemisorbed by a 1:1 mechanism with silanols. These residual halogens are also high energy sites for ethanol adsorption because of the polar nature of their bonding to silicon. Although TPCS-treated samples have the highest concentration of residual silanols, ethanol adsorption is rather lower than expected, presumably because the benzene rings from the TPS groups lie flat at the surface and hence screen the silanols underneath from incoming adsorptive molecules.

After all the defects have been patched up, adsorption occurs on top of the modifier layer. The dominant molecular interactions at this stage are dispersion forces only, in those cases without residual chlorine atoms at the surface.

The potential for hydrogen bonding between adsorbed alcohol molecules themselves, however, causes an additional complication. This was resulted minimum in the plot of isosteric enthalpy of adsorption against coverage, which is sometimes below the heat of condensation of the alcohol<sup>36,38</sup>.

## Conclusion

Modification of aerosil with TMCS, TECS, DMDCS and TPCS reduces ethanol adsorption in the monolayer and multilayer regions. Consequently both the BET area and the multilayer thickness are reduced and governed by the concentration of accessible surface silanols and the shape and concentration of the modifier silyl groups at the surface in agreement with results from the derived BET constant. It is thought that the first ethanol molecules react with the most exposed silanols to give alkoxides, then their is formation of lot hydrogen bond with the silanols to form and develop adsorbed ethanol clusters and the final lot physically adsorbs on top of the silyl organic layer.

Further work should include investigation of ethanol adsorption on modified porous silica samples to reveal the effect of modified pores on the development of monolayer, multilayers and on the capillary condensation. Studies should also be extended using water in order to establish corresponding trends and compare the results with those from work with benzene and ethanol. This will help in understanding the mechanism of capillary condensation of polar adsorptives in autophobic systems in view of the potential applications in nanotechnology<sup>13,39-41</sup>.

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