

### CHARACTERISATION OF SILICA SURFACES III: CHARACTERISATION OF AEROSIL SAMPLES THROUGH ETHANOL ADSORPTION AND CONTACT ANGLE STUDIES

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**ABSTRACT.** Aerosil samples, heat treated and then silylated with various silanes at various temperatures have been characterised by adsorption of ethanol at 293 K. Adsorption isotherms were plotted and the BET specific surface areas were determined. Contact angles were measured by the captive bubble method at the three phase contact line in ethanol, on glass slides similarly modified. Silylation was found to alter the ethanol adsorptive properties 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 that of surface silyl groups.

**KEY WORDS:** Modified aerosil, Surface characterisation, Ethanol adsorption, Contact angle

#### 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 NMR [1], adsorption using various adsorptives, deuterium hydrogen exchange, thermal gravimetric and time of flight secondary ion mass spectroscopy (TOF-Sims) [2], and identified those originating from physically adsorbed water, free isolated silanols, and hydrogen bonded geminal and vicinal silanols [3].

Silica surfaces may be modified by removing surface silanol by heating or by irradiation with ultra violet light [2]. Alternatively, the surface silanols protons may be replaced with bulky organic groups producing a hydrophobic and non-polar surface [4-7]. The extent of hydrophobicity depends on the surface density of the added organic groups. Consequently, designed intermediate properties can be achieved by fractional hydrophobisation [5] 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 stabilisation, modification, and controlled release, thin and nano-structured film formation, and advanced material fabrication [8-10]. 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 [12], and selective rejection of chromium(VI) [13].

The questions that need to be answered are “what changes occur during modification and how do these changes affects the surface properties of the particles and hence their interaction

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with other materials such as alcohols?" How much of this information can we obtain from ethanol adsorption and contact angle measurements?

Adsorption of alcohols on siliceous materials has been investigated using spectroscopic methods under varying conditions [14-17]. At lower temperatures, physisorption mechanisms dominate; however, residual alkoxide groups have been detected at the surface [15, 16] 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 [16]. Clearly, surface silanols are directly involved in both mechanisms. Consequently, a change in their surface concentration and accessibility will directly affect the adsorption as well as the contact angle at the three phase contact line in alcohol.

This paper describes adsorption studies of ethanol on a non-porous silica aerosil, which is often used in research as a non-porous standard, modified using a variety of halogenated silanes including trimethylchlorosilane (TMCS) and dimethyldichlorosilane, (DMDCS), which generate surfaces with compact organic groups. A more open surface is expected from treatment with triethylchlorosilane, TECS, and triphenylchlorosilane, TPCS. Partial treatment to ¼ TMCS silylation was also used to vary the density of surface organic groups. The BET ethanol specific surface areas were determined as a function of these pre-treatments. Contact angles on similarly modified glass slides were also determined. 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.

## EXPERIMENTAL

Contact angles were measured at the three phase contact line in ethanol on glass slides by the captive bubble method using equipment described in detail elsewhere [18]. 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 [19].

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 [20].

The possible sources of error in the determination of the weight adsorbed (adsorption of the microbalance assembly, buoyancy and Knudsen flow effects [21, 22]) have been considered previously and found to be negligible. Similar conditions were used in the work reported here consequently errors will also be minimal.

### *Materials*

*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 [19].

*Ethanol.* Ethanol 99.95 % (BDH) was transferred directly to a reservoir bulb without further purification. It was out-gassed immediately using the freeze-thaw cycles [20] 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 [20]. 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 [19].

**RESULTS AND DISCUSSION***Contact angle*

Results from contact angle determination are given in Table 1.

Table 1. Contact angles on treated and untreated glass slides in ethanol.

Silane	T reaction (K)	$\phi_a$ advancing.	$\phi_r$ receding
NIL	673/653	0	0
TMCS	598/598	26	21
TMCS	653/653	28	22
TMCS	673/653	29	24
TECS	673/598	30	26
DMDCS	673/653	41	32

The contact angle values obtained in this work are generally lower than those obtained in water by Herzberg [23] using similar surfaces. This can be attributed to the different liquids, different solid surface pre-treatment and reaction conditions used (silylation, in Herzberg's work, included vapour phase adsorption at room temperature producing very polar surfaces with a possible maximum surface silanol concentration of 4.816 groups  $\text{nm}^{-2}$  [24, 25]. In this work, surface pretreatment and silylation was at 598 K or higher to give less polar surfaces. The contact angle size on a polar solid surface has been found to decrease with increasing polarity of the liquid used [5, 26].

The advancing contact angle was used for analysis in the present work because it more closely relates to the situation as ethanol vapour has just condensed. It has also been found to give values which are more reproducible than the receding angles [23]. Yun Seup and co-workers studying industrial nano-particles modified with octyltriethoxy silane found the advancing contact angle to increase with the surface concentration of the modifier group [25]. The advancing contact angle, in this work, shows that the higher the concentration of residual silanols (corresponding to lower evacuation temperature), the smaller the contact angle. The slides evacuated at 598 K exhibit the smallest contact angle of 26 degrees despite the higher concentration of grafted groups.

Silylation leaves a large quantity of silanols at the surface, under the silyl umbrellas (see Figure 1b, 1c, 1d and 1e) and in the defects which are left between the grafted groups [20]. Reduction of the concentration of these residual silanols is brought about by higher temperatures of evacuation, and by removal through reaction with silanes. In the latter case, DMDCS is a more efficient silanol remover, resulting in a higher contact angle here and with Herzberg and co-workers [23].

*Physisorption experiments*

Ethanol adsorption isotherms on aerosil were plotted before and after treatment with TMCS, 1/4TMCS, TECS, DMDCS and TPCS. In these experiments, ethanol was chosen as an adsorbate because of its polar and organic nature to monitor the varying specific interactions with varying silanol concentration. Hence the contact angle can be gradually altered by manipulating the silanol concentration, whilst the organic nature improves the interaction between the molecules and the modified surface. As a result, information about the variation of contact angle, of monolayer and multilayer adsorption can be obtained.

*Surface modification by various silanes*

The reaction scheme for the modification of aerosil with TMCS is given in Figure 1a, the products from modification using TPCS, TMCS, TECS, and DMDCS are given in Figures 1b, 1c, 1d, and 1e, respectively. Adsorbed group parameters are given in Table 2.

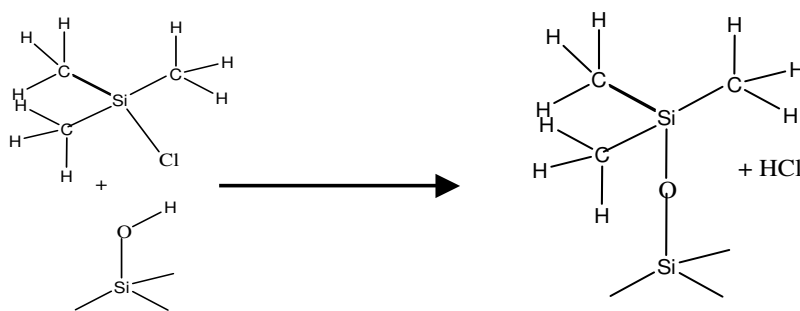


Figure 1a. The silylation reaction process.

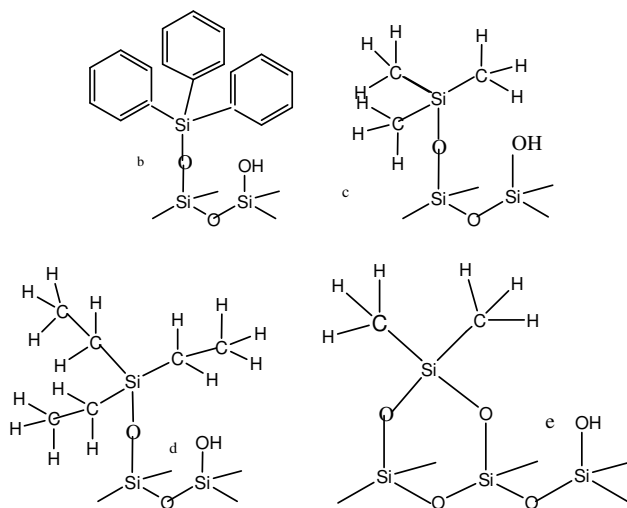


Figure 1. (b, c, d, e). The resulting surface grafted groups: b, triphenyl (from TPCS); c, trimethyl (from TMCS); d, triethyl (from TECS); and e, dimethyl (from DMDCS).

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 2 shows the various group concentrations at the surface obtained in this work and Figure 1a, shows the silylation process. The resulting structure and relative size of the groups together with residual silanols at the surface are given in Figure 1b to 1e.

Table 2. Adsorbed group parameters.

Silyl group/ evacuation T/K	Concn mmm <sup>-2</sup> ±0.01	Groups nm <sup>-2</sup> ±0.02	Area per 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 [34]
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 [37]

<sup>a</sup>Values calculated from liquid densities of the chlorinated silane. <sup>b</sup>Chemisorption to a quarter of the total adsorption.

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 m<sup>2</sup>g<sup>-1</sup>. The evacuation temperature before the chemisorption experiments was 673 K on most samples; in other cases they are shown in Table 2 together with the modifier.

The maximum silanol concentration at the surface under these conditions is around 8 mmm<sup>-2</sup> (milli-moles per square meter) [24]. This is equivalent to 4.816 groups per nm<sup>2</sup>; each silanol therefore occupies a minimum area of 0.21 nm<sup>2</sup>. 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 is in the range 3.7 to 4.5 mmm<sup>-2</sup> [38] or around 2.4 groups per nm<sup>2</sup> [28]. Thus, at most 50 % of the silanols can be replaced by TMS groups [20]. The level of residual silanols has been detected by isotopic exchange and infrared spectroscopy [29, 30]. Coverage by various silane molecules on a variety of silica samples, under specific conditions, has been discussed by Unger [31].

#### Ethanol isotherms

In the adsorption isotherms given, Figure 2 is for TMCS-treated, Figure 3 is for 1/4 TMCS treated, Figure 4 is for TECS-treated. Isotherm cross-plots between unmodified aerosil and modified samples, for comparison, for TMCS, TECS, TPCS, and DMDCS are given in Figures 3b, 4b, 5b and 5c, respectively. Figure 6 is the collected isotherms showing the various monolayers and multilayers regions for comparison.

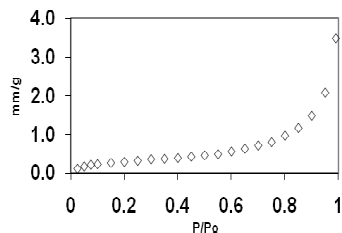


Figure 2. Ethanol adsorption isotherm at 293 K on aerosil pre-evacuated and TMCS-silylated at 598 K.

Adsorption 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. Isotherm cross-plots (Figure 3b, 4b, 5b, 5c) were obtained by plotting adsorption on a modified sample at a given pressure against that on the unmodified sample at the same pressure together with adsorption on virgin aerosil against itself for simple comparison.

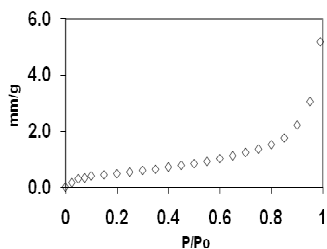


Figure 3a. Ethanol adsorption isotherm at 293 K on aerosil evacuated at 673 K and  $\frac{1}{4}$  TMCS-silylated.

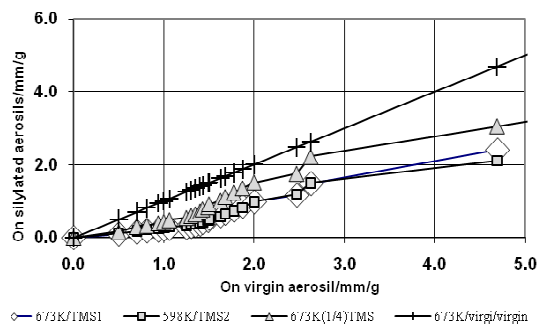


Figure 3b. Cross-plots of ethanol adsorption on virgin aerosil against adsorption on samples TMCS-modified under various conditions.

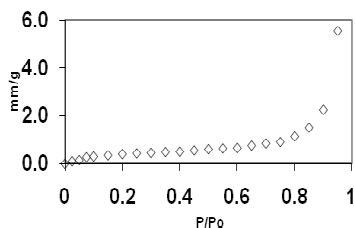


Figure 4a. Ethanol adsorption isotherm at 293 K on aerosil evacuated at 673 K and TECS modified.

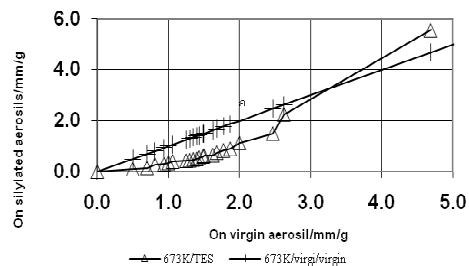


Figure 4b. Cross-plot of ethanol adsorption on virgin aerosil against adsorption on TECS modified sample.

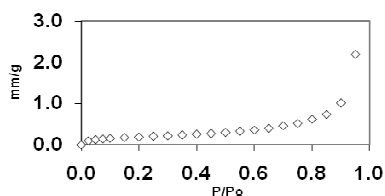


Figure 5a. Ethanol adsorption isotherm at 293 K on aerosil evacuated at 673 K and TPCS-silylated.

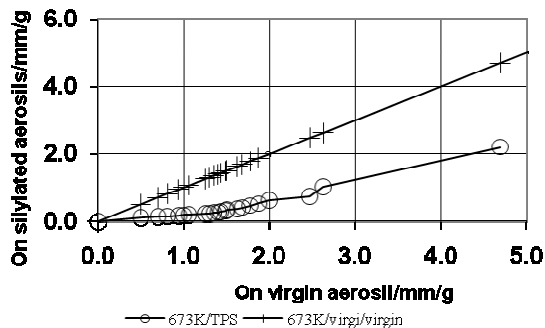


Figure 5b. Cross plot of ethanol adsorption on virgin aerosil against adsorption on TPCS-silylated sample.

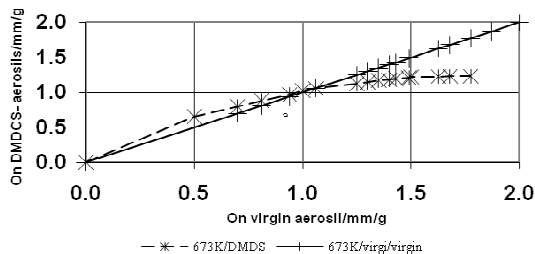


Figure 5c. Cross plot of ethanol adsorption on virgin aerosil against adsorption on a DMDCS-silylated sample.

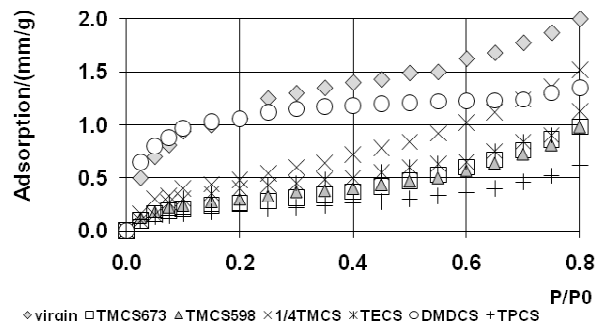


Figure 6. Collected smooth isotherms: adsorption of ethanol at 293 K on aerosil modified using various silanes. Samples were evacuated at 673 K or as shown above then silylated.

Ethanol has easier access to hidden silanols under the umbrellas of the surface silyl groups (Figure 1b, 1c, 1d, and 1e) in the modified silica samples than benzene [20]. Furthermore, it has stronger specific interactions with the silanols through hydrogen bonding. This is intermediate between physisorption and chemisorption. 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. In all cases, the cross-plots (Figure 3b, 4b, and 5b) show that adsorption by modified samples is consistently lower than that on the unmodified sample. The upward blip common to all cross-plots at 2.5 mm/g ( $P/P_0 \sim 0.8$ ) on the virgin aerosil axis probably represents the start of ethanol condensation. The cross-plot for DMDCS modified aerosil in Figure 5c is close to that of the virgin aerosil at both monolayer and multilayer regions because of the residual chlorine resulting from adsorption of DMDCS by loss of one chlorine rather than two.

#### *The shapes of the isotherms*

Type II isotherms were obtained for ethanol adsorption on all samples with various pre-treatments [32]. Table 3 summarises the changes in ethanol adsorption resulting from silylation, for comparative purposes

Ethanol adsorption on silica samples with the highest density of TMS surface groups is presented in Figure 2, while that with lower density of surface silyl groups by using larger TES groups is given in Figure 4. They both show low monolayer coverage and slow building of multilayers (slope of 1.0 see Table 3). In Figure 3, adsorption of ethanol on a sample with low concentration of TMS groups and a large number of deliberately saved residual silanols shows higher monolayer coverage and a faster developing multilayer region (slope of 1.5 see Table 3). However, there was a scatter of desorption points at high pressure probably due to capillary condensation at the points of mutual contact of the particles, and in the interparticle spaces created during the preparation of the samples into pellets. These spaces are too wide to give a clear hysteresis but are readily available for ethanol adsorption due to the low density of the TMS groups. In Figure 5 the effect of the large flat TPS groups, results in very low obscure knee and point B showing the tendency towards a type III adsorption isotherm. The multilayer plateau has a very small slope of 0.5 (see Table 3).

Figure 6 is a collection of isotherms in the monolayer and multilayer regions showing the relative effect on ethanol adsorption of the various modifiers on the development of these regions. Clearly, monolayer development is fastest for DMDCS- treated aerosil showing a clear



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. However, the multilayer plateau is almost flat, indicating the tendency towards type I isotherm probably because DMDCS is a more effective remover of silanols. However, the residual silanols are not so well screened by the more rigidly fixed DMS surface groups (Figure 1e).

Therefore, silylation of the aerosil surface reduces its ethanol adsorption with an effectiveness trend of 673/653 TPCS > 673/653 TMCS > 598/598 TMCS > 673/653 TECS > 673/598 > 1/4TMCS (Table 3 columns 6 and 7). 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.

Table 4. Summary of the decrease in adsorption due to treatment with silanes.

Figure	Modifier silane/temp evacuation/K	Point B mm/g monolayer	Slope $p/p_0$ (0-0.8)	P/P <sub>0</sub> = 0.4 mm/g end monolayer	P/P <sub>0</sub> = 0.4 treated/untreated %	P/P <sub>0</sub> 0.8 mm/g, end of multilayer
6	TMCS/673	0.38	1.0	0.42	29	1.02
2	TMCS/598	0.40	1.0	0.44	30	1.04
3a	1/4 TMCS/673	0.68	1.5	0.76	52	1.62
4	TECS/673	0.52	1.0	0.57	39	1.20
5	TPCS/673	0.26	0.5	0.28	19	0.64
6	Nil/673	1.40	2.0	1.46	100	2.1

#### The BET surface areas

The requirements for the suitability of a molecule in surface area determination by the BET method have been discussed [20]. They include the variation of molecular shape and hence cross-sectional area, molecular polarity and hence specific interactions with 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 sample BET plot of  $\{P/P_0/(X_a(1-P/P_0))\}$  against  $P/P_0$  ( $X_a$  represent moles of ethanol adsorbed on the silylated aerosil per gram of the adsorbent) is given in Figure 7 and the results for various samples are given in Table 4.

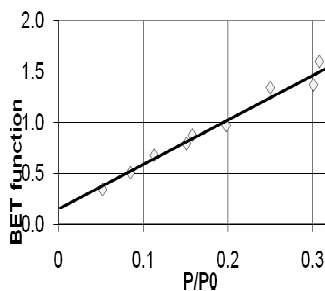


Figure 7. BET plot for ethanol adsorption at 293 K on aerosil evacuated at 673 K and TMCS-silylated.

Table 4. A summary of the results of BET surface areas, in  $\text{m}^2\text{g}^{-1}$  and C constants of aerosil, for the surface treatments used in this study.

Evacuation/silylation Temp. K	Area/ $\text{m}^2\text{g}^{-1}$	BET C constant
NIL-673 K	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 are in brackets ( ).

The BET surface areas were determined in the same way as for the adsorption of benzene [30], 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 using a value of  $0.28 \text{ nm}^2$ , obtained from a similar adsorbent [33], for the cross-sectional area of an adsorbed ethanol molecule. The calculated specific surface area of the untreated aerosil is then  $104.5 \text{ m}^2\text{g}^{-1}$ . This is much smaller than the  $199.3 \text{ m}^2\text{g}^{-1}$  obtained for adsorption of benzene [20], and smaller than the value of  $170 \text{ m}^2\text{g}^{-1}$  obtained for the adsorption of nitrogen at 77 K [34]. 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 the 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 [33, 35].

The strong specific and localized adsorption through hydrogen bonding between the surface silanols and ethanol [36, 37] is reflected in the higher isosteric heat of adsorption of  $51.8 \text{ kJ mol}^{-1}$  compared to  $28.3 \text{ kJ mol}^{-1}$  for benzene at half coverage [37]. Kiselev and Babkin [33] found 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 chemisorbed 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 overestimated, as in the case with benzene [20].

*Effects of modification on ethanol adsorption*

A summary of the changes resulting from silylation is given in Table 3. The surface concentrations of the various silyl groups on aerosil are given in Table 2. 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 (Table 3 column 6). Isotherms in Figure 6 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 4. 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 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, again indicating that the surface area trend is identical to the residual surface silanols concentration trend. It is believed [38] 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 C constant values given in Table 4, and in the trend of isosteric enthalpy of adsorption obtained by various workers [29, 32]. Specific orientation of the initial molecules adsorbed at the surface has also been used in explaining the behaviour of polar molecules adsorbed on alumina [39].

The trend for the BET C constant, given in Table 4, 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 (see Figure 1b).

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 found to result in a minimum in the plot of isosteric enthalpy of adsorption against coverage, which is sometimes below the heat of condensation of the alcohol [36, 38].

## CONCLUSIONS

Contact angle measurements confirm that modification of silica with TMCS, TECS, or DMDCS increases the size of the advancing contact angle in ethanol according to the trend DMDCS > TECS > TMCS. Furthermore, modification with TMCS, TECS, DMDCS, and TPCS reduces adsorption for ethanol in the monolayer and multilayer regions. Consequently both the BET area and the multilayer thickness are reduced to extents governed by the concentration of accessible surface silanols which is controlled by the physical size, shape and concentration of the modifier silyl groups at the surface, in agreement with results from the contact angle determination and the derived BET C constant.

The reduction in surface area may be responsible for the reduction in inter-particle contact and the increase in inter-particle separation distance which depends on the size of the modifier

group. Hence modification will lower the attractive interaction thus reducing particle agglomeration [7] and hence minimising powder sintering, which is a big problem in industry.

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. Particular attention should be paid to the effect of the polarity of the adsorptive, in the presence of the various surface silyl groups, to the development of hysteresis and to the pore size analysis under these conditions. Studies should also be extended to 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 behaviour of modified particle surfaces in view of the large number of current and potential applications in nanotechnology [7, 40–41].

This work offers two methods with potential as standards for the estimation of surface polarity; firstly using fractional hydrophobisation with a suitable modifier such as TMCS and secondly by varying the size of or the type of the modifier. Surface polarity can then be estimated using contact angle size in a suitable liquid or by adsorption of a suitable adsorptive at monolayer or multilayer region.

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