Investigation of the behaviour of water on the surface of modified silica using differential scanning calorimetry

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Abstract

The melting behaviour of water in contact with 60 Å, 150 Å, and 300 Å silica surfaces was studied using differential scanning calorimetry. In addition to the melting of bulk water, peaks that are diagnostic of the interaction of water with the surface are observed. The behaviour of these peaks as a function of the properties of the silica surface have shown that the pore size and surface activity have the greatest effect on the behaviour of water. This behaviour was compared to the melting behaviour of water on the surface of the 60 Å and 300 Å silicas modified with alkyl silane ligands. The silicas were modified with increasing bonding densities of trimethylsilane, octylsilane, and octadecylsilane. The behaviour of the melting peaks associated with the water perturbed by the surface was altered as the bonding density and the chain length were increased. The modification of the surface resulted in the prevention of the interaction of water with the surface silanols. The longer chains also blocked the silanol sites by steric hindrance of the surface.

Keywords: Silica; Surface–water interaction; Stationary phases, LC; Water–surface interaction; Silanol groups

1. Introduction

The goal of this work was to evaluate the properties of water associated with the surface of modified amorphous silica. Differential scanning calorimetry was used to study the melting behaviour of water on the surface of 60 Å, 150 Å and 300 Å silicas. These results were then compared to the melting behaviour of water on the surface of the 60 Å and 300 Å silicas modified with trimethyl, octyl and octadecyl silane groups. Changes in the melting behaviour of water were used as an indication of changes in the interaction of water with the silica surface caused by the modification.

An understanding of the interactions at the modified silica interface used as a stationary phase in RPLC is of great importance in the elucidation of the mechanisms of solute retention. An understanding of the processes that control the selectivity and efficiency will allow the manipulation of the interfacial properties to give improved separations. Many studies have characterized the nature of the interactions that occur in the interface between the modified silica stationary phase and mobile phase solvent. Interactions are possible with the surface active sites of the porous silica support, the bonded phase, the solvent associated with the bonded phase, and the bulk solvent. The forces that govern the retention and selectivity of a solute involve a complex synergy

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of all of these interactions. The role of water in this complex system has not been studied in detail.

The water in the near-surface region of silica can influence many of the interactions at the surface. The water on the surface affects the reactions used to modify the surface with alkyl silanes. It plays a role in the reactivity of the silanols on the surface, and is the driving force in the polymerization reactions between silane modifiers in solution. On the modified surface the water affects the activity of the unreacted silanols and also plays a role in the structuring of the interface. It has been inferred that the structuring of water in the near-surface region plays a role in the selectivity of the surface, and the dynamics of the stationary phase–mobile phase interactions. Surface water would thus play a role in the selectivity and retention of solutes in a chromatographic system. The distance that these interactions extend away from the surface and how this can be altered by the presence of alkyl-bonded phases would be of interest in understanding the effect that surface water has on chromatographic separations.

There are many different silanol sites on the surface of amorphous silica. Silanols can exist on the surface as isolated silanols, vicinal silanols, geminal silanols and siloxane linkages which are considered hydrophobic. It has been postulated that some silanol sites are more reactive than others [1–4]. The reactivity will depend on the water associated with the silanol, and the way in which the geometry of the surface allows the silanols to interact with each other. A variety of physical and chemical methods can be used to determine the surface concentration of silanols [5,6]. It is generally agreed that a fully hydroxylated surface contains 8 ± 1 $\mu m/m^2$ of silanols independent of the origin, type and structural characteristics of the silica [7,8].

Investigations of the properties of water at the surface of oxide materials have shown that water associated with these surfaces exhibits properties that differ from those of bulk liquid water. The density of water in the near-surface region has been found to be lower than the density of bulk water [9]. The viscosity of water measured near clay and quartz surfaces has been found to be as much as 20 times that of bulk water [10]. The dielectric constant dramatically decreases at distances less than $1-2$ μm from the surface of mica [11], and the thermal

diffusion of water films is greatly decreased [12]. NMR relaxation studies have shown that there is reduced rotation of water films, and that the mobility of water is greatly reduced [13,14]. The heat capacity of water in association with a variety of silica surfaces has also been shown to be 25% greater than that of bulk water [15].

The adsorption and desorption of water from the surface of silica has also yielded useful information about the interaction of water with the surface. It has been found that heating silica under reduced pressure conditions results in the removal of several types of water. Physically adsorbed water starts to be removed as low as room temperature (25°C). For macroporous silicas this process should be complete at 120°C. For highly porous silica, it is necessary to sometimes heat to 150°C and 300°C to remove all physically adsorbed water. Dehydroxylation of silica by condensation of vicinal hydroxyl groups occurs almost simultaneously with the removal of physically adsorbed water. Above 175°C dehydroxylation of vicinal groups is certainly occurring, and by 500°C all vicinal groups are completely condensed. All of the dehydroxylation reactions mentioned up to this point are reversible. If the silica is exposed to a positive pressure of water vapor, the surface can be rehydroxylated. If the heating process is continued above 600°C, condensation is favoured by the lateral mobility of the surface silanols, and by 1200°C the surface is completely dehydroxylated [16]. It has also been shown that the adsorption is more dependent on the number of surface hydroxyls than the surface area or the porosity of the silica [17]. For highly hydroxylated silicas it is believed that the first water molecules are adsorbed by double hydrogen bonding to surface silanols. As water coverage is increased formation of clusters of 5–6 water molecules are favoured [18]. For surfaces sparsely populated with silanols water molecules will cluster about water molecules already on the surface [19].

The freezing and melting of water near silica surfaces has also shown anomalous behaviour. A layer of non-freezing water close to the surface has been observed as low as -194°C. Three layers of water close to the surface have been hypothesized. The layer closest to the surface does not seem to crystallize even at very low temperatures. The middle layer does exhibit a phase transition, but at a

temperature and energy of transition lower than that of bulk water. The outermost layer exhibits all the properties of bulk water [14]. The thickness of the layers in which the properties of water close to the surface have been different to that of bulk water depends on the type of silica and the technique used to investigate the system. The theories regarding the cause of these observations are varied. The differences have been attributed to the fact that adsorption of water depends critically on the arrangement of surface hydroxyl groups which can enhance or destroy the hydrogen-bonding network of water [20]. The variation in the results observed could also be due to differences in the number and geometry of the silanol sites present in the silicas used in these studies.

The modification of the silica surface with alkyl silanes does not completely deactivate the silica surface. It has been found that the maximum coverage attainable with the smallest modifier (trimethyl) is usually 60–70% of the 8 ± 1 μm/m^2 of silanols present [21]. This is due to the inaccessibility of some of the pore volume to the bonding reagent and the steric hindrance of the side groups which prevent further reaction. The residual silanols are accessible to some analytes and these interactions have been implicated in the degradation of the separation of basic amines as evidenced by the asymmetry of the elution peak [22,23].

The forces that govern the retention and selectivity of a solute involve a complex synergy of interactions with the residual silanols on the surface, the bonded alkyl phase, and the solvent molecules. The role of water in this complex system has not been studied in detail. There have been observations of unusual behaviour that have implied that the properties of water in the near-surface region of modified silicas differ greatly from those of bulk water. Lochmuller and Marshall [24] and El Hassan and Burke [25] have noted shifts in the spectrum of bound probe molecules on the surface of silica and have attributed this to a layer of very structured water in the near-surface region. NMR studies by Gilpin and Gangoda [26] have found that the bonded phases are in a very rigid environment when totally solvated with water. It has been postulated that the changes observed in the behaviour of highly polar solutes in the near-surface region as a function of the alteration of the

bonded phase density and functionality are due to the reorganization of the water-rich region that is associated with the residual silanols. It has also been postulated that the structuring of the water layer may be increased at lower temperatures causing the greater exclusion of organic modifier, reduced mass transfer between mobile and stationary phases and reduced mobility of all species in this region. The ability of water molecules to interact strongly with the surface silanols will also play an important role in the re-equilibration of the interphase when switching from mostly aqueous to mostly organic mobile phases [27–31]. The degree of association of water with the bonded stationary phase from binary acetonitrile-water, and methanol-water mobile phases has also recently been studied with deuterium NMR spectroscopy [32]. Small changes in the relaxation times observed for the solvents in contact with the bonded stationary phase, were attributed to the association of the water with the residual silanols on the surface.

One technique that can be used to study the phase changes of solids and liquids is differential scanning calorimetry (DSC). The material and construction of the DSC ovens are carefully chosen to ensure a small thermal mass and rapid thermal conductivity. Heat is transferred at a constant rate from the ovens to the purge gas of high thermal conductivity and, thence, to an aluminum block which is usually cooled or at room temperature. This arrangement provides a stable thermal background so that small changes in the heat provided to the ovens by the heaters can be detected. When a sample undergoes a phase change or a chemical reaction that involves the absorption or release of heat, the power changes that occur for the ovens can be recorded and are directly related to the heat lost or gained by the sample.

In this study the melting behaviour of water at 60 Å, 150 Å and 300 Å silica surfaces has been investigated using differential scanning calorimetry. In addition to the bulk water melting behaviour, other events that we believe to be characteristic of the interaction of water with the surface were observed. The behaviour of these peaks were studied as a function of the water-to-silica ratio. In addition, the observed behaviour was compared to properties of the silica surface such as the pore size, surface area, and surface activity. The 60 Å and 300 Å

silicas were monomerically modified with trimethyl, octyldimethyl and octadecyldimethyl groups. The effects of bonding density and chain length were studied. The changes in the behaviour of the water upon modification of the surface indicates that the hydrogen bonding of the water with the surface silanols is a major contributor to the observed behaviour.

2. Experimental

2.1. Reagents

Octadecyldimethylchlorosilane (Lot 5688), octyldimethylchlorosilane (Lot 81-1037-3), and trimethylchlorosilane (Lot 100–700) were obtained from Petrarch (Bristol, CT, USA) and used without further purification. Analytical reagent grade toluene was obtained from EM Science (Gibstown, NJ, USA), filtered, then distilled and stored under dry argon just before use. HPLC-grade isopropanol and methanol were obtained from Baker (Phillipsburg, NJ, USA). Water was deionized, and distilled twice. The second distillation was from a basic potassium permanganate solution. All solvents brought into contact with silica particles were filtered using 0.45-μm PTFE membrane filters from Millipore (Bedford, MA, USA).

2.2. Silica

The silicas used were from Analytichem International (Harbor City, CA, USA) Lot 138 (60 Å, 8 μm, 433 m^2/g), from Davidson Chemical division of Grace (Baltimore, MD, USA), Davisil grade 215HPOX1821 Lot 1 (150 Å, 15 μm, 266 m^2/g), and from Shandon Southern Products (Cheshire,

UK) Hypersil WP300 Batch 85-1-08 (300 Å, 10 μm, 39 m^2/g). The silicas were acid washed when received from the manufacturer, dried overnight in a vacuum oven at 120°C, and stored in a desiccator. The properties of these silica materials are summarized in Table 1.

The pore size and particle size are provided by the manufacturer. The specific surface areas are measured by nitrogen adsorption if not provided by the manufacturer. The specific pore volume was measured by the method of Fisher and Mottlau [5] where silica samples between 0.5–1.0 g are weighed in a small Erlenmeyer flask and titrated with ethanol with stirring. By dropwise addition of liquid, the pore volume of the sample is gradually filled and the endpoint is indicated by the sticking of the silica particles. The precision of the method is 20% and the reproducibility is 10%.

2.3. Silica modification and determination of bonding density

There are many procedures that have been developed for the modification of silica with organosilanes. Most of these schemes contain the follow steps in common [33]: acid washing of the silica to remove metal cations; pre-drying of the silica at temperatures of between 110°C and 150°C to remove excess water; refluxing the silica in a predried polarizable solvent such as toluene; use of an acid scavenger or degassing the mixture with an inert gas to remove the hydrochloric acid produced during the reaction. A five-fold excess of silanizing reagent, and long reaction times of the order of 24–48 h, are the conditions used to achieve maximal coverage of the silica surface, which has been estimated to be about one half of the total silanols present (8 ± 1 μm/m^2).

The aim of this experiment is to gain an insight

Table 1
Properties of 60 Å Analytichem, 150 Å Davisil and 300 Å Hypersil silicas

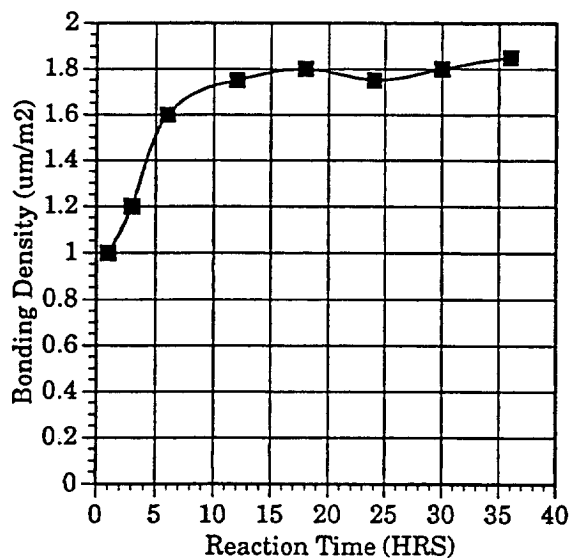| Silica source	Pore size (Å)	Particle size (μm)	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)	Surface silanols (μmol/g)
Analytichem	60	8	433	2.15	3464
Davisil	150	15	266	2.19	2128
Hypersil	300	10	39	1.38	312

Fig. 1. Effect of reaction time on the bonding density of octyldecylsilane on 60 Å silica.

into the changes in the behaviour of water as the surface is gradually deactivated. Maximal derivitization is not the goal here, but a series of increasing bonding densities starting with very low coverages and proceeding until no more changes in the behaviour of water are observed as a function of the

bonding density. One recommended way to reduce the surface coverage is to carry out the reaction at room temperature [34]. One can also use a five-fold excess of reagent, and remove aliquots of the reaction mixture at prescribed times or use a limited amount of reagent, and a fixed reaction time. Both methods were investigated and it was found that the most consistent and controllable low-bonding densities were obtained from the latter method, where a limited amount of reagent was used and the reaction time kept uniform. The preliminary experiments also showed that the bonding density increased slowly as a function of the reaction time at reaction times of 6 h or less, and increasing the reaction time to 24 h did not change the bonding density that much (Fig. 1).

The apparatus in Fig. 2 was used for the synthesis of low-bonding-density materials. A less than stoichiometric amount of silane in toluene was mixed with the silica and placed in a pear-shaped flask. The apparatus was purged with dry argon through a capillary suspended at the bottom of the flask. The purging removes the HCl produced by the reaction, while gently stirring the mixture. The reaction was allowed to run for 6 h. The silica was then vacuum filtered using a 0.45-μm PTFE filter (Millipore, Bedford, MA). The silica was then washed with ten 10-ml portions of dry, filtered toluene, five 10-ml

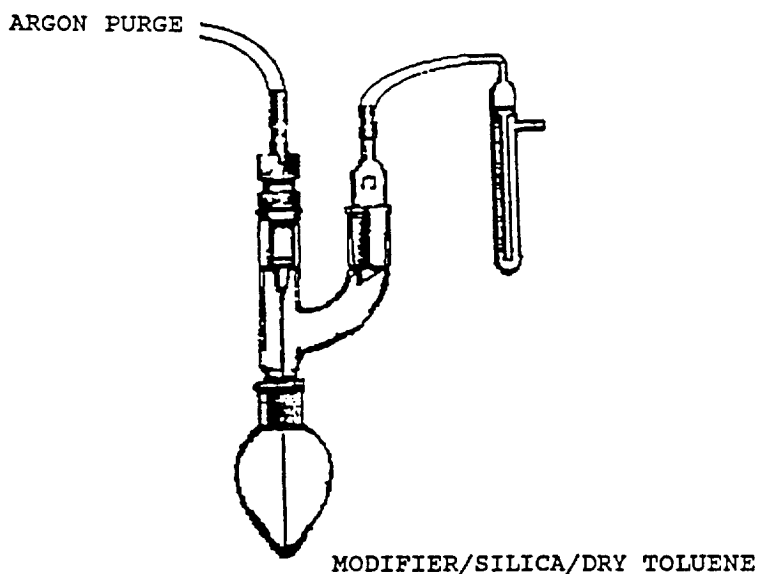Fig. 2. Reaction apparatus employed in the modification of silica surfaces.

Table 2
Bonding densities on 60 Å silica (μm/m^2)

TMCS	C_8	C_{18}
0.58	0.38	0.66
1.12	0.74	0.91
1.69	1.22	1.48
2.00	1.40	1.61
2.44	1.71	1.76
3.12	2.28	1.91
		2.73

portions of filtered isopropanol, and five 10-ml portions of filtered methanol. The silica was then transferred to a 4-dram vial and dried in a vacuum oven at 120°C at reduced pressure (~0.1 mmHg; 1 mmHg = 133.322 Pa) for 24 h, and then stored in a desiccator.

The percent carbon on the derivatized surface was obtained by combustion analysis with a Perkin-Elmer Elemental Analyzer Model 2400, using 3,5-dibenzoic acid as a standard. The coverage was calculated using the following formula

Coverage (μm/m^2)

$$= \frac{X(10^6)/(12.01n)}{\{1 - [X(M_r - 1.008)/(12.01n)]\}SA}$$

where X is the mass fraction of carbon, n is the number of carbons in each bonded group, M_r is the formula mass of the alkylsilyl radical and SA is the surface area of the silica.

The two silicas were both derivitized with trimethychlorosilane, octyldimethylchlorosilane, and octadecyldimethychlorosilane. In addition, reaction blanks where no silane reagent was added to the silica were also put through the whole reaction process. The coverages obtained for the materials

Table 3
Bonding densities on 300 Å silica (μm/m^2)

TMCS	C_8	C_{18}
1.47	0.39	0.36
1.74	0.69	1.07
2.13	1.39	1.19
2.14	1.56	1.33
2.39	1.83	2.80
3.97	2.13	

synthesized are shown in Table 2 (60 Å silica) and Table 3 (300 Å silica).

3. DSC analysis

All DSC measurements were carried out with a Perkin-Elmer DSC 7 instrument, controlled by a TAC 7/3 interface and a 3700 data station. Data were collected and analyzed with the Delta Series DSC 7 software. The DSC instrument was, unless otherwise specified, run under sub-ambient temperature conditions with liquid-nitrogen cooling. The sample chamber was purged with dry helium at 20 cm^3/min, and the sample handling dry box was purged with dry nitrogen at 20 p.s.i. (1 p.s.i. = 6894.76 Pa). The DSC was calibrated with Indium (m.p. = 156.6°C, 28.45 J/g), and n-heptane (m.p. = −90.56°C, 140.16 J/g).

3.1. Sample preparation

Both modified and unmodified silica samples were dried overnight in a vacuum oven at 120°C. Scott and Traiman [16] have shown that is sufficient to remove all physically adsorbed water from the surface. Any water remaining on the surface is very tightly bound and will only start to be removed at 200°C. This process is not complete until 650°C, whereas dehydroxylation by condensation of vicinal groups is believed to be occurring at temperatures as low as 175°C. Silica samples were prepared using a Mettler AE240 semimicro balance in a dry box purged with dry nitrogen. Silica was weighed into the sample pans and then rehydrated by the addition of water with a microsyringe. The smallest amount of water that was observed to give a melting curve with the DSC was 0.25 g of water per g of silica. This was well above the smallest amount of water that could be added with the microsyringe. Thus, other methods of rehydration such as vapor deposition were not explored. All samples were sealed in Perkin-Elmer DSC volatile sample pans (PE NO0219-0062), agitated to mix thoroughly, and allowed to equilibrate overnight before analysis. Both cooling and heating curves were recorded at a scan rate of 10°C/min unless otherwise noted. The temperature range scanned was 25°C to −50°C and

from −50°C to 25°C. For most of the cooling curves very complex freezing behaviour was observed. Supercooling occurred, and the temperature at which the water froze was not reproducible. For these reasons freezing curves are not usually used for analysis. All of the thermal behaviour discussed will be based on the melting behaviour of water.

4. Results and discussion

Freezable water that can be distinguished from bulk water by a change in the bulk parameter such as the freezing or melting point is often referred to as a cluster or droplet. The size of the cluster will determine the type of freezing and melting behaviour exhibited. If water molecules aggregate in large enough clusters they will exhibit the properties of bulk water, while smaller aggregates may not. 'Bound' water molecules specifically associated with silanol sites are not expected to freeze, since freezing is a cooperative function of water aggregates. When small amounts of water are adsorbed in a restrictive environment such as a polymer or silica pore, it is expected that hydrogen bonding and aggregation will be affected. Space restrictions due to the constraints of the narrow pores may then preclude the formation of ice crystals from the adsorbed water. The water will not be able to freeze since this involves a more structured, expanded network of hydrogen bonding. In addition, there may also be kinetic difficulties in nucleating crystallization of ice clusters of limited size [35]. The anomalous freezing and melting behaviour observed for water has also been attributed to a mobile liquid-like layer containing bifurcated H bonds and odd-sided polygons that exist on the surface of ice between −10°C and 0°C. The increased number of water molecules in the surface region, due to these small clusters might also contribute a proportionately greater amount of liquid fraction below the normal freezing point, and this surface 'melting' may be the source of the observed behaviour [36].

The water molecule is ideally suited to engage in hydrogen bonding because it can act both as a donor and as an acceptor of hydrogens. In the crystal structure of hexagonal ice 1H that exists at atmospheric pressure and above −80°C each water mole-

cule in the ice crystal is hydrogen bonded to 4 nearest neighbors with tetrahedral symmetry. The melting of ice 1H to form liquid water does not fully destroy this extended hydrogen bond network. It is believed that the majority of the hydrogen bonds survive the trauma of melting. During melting, rigidity is replaced by fluidity, and molecules are much freer to diffuse and change orientation. The density increases by 9% and the mean separation of nearest neighbors increases by 0.1 Å. It is believed that only about 10% of the hydrogen bonds rupture upon melting, and there is persistence of the hydrogen bond order well beyond the melting transition [37]. The literature value for the melting of pure ice 1H occurs at 0°C with an enthalpy of 322 J/g [38]. The average melting behaviour of more than 20 samples of water ice observed with the differential scanning calorimeter in our laboratory occurred at −1.0±0.5°C with an enthalpy of melting of 323±9 J/g.

A comparison of the melting behaviour of water unperturbed by the interactions with the silica surface, and water associated with the surface of the 3 silicas used in this study is shown in Fig. 3. There is a melting peak at around 0°C (peak a) which is the melting of bulk-water ice. In addition there is a smaller peak at a lower temperature (peak b), and a shoulder (peak c) on the high-temperature side of the bulk-water melt. Peak b is most apparent in the 60 Å and 150 Å silicas, and peak c is most apparent in the 300 Å silica. We believe that the behaviour of peaks b and c are representative of the interactions of the water at the silica surface, and can be used to probe the behaviour of water at the surface as a function of the properties of silica.

The onset temperature for the surface water peak on the 60 Å silica was observed at −21.2±6.8°C, for the 150 Å silica it was observed at −10.2±1.5°C. The shoulder on the high-temperature side of the bulk water peak that was observed for the 300 Å silica had an onset temperature of 1.9±0.8°C. Except for the very broad peaks at low water–silica ratios, and overlapping peaks where the onset temperature is difficult to determine, the onset temperatures do not vary more than ±2°C for a variety of sample sizes and for samples analyzed over several months. The onset temperatures for the bulk water peak on each silica vary from −2.1°C to −1.5°C.
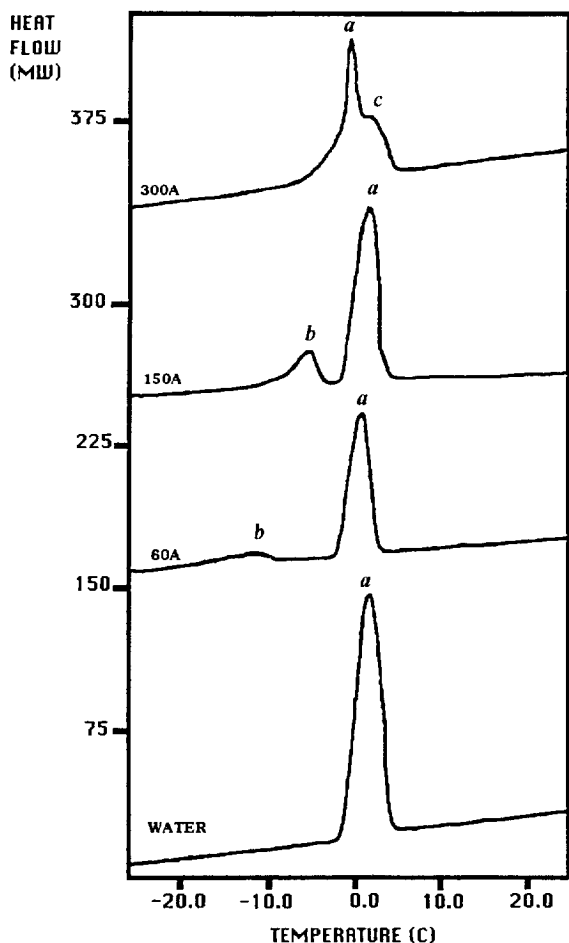
Fig. 3. Melting behaviour of water on the surface of 60 Å, 150 Å and 300 Å silicas. Samples are approximately 1 g of water per g of silica. a = bulk-water melt; b and c = surface-water melt.

These values fall within 2°C of the experimentally determined value of the onset temperature of bulk water which is within the variation of temperatures expected in this experiment.

Some may argue that the observed changes in the freezing and melting behaviour of water in contact with surfaces and in very small pores may just be due to simple colligative effects. The molal freezing point depression constant for water is 1.86 K kg/mol, and the expected theoretical freezing point depression for the range of silica water ratios that we have studied has been compared to the experimental results observed for the melting of water ice (assuming that the freezing and melting points would be

equivalent). From theory the colligative freezing point depression decreases linearly as the silica water ratio is increased. This is not what we observed experimentally. First, there are two peaks, the bulk water melt and another peak shifted to a lower temperature. For each silica, the onset temperature of the peak at lower temperatures remains constant as the silica water ratio is adjusted. The onset temperature shifts only when a different silica is analyzed. This indicates that the phenomenon is a result of some change in the interaction of water with the silica, dependent on the properties of the silica itself. Water peaks with a freezing point as low as −35°C, in addition to the bulk-water behaviour, have been observed for many porous systems similar to silica. The observations of this behaviour in soils and polymer membranes have been attributed to the perturbation of water behaviour by the surface of these matrices, and not to simple colligative behaviour [20].

There has also been speculation that the observed behaviour of water on silica surfaces is due to the formation of a gel layer on the surface formed by the dissolution of the silica. Israelachvili [39] has measured the forces between two molecularly smooth mica plates immersed in an aqueous solution. At distances of less than 30 Å short-range repulsive forces which were attributed to the hydration of ions at the mica water interface were observed. This behaviour was attributed to the enhanced structure of water in thin films. Mica does not form a gel layer on the surface, so the observed behaviour could not be caused by this phenomenon. Similar hydration effects were also observed when the forces between two silica disks are measured [11,12].

The question remains as to what causes the observed behaviour of water ice in these systems. The interaction of water with the silica surface could prevent the formation of the extended hydrogen bond network of water ice crystals in two ways. The very small pores offer a restricted space which would not allow the water to expand during freezing. An alternative explanation would be that because the water is strongly associated with the silanols on the surface it cannot undergo the cooperative aggregation necessary for the phase change. It may also be possible that both factors contribute to the observed behaviour. Several layers of water with different

freezing and melting properties have been observed in the literature, but the thickness of the layers that have been reported have widely varied. We have studied the melting behaviour of the water peak which we believe to be characteristic of the inter-action of water with the surface of silica as a function of the water-to-silica ratio. We have corre-lated the melting behaviour to the pore size, pore volume, surface area, and surface activity of 3 silicas with varying surface properties to determine which one has the most effect on the behaviour of water on the surface.

4.1. Factors affecting the behaviour of water on the surface of silica

The water-to-silica ratio was varied from amounts where only the surface water behaviour was ob-served (0.25 g of water per g silica) to well past the point where the bulk melting peak at 0°C was observed. Representative curves for the trends ob-served for the 60 Å silica are shown in Fig. 4. It can be seen that at very low levels of water, only the small peak (peak b) at $-21.4°C$ is observed. As more water is added to the sample, the bulk water peak (peak a) starts appearing and continues to grow as water is added. The area under the peak and the amount of water added to the sample can be used to calculate the enthalpy of melting of peak b at $-20°C$. The value obtained for this peak on 60 Å silica was 160.4 J/g. Similar behaviour was observed for the 150 Å silica as shown in Fig. 5. The onset of melting of peak b was $-10.2°C$ and the enthalpy of melting was 241.2 J/g. The representative curves for the 300 Å silica are shown in Fig. 6. The behaviour of water on this silica surface exhibited significantly different behaviour. Instead of a small peak (peak b) at lower temperatures, a shoulder (peak c) at 1.9°C was observed on the higher-temperature side of the bulk water peak. In some of the 60 Å and 150 Å silica water samples there were also indications of a shoulder (peak c) on the high-temperature side of the bulk water peak (peak a). This shoulder was very slight and difficult to distinguish from the bulk water peak. The enthalpy of melting could not be accu-rately determined because of overlap with the bulk water melt, but was estimated to be 159.6 J/g. The onset temperatures and enthalpy of melting for the
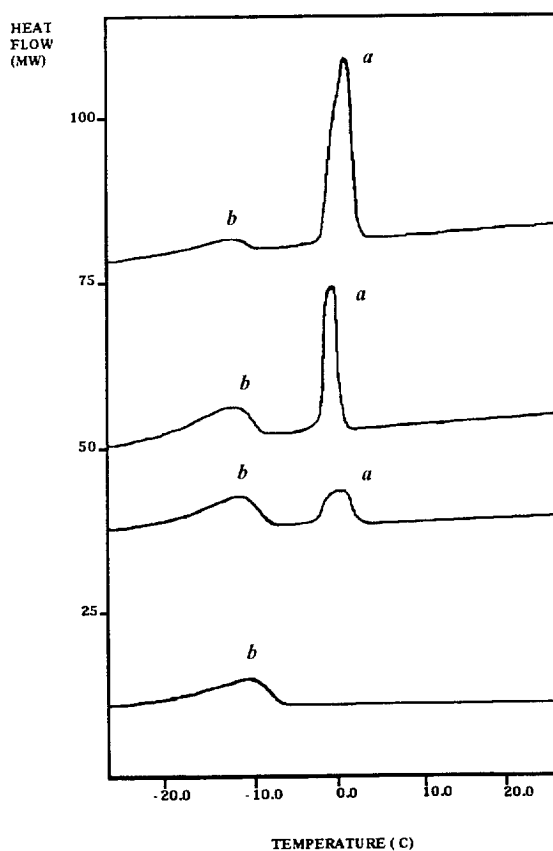

Fig. 4. Melting of water on 60 Å silica as a function of sample size. a = bulk-water melt; b = surface-water melt.

small peak that we believe to be indicative of surface-water behaviour are summarized in Table 4.

The enthalpy of melting of the bulk water in these samples can now also be calculated by taking into account how much water is associated with the surface-water peak compared to the bulk-water peak. These values are also shown in Table 4 and are close to the experimentally determined value of 322 J/g. The enthalpy of melting for the various forms of water ice can be estimated from the phase diagram of water [40], the highest value for ice I can be estimated as 334 J/g, and the lowest value for ice III can be estimated as 311 J/g. The values obtained for the bulk water on silica lie well within these parameters, and the slight variations are within experimental error.

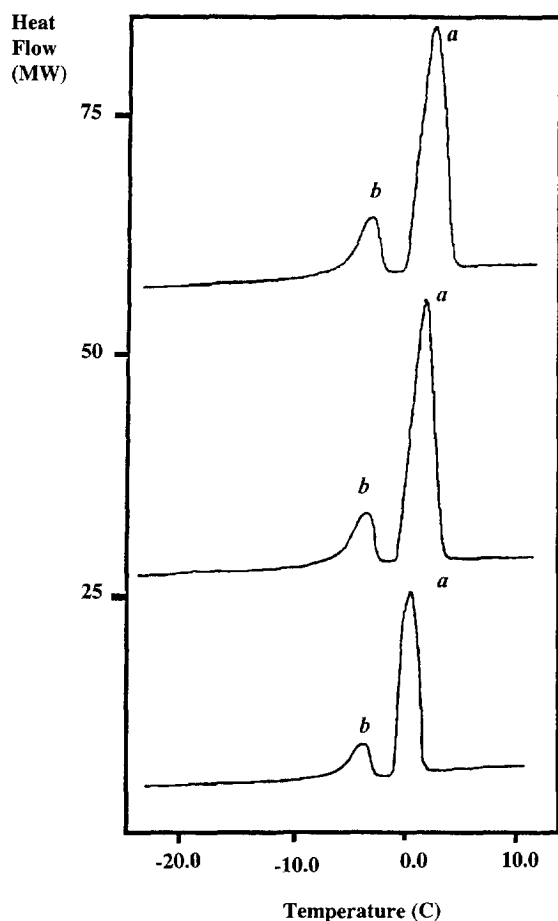The observed enthalpy of melting for the surface-water peaks are all smaller than those for bulk water.

Fig. 5. Melting of water on 150 Å silica as a function of sample size. a = bulk-water melt; b = surface-water melt.

Fig. 6. Melting of water on 300 Å silica as a function of sample size. a = bulk-water melt; c = surface-water melt.

The explanation of this behaviour could be that the water in the near-surface region is constrained by the surface morphology so as not to achieve the co-operative association of water molecules that can be manifested as bulk-water behaviour. Thus, during the phase transition, less water–water hydrogen bonds are being broken. The other consideration is that the observed behaviour is a combination of effects from both the dissociation of water–water hydrogen bonds of bulk water, and the dissociation of the hydrogen bonds of water associated with silanols on the surface. According to Bolis [18] the association of water via one hydrogen bond to a silanol on the surface results in an enthalpy of adsorption lower
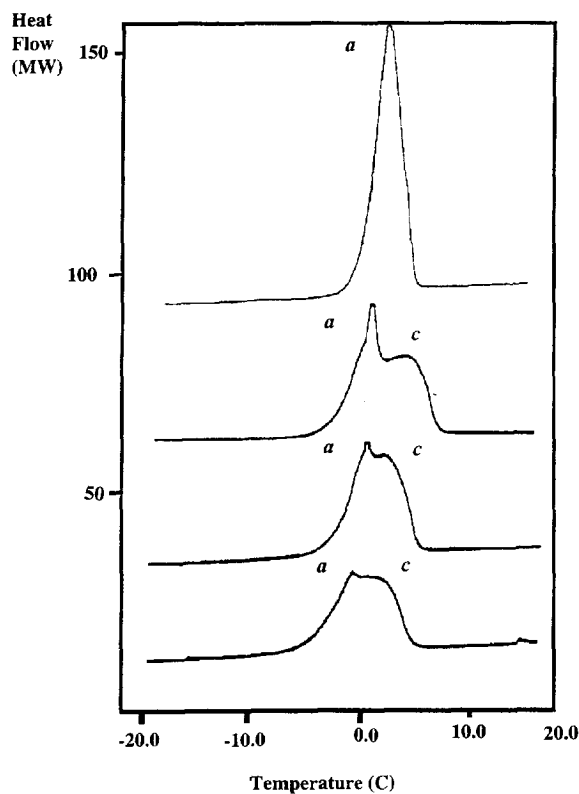
than the latent enthalpy of the liquefaction of water from the vapor phase. Using this reasoning it can be assumed that the strength of a hydrogen bond between a water molecule and silanols on the surface is weaker than the hydrogen bond between two water

Table 4
Comparison of properties of water on silicas of varying pore size

Silica	60 Å	150 Å	300 Å
Onset temperature surface-water peak (°C)	−21.2	−10.2	1.9
Onset temperature bulk-water peak (°C)	−1.5	−2.1	−2.1
Enthalpy of melting of surface water (J/g)	160.4	241.2	159.6
Enthalpy of melting of bulk water (J/g)	325.9	309.7	315.7

molecules. Bolis also attributed an enthalpy of melting close to that of the melting of bulk ice as being due to the melting of multilayers of water on the silica surface.

The constraints of a porous environment would also prevent the water molecules from achieving the extended hydrogen-bonded network of bulk ice. Water expands upon freezing, and this could be prevented by a narrow-pore geometry. Water in small pores would thus not freeze completely and would melt at lower temperatures. The temperature at which these water samples melt is indicative of the ability of the water in the near-surface region to freeze in the fully hydrogen-bonded configuration of bulk-water ice. If the water cannot attain the extended hydrogen-bonded structure that is favored by bulk-water ice it will not melt at close to 0°C, but at a lower temperature.

We have observed that the onset temperature of the peak associated with surface-water behaviour decreases as the pore diameter of the silica is decreased. This is consistent with the hypothesis that the narrower the pore the less water will be able to freeze, and the lower the onset of melting. If one compares the peak area to the percent pore volume filled, the trend for the surface-water peak is to increase to a maximum and then either plateau or slowly decrease. The trend for the bulk-water peak is to slowly increase to a plateau. The point where these curves cross is the point at which the amount of water on the surface has been increased to where bulk-water behaviour begins to be observed. For the 60 Å silica, this corresponds to ~50% of the pore volume filled, and the 150 Å silica shows this behaviour at ~75% of the pore volume filled. For the 300 Å silica, the crossover of the curves represents the point at which the shoulder representing the surface-water peak is no longer distinguishable from the bulk-water peak, and this occurs at 90% of the pore volume filled. For the 60 Å and 150 Å silicas the percent pore volume filled corresponds roughly to the ratio of the enthalpy of the surface-water peak to the enthalpy of the bulk-water peak. This does not hold for the 300 Å silica, but it must be remembered that the measurements made for the 300 Å silica represent the estimation of the peak area of a small shoulder on a large peak, which is subject to larger errors.

Fully hydroxylated silica has 8 $\mu m/m^2$ of surface hydroxyl groups, independent of the origin, and the structural characteristics of the silica [8]. The concentration of silanol sites is thus related to the surface area of the silica. This information for each type of silica studied is shown in Table 1. The silica with the largest number of surface silanols is the one which shows the greatest shift in the onset temperature, and the lowest enthalpy of melting of the surface-water peak. If the observed behaviour is the result of the interaction of the water with the surface silanols this would be the expected behaviour. The silica with the most silanol sites would have the largest interaction with the water molecules and would thus prevent the freezing of water to bulk ice most effectively. The melting point would thus be shifted the most from the melting point of bulk water. Since the silanol–water hydrogen bond has a smaller enthalpy of dissociation than the water–water hydrogen bond, the enthalpy of melting of the water associated with the surface would also be lowest on the silica with the most silanol sites. This would be attributed to the larger quantity of silanol–water hydrogen bonds compared to the water–water hydrogen bonds.

In summary, these studies have shown that by varying the amount of the silica–water ratio, we can probe the effects of different properties of the silica on the behaviour of water in the near-surface region. Thus, it can be seen that 60 Å silica, which has the smallest pore size and highest silanol activity, has the greatest effect on the freezing and melting of water. The water on this surface is most perturbed and thus shows the lowest melting point and enthalpy of melting. For the 150 Å silica, which has a larger pore size and silanol activity, the water freezes and melts at a higher temperature than the water on the 60 Å silica, but below that of bulk water. For the 60 Å and 150 Å silicas it seems likely that the water is constrained on one side by the interactions with the surface silanols, and at the other by the narrowness of the pores. This will cause it not to freeze completely and, thus, melt at a lower temperature. For 300 Å silica, with the largest pore size and the lowest silanol activity, the surface water melts as a shoulder on the higher-temperature side of the bulk water peak.

4.2. Effect of the modification of silica on the behaviour of water on the surface

The discussion of the effect of surface modification will first focus on the behaviour of water on the modified 60 Å silica (Analytichem, 60 Å pore, 8 μm particle, 433 m^2/g specific surface area, 2.15 cm^3/g specific pore volume). The unmodified silica showed the presence of a bulk-water peak at $-1.5°C$, and a surface-water peak at $-21.2°C$. For the purpose of comparison, the silica-water ratio in the following 3 figures are all approximately 1 g of water per 1 g of modified silica.

The bonding of the trimethylchlorosilane to the surface of silica was the shortest chain studied. The effect of increasing the bonding density of the trimethyl group on the behaviour of water is shown in Fig. 7. At very low bonding densities (0.58–1.12

μm/m^2 = ~10% of 8 μ/m^2), the behaviour of water is very similar to the behaviour on the unmodified surface. There is a bulk water peak at $-0.4°C$, and a surface-water peak at $-19.7°C$. As the bonding density is increased up to 2.44 μm/m^2 (~30% of 8 μm/m^2) the behaviour does not change significantly. As the bonding density is increased to 3.12 μm/m^2 (~40% of 8 μm/m^2) a bulk-water peak is observed, along with a shoulder on the higher-temperature side of the bulk-water peak. This shoulder is similar to the peak observed for water on the unmodified 300 Å silica.

The results of immobilization of an octyldimethyl group on the surface of the 60 Å silica are shown in Fig. 8. At bonding densities of 0.74 μm/m^2 (~10% of 8 μm/m^2) and less, a bulk-water peak at $-0.5°C$ and a surface-water peak at $-21.0°C$ are observed. When the bonding density is increased to 1.71 μm/
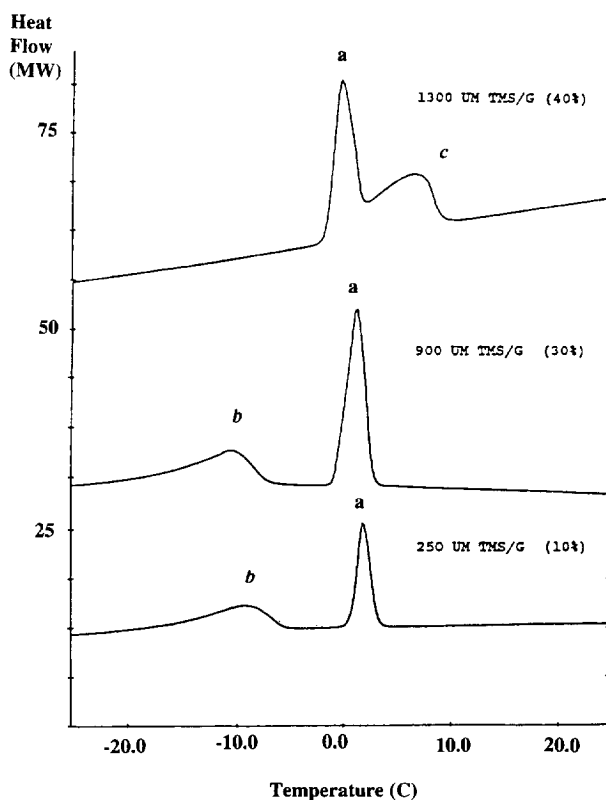

Fig. 7. Effect of the bonding density of trimethylsilane on the behaviour of water on 60 Å silica. Samples are approximately 1 g of water per g of silica. a = bulk-water peak; b and c = surface-water peaks.
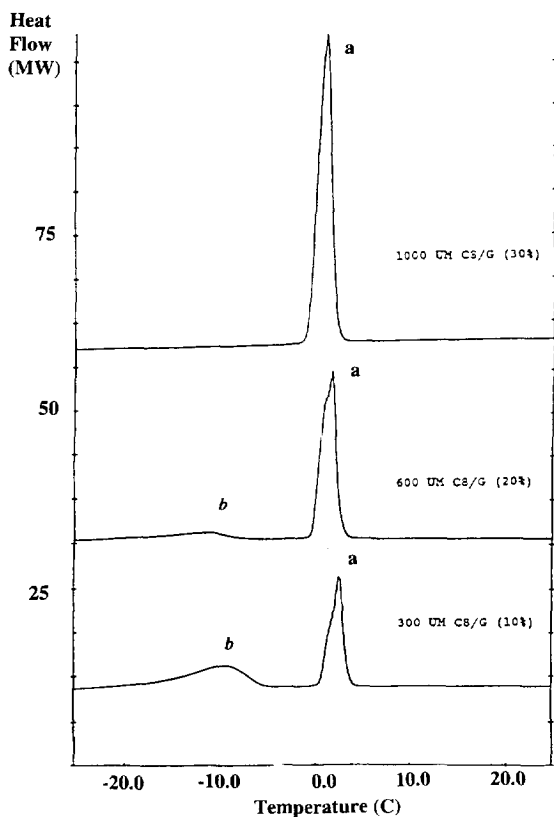
Fig. 8. Effect of the bonding density of octylsilane on the behaviour of water on 60 Å silica. Samples are approximately 1 g of water per g of silica. a = bulk-water peak; b = surface-water peak.
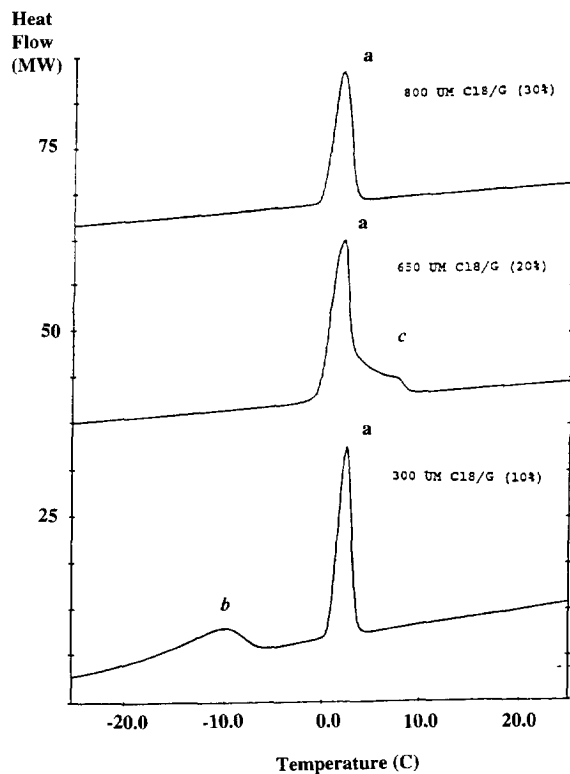

Fig. 9. Effect of the bonding density of octyldecylsilane on the behaviour of water on 60 Å silica. Samples are approximately 1 g of water per g of silica. a = bulk-water peak; b and c = surface-water peaks.

m^2 (~20% of 8 μm/m^2) both peaks are still present, but the surface-water peak is much closer to the baseline. When the bonding density has been increased to 2.28 μm/m^2 (~30% of 8 μm/m^2), the only peak observed is that of the bulk-water peak.

One now looks at the behaviour of water on the octadecyldimethyl-modified 60 Å silica (Fig. 9). At low bonding densities 0.66–0.91 μm/m (~10% of 8 μm/m^2) a bulk-water peak at -0.3°C and a surface-water peak at -20.3°C are observed. In the range 1.48–1.61 μm/m^2 (~10 and 20% of 8 μm/m^2) only the bulk-water peak is observed. The surface-water peak may be present, but is probably not distinguishable from the baseline. When the bonding density is increased to 1.76 μm/m^2 (>20% of 8 μm/m^2) a bulk-water peak is observed in addition to a shoulder

on the high-temperature side of the bulk-water peak. When the bonding density is increased to 2.73 μm/m^2 (~30% of 8 μm/m^2), only the bulk water peak is observed.

The effect of the bonding density of the 3 modifiers on the behaviour of water on the 300 Å silica (Shandon, 300 Å pore, 10 μm particle size, 39 m^2/g specific surface area, 1.38 cm^3/g specific pore volume) are summarized in Fig. 10. The short-chain modifier (trimethyl) can be bonded up to 3.79 μm/m^2 (~50% of 8 μm/m^2), and the behaviour is still the same as that for the unmodified silica, i.e., a shoulder is observed at the high-temperature side of the bulk-water peak. The medium-chain modifier (octyldimethyl) still shows similar behaviour to the unmodified silica up to a bonding density of 1.83 μm/m^2 (~20% of 8 μm/m^2), although the mag-
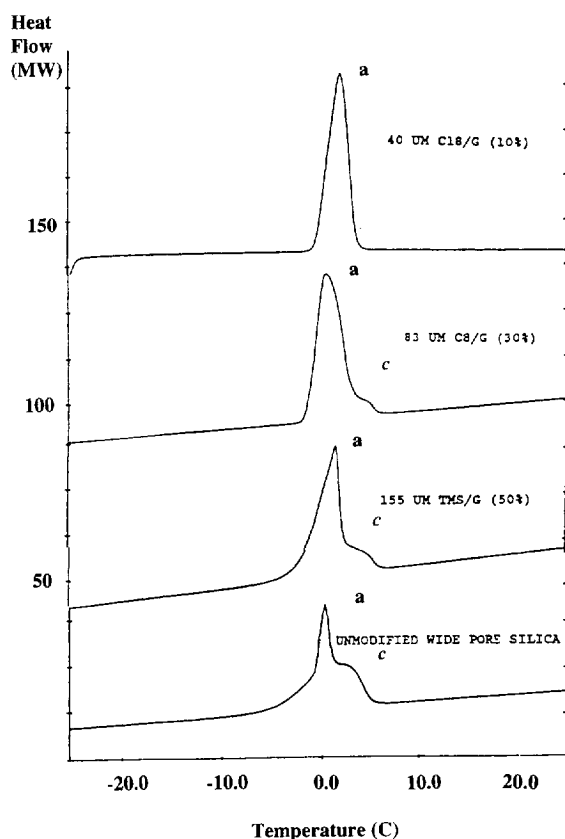
Fig. 10. Effect of the modification of the surface of 300 Å silica on the behaviour of water. Samples are approximately 1 g of water per g of silica. a = bulk water peak; c = surface water peak.

nitude of the shoulder has been diminished. In contrast, the long-chain modifier (octadecyldimethyl) shows that the shoulder has disappeared even at very low bonding densities of 1.06 μm/m^2 (~10% of 8 μm/m^2), and only bulk-water behaviour is observed with no shoulder present.

A comparison of the relative amounts of each modifier needed to change the behaviour of the surface-water peak is a way to study the effect of chain length on the interaction of the water with the surface. On the 60 Å silica, only 20% of 8 μm/m^2 of the octadecyldimethyl group is needed to reach the point where the surface-water peak changes significantly. For the octyldimethyl groups no significant change is observed. For the trimethyl groups 40% of 8 μm/m^2 coverage is needed before a significant change is observed. Thus, the shorter the

chain the more modifier is needed to block the access of the water molecules to the surface. For the very long chains, the chains have a tendency to fold and kink, thereby sterically limiting the access of the water to the surface. The reasons that a significant change was not observed with the intermediate octyldimethyl chains are twofold. Firstly the range in which the behaviour is observed in the octadecyldimethyl case is very small. The range of bonding densities necessary to observe this behaviour in the octyldimethyl case may not have been studied. Secondly, the bonding densities of the octyldimethyl could have been too low to observe this behaviour. The maximum bonding density studied for octyldimethyl was 30% of 8 μm/m^2 and this could have been the region similar to the octadecyldimethyl case between 10–20% of 8 μm/ m^2 where the surface-water peak observed at lower temperatures than the bulk-water peak was too broadened to be discernible from the baseline. Thus, a significant change in the interaction of the water on the octyldimethyl phase may be causing bonding densities greater than 30% of 8 μm/m^2. This is consistent with the behaviour observed for the other two modifiers, and with the behaviour of octyldimethyl observed in the literature [29], where it has been noted that the octyl chain behaves more like the trimethyl group then the octadecyl group. This has been attributed to the inability of the octyl chain to fold and kink like the octadecyl chain.

The properties of water on the surface of the modified 60 Å silica are shown in Table 5. The values are in reasonable agreement with those ob-

Table 5
Properties of water on modified 60 Å silica

	Enthalpy (J/g)	Onset temp. (°C)
Surface water		
Silica	160.43	−21.2
TMCS	157.93	−19.7
C$_8$	159.05	−21.0
C$_{18}$	156.82	−20.2
Bulk water		
Silica	322.61	−1.5
TMCS	322.33	−0.4
C$_8$	322.87	−0.5
C$_{18}$	322.83	−1.5

tained for water on the surface of unmodified silica. The onset temperatures of all 3 peaks are usually within 1°C of the onset temperature of the peaks observed on the unmodified material. Similarly, the peak widths are within 5°C of the peak widths observed on the unmodified silica. For the cases where only bulk-water behaviour is observed, the enthalpy of melting of the bulk-water peak is within 0.5 J/g of the bulk water value (322.6 J/g). The enthalpy of melting of the surface-water peak on the modified 60 Å silica averaged 157.9 J/g, whereas on the unmodified silica the enthalpy of melting averaged at 160.4 J/g. It is interesting to note that the enthalpy of melting of the bulk-water peak observed on the octadecyldimethyl modified silica with bonding densities in the range 1.48–1.61 μm/m^2 (10–20% of 8 μm/m^2) is usually just slightly less than the bulk-water value. This supports the hypothesis that the surface-water peak has been broadened until it has blended into the baseline, and the contribution of the enthalpy of melting of the surface-water peak serves to lower the value of the calculated enthalpy of bulk water.

The properties of water on the surface of the modified 300 Å silica are shown in Table 6. The onset temperature for the bulk-water melt for all modifications was within 0.5°C of the bulk-water peak. For the surface-water peak the onset temperature varied over a 1.5°C range, but since in most cases the surface-water peak was a shoulder on the bulk-water peak, the onset temperature was difficult to determine accurately. The peak width decreased as the chain length of the modifier was increased for

Table 6
Properties of water on modified 300 Å silica

	Enthalpy	Onset temp. (°C)
Surface water		
Silica	159.6	1.9
TMCS	258.0	2.6
C$_8$	303.9	3.3
C$_{18}$	314.2	1.4
Bulk water		
Silica	315.7	−2.1
TMCS	318.8	−2.0
C$_8$	314.5	−1.6
C$_{18}$	317.4	−1.7

both the bulk- and surface-water melts. The enthalpy of melting of the bulk-water peak did not change much compared to the unmodified silica. The enthalpy of melting of the surface-water peak gradually increased from the unmodified silica value up to the value that was close to the enthalpy of melting of the bulk water. The changes observed in the properties of the surface-water peak as the length and bonding density of the modifier are increased is indicative of the ability of the water in the near-surface region to exhibit bulk-water properties when the interactions with the surface silanols are blocked.

5. Conclusions

We have shown that the measurement of the melting behaviour of water in contact with the surface of silica can be used to study the effect of the surface on the properties of water. We have studied this phenomenon as a function of the pore size, surface area and silanol activity of the silica. We have found that the interaction with the surface silanols on one side and the constrictive environment of the pores on the opposite side prevent water molecules from achieving the cooperative association and extended hydrogen-bonding structure associated with freezing to bulk ice. The subsequent melting behaviour thus occurs at a lower temperature and with a lower enthalpy of melting than that observed for the bulk ice/water transition. The investigation of the effect of modifying the surface of silica on this behaviour was useful in understanding the effect of the attenuation of water behaviour by the surface.

The modification of the two silica samples of varying properties with alkyl modifiers of increasing chain length has given an insight into several factors that affect the behaviour of water on silica. The most important conclusion was the confirmation of the importance of the silanol activity on the behaviour of water. The modification of the surface with alkyl silane groups will prevent the interaction of water with surface silanols. We have found that as the bonding density is increased, the surface-water peak is drastically altered, proving that the hydrogen bonding of water with the surface silanols is one of the major reasons for the observed changes in the behaviour of water in the near-surface region. For

the 60 Å silica with very high surface area, the combination of the high surface activity and the curvature of the surface would make it possible for more than one silanol at a time to hydrogen bond with water. This water will be very tightly held. We observed this water freeze and melt at a much lower temperature than bulk water. In the 150 Å silica where the lower silanol activity and surface curvature would allow for maybe only a few silanols at a time to interact with the water, the water in the near-surface region is slightly less constrained and would be able to freeze and melt at a higher temperature than the water on the 60 Å silica, but below that of bulk water. For the 300 Å silica, the low surface area, low surface activity and low surface curvature ensure that the possibility of the water being able to hydrogen bond with more then one silanol is very small. Thus, the water in association with this surface can behave like bulk water, but a small number of hydrogen bonds with isolated silanols on the surface have to be broken before the water in contact with the surface can melt. We believe this to be the source of the shoulder on the higher-temperature side of the bulk-water peak. This hypothesis is supported by the results of the bonding experiments, where, as the surface is deactivated, it becomes possible for the water to interact with only the isolated silanols. It was observed that as the bonding density was increased, with the concomitant decrease in silanol activity, the behaviour of water changed from the behaviour observed on the 60 Å silica to the behaviour observed on the 300 Å silica. This is consistent with the hypothesis that the water-melting peak observed at the melting temperature below that of bulk water was water that was associated with more than one silanol on the surface, which, in conjunction with the curvature of the surface, prevented the water in the near-surface region from achieving the extended hydrogen-bonding structure of bulk water. This also confirms that the shoulder on the high-temperature side of the bulk-water melt is due to the interaction of water with isolated silanols, which does not preclude the formation of bulk-water ice, but does hold the water to the surface. Thus, the behaviour of water goes from the pre-peak which represents the interaction of water with more than one silanol, to the shoulder on the higher-temperature end of the bulk-water peak,

which represents the interaction of water with isolated silanols.

On the silica with high surface activity, the bonding density had to be increased to over 30% of the fully hydroxylated surface with the trimethy modifier to result in marked changes in the behaviour of the surface water, whereas with the octadecyl modifier only 20% needed be modified. Similarly, on the low-surface-activity material the deactivation with ~50% of the fully hydroxylated surface with the trimethyl modifier did not completely remove the influence of the surface on the water, while at bonding densities of only ~15% of the fully hydroxylated surface with C_{18} we observed the disappearance of the surface-water peak. This reflects the importance of the chain length on the deactivation of the surface; the longer chain can sterically hinder access to the surface in addition to being hydrophobic and repelling the water from the silanols.

The deactivation probably occurs first on the most active silanol sites. Some active silanol sites probably still exist on the surface of the modified material since the modifier already on the surface would tend to sterically hinder the reactions of neighboring silanols. Another consideration is whether the modification of the surface is homogeneous, or whether the modifier chains are clustered in patches on the surface. The water behaviour on the 60 Å silica with high silanol activity reflects the gradual isolation of silanols that are still accessible to water, surrounded by alkyl chains. Whether or not this is occurring in clusters or homogeneously over the surface will depend on the initial distribution of the silanol sites, which, at this time, is unknown. The enthalpy of melting, the onset temperature and the width of the peaks for both surface and bulk water were close to the values obtained for water on the unmodified surface or in the pure form. The changes observed were in the types of peaks observed.

These studies have shown that water does interact very strongly with the silica surface, with properties differing from bulk water in the near-surface region. The interaction of the water with the surface persists even when the surface of the silica has been modified, because of the presence of residual silanols. The interaction of solutes with the stationary phase in RPLC will be influenced by the presence of this

water on the surface. This is especially important for solutes that are retained in the region closest to the surface. Since RPLC is not often performed with purely aqueous mobile phases, it would be extremely interesting to study how the melting behaviour of solvent mixtures such as methanol water and acetonitrile water would be affected by close proximity to alkyl-modified and unmodified silica surfaces. This would give a further insight into the interactions at the modified-silica interface that could affect the RPLC separation. We are continuing to investigate the properties of water at the modified silica interface under these conditions.

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