172. Rapid Silylation of a Glass Surface: Choice of Reagent and Effect of Experimental Parameters on Hydrophobicity

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(15.VI.82)

Summary

The silylation of the surface of sodium borosilicate glass was investigated under conditions that might be applied to the fabrication of ion-selective microelectrodes of the liquid membrane type such as are used in physiology. Silylation was carried out for 15 min at different temperatures and with six different silanes. The hydrophobicity was measured and found to be greatest with reaction temperatures of 200–350°, the effectiveness of the different silylating agents being in the (increasing) order: trimethylchlorosilane, tributylchlorosilane, (dimethylamino)trimethylsilane, hexamethyldisilazane, dimethyldichlorosilane, bis (dimethylamino)dimethylsilane. The results give evidence of a catalytic effect of basic amine groups and show that the reactivity of the surface of freshly drawn glass is increased by acid leaching.

Introduction. – A widely used method for increasing the hydrophobicity and electrical resistivity of a glass surface is to make it react with a silane [1] [2]. One use of this reaction *(Fig. 1)*, where the requirements are particularly stringent, is in the treatment of glass micropipettes for ion-selective microelectrodes of the liquid membrane type [3] [4]. Such electrodes are now widely used in medical research (*e.g.* [5] [6]). Most studies of silylation have been done with the least complex glass,
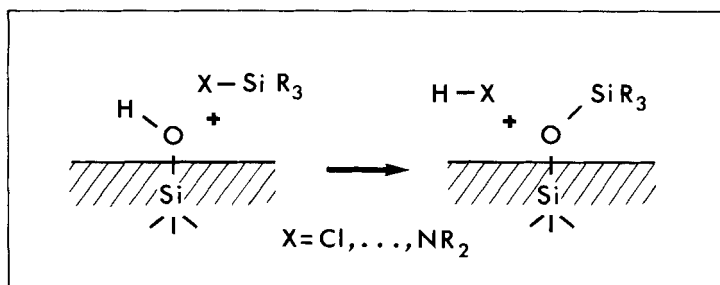

Fig. 1. *Silylation reaction scheme, taking place at the surface of a silicate glass between hydroxyl groups and a silane with reactive group X and nonpolar groups R*

silica itself [7–9], but microelectrodes are normally made of a sodium borosilicate glass, *Pyrex*, which is likely to behave differently. Further, certain promising aminosilanes have only recently become available commercially. Hence, with the ultimate aim of optimizing the fabrication of ion-selective microelectrodes we tested the hydrophobicity of the *Pyrex* surface after treatment with different silanes and under a range of conditions. Based on the results in this paper, a recipe for silylating micropipettes has been developed and is described elsewhere [10].

Experimental approach. – Silylation of a glass surface replaces the H-atoms of the surface hydroxyl groups by covalently bound organosilyl groups, as illustrated in *Figure 1*. We used the following silanes: trimethylchlorosilane (TMCS), tributyl-chlorosilane (TBCS), dimethyldichlorosilane (DMDCS), (dimethylamino)trimethyl-silane (DMATMS), hexamethyldisilazane (HMDS), bis(dimethylamino)dimethyl-silane (BDMADMS). TMCS has been most studied in the past [8] [9]. TBCS [11] [12] was chosen to test the effect of longer non-polar groups (R in *Fig. 1*). DMDCS has two reactive Cl-atoms so theoretically it can react with two surface hydroxyl groups. The aminosilanes DMATMS, HMDS and BDMADMS were chosen to test the effect of a basic leaving group.

On a completely hydroxylated silica surface the concentration of hydroxyl groups is about 8 μmol/m^2 [7–9]. A maximum of only about 4 μmol/m^2 of these groups can react with silanes, because steric hindrance will not allow a greater density of organosilyl groups, even in the case of the least bulky substituent [Si(CH$_3$)$_3$]. With silanes with two reactive groups geometrical constraints further limit the coverage. For surfaces of silica the maximum coverage is obtained after several hours [7] but the hydrophobicity can come close to its final value after the first few minutes [13]. Since, in the fabrication of ion-selective microelec-trodes, a rapid method would be more convenient, we chose to silylate all the samples for only 15 min. *Pyrex* glass was chosen because it is normally used for ion-selective microelectrodes, its electrical resistivity being sufficiently high, its mechanical strength adequate and its softening point not inconveniently high. To measure the hydrophobicity we used a cylindrical surface (the interior of a capillary) and measured the capillary rise (or depression) of distilled water. The cosine of the contact angle θ was then calculated as described in the experimental part. The silylation was carried out in sealed glass ampoules each containing three capillaries and a drop of silane.

Results and discussion. – *1. Comparison of silylating agents. Figure 2* shows the different curves of cos θ as a function of silylation temperature; the more hydro-phobic the surface is the more negative is cos θ. In every case the optimum tem-perature was in the range 220–350°. The silanes gave increasing hydrophobicity in the order TMCS, TBCS, DMATMS, HMDS, DMDCS, BDMADMS. For TMCS and TBCS the reaction is of the same type, but the latter has longer hydrophobic groups. On the one hand, steric hindrance by the butyl chains would tend to reduce the proportion of surface hydroxyl groups that can react, on the other, the non-polar layer will be thicker. Evidently, the effect of the latter predominated in these tests (see [11] [12]).
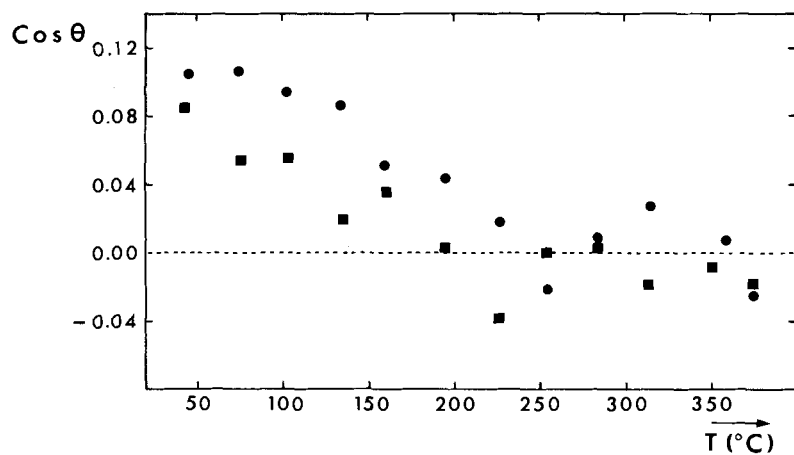
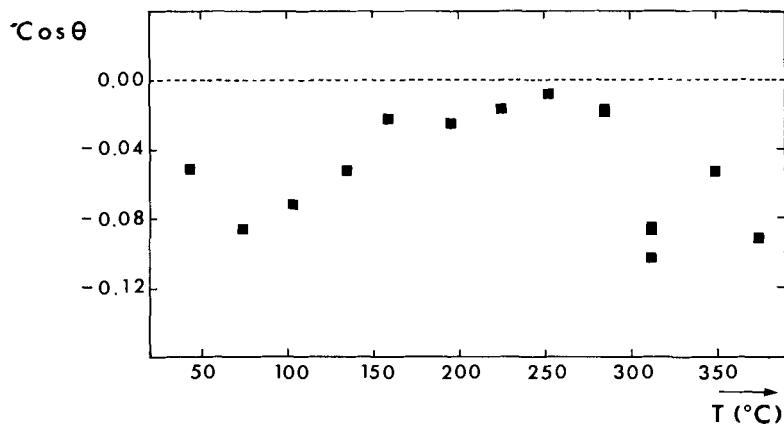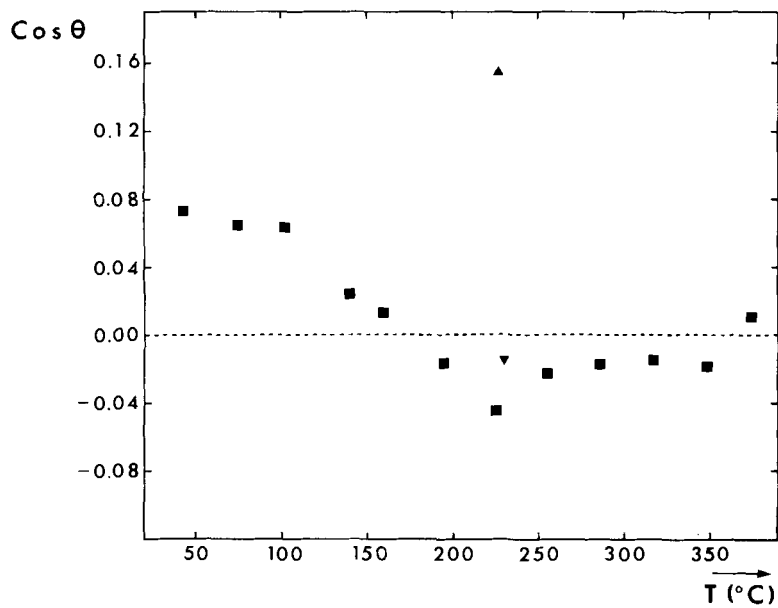Fig. 2a. TMCS (●) and TBCS (■)

Fig. 2b. DMDCS

Fig. 2c. DMATMS. (▲), (▼): values obtained without and with acid leaching after pulling.
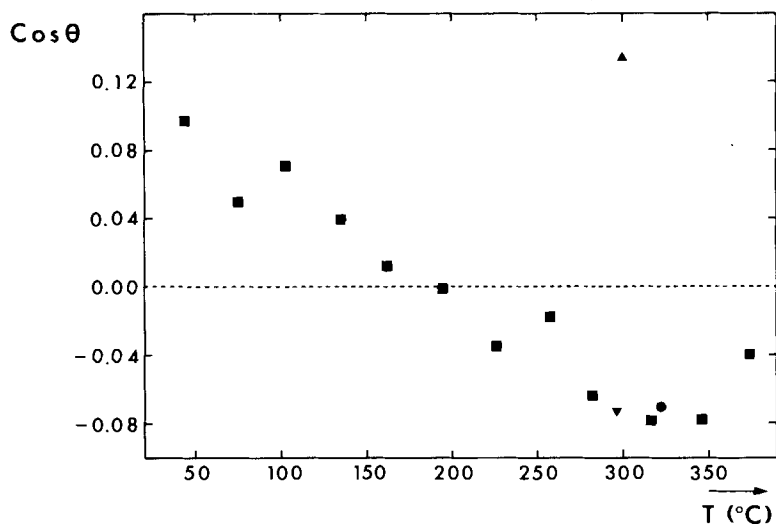
Fig. 2d. HMDS.
(▲), (▼): values obtained
without and with acid leaching
after pulling. (●): value
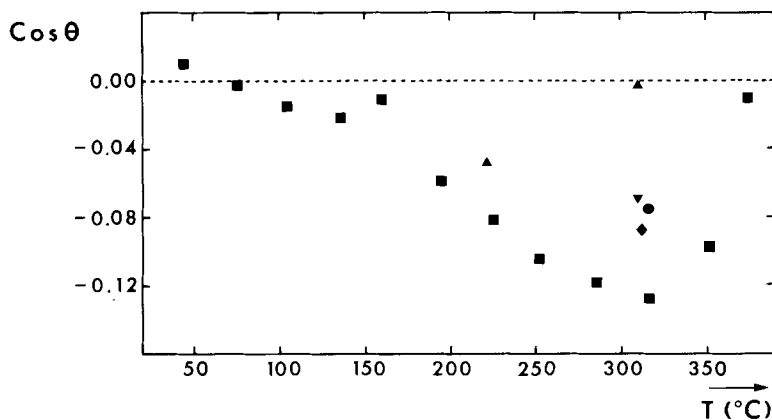obtained with an acid leaching
of 15 min after pulling.

Fig. 2e. BDMADMS.
(▲), (▼): values obtained
without and with acid leaching
after pulling. (◆): value
obtained with acid leaching
for 15 min and (●) for
60 min.

Fig. 2a–e. *Values obtained for cosθ as a function of temperature for each silane.* Each point in the curves is a mean value obtained with three different capillary tubes giving, each one, 5 measurements. Except where mentioned, the capillaries were the standard aged ones that were acid leached for 24 h and washed as described in the *Experimental Part.*

Of the monofunctional silanes used, the aminosilanes were superior to the chlorosilanes. The comparison is most direct in the case of TMCS and DMATMS, where the silylated surfaces have the same structure and the observed difference is presumably due to the degree of completion of the reaction. This accords with earlier observations that silylation of silica can be catalyzed by ammonia [14] [15] or basic amino groups produced in the reaction [15]. A scheme for the mechanism has been proposed [7]. HMDS, which should also give the same final surface structure, produced surfaces even more hydrophobic than those treated with DMATMS, a possible reason being that the by-product with HMDS (NH_3) will

be a better catalyst [7] than that with DMATMS ((CH$_3$)$_2$NH). Two of the silanes were bifunctional: DMDCS and BDMADMS, and these should have given the same structure if both of the functional groups reacted. However, there is evidence that, at least for DMDCS, about 40% of the molecules bound to the surface still have one of the two groups unbound and exposed [9] [16] [17]. These exposed groups would react readily with water, and, if still present, must have reacted with the water used for measuring the hydrophobicity. However, the minimum in cos θ at about 70 °C with DMDCS suggests that there was some polymerization with traces of water in the reaction ampoules. These polymers may have been physically or chemically bound to the surface, producing, in either case, multimolecular layers that could account for the high hydrophobicity. Again, as for the monofunctional silanes, the aminosilane was superior to the chlorosilane.

2. Modification of the glass surface before silylation. For the tests described so far, the capillaries were first leached in HNO$_3$ for 24 h and then washed in distilled water. The intention was to have all the capillaries in the same state of cleanliness and surface structure. However, in making a microelectrode, the capillary is heated to its softening point (for 10–30 seconds), pulled into two micropipettes and rapidly cooled. In the region of interest, the tip of the micropipette, the surface area of the glass is increased and material from the bulk is exposed. The ratio of the new surface area to the original one may be calculated as follows. Let the initial external and internal radii of the capillary be A and B, and the final radii at the tip be a and b. Experimentally it is observed that $a/b = A/B$. For the capillary tube, the ratio of the area of the internal surface S to the volume V is:

$$S/V = 2B/(A^2 - B^2) \tag{1}$$

Similarly at the tip of the pipette, the ratio of the internal surface s to the volume v is:

$$s/v = 2b/(a^2 - b^2) \tag{2}$$

In the pulling, the internal surface area of the volume of glass v is increased by a factor

$$R = (s/v) \cdot (S/V)^{-1}$$

Substituting (1) and (2) gives

$$R = (A - B)/(a - b) \tag{3}$$

Typically, a capillary has $A = 1$ mm, $B = 0.5$ mm and it is pulled into a micropipette whose tip has $a = 0.2$ μm, $b = 0.1$ μm. In this case $R = 5,000$. Thus, all but 0.02% of the surface is newly exposed glass; this surface will have a structure different from that of the surface of acid leached capillaries. It is desirable to silanize micropipettes as soon as possible after pulling because. a) They are less likely to be contaminated by dust. b) Although the bulk resistivity of *Pyrex* is generally thought to be adequate for microelectrodes (but *cf.* [18]) it is reduced when the

glass is hydrated. Because the wall thickness near tip may be less than 1000 Å, it is possible that with time the entire thickness of the wall could become hydrated. c) In practice, it is more convenient to make microelectrodes rapidly.

We therefore made tests on capillaries that were freshly drawn from thicker tubing, silylating the surfaces at temperatures that had been found to be optimum for the washed capillaries. In these experiments the new surface area was only about three times that of the initial surface area. However, from what has been previously established about the surface of glass, even the 'old' parts of the surface must have had a structure similar to that of the newly exposed glass. As the glass is heated, physically adsorbed water is driven off above ca. 100°. Above 200° dehydroxylation begins; above 400°, still well below the softening point of Pyrex (850°), it will proceed rapidly [8] [9] [19].

The results are shown by additional points in Figures 2c–e. When the glass was silylated after heating and pulling, without any intermediate treatment, $\cos \theta$ tended to be positive, and, in addition, the scatter in the values (for a given silane) was greater than for the washed capillaries. When the capillaries were acid-leached for 15 min before silylation (but after drawing) $\cos \theta$ was brought most of way down to its previous value; the treatment was virtually complete in 1 h. After either pulling or heating, the surface of the glass would have lacked reactive hydroxyl groups. In addition, there will have been an increase in the concentration of alkalis and oxides at the surface, either by heat-facilitated diffusion [20] or, as the surface area increased, by bulk movement of glass. Subsequently, some of the more volatile components may have evaporated or reacted with air [19]. Hence, acid leaching is useful not only to protonate siloxane groups, but also to remove many of the components that would otherwise tend to reduce the electrical resistivity of the surface. It will do this either by exchanging alkali cations for protons, or by dissolving oxides and salts.

Conclusion. – The results show that on Pyrex, as on silica, aminosilanes react better than chlorosilanes. Within these two classes, silanes with two functional groups produced surfaces more hydrophobic than those produced by monofunctional silanes. As expected, the surface of Pyrex is more dependent on its history than that of silica: after it is drawn, acid leaching for 15 min greatly favors the reaction.

Experimental Part

A few hundred capillary tubes of Pyrex (Corning USA, code 7740) were cut into 3.5 cm lengths. The mean internal radius was 0.38 mm (S.D. 0.01 mm). The tubes were then acid-leached in HNO_3 (Merck, 60%) for 24 h, rinsed 3 times with water distilled in glass and dried overnight at 60° in a flow of N_2. The silylation was carried out in Pyrex ampoules, internal diameter 4 mm and body length about 55 mm. The ampoules were washed and dried in the same way as the capillaries. Three capillary tubes were placed in each ampoule and a drop of silane added. The ampoules were then placed in liquid N_2, evacuated to 10^{-2} Torr, and sealed. The sealed ampoules were heated in the oil jacketed chamber shown in Figure 3 for 15 min, then opened and the capillary tubes washed with ether and dried overnight at 60° in a flow of N_2. For the experiments on freshly drawn capillaries, Pyrex tubes with an internal diameter of 3 mm were softened in a vertical oven with a heating element of Pyrox 2000 (CENF/SEAMA, BP6 Fontenay-aux-Roses, F-92260) and pulled down with
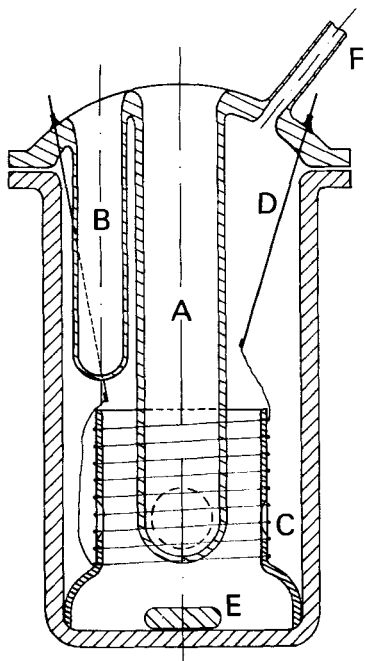
Fig. 3. *Section of the oil bath.* A platinum heating coil C is wound on an annular former that rests on the floor of the oil bath. The oil (*Aseol Trans S* 16-922, CH-3001 Bern) is stirred by magnetic stirrer E and can circulate through holes in the annular former (one of which is shown by a dashed circle). The ampoule containing the capillary tubes to be silanized is placed in cylindrical well A. The temperature is monitored by a thermocouple in well B. Tube F conducts oil vapours away from the apparatus and allows the oil to expand. The temperature was the same, to within 1°, at all points in well A. The platinum heating coil was connected to tungsten wires D which were sealed in the glass. The lid of the oil bath was clamped in position. The total height of the apparatus was 8 cm.

a weight to an internal diameter of about 0.3 mm. The silanes used were obtained from *Fluka AG* (CH-9470 Buchs) apart from the TBCS which was obtained from *Pfaltz & Bauer,* Inc. (375 Fairfield Ave., Stamford, Conn. 06902 USA).

The apparatus for measuring the contact angle is shown in *Figure 4b.* Filtered, glass-distilled water was contained in a cylindrical polystyrene vessel with a white polyethylene cap C. The silylated capillary tube t was pushed through a hole in the cap, which sealed hermetically, and advanced 5 mm into the water. The pressure in the vessel could be controlled by changing the
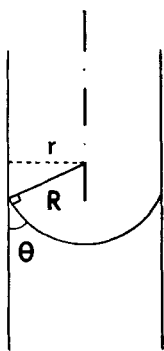

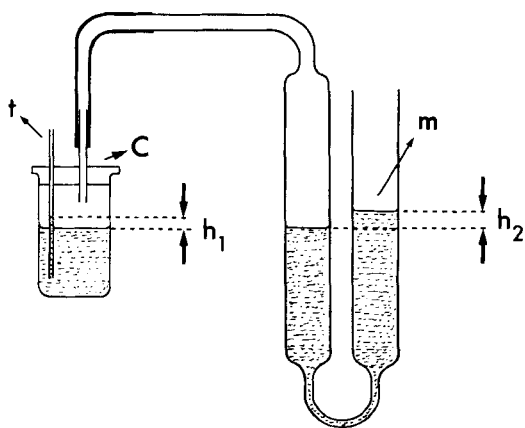Fig. 4a. *Geometrical parameters for calculating contact angles*

Fig. 4b. *Apparatus for determining contact angles* (See text for details)

amount of water in the manometer m. The procedure was to increase the pressure until the water rose up the capillary a few mm beyond the external water level, then to reduce the pressure so that the column fell back to about 1 mm above the external level. The vessel was mounted on a flimsy support and an equilibrium height could be obtained by tapping the vessel vertically with a finger. Heights h_1 and h_2 were measured and the pressure head h across the surface in the capillary was calculated. Water was then removed from the open side of the manometer and another measurement made with the column slightly lower in the capillary. Five to ten measurements were made in this way on each capillary. The water was replaced at least once every 60 min. The temperature was 23°. The cosine of the contact angle (see Fig. 4a) was calculated using the formula $\cos\theta = \rho g h r / 2T$ where θ is the contact angle, ρ is density of water, g is 981 cm $\cdot$ s^{-2}, r is the radius of the capillary and T is the surface tension of the water taken as 72 dynes cm^{-1}.

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