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CHARACTERIZATION OF FUSED-SILICA CAPILLARY TUBING BY CONTACT ANGLE MEASUREMENTS

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SUMMARY

The capillary rise method has been used to obtain contact angle measurements on untreated fused silica and fused silica treated with a variety of deactivating reagents. The contact angle data were used in the construction of Zisman plots which allowed characterization of the wettability of the surfaces by their critical surface energies. The wettability of raw fused silica was found to be widely variable which adversely affects attempts to fully deactivate the surface. Hydrothermal treatment of the fused silica with nitric acid was found to be adequate for cleaning and hydroxylating the surface so as to allow complete deactivation. Simple silylating reagents, cyclic siloxanes, and polysiloxanes covering a wide range of polarity were used and evaluated as deactivating reagents.

INTRODUCTION

The production of high-efficiency capillary columns requires that the stationary phase be deposited as a thin, homogeneous film on the surface of the capillary tubing. To ensure a reasonable column lifetime, the stationary phase film must retain its uniformity through repeated temperature programming and large volume injections of a wide range of solvents. The ability of the column to resist performance degradation due to high-temperature rearrangement or washout of the phase can be dramatically improved by cross-linking or immobilizing the stationary phase inside the column. However, the initial attainment of a smooth, homogeneous film is dependent upon the ability of the stationary liquid to completely wet the surface of the tube wall. The importance of this wettability was first suggested in 1962 by Farre-Rius *et al.*[1] who used the concept of a Zisman plot[2] to determine the critical surface energies of various tubing materials. Since that time, a number of workers have used this method to determine the degree of wetting of glass surfaces by stationary phases[3–8].

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The technique of capillary rise has been used for the characterization of actual capillaries made of glass[4,9-11] and fused silica[11,12].

Because of the relatively high surface energy of fused silica[11], most stationary phases will wet the surface. However, columns coated without deactivation of the surface most often show undesirable activity toward sensitive analytes. Efforts to deactivate the surface while maintaining or enhancing wettability have been at the forefront of capillary column research for many years now.

Wettability of capillary columns by stationary phases can generally be enhanced in one of two ways: roughening the interior surface of the tubing or chemical modification of the surface. Increased roughness has been related to increased wettability by a roughness factor introduced by Wenzel[13] and further discussed by Cassie[14]. Roughening can be accomplished either by etching the inside surface or by deposition of a microcrystalline structure on the surface. These methods are summarized by Lee et al.[15] but are generally not applicable to fused-silica tubing material.

Chemical modification of fused silica is at present the most satisfactory technique for both the deactivation and the enhancement of wettability of the surface. Replacement of surface hydroxyl groups with silyl ether groups (silylation) containing functional groups similar or identical to those in the stationary phase is the most successful. Simple silylating reagents such as disilazanes, disiloxanes, and chlorosilanes have been widely used[16-19]. Other useful deactivating procedures include the thermal degradation of polysiloxane stationary phases[20] and the thermally induced ring opening of cyclic siloxanes[21-23].

In this paper we report the use of the capillary rise method to obtain data for the construction of Zisman plots to characterize both raw fused silica and fused silica subjected to various hydrothermal and deactivation procedures. Consistent with the high degree of surface coverage demonstrated, highly efficient and inert capillary gas chromatographic (GC) columns are produced which show chromatograms free from both reversible and irreversible adsorption of nanogram levels of alcohols, amines and acids.

THEORY

The theory of wetting at the solid–liquid interface is discussed in detail by Shaw[24] and Adamson[25] and summarized[11] elsewhere. For the sake of brevity, we present only the salient features here.

In the wetting of a solid by a liquid, the liquid spreads so as to increase the solid–liquid and liquid–gas interfacial areas while decreasing the solid–gas interfacial area. The surface tension of a liquid, γ_l, is the force per unit length on the liquid surface that opposes the expansion of the liquid surface area.

At a liquid–solid–gas interface there is a characteristic contact angle θ. The contact angle is defined as the angle formed between the tangent to the liquid drop and the solid surface, as drawn through the liquid. For a liquid that completely wets the surface the contact angle is zero. The tendency for the liquid not to wet the surface increases with the contact angle. This situation arises when the cohesive forces of the liquid are greater than the adhesive forces between the liquid and solid. Therefore, the contact angle is an inverse measure of the wettability of the solid by the liquid.
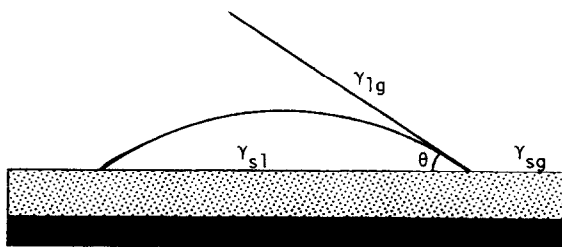
Fig. 1. Drop of liquid in contact with a solid surface showing surface tension of the liquid in equilibrium with its vapor (γ_{lg}), surface tension of the solid in equilibrium with vapor (γ_{sg}), surface tension of the solid in equilibrium with the liquid (γ_{sl}), and the contact angle (θ).

Fig. 1 shows a liquid drop in equilibrium with a solid surface and gas. At equilibrium the three interfacial tensions must balance along the line of contact (Fig. 2) so that:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta \qquad (1)$$

where γ_{sg} is the surface tension of the solid in equilibrium with gas (vapor of the wetting liquid); γ_{lg} is the surface tension of the wetting liquid in equilibrium with its vapor; and γ_{sl} is the surface tension of the solid in equilibrium with the liquid.

Rearranging eqn. 1 gives the so-called Young's equation:

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \qquad (2)$$

Young's equation holds only if the solid is partially wet by the liquid; it fails if the solid is completely wet ($\cos\theta = 1$) or if the solid is not wet at all ($\cos\theta < 0$). The cosine of the contact angle can thus be used as a direct measure of the surface wettability.

The determination of θ (or $\cos\theta$) for liquids in contact with the inner surface of fused-silica capillary tubing can be made accurately by the technique of capillary rise since fused silica is inherently straight.

A capillary tube of radius r is shown immersed in a liquid of density ρ in Fig. 3. If the liquid at least partially wets the tube, the liquid rises. It continues to rise until the force due to the surface tension which is pulling the liquid upward is coun-
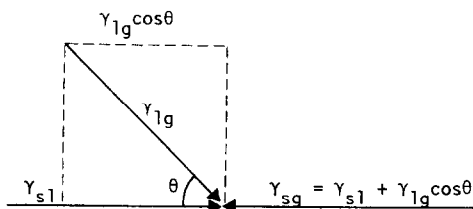

Fig. 2. Vector diagram illustrating the balance of the solid–liquid–gas interfacial tensions at equilibrium.
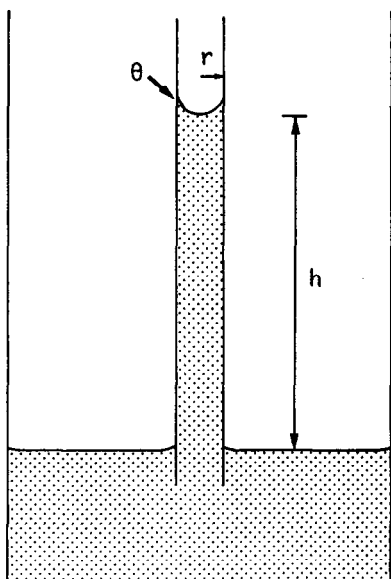
Fig. 3. Diagram of capillary rise experiment showing fused-silica capillary immersed in a reservoir of liquid (methanol–water mixtures).

terbalanced by the downward pull of the force of gravity. The height of rise of liquid in the tube is represented by h and is measured from the surface of the liquid to the lowest point of the meniscus. Only the vertical component of the upward force is effective in causing the liquid to rise up the capillary so that the upward force is $2\pi r \gamma_l \cos \theta$. The downward force is given by $\pi r^2 h \rho g$ where g is the acceleration of gravity. As before, at equilibrium these forces must balance so that:

$$2\pi r \gamma_l \cos \theta = \pi r^2 h \rho g \qquad (3)$$

or

$$\cos \theta = \frac{h \rho g r}{2\gamma_l} \qquad (4)$$

The exact solution for capillary rise[25] includes a correction for the deviation of the meniscus from sphericity and would use the density difference $(\Delta \rho)$ between the liquid and the surrounding vapor instead of simply the liquid density. Good discussions of experimental aspects of the capillary rise method have appeared in the literature[26,27].

A useful parameter for characterizing the wettability of solid surfaces is that of the critical surface tension (or energy), γ_c, as proposed by Zisman and co-workers[2,28]. Critical surface energies are obtained from plots (Zisman plots) of $\cos \theta$ vs. γ_l for various liquids. In most cases these plots are linear and can be extrapolated to zero θ ($\cos \theta = 1$). The γ_l value corresponding to $\cos \theta = 1$ was proposed by Zisman to be characteristic of the particular solid and was designated the critical surface tension. The significance of the critical surface energy is that, in general, liquids with

$\gamma_l \leqslant \gamma_c$ will completely wet the surface while liquids with $\gamma_l > \gamma_c$ will wet the surface incompletely.

If the surface under investigation is heterogeneous, *i.e.*, composed of two types of material, then the observed contact angle for the composite surface is given by:

$$\cos \theta_{obs} = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2 \tag{5}$$

assuming the heterogeneities are effectively averaged and σ_1 and σ_2 are the fractional surface areas of each type of material with their respective contact angles (θ_1 and θ_2). The slopes of the Zisman plots can be used to determine the relative coverage of the two surface types if $\theta = 0$ for one of the surface structures and γ_c is the same for both the heterogeneous surface under study and a surface comprised of entirely type 1 structures, as has been described by Bartle *et al.*[11]. For this limiting case, if $\theta_2 = 0$ for the bare silica surface, then the magnitude of $\cos \theta_{obs}$ will decrease as σ_1 increases. As a result, the relative degree of surface coverage of the type 1 groups on two surfaces can be assessed from the ratio of the slopes of the two Zisman plots by the relationship:

$$\sigma_1 = \frac{\cos \theta_{obs} - 1}{\cos \theta_1 - 1}$$

$$= \frac{\text{slope of Zisman plot for heterogeneous surface}}{\text{slope of Zisman plot for type 1 surface}} \tag{6}$$

This type of approach is used to assess the relative surface coverage of fused silica by different classes of silylating reagents carrying the same functional groups; the more negative the slope, the higher the relative surface coverage.

EXPERIMENTAL

Fused-silica capillary tubing (0.25 mm I.D.) was obtained from Polymicro Technologies (Phoenix, AZ, U.S.A.). Deactivating reagents used were: trimethylchlorosilane, hexamethyldisiloxane, octamethylcyclotetrasiloxane (D_4), octamethylcyclotetrasilazane, tetravinyltetramethylcyclotetrasiloxane, (3,3,3-trifluoropropyl) methylsiloxanes (mixed cyclics, F_3/F_4), octaphenylcyclotetrasiloxane (Ph_4), and tetrakis (β-cyanoethyl) tetramethylcyclotetrasiloxane from Petrarch Systems (Bristol, PA, U.S.A.); hexamethyldisilazane (HMDS) and hexamethylcyclotrisiloxane (D_3) from Aldrich (Milwaukee, WI, U.S.A.); SF-96 (dimethylpolysiloxane) and Carbowax 20M from Foxboro/Analabs (North Haven, CT, U.S.A.); Superox 20M and Superox 4 from Alltech/Applied Science (Deerfield, IL, U.S.A.); and diphenyltetramethyldisilazane (DPTMDS) from Fluka (Hauppauge, NY, U.S.A.).

Fused-silica treatment

Some tubing was rinsed with water followed by methanol while other tubing was subjected to intense hydrothermal treatment at 200°C with 20% nitric acid before deactivating as described elsewhere[29]. In all cases the tubing was dehydrated at 225°C for 90 min under nitrogen flow before proceeding.

To accomplish deactivation, a plug of the deactivating reagent was pushed

through the column with nitrogen. Reagents which are liquids at room temperature were used neat with the column ends flame-sealed immediately after expelling the reagents. Solid reagents were dissolved in either methylene chloride or pentane and the ends were sealed after 30 min of drying under nitrogen flow at 25°C for pentane and 40°C for dichloromethane solutions. Tubing to be heated above 350°C was wrapped in a protective jacket of aluminum foil and purged with nitrogen while

TABLE I

SUMMARY OF CRITICAL SURFACE ENERGY (C.S.E.) DETERMINATIONS FOR VARIOUS DEACTI-VATION REAGENTS AND CONDITIONS

Surface	Deactivant	Fused silica pretreatment	Temp. (°C)/Time (h)	C.S.E. (dyn/cm)	Slope ($\times 10^{-3}$ cm/dyn)
1	None	None		28–48	
2	None	a§		44	
3	None	b§		46	
4	D_4*	a	400/1.5	23	−35
5	D_4*	b	400/1.5	21	−37
6	D_4	b	400/1.5	21	−68
7	D_3*	a	410/2	23	−49
8	D_3	b	400/1.5	21	−9
9	Hexamethyldisiloxane	b	400/1.5	21	−73
10	TMCS	b	400/1.5	21	−53
11	TMCS	a	150/0.5	25	−38
12	SF-96	b	400/1.5	20	−73
13	HMDS	b	400/1.5	20	−77
14	Octamethylcyclotetra-silazane (2% in pentane)	b	400/1.5	20	−80
15	Tetravinyltetramethyl-cyclotetrasiloxane (10% in pentane)	a	390/1.5	22	−54
16	F_3/F_4	b	400/1.5	22	−54
17	DPTMDS	a	400/10	25	−40
18	DPTMDS	b	400/10	26	−58
19	Ph_4 (10% in dichloromethane)	a	400/1.5	29	−49
20	Tetrakis (β-cyanoethyl) tetramethylcyclotetra-siloxane (2% in dichloromethane)	b	280/16	32	−24
21	Cyclic mixture**	b	400/1.5	28	−46
22	Polysiloxane***	b	400/1.5	21	−65
23	Carbowax 20M (2% in dichloromethane)	b	280/16	43	−8
24	Superox 20M (2% in dichloromethane)	b	280/16	44	−16
25	Superox 4 (0.25% in dichloromethane)	b	280/16	34	−14

* Measured with homologous series of alkanes.
** 7% Tetrakis (β-cyanoethyl)tetramethylcyclotetrasiloxane, 7% Ph_4, 2% tetravinyltetramethylcyclo-tetrasiloxane, and 84% D_4-2% in dichloromethane.
*** 7% Cyanoethyl, 7% phenyl, 1% vinyl, 85% methyl polysiloxane–2% in pentane.
§ Treatment a: water followed by methanol rinse. Treatment b: HNO_3 at 200°C for 10 h.

TABLE II

SURFACE TENSIONS (γ_l) AND DENSITIES (ρ) OF THE METHANOL–WATER MIXTURES USED IN THE CAPILLARY RISE EXPERIMENTS[30]

Composition methanol–water	γ_l (dyn/cm)	ρ (g/ml)
100:0	22.1	0.792
90:10	24.9	0.820
75:25	28.3	0.859
70:30	29.7	0.872
60:40	32.6	0.894
50:50	34.9	0.916
25:75	45.8	0.962
20:80	51.6	0.967
10:90	58.5	0.982
0:100	72.0	1.000

others were placed in an oven directly and heated at 10°C/min to various final temperatures and held for various lengths of time. After cooling to room temperature, the columns were rinsed with dichloromethane and briefly dried at 100°C under nitrogen flow. The individual conditions are noted in Table I.

The capillary rise method was used to measure the advancing contact angle of methanol–water mixtures on the various surfaces at a temperature of 25° ± 1°C. Surface tensions and densities of the mixtures are listed in Table II. The height of rise of the meniscus from the surface of the liquid was measured to ±0.01 cm with a cathetometer. Approximately 15 ml of solution was placed in a 100-ml color comparison tube and supported on a ring stand. A thermometer was placed through one hole of a three-hole No. 6 rubber stopper, a right angle 1/4-in. open glass tube placed through another hole and a 1/8-in. Swagelok union was threaded through the third hole. Sections of fused silica were held in place in the 1/8-in. union with a 1/8 in. × 0.4 mm graphite reducing ferrule. Frontal illumination against a white background allowed easy location of the meniscus in the capillaries.

RESULTS AND DISCUSSION

In utilizing the contact angle approach for characterizing fused-silica surfaces, there are several characteristics that must be emphasized. First of all, γ_c need not be independent of the probe liquids used and data obtained from Zisman plots using different liquids should not be quantitatively compared. This is apparent from a comparison of surfaces 5 and 6. Secondly, any data point for which cos θ = 1 cannot be used since γ_c must be obtained from extrapolation and finally, the extrapolation to γ_c should be kept short and in the linear region. There are some wettability studies which have appeared in which one or more of these guidelines apparently have been ignored.

The linearity of all the Zisman plots reported in this study was quite good. Correlation coefficients were 0.990 or better for all plots except for surface 7 which had a correlation of 0.98.

As previously mentioned, the exact solution for capillary rise takes into ac-

count a correction for the deviation of the meniscus from sphericity. For capillaries of 0.25 mm I.D., this correction would have added only 0.004 cm to the actual height measured and in all measurements here it was neglected. This factor, along with a small error encountered by not being able to exactly locate the level of the surface of the reservoir when sighting through the glass reservoir, can be corrected for by applying calibration measurements on capillaries of identical diameters with liquids which completely wet the surface[9-12]. Values obtained from eqn. 4 differed by less than 0.01 in cos θ from those obtained using calibration and thus calibration was deemed not necessary.

Critical surface energies and the slopes of the Zisman plots are given in Table I. As seen from the first entry, the critical surface energy of the raw fused silica is widely variable with values ranging from 28 to 48 dyn/cm. The majority of test pieces were determined to have energies in the low to mid 40's. These values are lower than those found by Lee and co-workers[11] who measured surface energies for some tubing to be greater than 72 dyn/cm. It is known that clean glass is a high energy surface[31], but as a result of this high energy the glass surface can easily be converted to a lower energy surface through adsorption and hydration[32,33]. Such processes can certainly occur during the handling and storage of the fused silica and are the probable cause for the discrepancies in wettability noted between different manufacturers of fused silica and also within material from the same manufacturer. This variability is also suspected to be the major factor in irreproducible deactivations and coatings noted by us and others[29,34].

Rinsing the fused silica was effective in restoring a moderately wettable surface (No. 2) but still showed insufficient deactivation (compare surface 4 with 5, 7 with 8, and 10 with 11). Methods to activate the raw fused-silica were investigated[29] and a 20% nitric acid hydrothermal treatment at 200°C for 10 h was found to yield a reproducible high energy surface (No. 3) that could be completely deactivated.

Eqns. 5 and 6 can be used to compare the relative surface coverages for surfaces that have the same γ_c. Comparing the extent of methylation for various deactivating reagents by this approach shows that for surfaces with $\gamma_c = 21$ dyn/cm (surfaces 6, 8, 9 and 10) the degree of coverage appears to decrease in the order hexamethyldisiloxane > D_4 > TMCS > > D_3. For surfaces with $\gamma_c = 20$ dyn/cm (surfaces 12–14) the degree of coverage appears to decrease in the order octamethylcyclotetrasilazane > hexamethyldisilazane > SF-96. It should be noted that the differences among any of these are not large and all are adequate for a high degree of surface coverage. The only treatment which failed to give a high degree of coverage was the D_3 (surface 8).

The high degree of deactivation of fused silica with D_4 is evident from a comparison of surfaces 5 and 6. The equivalence of γ_c for D_4 treated surfaces measured with alkanes (No. 5) and methanol–water mixtures (No. 6) is indicative of the film building tendency of cyclic siloxane deactivants as noted by Blomberg[35] and Lee et al.[36]. As discussed by Kováts and co-workers[9,10], the shielding of a siliceous surface by bonded methyl silyl groups is insufficient to prevent the interaction of polarizable and polar wetting agents (such as the methanol–water mixtures) with the bare silica surface. As a result, as the underlying dipole layer becomes more and more shielded, the difference between γ_c measured with alkanes and γ_c measured with more polar liquids will decrease.
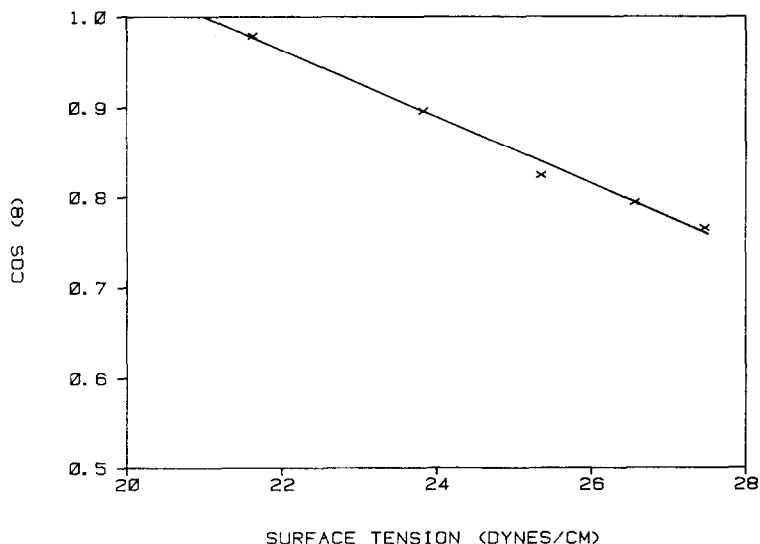
Fig. 4. Zisman plot obtained from fused silica hydrothermally treated with nitric acid and deactivated with D_4 (surface 6).

The Zisman plot for D_4 on an acid treated fused-silica surface (6) is shown in Fig. 4. Fig. 5 shows a chromatogram of the Grob comprehensive test mix II[37] on this same surface coated with OV-73 and cross-linked with azo-tert.-butane (ATB). The excellent inertness of the column is evident from the perfect elution (height and
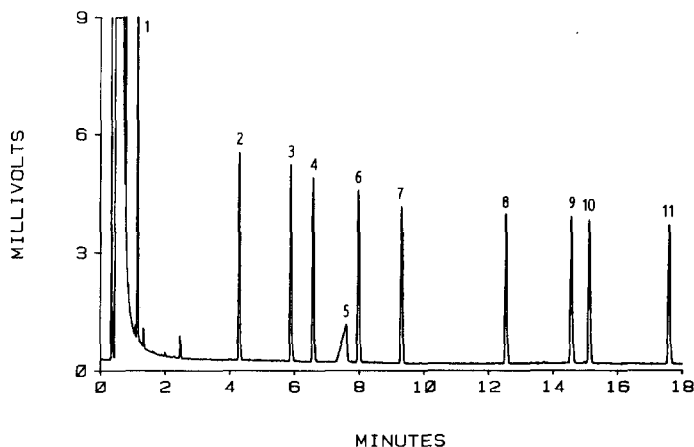

Fig. 5. Chromatogram of Grob Test Mix II. Column: 10 m × 0.25 mm I.D. fused silica, hydrothermally treated with 20% nitric acid at 200°C for 10 h, D_4 deactivated, coated with OV-73 (0.25 μm) and cross-linked with azo-tert.-butane. Temperature programmed from 40° to 130°C at 5°/min with H_2 carrier gas at 50 cm/s (measured at 40°C); 1 μl injection split 20:1; flame ionization detection. Peak identifications: 1 = 2,3 butanediol (2.7 ng), 2 = n-decane (1.4 ng), 3 = 1-octanol (1.8 ng), 4 = 2,6 dimethylphenol (1.6 ng), 5 = 2-ethylcaproic acid (1.9 ng), 6 = 2,6 dimethylaniline (1.6 ng), 7 = n-dodecane (1.5 ng), 8 = methyl decanoate (2.1 ng), 9 = dicyclohexylamine (1.6 ng), 10 = methyl undecanoate (2.1 ng), 11 = methyl dodecanoate (2.1 ng).

symmetry) of all the components of the mixture except for the free acid which is obviously overloaded. Examination of the area counts for the 2-ethylcaproic acid peak shows no evidence of irreversible adsorption.

Surfaces 4, 5; 7, 8; and 10, 11 cannot be compared by using the slopes of the Zisman plots since the critical surface energies are not the same. At first glance this might appear to be a failure of eqns. 5 and 6. However, this is not the case since in obtaining 6 from 5 it was assumed that the surface contained only two types of surface structures; one that was completely wet ($\theta_2 = 0$) and one that was incompletely wet ($\theta_1 > 0$). The values of γ_c obtained for surfaces 4, 7, and 11 are indicative of more than two types of surface structures present on the fused silica. Therefore, eqn. 5 must be expanded to include at least one additional term:

$$\cos \theta_{\text{obs}} = \sigma_1 \cos \theta_1 + \sigma_2 \cos \theta_2 + \sigma_3 \cos \theta_3 \tag{7}$$

where σ_3 is now the fractional area occupied by the type 3 surface and θ_3 is the contact angle characteristic of this surface. To probe the methylated surfaces, methanol–water mixtures were used which covered the range of 22–30 dyn/cm. If we arbitrarily assign σ_1 to be the fractional area occupied by methyl groups ($\gamma_c = 21$ dyn/cm) we see that each of the probe liquids used will incompletely wet σ_1. If σ_2 is the fractional area occupied by the bare silica surface (which is composite but is treated as a single structure, $\gamma_c \approx 45$ dyn/cm) each of the probe liquids used completely wets σ_2. If σ_3 were completely wet by the range of liquids used then eqn. 6 would still hold. Therefore, the surface energy of the structure giving rise to σ_3 must lie within the range of the surface tensions of the probe liquids used. In cases such as this the success of deactivation must be judged by the value of γ_c and not the slope of the Zisman plot. Whatever the surface structure is that gives rise to this phenomenon, the water and methanol rinses were not sufficient to remove it whereas the 20% nitric acid treatment was. This type of hydrothermal treatment then appears to be a necessary precaution to not only fully hydroxylate the surface[29] but also to clean it.

The surface energy of fused silica can be increased from 21 dyn/cm by the use of deactivants with functional groups more polar than methyl groups. Surface 16 was deactivated with (3,3,3-trifluoropropyl) methyl cyclic siloxanes which yields a surface compatible with the trifluoropropyl containing phases such as OV-210 and OV-215[22,38].

Higher surface energies are obtainable by utilizing deactivants with phenyl substituents. The entirely phenyl substituted cyclic tetramer (Ph$_4$) gave a critical surface energy of 29 dyn/cm. Diphenyltetramethyldisilazane (surfaces 17 and 18) is an excellent silylating reagent for introducing some phenyl substitution onto the surface. The conditions used here for the fused silica are analogous to those developed by Grob and Grob[17] for glass. As expected, the surface which was acid treated prior to deactivation is superior to the rinsed surface. We have used this deactivation procedure with only a 90 min hold at 400°C successfully with OV-73 as the liquid phase.

Recently there has arisen some controversy over the use of DPTMDS in improving wettability of glass and fused silica surfaces. Rutten et al.[39] have claimed that silylation with DPTMDS at temperatures of 400°C yields a surface identical to that formed when HMDS is used due to the loss of phenyl groups by DPTMDS. Our

results clearly demonstrate the increased wettability resulting from silylation with DPTMDS (surface 18 over surface 13) at least with fused silica as the substrate. These quantitative results are in agreement with the recent qualitative studies of Grob and co-workers[40,41].

The most polar cyclic siloxane we have used for deactivation is the tetrakis (β-cyanoethyl)tetramethylcyclotetrasiloxane (surface 20). A reaction temperature of 280°C for 16 h gives a good deactivation with a surface energy of 32 dyn/cm.

The Carbowax pyrolysis procedure of Cronin[42] was studied and compared with identical treatments for Superox 20M and Superox 4 (surfaces 23–25). The Carbowax 20M and Superox 20M both give very high surface energies which would be wettable by most stationary phases commonly used in fused-silica capillary columns. However, the temperature limit of a Carbowax 20M or Superox 20M pre-treated column would now be that of the deactivation layer (about 250°C) and not that of the stationary phase. Also, the polarity of columns coated with the more non-polar phases is affected by the polyethylene glycol (PEG) pretreatment. For these reasons the PEG type deactivating procedures are not commonly used. There is a current interest in our laboratory in the use of these materials for the deactivation of fused-silica columns for supercritical fluid chromatography where the increased strength of the mobile phase as compared to GC minimizes the observance of column polarity changes and where column temperatures rarely exceed 150°C. Preliminary results with Carbowax 20M deactivation coupled with a cross-linked film of OV-1701 are quite encouraging[43].

Because of its higher molecular weight (4×10^6), Superox 4 has been used for production of glass and fused-silica columns of moderate to high polarity[44–46]. In our experience Superox 4 does not yield surfaces with as high a surface energy as Carbowax 20M or Superox 20M. Solutions of Superox 4 used for dynamically coating the capillaries for deactivation were more dilute than the Carbowax 20M and Superox 20M solutions due to the very high viscosities of the Superox 4 solutions.

The final comparison to be made is between the use of an intermediate polarity phase for polysiloxane degradation type deactivation *versus* a mixture of cyclic siloxanes. The stationary phase was synthesized utilizing cyclic siloxanes as the starting materials by a procedure described elsewhere[47]. The phase was cyanoethyl–phenyl–methyl–vinyl polysiloxane (cyanoethyl analog of OV-1701) (7:7:85:1). The mixture of cyclics used for deactivation was made to give equivalent percentages of each functional group from tetrakis (β-cyanoethyl)tetramethylcyclotetrasiloxane, tetra-vinyltetramethylcyclotetrasiloxane, Ph_4, and D_4. As seen from a comparison of surfaces 21 and 22, the use of the cyclic mixture yielded a fused-silica surface of mod-erately high energy which produced a stable and efficient column when coated with the phase. The polysiloxane degradation of the phase yielded a surface with very low energy (equivalent to methylation with a high surface coverage, see surface 6, etc.) which could not be coated efficiently with the phase. A similar phenomenon was noted for OV-17 on fused silica by Verzele *et al.*[48]. Presently we are unable to explain this observation.

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