# CORRELATIONS OF SURFACE MEASUREMENTS WITH THE CHROMATOGRAPHIC PERFORMANCE OF CHEMICALLY MODIFIED GLASS CAPILLARY COLUMNS

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SUMMARY

  Wetting phenomena for different liquids were studied on various surfaces "tailored" by the permanent bonding of selective monolayers of silanes to the inner wall of glass capillaries. Surfaces were characterized by graphing the cosine of advancing contact angle on differently modified glass against liquid surface tension. The thicknesses of coated films of stationary phases, measured chromatographically, were found to be in good agreement with those calculated from the Fairbrother–Stubbs equation. However, the presence of the monolayers significantly alters the surface characteristics of the glass, and the chromatographic performance of capillary columns the reflects the film homogeneity, which was found to be a sensitive function of the chemical similarities between the surface structure and the phase. The mechanism of compatibility proposed earlier for the wettability of glass capillary walls is discussed in terms of both the surface phenomena described and a molecular model of the modified surface.

INTRODUCTION

  Surface wetting phenomena are among the most important subjects of study in chromatography. To achieve high separation efficiencies with gas chromatographic columns, a uniform and homogeneous stationary-phase layer on the supporting solid must be obtained. Wetting phenomena are particularly critical for glass capillary columns, and these problems have been discussed in a review article by Novotny and Zlatkis[1]. In the same way, improved wettability would also be beneficial for ordinary chromatographic materials (diatomaceous earths, silica gels, glass beads, etc.) in terms of better efficiency and deactivation. According to the theoretical model of Giddings[2], a solid support is first coated with a thin layer of the stationary phase, if this process is allowed by the surface wettability, before any further accumulation of the liquid into the pores takes place.

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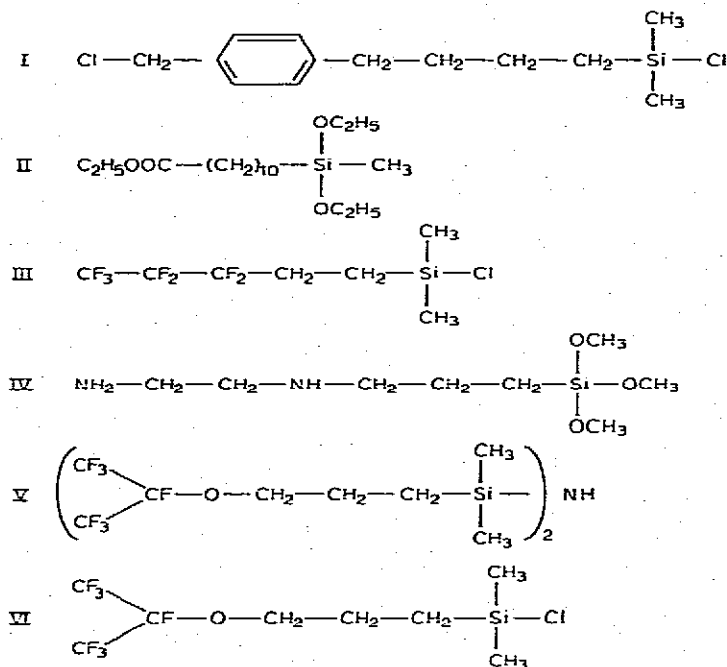
While wettability problems with glass capillary columns can be solved to a certain degree by the general approach of increasing the roughness of the glass surface[3,4] with corresponding decrease of liquid contact angles on thermodynamic grounds, the molecular basis of wetting cannot be overlooked. Based on our previous experimental evidence[4,5] a general surface model for modified glass has been suggested[1] in which a permanently bonded monolayer should be attached to the silica framework, while the "exposed" portions of the attached molecules should be available to comply with the polarity or other property of a given stationary phase. While hydrophobic monolayers prepared by simple trialkylsilylation can be used with non-polar phases[4], only limited success was achieved with more polar substrates because of the unavailability of suitable silanes. Recently, however, a universal experimental realization of this above model has been described[6], in which dimethylchloro[4-(4-chloromethylphenyl)butyl]silane (I) is reacted with the surface hydroxyl groups; the benzylic chlorine atom is then replaced, in subsequent reactions, by suitable groups compatible with the stationary phase. Only qualitative proof of the validity of this approach was presented[6] as reflected in the improved efficiency of glass capillary columns coated with several polar stationary phases.

Consequently, the main objective of the present work has been to verify the compatibility concept[1] in a more quantitative fashion. If it indeed implies that chemical similarities between the wall of capillary columns and the stationary phase are conducive to an efficient spreading of the latter, such phenomena should be reflected in the surface characteristics. Therefore, the contact angles of various liquids on differently "tailored" surfaces were measured together with respective surface tensions where necessary, and these were then correlated with chromatographic measurements. It is found that both chromatographic efficiencies and measurements of the average film thickness[7] in glass capillary columns strongly support the validity of the compatibility concept. A discussion of the molecular basis of wetting is presented, and a model of the surface is used to explore relevant phenomena at the molecular level.

EXPERIMENTAL

Soda-glass capillaries, 14–25 m · 0.2 mm I.D., were filled with a solution of compound I in dry benzene and the surface groups were allowed to react before washing with benzene and acetone. Further reactions of the surface-bonded –CH$_2$Cl groups[6] were then carried out by: (a) hydrolysis with potassium carbonate in tetrahydrofuran–water before successive washings with a series of solvents of decreasing polarity; (b) treatment as in (a) followed by esterification of the hydroxyl groups with benzoyl chloride and subsequent washing as in (a); (c) reaction with potassium cyanide before washing as in (a); and (d) reaction with a weak solution of ammonium hydroxide before washing as in (a).

Other capillaries were filled with benzene solutions of: (e) diethoxymethyl-(10-ethoxycarbonyldecyl)silane (II); (f) 3,3,4,4,5,5,5-heptafluoropentyldimethylchlorosilane (III); (g) N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (IV); and (h) a 1:1 mixture of 1,3-di(3-heptafluoroisopropoxypropyl)tetramethyldisilazane (V) and (3-heptafluoroisopropoxypropyl)dimethylchlorosilane (VI); after reaction, the capillaries were washed with benzene and acetone. In a capillary, treated (i) as in (h), hydrolysis was carried out by means of an HCl solution in methanol (in order to yield

I $\quad Cl-CH_2-$ ⟨benzene ring⟩ $-CH_2-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-Cl$

II $\quad C_2H_5OOC-(CH_2)_{10}-\overset{\overset{\displaystyle OC_2H_5}{|}}{\underset{\underset{\displaystyle OC_2H_5}{|}}{Si}}-CH_3$

III $\quad CF_3-CF_2-CF_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-Cl$

IV $\quad NH_2-CH_2-CH_2-NH-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle OCH_3}{|}}{Si}}-OCH_3$

V $\quad \left( \overset{CF_3}{\underset{CF_3}{}}CF-O-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}- \right)_2 NH$

VI $\quad \overset{CF_3}{\underset{CF_3}{}}CF-O-CH_2-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}-Cl$

different types of surface hydroxyl groups), and followed by washing with methanol and acetone. All capillaries were finally dried by passing dry nitrogen gas at 50 .

Procedures described elsewhere were used to prepare (j) acetone-washed[8]; (k) chromic acid-washed[1]; and (l) silanized[7] 20 m · 0.2 mm I.D. capillaries.

*Physical measurements*

The surface tensions of stationary phases and stationary phase solutions were measured by the capillary-rise method using capillaries (k) above; calibrating liquids were analytical grade toluene and chloroform.

Contact angles were measured by the capillary-rise method on segments of the columns later used in coating experiments. The meniscus height was measured with a cathetometer with the tangent to the centre of the meniscus normal to the perpendicular in both surface-tension and contact-angle measurements.

Densities and viscosities were measured with a pyknometer and a Ubbelohde suspended-level viscometer, respectively[7].

*Coating of capillary columns*

The dynamic method was used, as described previously[8], with the coils hanging vertically. The required plug velocity for a given film thickness was calculated from the Fairbrother–Stubbs equation[7-9] using values of the physical properties listed in Table I.

*Gas chromatographic measurements*

Capacity-ratio and column efficiency measurements were made on a Varian Model 1400 gas chromatograph with modified injector and detector manifold. Injec-

TABLE I

PROPERTIES OF 10% v/v STATIONARY-PHASE SOLUTIONS AT 25°
For details of the surface treatments, see Experimental.

| Stationary phase | Solvent | Density $(kg/m^3)$ | Surface tension $(10^{-2} N/m)$ | Viscosity $(g/m \cdot sec)$ | Chemical treatment of the glass surface where zero contact angles are obtained |
|---|---|---|---|---|---|
| Ucon oil 50-HB-2000 | Toluene | 883 | 2.80 | 1.39 | (a), (c), (i) |
| 2,2'-Oxydipropionitrile | Toluene | 880 | 2.79 | 0.70 | (a), (c) |
| Dinonyl phthalate | Toluene | 873 | 2.80 | 0.66 | (b), (e) |
| Triethanolamine | Methanol | 821 | 2.32 | 0.84 | |
| Silicone oil OV-210 | Acetone | 824 | 2.12 | 0.80 | (f) |
| 1,2,3-Tris(cyanoethoxy)propane | Methanol | 822 | 2.25 | 0.75 | (c) |

tions of 1 μl of benzene headspace were made with nitrogen carrier gas, a split ratio of 1:200, and injector and detector temperatures of 130°. Specific retention volumes, $V_g$, for 2,2'-oxydipropionitrile, Ucon oil 50-HB-2000, and OV-210 silicone oil were determined with previously described equipment[7], and film thicknesses, $d_f$, were derived by combining values of the capacity ratio, $k$, and $V_g$ measured at the same temperature.

## RESULTS AND DISCUSSION

### Contact angles

Characterization of the chemically modified capillary surfaces was attempted by plotting $\cos \Theta$ (where $\Theta$ is advancing contact angle, Tables I and II) against $\gamma$ (surface tension) for various stationary phases, stationary-phase solutions, and miscellaneous liquids[10,11]. Untreated (i.e. merely acetone washed) glass shows effects expected of a heterogeneous surface (Fig. 1). A slightly greater degree of wetting ($\Theta = 0$, $\cos \Theta = 1$) is evident with this glass as compared to the literature value[12] of the critical surface tension, $\gamma_c$ (the maximum value of $\gamma$ at which $\Theta = 0$ (ref. 10)), obtained for Pyrex glass, but there is wide scatter in this graph. Autophobic effects[13,14] apparently operate for the esters di(2-ethylhexyl) sebacate and dinonyl phthalate.

On the other hand, surfaces treated by silanization with trimethylchlorosilane; compound III; a mixture of V and VI; V and VI followed by hydrolysis with HCl; I treated first to yield hydroxy structures and then followed by reaction with benzoyl chloride; and I followed by reaction with ammonia, all gave more regular $\cos \Theta$ vs. $\gamma$ behaviour (Figs. 2–6, and Tables II and III). The autophobic behaviour of esters is generally suppressed, and straight lines with good correlation coefficients (Table III) may be drawn through the points for which $\gamma$ (liquid) is greater than $\gamma_c$ (surface). The intercept on the $\cos \Theta = 1$ axis gives the value of $\gamma_c$ (Table III); for our surfaces covered with surface bonded $-Si(CH_3)_3$, $-Si(CH_3)_2CH_2CH_2CF_2CF_2CF_3$ and $-Si(CH_3)_2-CH_2CH_2CH_2CH_2-C_6H_4-CH_2OOC-C_6H_5$ groups, these values are very close to $\gamma_c$ for corresponding monolayers and crystal structures reported in the literature (Table III), so that a fairly complete coverage of the surface is suggested. The gradients of the rectilinear plots shown in Figs. 2–6 are all similar.

TABLE II

CONTACT ANGLES ON CHEMICALLY TREATED SODA-GLASS SURFACES AT 25°

For details of the surface treatments, see Experimental.

| Stationary phase or standard liquid | Density (kg/m³) | Surface tension (10⁻² N/m) | Contact angle (±10°) on variously treated soda glass | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | (a) | (b) | (c) | (d) | (e) | (f) | (g) | (h) | (i) | (j) | (k) | (l) |
| Silicone oil SF-96 | 954 | 2.06 | 12 | 0 | 19 | 23 | 21 | 27 | 20 | 25 | 16 | 0 | 0 | 0 |
| Ucon oil 50-HB-2000 | 1051 | 3.57 | 0 | 0 | 0 | 27 | 59 | 46 | 33 | 52 | 25 | 0 | 0 | 38 |
| 2,2'-Oxydipropio-nitrile | 1045 | 4.81 | 20 | 28 | 27 | 59 | 60 | 65 | 59 | 73 | — | 42 | 0 | 72 |
| Di(2-ethylhexyl) sebacate | 912 | 3.22*** | 22 | 20 | 35 | — | 27 | — | — | — | — | 31 | 22 | 36 |
| Dinonyl phthalate | 964* | 2.88 | 17 | 15 | 24 | 16 | 23 | 39 | 0 | 43 | 0 | 30 | 15 | 35 |
| Triethanolamine | 1119 | 4.90 | 20 | 26 | 36 | 50 | 66 | 64 | 58 | 73 | 56 | 21 | 0 | 61 |
| Silicone oil OV-210 | 1190 | 2.19 | 10 | 0 | 0 | 16 | 0 | 38 | 0 | 28 | 39 | 0 | 0 | 0 |
| 1,2,3-Tris(cyano-ethoxy)propane | 1114 | 5.19§ | 37 | 44 | 30 | 50 | 78 | — | — | — | — | 44 | 30 | 67 |
| Formamide | 1129** | 5.79** | 31 | 37 | 27 | 61 | 74 | 65 | 50 | 77 | 67 | 0 | — | 59 |
| Water | 997** | 7.20** | 41 | 63 | 45 | 81 | 78 | 85 | 62 | 92 | 56 | 33 | — | 68 |
| Glycerol | 1258** | 6.29** | 33 | 45 | 41 | 68 | 77 | 85 | 59 | 88 | 67 | 14 | — | 71 |
| Toluene | 863** | 2.74** | 0 | 0 | 0 | 0 | 0 | 40 | 0 | 40 | 0 | 0 | 0 | — |
| Methanol | 787** | 2.22** | — | — | — | — | — | — | — | 0 | — | — | — | — |

  * Value from ref. 33.
 ** Values from refs. 34 and 35.
*** Value from ref. 36.
  § Based on θ = 30° on chromic acid-washed glass (ref. 37).
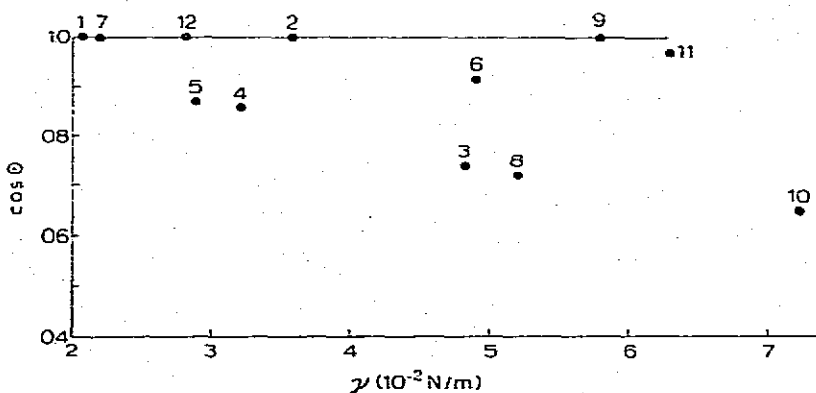


Fig. 1. Graph of cos θ against γ for acetone-washed glass (treatment (j)). 1 = Silicone oil SF-96; 2 = Ucon oil 50-HB-2000; 3 = 2,2'-oxydipropionitrile; 4 = di(2-ethylhexyl) sebacate; 5 = dinonyl phthalate; 6 = triethanolamine; 7 = silicone oil OV-210; 8 = 1,2,3-tris(cyanoethoxy)propane; 9 = formamide; 10 = water; 11 = glycerol; 12 = toluene; 13 = methanol; 14 = 10% v/v Ucon oil 50-HB-2000 in toluene; 15 = 10% v/v 2,2'-oxydipropionitrile in toluene; 16 = 10% v/v dinonyl phthalate in toluene; 17 = 10% v/v silicone oil OV-210 in acetone; 18 = 10% v/v 1,2,3-tris(cyanoethoxy) propane in methanol; 19 = 10% v/v silicone oil in toluene.
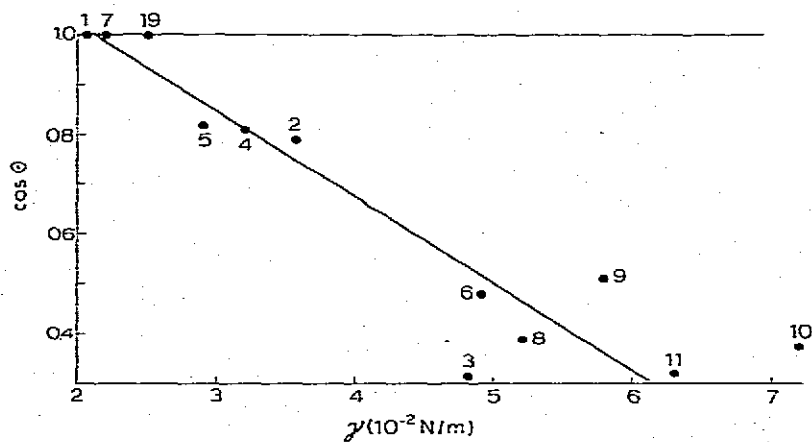
Fig. 2. Graph of cos Θ against γ for silanized glass (treatment (l)). For explanation of the numbers see legend to Fig. 1.
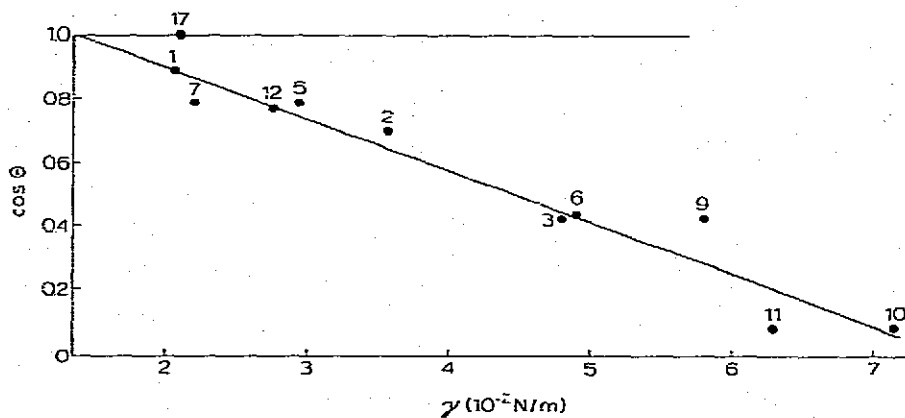


Fig. 3. Graph of cos Θ against γ for glass with bonded –Si(CH₃)₂CH₂CH₂CF₂CF₂CF₃ groups (treatment (f)). For explanation of the numbers, see legend to Fig. 1.
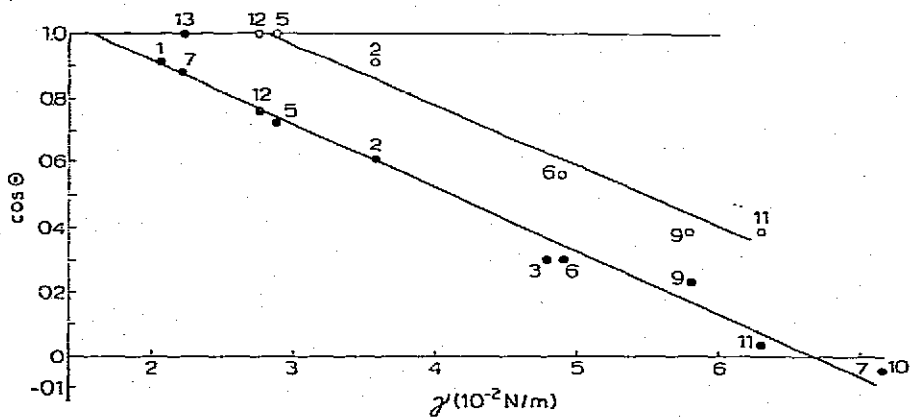


Fig. 4. Graph of cos Θ against γ for glass with (●) bonded –Si(CH₃)₂CH₂CH₂CH₂OCF(CF₃)₂ groups (treatment (h)), and for glass similarly treated and then hydrolyzed (treatment (i)) (○). For explanation of the numbers, see legend to Fig. 1.
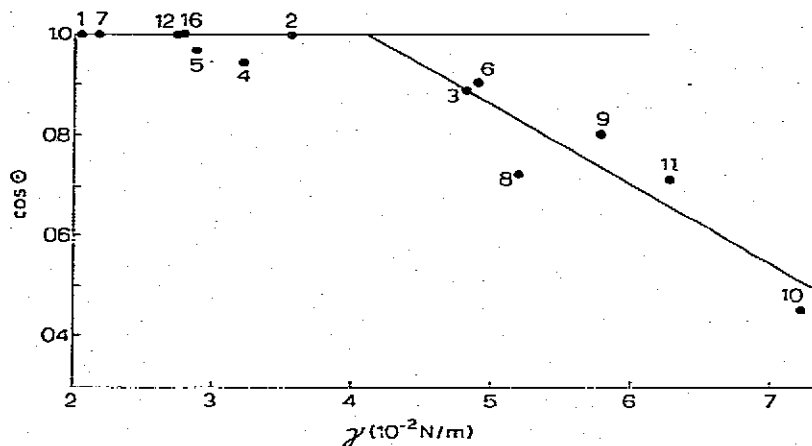
Fig. 5. Graph of cos $\Theta$ against $\gamma$ for glass with bonded $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2OOC-C_6H_5$ groups (treatment (b)). For explanation of the numbers, see legend to Fig. 1.

On the other hand, surfaces covered with $-Si(CH_3)_2CH_2CH_2CH_2CH_2-C_6H_4-CH_2OH$ and $-Si(CH_3)_2CH_2CH_2CH_2CH_2-C_6H_4-CH_2CN$ groups show rectilinear cos $\Theta$ vs. $\gamma$ plots (Figs. 7 and 8), but with smaller negative gradients than the earlier graphs (Table III). $\gamma_c$ for both is approximately $3.5 \cdot 10^{-2}$ N/m. Esters show some degree of autophobia on both surfaces, and 2,2'-oxydipropionitrile still shows an appreciable $\Theta$ on the surface containing cyano groups.

Anomalous cos $\Theta$ vs. $\gamma$ relationships were observed for surfaces treated with compounds II and IV. It should be noted that a multilayer surface coverage is expected with these compounds due to the formation of polymers, and complicated solvation
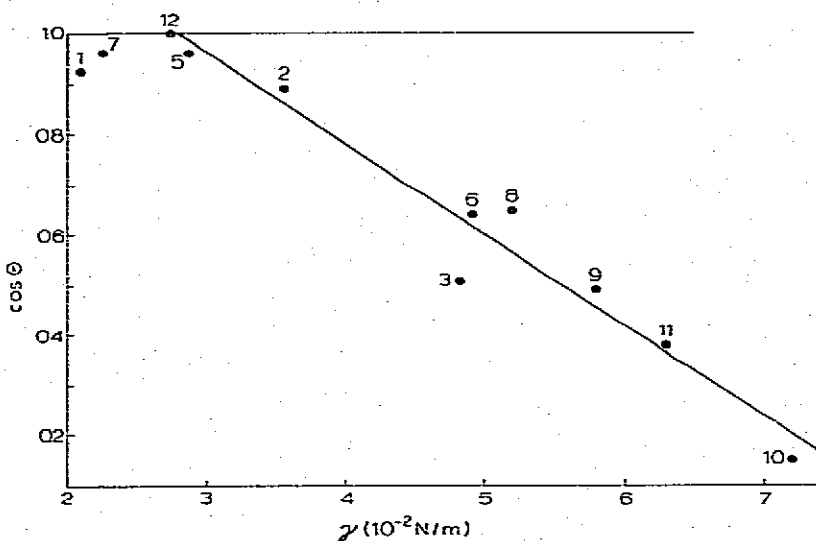
Fig. 6. Graph of cos $\Theta$ against $\gamma$ for glass with bonded $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2NH_2$ groups (treatment (d)). For explanation of the numbers, see legend to Fig. 1.

TABLE III

DATA DERIVED FROM GRAPHS OF cos $\Theta$ AGAINST $\gamma$ FOR CHEMICALLY TREATED SODA-GLASS SURFACES

| | *Treatment* | | | | | | | |
| | *(a)* | *(b)* | *(c)* | *(d)* | *(f)* | *(h)* | *(i)* | *(l)* |
|---|---|---|---|---|---|---|---|---|
| Gradient/mN$^{-1}$ | $-7$ | $-16$ | $-7$ | $-18$ | $-17$ | $-20$ | $-19$ | $-18$ |
| $10^2 \gamma_c$/Nm$^{-1}$ | 3.6 | 4.1[*] | 3.3 | 2.8 | 1.5[**] | 1.7[**] | 2.9 | 2.1[***] |
| Number of points | 7 | 6 | 7 | 9 | 11 | 11 | 6 | 9 |
| Correlation coefficient | $-0.90$ | $-0.91$ | $-0.89$ | $-0.98$ | $-0.97$ | $-0.99$ | $-0.99$ | $-0.88$ |

   [*] *cf.* $\gamma_c = 4.3 \cdot 10^{-2}$ N/m (ref. 10) for polyethylene terephthalate; $4.0 \pm 0.2 \cdot 10^{-2}$ N/m (ref. 12) for polyethyleneglycal terephthalate.

   [**] *cf.* $\gamma_c = 1.7 \cdot 10^{-2}$ N/m for surface composed of $-CF_2-$ and $CF_3$ groups (ref. 10).

   [***] *cf.* $\gamma_c = 2.2 - 2.4 \cdot 10^{-2}$ N/m for monolayer composed of $-CH_3$ groups; $2.0 \cdot 10^{-2}$ N/m for $-CH_3$ crystal surface (ref. 10).
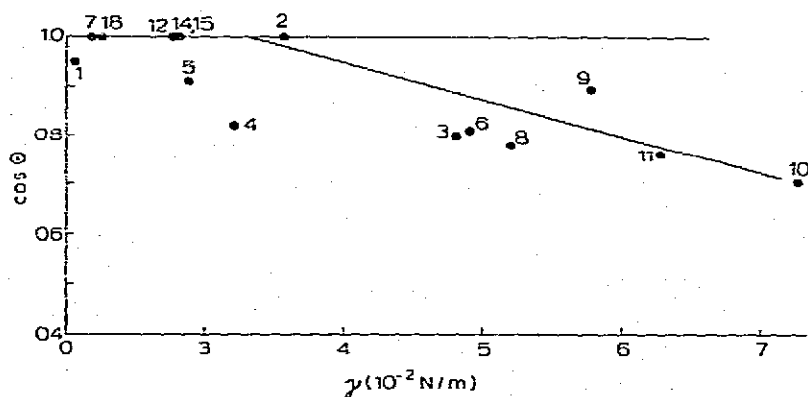


Fig. 7. Graph of cos $\Theta$ against $\gamma$ for glass with bonded $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2OH$ groups (treatment (a)). For explanation of the numbers, see legend to Fig. 1.
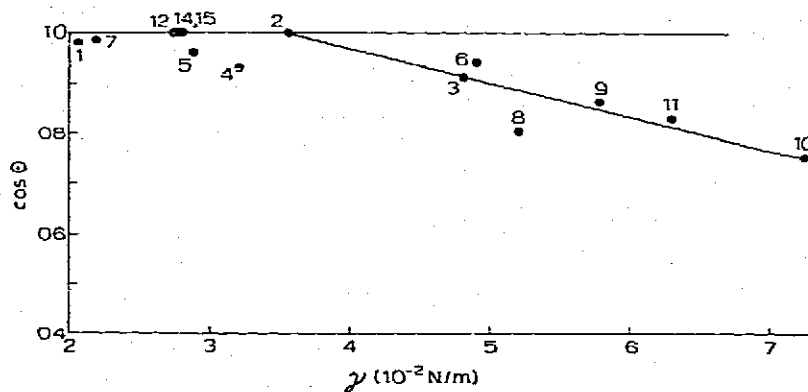


Fig. 8. Graph of cos $\Theta$ against $\gamma$ for glass with bonded $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2CN$ groups (treatment (c)). For explanation of the numbers, see legend to Fig. 1.

phenomena[15] may complicate the measurements. Surface hydrolysis of the ester groups with II may also be implicated.

Hydrolysis of the ester groups in capillaries with bonded $-Si(CH_3)_2CH_2CH_2-CH_2CH_2-C_6H_4-CH_2OOC-C_6H_5$ groups was observed and studied in detail (Fig. 9); the rise of the water level in capillary-rise experiments did not follow the Washburn equation[16] as in the case for capillaries in which no surface reaction occurred (e.g. with bonded $-Si(CH_3)_2CH_2CH_2CH_2CH_2-C_6H_4-CH_2OH$ groups —Fig. 9), and continued to increase as the ester groupings were hydrolysed to hydroxyl groups for which the contact angle is smaller and the meniscus height greater. A more rapid increase in level was observed for 0.1 $M$ hydrochloric acid in the ester-bonded capillary, consistent with a greater reaction rate for the hydrolysis. Such observations are, of course, strong evidence for the presence of the ester groups after the sequence of reactions outlined in Experimental.
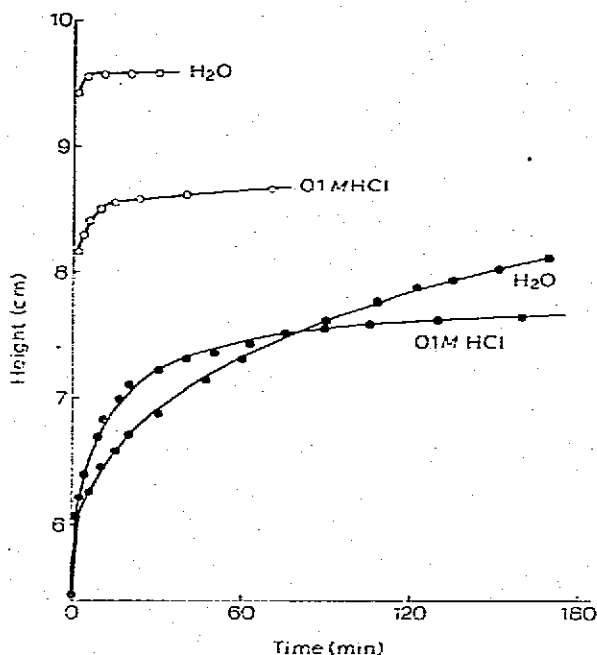


Fig. 9. Graph of height of liquid in capillary tube against time for glass with bonded $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2OOC-C_6H_5$ (●), and $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2OH$ groups ( ).

*Gas chromatographic properties of treated capillaries*

The properties (Table IV) of columns coated with plugs of stationary-phase solutions at coating rates appropriate to give film thicknesses near $1.5 \cdot 10^{-7}$ m demonstrate clearly the importance of column pretreatment to give a surface compatible with the coated phase. For example, 2,2'-oxydipropionitrile coated on untreated glass results in a poor column, but much improved column efficiency is achieved on a surface with bonded cyano groups. In both cases, the measured[7] film thickness is very near

TABLE IV

PROPERTIES OF SODA-GLASS CAPILLARY COLUMNS (I.D. 0.2 mm) WITH VARIOUS TREATMENTS AND COATINGS

For details of the surface treatments, see Experimental.

| Column length (m) | Surface treatment | Bonded surface groups | Stationary phase | Calculated thickness ($10^{-7}$ m) | Measured k-value (benzene) | Experimental thickness ($10^{-7}$ m) | Efficiency for benzene (plates/m) | Remarks |
|---|---|---|---|---|---|---|---|---|
| 14 | (j) | None | Ucon oil 50-HB-2000[*] | $1.8 \pm 0.1$ | 1.15 (53°) | $2.1 \pm 0.1$ | 140 | Visible droplets |
| 11 | (a) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2OH$ | Ucon oil 50-HB-2000 | 1.9 | 1.15 (53°) | 2.1 | 2100 | |
| 14 | (c) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2CN$ | Ucon oil 50-HB-2000 | 1.8 | 1.14 (53°) | 2.1 | 900 | |
| 17 | (i) | $-Si(CH_3)CH_2CH_2OH$ | Ucon oil 50-HB-2000 | 1.5 | 0.86 (53°) | 1.6 | 1100 | |
| 15 | (j) | None | 2,2'-Oxydipropio-nitrile[**] | 1.4 | 0.51 (53°) | 1.4 | 170 | Visible droplets |
| 16 | (c) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2CN$ | 2,2'-Oxydipropio-nitrile | 1.3 | 0.40 (53°) | 1.1 | 1100 | |
| 15 | (a) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2OH$ | 2,2'-Oxydipropio-nitrile | 1.2 | 0.41 (53°) | 1.1 | 300 | Visible droplets |
| 15 | (j) | None | Silicone oil OV-210[***] | 1.4 | 0.30 (53°) | 1.6 | 2300 | |
| 16 | (f) | $-Si(CH_3)_3CH_2CH_2CF_2CF_2CF_3$ | Silicone oil OV-210 | 1.3 | 0.30 (53°) | 1.6 | 1400 | |
| 17 | (b) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2-OOC-C_6H_5$ | Dinonyl phthalate[§] | 1.4 | 1.61 (28°) | 1.1 | 220 | Slight tailing |
| 19 | (e) | $-Si(CH_3)_3(CH_2)_4-COOC_2H_5$ | Dinonyl phthalate | 1.4 | 1.50 (22°) | 1.0 | 360 | Tailing |
| 18 | (d) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2NH_2$ | Triethanolamine | 1.4 | 0.22 (47°) | ... | 60 | |
| 20 | (g) | $-Si-CH_2CH_2NHCH_2CH_2NH_2$ | Triethanolamine | 1.6 | 0.24 (47°) | ... | 150 | |
| 14 | (e) | $-Si(CH_3)_3(CH_2)_4-C_6H_4-CH_2CN$ | 1,2,3-Tris(cyano-ethoxy)propane | 1.5 | 0.34 (53°) | ... | 260 | |

[*] $V_g = 21.7 \cdot 10^{-3}$ m³/kg.
[**] $V_g = 14.8 \cdot 10^{-2}$ m³/kg.
[***] $V_g = 6.7 \cdot 10^{-2}$ m³/kg.
[§] $V_g = 69.2 \cdot 10^{-2}$ m³/kg (ref. 33).

that calculated from the Fairbrother–Stubbs relation, but compatibility of the surface and the stationary phase induces film homogeneity.

Similar results were observed for columns coated with Ucon oil 50-HB-2000 (a polypropylene glycol). Poor efficiency on untreated glass was observed, while considerably improved results were obtained on the $-Si(CH_3)_2CH_2CH_2CH_2CH_2-C_6H_4-CH_2OH$ bonded surface. On the other hand, attempts to make such columns with $d_f$ near $2.5 \cdot 10^{-7}$ m, by changing the parameters of the Fairbrother–Stubbs equation, failed. The range of stabilizing action of the hydroxyl group-containing surface is evidently comparatively limited. Similar effects have been observed[17] for trimethyl-silanized columns coated with SF-96 methyl silicone oil and Apiezon L. Thicker films may be prepared by increasing the surface area (e.g by etching) before a selective treatment.

The compatibility effect is remarkably specific, and complements, and may even over-ride, the requirement that contact angle be small for the stationary phase on the glass surface. For example, 2.2′-oxydipropionitrile has non-zero $\Theta$ (27°) on the compatible surface which it coats successfully: $\Theta$ for this phase on $-Si(CH_3)_2CH_2CH_2-CH_2CH_2-C_6H_4-CH_2OH$ bonded glass is similar (20°), but a much lower column efficiency is observed. Conversely, Ucon oil has $\Theta = 0$ on both hydroxy and cyano surfaces, but a lower column efficiency is observed in this case for the column with the surface containing cyano groups.

The interplay of contact angle and compatibility effects is further demonstrated by columns coated with the fluorinated silicone polymer OV-210. This phase has low $\gamma$ ($2.19 \cdot 10^{-2}$ N/m) and coats untreated glass quite well, so that a column of good efficiency is obtained. However, a surface treated with $-Si(CH_3)_2CH_2CH_2CF_2-CF_2CF_3$ groups has $\gamma_c$ ($1.5 \cdot 10^{-2}$ N/m) below even the $\gamma$ value for OV-210, and contact angle $\Theta = 38°$ for this liquid. The increased compatibility of the phase and fluorinated surface, however, results in only a relatively small decrease in column efficiency. Similarly, another surface compatible with Ucon oil is the one containing hydroxy groups prepared through the hydrolysis of $-Si(CH_3)_2CH_2CH_2CH_2-O-CF(CF_3)_2$ with dilute HCl: although $\Theta$ is 25°, a fairly efficient column can be prepared.

Regrettably, compatibility is not always ensured by merely matching functional groups of the stationary phase with those of the surface: 1,2,3-tris(cyanoethoxy) propane has structure somewhat analogous to that of 2,2′-oxydipropionitrile, has similar $\Theta$ on the cyano-treated glass (30°), but gives poor columns. In the same way, attempts

$$CH_3$$
$$|$$
to find surfaces compatible with dinonyl phthalate through $-Si-(CH_2)_{10}-COOC_2H_5$
$$|$$

and $-Si(CH_3)_2CH_2CH_2CH_2CH_2-C_6H_4-CH_2OOC-C_6H_5$ were unsuccessful. In any case, the observed surface hydrolysis of the ester linkage makes use of these compounds for practical chromatography rather limited. The treatment previously described by us[5], in which an allylsilane layer is bonded to the glass and oxidized in situ appears to provide a suitable surface for dinonyl phthalate. No surface compatible with triethanolamine was found in this study. However, gas-phase etching which was previously shown to aid the spreading of triethanolamine[4] may be combined with a selective treatment in order to bring about better efficiency.

*The molecular basis of compatibility*

A solid surface may alter the structure of an adjacent liquid layer over a distance of up to about $10^{-7}$ m (refs. 18, 19). This phenomenon is thought to be caused by the induction by the solid surface of a molecular long-range orientation in the vicinal liquid. This condition alters the viscosity[20,21], thermal conductivity[22], and dielectric constant of liquid surface zones. These effects cannot be explained on the basis of long-range dispersion forces extended from the solid surfaces, which are calculated to have much smaller effects[23,24]. A more forceful explanation involves molecular rotation restriction in oriented surface zones[25]. For example, the rotational movement of an adsorbed or surface-bonded molecule is restricted about at least one axis, and the intermolecular distance to the next layer in the film is decreased compared with conditions in the bulk liquid in which rotation is free. A reduction in chemical potential is expected, and the decreased distance gives rise to an excess dispersion interaction. In this way, many molecular layers can be built up, but with increasing distance from the solid surface the rotations about other molecular axes become important and stabilizing excess interactions are diminished[25].

Moreover, the stability of certain dispersions has been explained by the existence of an oriented layer, of the liquid crystal type, of alkylbenzene molecules lying parallel to a graphite surface, and extending some distance from it[26]. Boundary layers with specific properties may also be formed for nonpolar compounds under the influence of adsorbed monolayers of polar compounds of similar structure[27]. Boundary layers are thus well-documented for low-molecular-weight materials, and their existence would explain our observations of film stability in capillary columns. The necessary similarity of functional groups in a surface modifying monolayer and the stationary phase may then be explained by molecular packing. This proposal was tested by model building.

*A model of the chemically modified glass surface*

It is usually supposed that the structure of silicate glasses can be represented by the assumptions that the basic units are silica groupings in which alkali and other basic oxides are distributed, and that the whole is bonded together through oxygen atoms. The mean spacing between the slightly irregularly arranged $SiO_2$ tetrahedra is rather wider than the regular spacing in the silica allotrope tridymite which obtains in vitreous silica[28,29]. A glass surface etched by NaOH was reported by Liberti[3] to have a basic silica structure. Accordingly, a model planar silicon oxygen network was chosen to represent a glass surface with standard bond distances[30] (see p. 49). Such a structure could accomodate eight hydroxyl groups per unit area ($10^{-18}$ m², i.e. 100 Å²), but in practice (Table V), smaller numbers are available for bonding, and a figure of four (of which half were assumed geminal) per unit area was taken as best in keeping with other work. A possible model for a chemically modified surface was then constructed by bonding $-Si(CH_3)_2(CH_2)_4-C_6H_4-CH_2CN$ groups through all non-geminal and half of the geminal $-O(H)$ groups of the network (Fig. 10) lower layer. Bonding to geminal groups is unlikely on steric grounds; reduced numbers of silane groups with bulky constituents were found by Unger[31] to bond to glass surfaces (Table V).

Fig. 10 shows that this procedure leads to a surface effectively comprised of fairly widespread cyano groups. Stationary phase molecules with cyano groups such
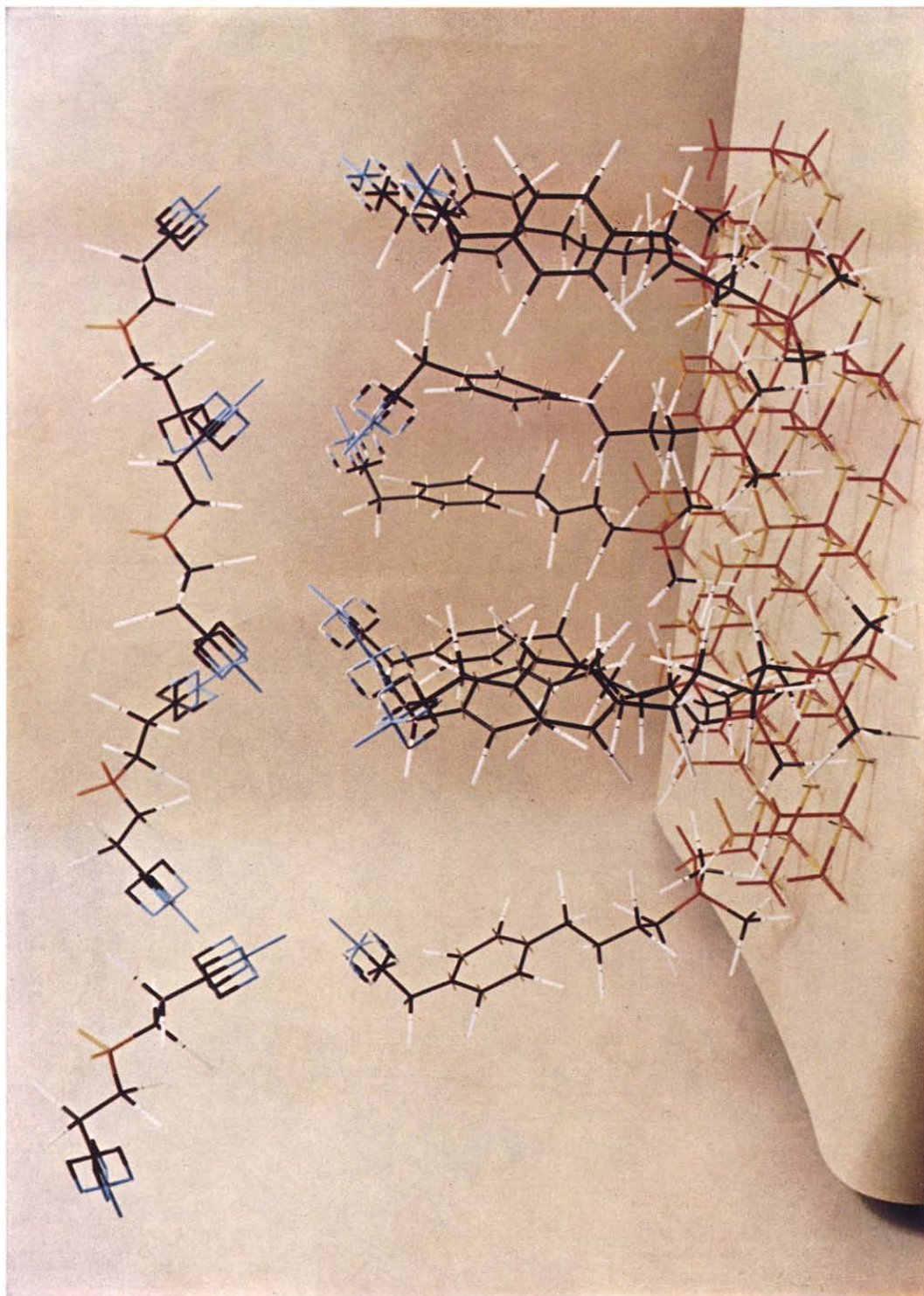
Fig. 10. Model of glass surface with bonded –Si(CH₃)₂(CH₂)₃ C₆H₄ CH₂CN groups coated with 2,2′-oxydipropionitrile. Colour code: red, silicon; yellow, oxygen in basic silica framework; red-orange, oxygen; orange-yellow, oxygen in free silanol groups; white, hydrogen; black, carbon; blue, nitrogen. Lower layer = modified surface; upper layer = first molecular layer of 2,2′-oxydipropionitrile.
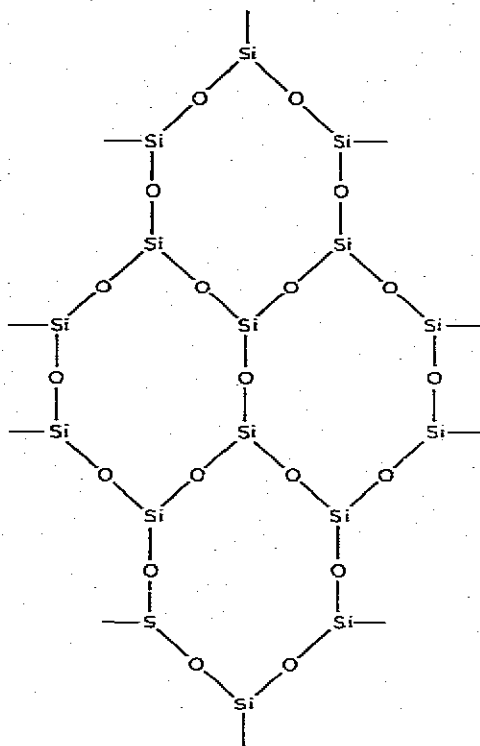
as 2,2'-oxydipropionitrile (upper layer in Fig. 10) adsorbed on such a surface are thus constrained to locations specified by the packing of like groups. Thus, the oriented surface zones necessary for the formation of stable layers of a compatible phase on chemically modified glass may arise.

TABLE V

ESTIMATES OF NUMBERS OF SURFACE HYDROXYL GROUPS PER UNIT AREA ($10^{-18}$ m$^2$ = 100 Å$^2$) ON SILICA SURFACE

| Method | Number per $10^{-18}$ m$^2$ | | | Reference |
|---|---|---|---|---|
| | Isolated | Vicinal | Total | |
| Crystal structure | | | 8 | 38 |
| Model | | | 8 | This work |
| $^2$H$_2$O exchange | 2.5 | 2.5 | 5 | 39 |
| Gravimetry | | | 6.8 | 3 (Etched glass) |
| Reaction with SiCl$_2$(CH$_3$)$_2$, TiCl$_4$ and BCl$_3$ | 1.4 | 3.2 | 4.6 | 40 |
| Reaction with SiCl(CH$_3$)$_3$ | | | 3–4 | 41 |
| Reaction with SiCl$_3$(C$_6$H$_5$) | | | 2.5 | 31 |

CONCLUSIONS

The previously suggested compatibility model for rationalizing wetting phenomena in glass capillary columns has now been tested with a series of monolayers of

different structures and with liquids of different polarities. Although contact angles may be generally decreased through suitable surface modifications, zero values (which are the thermodynamic indication of an ideal wetting) are difficult to achieve. This study underlines the great importance of chemical similarities between the surface and the wetting liquids for the preparation of homogeneous films inside cylindrical glass tubes. It appears that the contact angle and the chemical compatibility interplay in the wetting effect. The chromatographic efficiencies obtained with stationary-phase films on suitably modified monolayers give strong support to the high selectivity of "tailored" surfaces.

Consequently, stationary phases of different polarities can be effectively coated inside glass capillaries, thus creating homogeneous films of the order of $10^{-7}$ m thick. "Compatibility" of the surface and wetting liquid must still be understood in a broader sense: the molecular mechanism of wetting may be attributed to quite complex phenomena among which boundary-induced long-range order is particularly important, and each matching of the "tailored" surface and the wetting liquid should be treated separately. A combination of surface roughness and selective chemical modification appears necessary for inducing better adhesion of thicker liquid films[17]. Temperature changes (e.g. temperature programming in gas chromatography) should theoretically effect the film homogeneity[32] less for a "tailored" surface than for ordinary heterogeneous glass. However, the validity of this prediction has yet to be verified experimentally.

## ACKNOWLEDGEMENTS

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