PREPARATION OF THICK-FILM GLASS CAPILLARY COLUMNS BY THE DYNAMIC COATING PROCEDURE

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SUMMARY

The capacity for non-polar stationary phases of the silanized inner surfaces of glass capillary columns is shown to be restricted to a $2-3 \times 10^{-7}$ m thick film. However, geometrical modification of a soda-glass surface by etching with HCl gas before silanization allows non-polar silicone-oil films to be prepared with average thickness (in good agreement with those predicted from the Fairbrother–Stubbs relation) as high as 14×10^{-7} m. Such films are stable even after conditioning at 190°, and the column efficiencies, near 3000 theoretical plates per meter, were maintained. Van Deemter plots are similar for columns with average film thicknesses between 1 and 14×10^{-7} m, thus suggesting that the surface developed through the geometrical modification is still covered with a relatively thin film of stationary phase.

INTRODUCTION

The distribution of a stationary phase coated on the inner wall of a capillary column as a smooth and uniform film is the main factor in determining the column efficiency. The average film thickness, d_F, is taken into account in the Golay equation[1] since the capacity ratio, k, which appears in the mass-transfer terms is a function of d_F ($k = K/\beta$ and $\beta = r/2d_F$, where K is the thermodynamic partition coefficient, β is the column phase ratio, and r is the column radius). The resistance to mass transfer in the liquid phase, C_L, should increase with increasing film thickness. The C_L term becomes negligible as compared to the resistance to mass transfer in the gas phase, C_G, for very thin films of stationary phases.

In any practical separation problem, both the number of theoretical plates to effect a given resolution and k must be considered simultaneously[2]. It is therefore of considerable practical importance to control d_F over a relatively extensive range, while still maintaining a regular distribution of phase along the entire column length. Thus, while thin-film columns with thermostable phases are essential in the analysis of high-boiling compounds, an increased column capacity (through decreased phase ratio) is often pointed out as a distinct advantage of support-coated open-tubular columns for some applications.

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In the most desirable situation, efficient films of variable thickness should be available with stationary phases of different polarities such as are needed for any particular separation problem. Nevertheless, the usual approaches to the preparation of capillary columns are rather empirical since the unmodified surface does not allow for the controlled deposition of a liquid film. It turns out that both the geometrical and the chemical nature of the capillary inner wall are of great importance in wetting phenomena. Consequently, these are also the factors which determine the spreading efficiency and film thickness.

It is believed that the presence of certain surface structures may influence properties of coated liquids only up to a distance of about 10^{-7} m (refs. 3–5) from the surface. These physical forces which are primarily responsible for the molecular mechanism of wetting are expected to be reduced rapidly with increasing further distance, thus causing the excess of liquid deposited inside the capillary tube, by either the static or the dynamic coating procedure, to form irregular layers, waves, lenses, etc. Now, while a suitable surface modification with functional groups matching the properties of the wetting liquid is important in maintaining a stable thin layer, this approach does not permit formation of thicker stable films[7–8]. In this and previous work [6,7] we have shown that the hydrophobic surfaces of silanized glass columns cannot be coated with stable layers of non-polar liquids with a thickness greater than between 2 and 3×10^{-7} m. We now show, however, that stable, thick films up to at least 14×10^{-7} m of a methylsilicone oil can be obtained if the surface is etched[9] before being modified further by trimethylsilylation.

We have previously reported[6,7,10] that the Fairbrother–Stubbs relation[11] is applicable to the dynamic coating of glass capillary tubes; provided that the surface possesses enough "capacity" for the spreading of a wetting liquid, the film thickness is given by

$$d_F = \frac{rc}{200} \cdot \left(\frac{u\eta}{\gamma} \right)^{\frac{1}{4}} \tag{1}$$

where c is the concentration (vol. %) of the stationary phase in the coating solvent, u is the linear velocity of the coating plug, η is the viscosity, and γ the surface tension of the coating liquid. The film thickness is most conveniently increased by increasing c or u, or a combination of both. The validity of this equation has been carefully examined[7] with thicknesses of about 2×10^{-7} m or less on chemically modified, but unetched glass.

EXPERIMENTAL

Preparation of glass capillary columns

Pyrex and soda-glass capillaries with 0.2 mm I.D. and 15–20 m long were prepared by the usual cleaning and drawing procedures[12,13]. Some of the soda-glass capillaries were etched[9,14] at 350° with pure dry HCl gas, and others with mixtures of either 1% or 10% HCl in nitrogen at the same temperature. All capillaries were then silylated with a mixture of hexamethyldisilazane and trimethylchlorosilane vapours[9], and then coated by the dynamic method at various velocities in order to deposit a stationary-phase film of the desired thickness on the inner capillary wall in accor-

dance with the Fairbrother–Stubbs relation (eqn. 1). Soda-glass capillaries were coated with 10 and 20% v/v solutions of GE SF-96 methylsilicone oil in toluene, and Pyrex capillaries with a 12.8% v/v solution of hydrocarbon grease Apiezon L in cyclohexane.

Chromatographic measurements and calculations

Values of k for benzene with Apiezon L columns were measured as described elsewhere[7], and for the SF-96 column at 28°, with a Varian Model 1400 gas chromatograph with modified injector and detector manifold, both kept at 130°. Nitrogen was used as carrier gas, and 1-μl headspace samples were injected with 1:200 split ratio. Efficiencies were determined for selected columns over a range of carrier-gas velocities calculated from the retention time of methane. Both the numbers of theoretical plates and the k values were again measured after a number of columns had been conditioned overnight at temperatures up to 190°. Experimental film thicknesses at column coating temperature were determined from the formula[7]

$$d_F = \frac{273rk}{2T\rho V_g}$$ (2)

where V_g is the specific retention volume for the stationary phase obtained on a packed column, at the column test temperature T, and ρ is the density of the phase at column coating temperature.

Densities and viscosities were determined, respectively, with a pyknometer and an Ubbelohde suspended-level viscometer[7]; surface tensions were determined by the capillary-rise method and contact angles by the capillary-rise and tilting-plate methods[7]. Values of these physical properties (Table I) were then substituted in eqn. 1 to yield calculated values of d_F for comparison with those measured experimentally.

TABLE I

PROPERTIES OF STATIONARY-PHASE SOLUTIONS AT COLUMN COATING TEMPERATURES

Stationary phase	Temperature (°C)	Solvent	Concentration (% v/v)	Density (g/ml)	Viscosity (10^{-3} kg/m·sec)	Surface tension (10^{-2} N/m)
SF-96 *	25 ± 1	Toluene	10	0.874	1.42	2.53
SF-96	25 ± 1	Toluene	20	0.888	3.14	2.40
Apiezon L **	22 ± 1	Cyclohexane	12.8	0.788	1.81	2.51

* Contact angle = 0 on both etched and silanized, and unetched and silanized soda glass.
** Contact angle = 0 on unetched and silanized Pyrex glass.

RESULTS AND DISCUSSION

Graphs of experimental d_F values against the values calculated, for Apiezon L (Fig. 1) and SF-96 (Fig. 2), show clearly the limited surface capacity of unetched glass. In spite of the hydrophobic nature of the glass surface after silanization
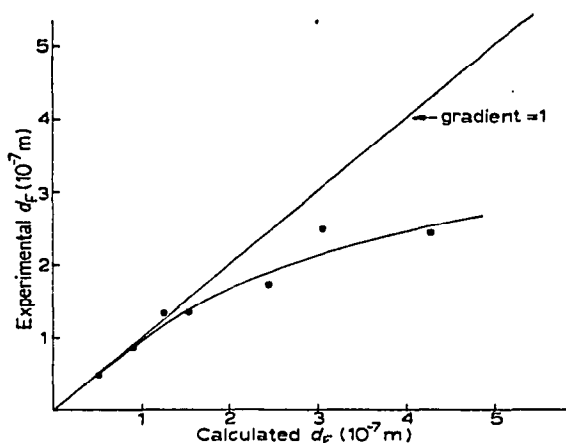
Fig. 1. Graph of experimental film thickness against thickness calculated from eqn. 1 for silanized Pyrex glass capillaries coated with Apiezon L.
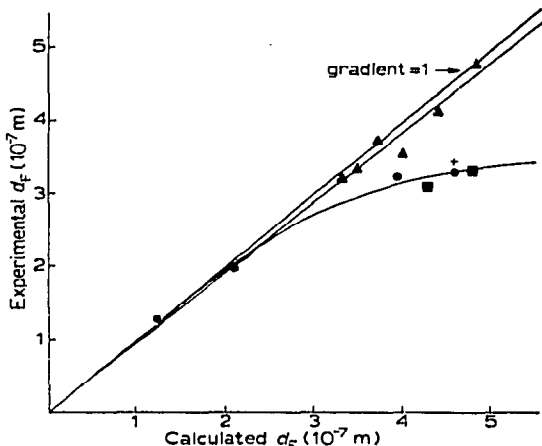
Fig. 2. Graph of experimental film thickness against thickness calculated from eqn. 1 for silanized soda-glass capillaries coated with SF-96 silicone oil. ●, Unetched; +, etched with 1% HCl in nitrogen for 5 h; ■, etched with 10% HCl for 5 h; ▲, etched with pure HCl.

and its chemical compatibility with non-polar stationary phases, the surface adhesion forces[8] are not strong enough to hold a layer thicker than about 3×10^{-7} m. Moreover, etching with the lower concentrations of HCl does not appear to bring about suitable geometrical modification of the surface (Fig. 2).

On the other hand, excellent agreement between theoretical and experimental d_F values was observed (Figs. 2 and 3) for capillaries of which the inner surface areas had been increased through more extensive etching with pure HCl. An etching
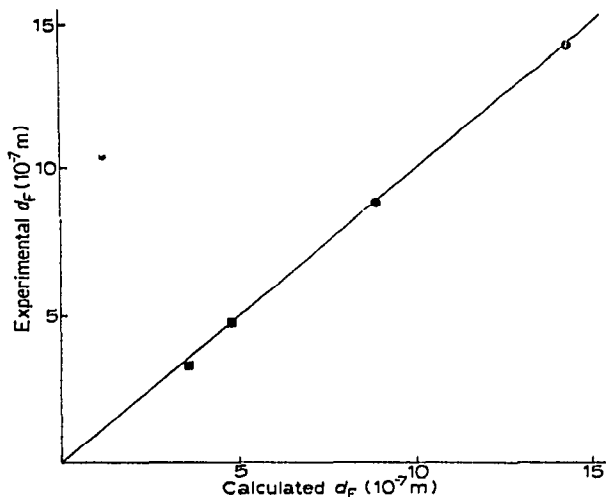

Fig. 3. Graph of experimental film thickness against thickness calculated from eqn. 1 for soda-glass capillaries etched for 5 h with pure HCl, silanized, and coated with SF-96 silicone oil. ■, Coated using 10% v/v solution in toluene; ●, coated using 20% v/v solution.

period of as little as one hour at 350° allowed columns with d_F values up to 5×10^{-7} m to be prepared; thicknesses as high as 14.2×10^{-7} m were obtained for capillaries etched for 5 h. Such capillaries are known to be opaque in appearance[14], and scanning electron microscopy[15] strongly suggests a regularly etched surface with the formation of cavities of the order of 10^{-7}–10^{-6} m deep. The data in Fig. 3, obtained with high stationary-phase concentration (Table I) and coating plug velocities, show that the validity of the Fairbrother–Stubbs relation is apparently not impaired even over the wide range of d_F values reported here. In fact, the upper limit of applicability corresponds to a value of the dimensionless group $(u\eta/\gamma = R)$ of 0.09 (ref. 16), whereas R did not exceed 0.02 in these experiments.

The efficiencies of fifteen columns coated with SF-96 silicone-oil layers with measured d_F in the range 1–15×10^{-7} m, were determined at a linear carrier-gas velocity of 12.0 cm·sec^{-1} and ranged between 2500 and 3600 (mean 3000) theoretical plates per meter; the differences in efficiency reflected merely the usual scatter encountered in the preparation of capillary columns. No significant changes in column efficiency were observed which could be clearly attributed to the film-thickness effect; k values for benzene at 28° ranged from 0.77 to 8.87. Figs. 4 and 5 show that Van Deemter plots measured for three columns with widely varying k values ($d_F = 1.2$, 4.8, and 14.2×10^{-7} m) were almost identical. These measurements were carried out without previous conditioning of the columns at high temperatures; however, no loss in efficiency or change in the HETP vs. carrier-gas velocity curve was observed after overnight conditioning at 190° even for the very-thickest-layer capillary (Fig. 5). A slight decrease in k values (less than 3%) was consistently observed after conditioning and is thought to arise from the removal of the low-molecular-weight material found in most polymeric stationary phases. For example, the original k value of 8.87 for a representative column with $d_F = 14.2 \times 10^{-7}$ m dropped only to 8.54 after conditioning, and this behaviour, coupled with efficiencies near 2500 theoretical plates per meter for a number of thick-film columns, suggests that the stability and regularity of the thick layers are both good.
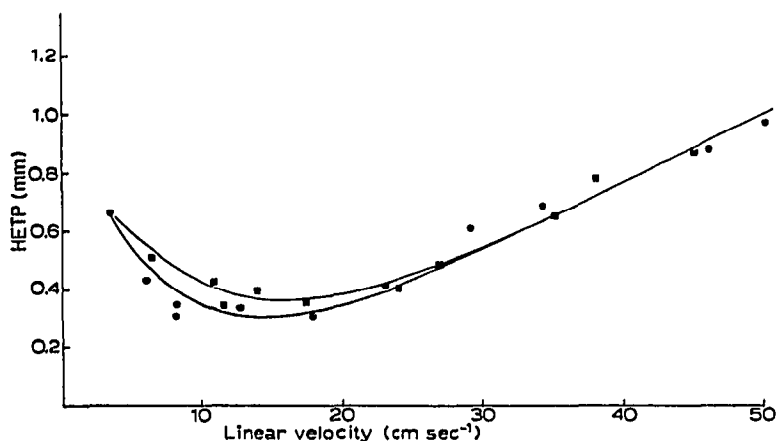

Fig. 4. Van Deemter plots for benzene measured at 28° on capillary columns coated with SF-96 silicone oil; carrier gas, nitrogen. ●, $d_F = 1.2 \times 10^{-7}$ m; ■, $d_F = 4.8 \times 10^{-7}$ m.
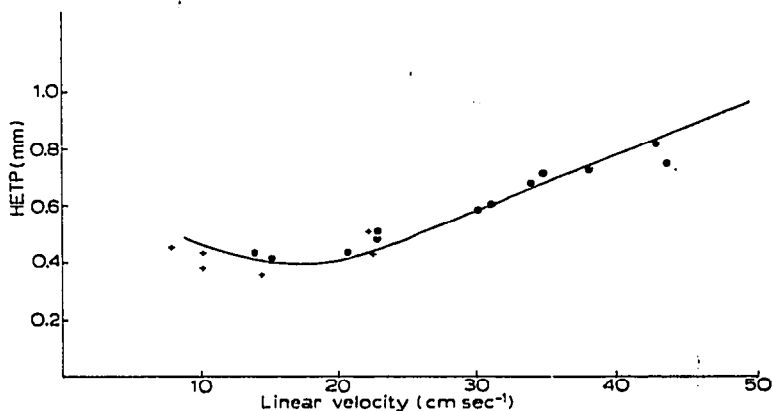
Fig. 5. Van Deemter plot for benzene measured at 28° on a capillary column coated with SF-96 silicone oil with $d_F = 14.2 \times 10^{-7}$ m; carrier gas, nitrogen. ●, Before conditioning; +, after conditioning overnight at 190°.

It should be emphasized that only average stationary-phase film thicknesses can be calculated from our chromatographic measurements, and that virtually nothing is known about the real distribution of the liquid coated on the capillary wall. If the theoretical model proposed by Giddings[17] for the distribution of liquid phases on diatomaceous supports applies here, it may be envisioned that the liquid phase will tend at first to coat on the available irregular (but chemically compatible) surface in a thin layer before filling the cavities created by the etching process. However, this model would be expected to lead to an increasing contribution to the HETP from the resistance to mass transfer in the liquid phase which could no longer be neglected. On the other hand, our observations (summarized in Fig. 4) suggest that C_L is similar over the full range of d_F reported here, and are consistent with apparently thicker average layers corresponding to a greater coverage of the etched surface with a still fairly thin film of the phase.

It has been suggested[13] that the combination of geometrical and selective modification is essential to glass-capillary column technology. While this work is limited to studies of relevant phenomena for a non-polar phase coated on a hydrophobic etched surface, a suitable combination of etching followed by selective chemical treatments[8,18] may be applicable to the preparation of glass capillary columns with controlled efficiency and capacity for a variety of stationary phases.

ACKNOWLEDGEMENTS

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