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INFLUENCE OF SURFACE TENSION ON THE HOMOGENEITY OF THE FILM OF STATIONARY PHASE IN GLASS CAPILLARY COLUMNS

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SUMMARY

The surface tensions of glass, stationary liquid and solvent affect the mode in which the film of a stationary phase is deposited on glass columns. The effects of the surface tensions of polar liquids and of the internal surface finish of the glass capillary formed before coiling on the quality of the film were studied. A procedure involving the so-called wettability coefficient is proposed for the evaluation of capillaries with surfaces modified prior to coating with a stationary phase.

INTRODUCTION

The homogeneous spreading of a stationary phase on the internal wall of a capillary is determined by the surface tensions of the construction material and of the stationary phase used, *i.e.*, by their interfacial tensions. If the surface tension of a stationary phase is lower than the critical surface tension of the solid surface, a homogeneous film of liquid should be created, which covers the entire capillary surface.

ANALYSIS OF THE PROBLEM

Surface tension is included in the relationship for the calculation of the thickness of the liquid film created by coating by means of the dynamic method[1]. The film thickness (assuming the presence of an even layer) depends on the capillary radius, coating velocity and surface tension of the stationary phase[2,3]. FAIRBROTHER AND STUBBS[4] derived the following relationship for the calculation of the film thickness:

$$d_F = \frac{c}{100} \cdot \frac{r}{2} \sqrt{u \frac{\eta}{\gamma}} \ . \tag{1}$$

where d_F is the film thickness, c is the concentration of the coating solution, r is the capillary radius, u is the linear coating velocity, η is the viscosity and γ is the surface tension of the solution. CONCUS[5] expressed the thickness of the film of liquid that remains in the capillary by the following expression:

$$d_F = 1.34 \ r \ (\eta u/\gamma)^{2/3} \tag{2}$$

Novotný *et al.*[2] found that the values obtained experimentally for the thickness of the film of stationary phase on the capillary column wall satisfy eqn. 1.

According to Young's equation[6],

$$\gamma_{23} = \gamma_{13} + \gamma_{12} \cdot \cos\theta$$

where subscripts 1, 2 and 3 indicate the liquid, the gaseous and the solid phases, respectively, and θ is the contact angle, the coating is perfect if the contact angle is zero. Critical surface tensions, for which $\cos\theta = 1$, are given in Table I for glasses

TABLE I

CRITICAL SURFACE TENSIONS OF PYREX GLASS SUBJECTED TO DIFFERENT TREATMENTS

Treatment	γ (dyne/cm)
Washed with acetone	28.0 ± 0.5
Cleaned with chromic–sulphuric acid	44.0 ± 1.0
Etched with NaOH	$32 - 34$
Carbonized according to GROB[12]	41

with various surface finishes[7,8]. It is obvious that the critical surface tension of a glass washed with chromic–sulphuric acid is 60 % greater than that of a glass washed with acetone. A monomolecular layer of impurities, *e.g.*, of water adsorbed on glass, changes the surface tension of the solid surface to such an extent that it causes unsatisfactory coating with liquid phases. If homogeneous coating of the glass capillary surface is to be obtained, then the surface tension of the coating solution should be lower than the critical surface tension of the glass. This requirement is reasonably satisfied during the coating with respect to low values of surface tensions of most solvents (see Table II) and to low concentrations of stationary phase in the coating solution. During the evaporation of the solvent, the surface tension of the solution increases gradually with increasing concentration of the stationary phase up to the value of the surface tension of the pure stationary phase. The values of the surface tensions of some stationary phases are also shown in Table II.

The value of the surface tension depends on the concentrations of the components on the surface of the mixture[6], so that it does not depend on the composition

TABLE II

SURFACE TENSIONS OF SOME SOLVENTS AND STATIONARY PHASES

Solvent	γ (dyne/cm)	Stationary phase	γ (dyne/cm)
n-Heptane	20.4	Squalane	29.95
Benzene	28.9	Polypropylene glycol	31.30
o-Xylene	29.1	Tritone	34.00
Dichloromethane	28.1	Diglycerol	50.30
Tetrachloromethane	25.6	Ucon oil (DLB-100-B)	28.3
Acetone	23.3	Tricresyl phosphate	40.9
Methyl alcohol	22.6	Dioctyl sebacate	32.2
		Bis-(2-ethylhexyl)phthalate	31.3
		Methylsilicone oil	19–20

of the mixture. Therefore, the surface tension can usually be expressed by the additive equation

$$\gamma = \gamma_1 x + \gamma_2(1 - x) = \gamma_2 + (\gamma_1 - \gamma_2)x \tag{3}$$

where γ, γ_1 and γ_2 are the surface tensions of the mixture and of components 1 and 2, respectively, and x is the proportion (w/w) of component 1. In most instances, empirical equations must be used, e.g.:

$$\gamma = \gamma_2 + kx + (\gamma_1 - \gamma_2 - k)x^2$$

or

$$\gamma = \frac{\gamma_2 + (k\gamma_1 - \gamma_2)x}{1 + (k - 1)x} \tag{4}$$

where the values of k are obtained by experimental measurements. In graphs expressing the dependence of γ on the composition of a binary mixture, a maximum or minimum appears mainly with mixtures in which the components have very similar values of γ_1 and γ_2.

The critical surface tension of the internal wall of a glass capillary is therefore decisive in determining the quality of the liquid film of the stationary phase. Glass capillaries with etched surfaces were coated with different stationary phases and values of the critical surface tension of the glass capillary were obtained experimentally. In order to obtain capillaries with the greatest attainable critical surface tension, some of the glass tubes were cleaned with chromic–sulphuric acid and the capillaries were compared. A procedure was suggested for the prediction of the probable properties of a capillary with a modified surface before it has been coated with stationary phase.

EXPERIMENTAL AND DISCUSSION OF RESULTS

Glass capillaries were drawn from tubes of Unihost glass (Czechoslovakia) in an apparatus designed according to DESTY et al.[9], and their radii were measured microscopically. The capillary surface was modified by etching with gaseous hydrogen fluoride produced by the thermal decomposition of trifluorochloroethyl methyl ether[10].

The wettabilities of both etched and non-etched capillaries were determined by measuring the capillary elevation of methyl alcohol in part of the capillary coil. The height of the liquid column was measured on the chord of the circle whose intercepts with the circle were represented by the height of the liquid in the vessel and by the upper meniscus. The capillaries were coated by the dynamic method[1] with the following solutions: 12 % (w/w) of DC-560 in acetone; 10 % (w/w) of PEG 400 in acetone; 6 % (w/w) of diglycerol in methyl alcohol; and 8 % (w/w) of a mixed phase (PEG 400–diglycerol, 1:1 w/w) in methyl alcohol. All the stationary phases were provided by Lachema, N.E., Brno. The surface tensions of the phases and their solutions were measured by the capillary elevation method.

Polyethylene tubes, 1 m long and 2 mm I.D., were packed with Chromosorb W coated with 5 % of DC-560, diglycerol and the mixed phase, respectively.

Glass capillary columns and packed columns were tested on a Carlo Erba gas chromatograph, Model C, equipped with a flame ionization detector at an operating

temperature of 50° for DC-560 and PEG 400 and 58° for diglycerol columns. Nitrogen was used as the carrier gas and its flow-rate was calculated from the retention time of methane.

Measured values of the surface tensions of the stationary phases and their solutions are given in Table III. It is obvious that the surface tension increases during evaporation of the solvent from the film of the solution on the capillary wall,

TABLE III

SURFACE TENSIONS OF PHASES AND THEIR SOLUTIONS AT 25°

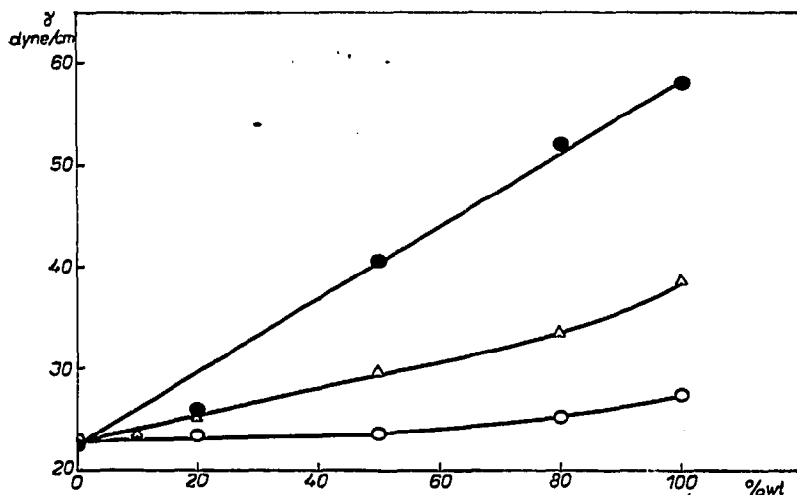| Solution	Concentration of phase (%, w/w)	Surface tension, γ (dyne/cm)
DC-560 in acetone	100	27.4
	80	25.2
	50	23.6
	20	23.3
	12	22.9
PEG 400 in acetone	100	38.4
	80	33.6
	50	29.4
	20	25.5
	10	23.4
Diglycerol in methyl alcohol	100	57.8
	80	51.6
	50	40.4
	20	26.0
	6	25.4
PEG 400 + diglycerol in methyl alcohol	100	47.0
	8	25.6

Fig. 1. Dependence of the surface tension γ, on the composition of solutions of the phases. ○, DC-560 in acetone; △, PEG 400 in acetone; ●, diglycerol in methyl alcohol.

by 20 % for the weakly polar phase DC-560, by 60 % for PEG 400, and by up to 120% for diglycerol. The capillary elevation method that was used gave values of the surface tensions of stationary phases that differed by 20% from those stated in the literature[6,8]. The increase in the surface tension with an increasing content of the phase in the solution is demonstrated in Fig. 1. The curve of γ corresponds with eqn. 3 with diglycerol, but it satisfies eqn. 4 better with the solutions of polyethylene glycol and silicone oil.

The surface tension was very close to the critical surface tension of glass, *i.e.*, 47 dyne/cm, with the mixed phase of polyethylene glycol and diglycerol. Fig. 2 shows that eventual changes in the composition of the mixture caused by the preferential sorption of one component on the glass do not influence the value of γ, as an extreme change in the composition of the adsorbed layer does not occur.
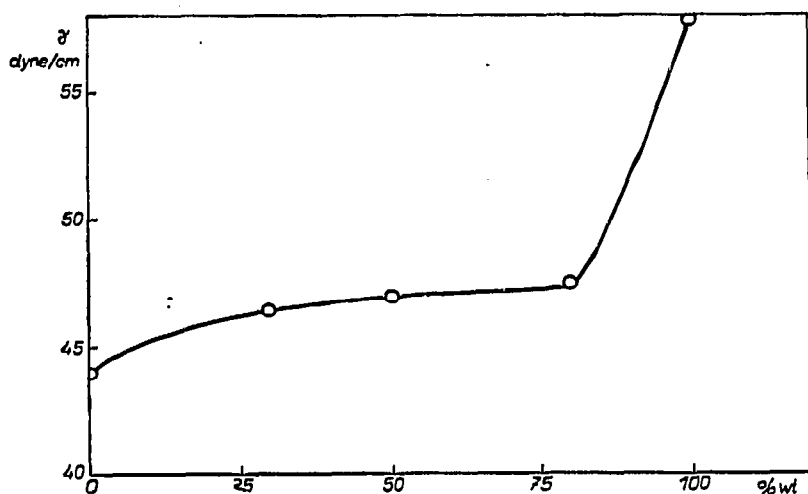

Fig. 2. Dependence of the surface tension of the mixture of PEG 400 and diglycerol (1:1, w/w) on its composition.

Wettability coefficient

In order to compare various types of solid flat surfaces, the roughness factor, defined as the ratio of cos θ of the same liquid on the two materials being compared, is used, and it varies in the range 1.05–1.10. The wettability coefficient, k_w, was proposed as being analogous to the roughness factor, and is defined by the ratio

$$k_w = \frac{\gamma'_e}{\gamma'}$$

where γ'_e is the interfacial tension of a solvent (in this work, methyl alcohol) and of the wall of an etched capillary, and γ' is the interfacial tension of the same liquid and of the wall of a non-etched capillary. The interfacial tension was calculated from Young's equation under the assumption that the contact angle, θ, is zero for methyl alcohol and glass. In order to calculate the interfacial tension, the surface tension of methyl alcohol was measured in part of the capillary coil; this measurement was always carried out on ten capillary coils simultaneously and the average and the standard deviation were calculated. The values of the interfacial tension and the wettability coefficient are given in Table IV.

TABLE IV

WETTABILITY COEFFICIENTS, k_w

Capillary number	Treatment	γ_e' (dyne/cm)	σ	γ' (dyne/m)	σ	k_w
1	Uncleaned	7.2	0.37	4.7	0.25	1.54
2		7.0	0.30	4.6	0.19	1.52
3		7.1	0.25	4.1	0.15	1.58
4		6.9	0.28	4.5	0.12	1.52
5		7.0	0.40	4.5	0.23	1.55
6	Cleaned	25.2	1.32	22.7	0.81	1.11
7		24.3	0.82	20.8	1.19	1.16
8		24.6	0.31	20.9	2.72	1.18
9		24.4	0.79	20.3	1.21	1.20
10		24.5	2.15	20.9	0.49	1.17

The wettability coefficient was used as a measure of a change in the interfacial tension of the system capillary wall–solvent, which is caused by the surface modification (by etching in the gaseous phase or by cleaning the tube with chromic–sulphuric acid and subsequent etching of the capillary wall). It was found that the coefficient k_w is clearly dependent on the extent of the capillary surface roughening caused by etching. It varies from 1.52 to 1.58 for capillaries that were not cleaned with chromic-sulphuric acid, and is lower for capillaries drawn from tubes cleaned with chromic-sulphuric acid, varying in the range 1.11–1.20.

The better the capability of the glass capillary surface has of forming a homogeneous film of the polar phase, the closer to unity is the wettability coefficient. This relationship can be used for the rapid evaluation of the capillary surface quality and for obtaining information on the approximate column efficiency after coating.

Coated capillary columns were tested by the injection of a mixture of ethyl, isopropyl and n-butyl alcohols. The number of theoretical plates, number of effective theoretical plates and capacity ratio were determined for n-butyl alcohol and are shown in Tables V and VI. The thickness of the film of the stationary phase was calculated according to the relationship

$$d_F = \frac{kr}{2V_g^0 \rho_l} \cdot \frac{273}{T}$$

where V_g^0 is the specific retention volume, ρ the density of the phase and T the absolute temperature. This relationship was derived for capillary columns from the relationship

$$V_g^0 = \frac{kv_g}{v_l \rho_l} \cdot \frac{273}{T}$$

where v_g and v_l are the volumes of the gaseous and the liquid phase, respectively. The specific retention volume was calculated according to the relationship used by McREYNOLDS[11]. When comparing the values given by McReynolds for DC-550, the straight line of the dependence of log V on $1/T$ is steeper for DC-560. This deviation is obviously caused by using various supports (Celite 545 and Chromosorb W) and by the addition[11] of a wetting agent, Poly-Tergent J-300. The film thickness was

calculated according to this equation, and the values given in Table V are in the range $1-2 \times 10^{-4}$ mm and it is evident that reproducibility of the capillary coating procedure can be obtained. However, these values are only hypothetical as they

TABLE V

FILM THICKNESSES, d_F

ϕ = mean value, σ = standard deviation.

Capillary number	Stationary phase	r (mm)	l (m)	k	$(n/m) \times 10^{-3}$	$(n_{eff}/m) \times 10^{-3}$	d_F (μm)
1	DC-560	0.137	24	3.1	2.1	1.3	0.1
2		0.117	25	6.4	0.3	0.2	0.2
3		0.146	14	8.5	1.3	1.1	0.2
4		0.142	22	8.4	1.0	0.8	0.2
5		0.125	29	7.2	1.0	0.8	0.2
					(ϕ=1.1; σ=0.40)	(ϕ=0.8; σ=0.18)	(ϕ=0.18; σ=0.008)
6	PEG 400	0.137	24	3.0	1.7	0.8	0.2
7		0.125	18.5	2.4	1.1	0.5	0.2
8		0.117	21	3.7	1.4	0.8	0.2
9		0.096	28	3.6	0.1	0.1	0.2
10		0.092	30	3.4	0.1	0.1	0.2
					(ϕ=0.9; σ=0.55)	(ϕ=0.5; σ=0.13)	(ϕ=0.2; σ=0)
11	Diglycerol	0.092	22	2.9	0	0	0.1
12		0.100	24	3.0	0.2	0.1	0.2
					(ϕ=0.1; σ=0.02)	(ϕ=0.05; σ=0.005)	(ϕ=0.15; σ=0.005)

TABLE VI

THICKNESS (d_F) OF THE FILM OF STATIONARY PHASE (1:1 MIXTURE OF PEG 400 AND DIGLYCEROL) IN GLASS CAPILLARY COLUMNS EITHER CLEANED OR NOT CLEANED WITH CHROMIC–SULPHURIC ACID

Capillary number	Treatment	r (mm)	l (m)	k	$(n/m) \times 10^{-3}$	$(n_{eff}/m) \times 10^{-3}$	d_F (μm)
1	Uncleaned	0.117	30	1.8	0	0	0.05
2		0.117	41	1.4	0.3	0.1	0.1
3		0.125	51	2.1	0	0	0.1
4		0.108	41	0.6	0.5	0.1	0.02
5		0.108	31	3.2	0.2	0.1	0.1
					(ϕ=0.2; σ=0.03)	(ϕ=0.06; σ=0.03)	(ϕ=0.07; σ=0.0014)
6	Cleaned	0.125	18	2.2	0.4	0.2	0.1
7		0.142	16.5	1.8	0.7	0.3	0.1
8		0.108	14.5	2.3	0.8	0.4	0.1
9		0.125	22.5	2.3	0.7	0.4	0.1
10		0.131	14	2.2	1.4	0.6	0.1
					(ϕ=0.8; σ=0.14)	(ϕ=0.7; σ=0.15)	(ϕ=0.1)

indicate the film thickness calculated assuming total coating of the capillary surface. The differences in the efficiencies of individual columns suggest clearly that although the amount of stationary phase that is coated on the capillary wall is always the same, various interfacial tensions cause decomposition or destruction of the film that was formed. The efficiencies of the capillary columns coated with diglycerol are very low in comparison with other phases, even though the amount of liquid on the wall is the same. Consequently, the surface tension of stationary phases is decisive for column efficiencies. As the surface tension of diglycerol is greater than the critical surface tension of the capillaries that were prepared, no efficient film can be formed on the capillary wall.

Values of the film thickness in the capillaries cleaned and not cleaned with chromic–sulphuric acid are given in Table VI. It is obvious that cleaning with chromic–sulphuric acid does not determine the physical roughness of the glass surface; this is influenced only by etching. A chemical change in the surface seems to be involved which is reflected in the efficiencies of capillary columns. The columns cleaned with chromic–sulphuric acid have efficiencies that are on average four times greater than those of uncleaned columns, which indicates that the wall was coated with liquid phase more uniformly.

CONCLUSION

The homogeneity of a film of stationary phase on a capillary wall is dependent on the surface tension of the stationary phase and the critical surface tension of the glass wall. It was shown experimentally that:

(i)   The homogeneity of the film of stationary phase on the capillary wall and the efficiency of the capillary column are dependent on chemical treatment (cleaning with chromic–sulphuric acid) of the glass tube prior to drawing;

(ii) only the phases whose surface tensions are lower than the critical surface tension of glass can form an efficient film on the capillary wall;

(iii) the quality of the internal capillary surface can be determined in advance, and thus also the capillary column efficiency obtained after coating, by measuring the surface tension of the solvent in a capillary coil.

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