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THE EFFECT OF COATING PARAMETERS ON THE QUALITY OF STATIONARY PHASE FILMS IN GLASS CAPILLARY COLUMNS

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SUMMARY

The influence of viscosity, surface tension and operational temperature on the thickness of stationary phase films in glass capillary columns coated by the dynamic method was studied. The analysis of the studied values was carried out and was proved experimentally.

INTRODUCTION

The thickness of the film of a stationary phase and its homogeneous spreading over the whole internal capillary surface are decisive factors in the separation efficiency of a capillary column. The film thickness is influenced by several factors which, for the dynamic coating method¹, are expressed by the following relation²:

$$d_F = \frac{c \cdot r}{200} \cdot \sqrt{u \frac{\eta}{\gamma}} \quad (1)$$

where d_F is film thickness, c the concentration of the coating solution (%), r the capillary radius, u the linear velocity of the flow of the solution through the capillary, η the viscosity of the solution and γ its surface tension.

KAISER³ transformed this relation into the form:

$$d_F = \frac{c}{100r} \cdot (0.265u + 0.25) \quad (2)$$

NOVOTNÝ *et al.*⁴ studied the effect of the suppression of the flow rate of the coating solution and found that the d_F values conformed to eqn. 1. He also showed a direct proportionality between the film thickness and the capillary radius. KAISER³ showed further the diagram of the dependence of the film thickness on the viscosity.

Surface tension, γ , and contact angle, θ , are decisive for the formation of a perfect film of the liquid on the wall of the capillary. Young's equation must hold for the equilibrium at the point of the contact of individual phases:

$$\gamma_{23} = \gamma_{13} + \gamma_{12} \cdot \cos \theta \quad (3)$$

where subscripts 1, 2, 3 indicate the liquid, atmosphere and capillary well, respectively. Critical surface tension, the surface tension for which the contact angle on the material is zero, was derived from this relation. These critical surface tensions were determined⁵ for the materials of the capillaries (Table I).

TABLE I

CRITICAL SURFACE TENSIONS (γ_c) OF SOME MATERIALS

Material	γ_c (dyne/cm)
Polytetrafluoroethylene	19
Stainless steel	24
Aluminium	27.4
Copper	27.0
Pyrex glass, cleaned with acetone	28.0
Polyethylene	33
Polyethylene terephthalate	40
Polyamide	41
Pyrex glass, cleaned with chromic acid	44

A rough internal capillary surface affects substantially the contact angle and LIBERTI⁶ introduced the coefficient of macroscopic roughening, r , which is defined as the ratio between the contact angles for smooth and roughened surfaces of the same material:

$$r = \frac{\cos\theta'}{\cos\theta} \quad (4)$$

where θ' and θ are contact angles for the rough and smooth surfaces, respectively. The values measured for some liquids on glass (taken from ref. 6) are listed in Table II.

The influence of surface tension

High efficiency of capillary columns is obtained with a film of the stationary phase covering the largest possible area of the capillary surface and having optimal and homogeneous thickness.

The surface tension of the coating solution must necessarily be lower than the critical surface tension of the coated wall for perfect capillary coating with the film. Even though the surface tension of the solution consists of the surface tensions of both the components (solvent and stationary phase), the characteristics of the

TABLE II

CONTACT ANGLES OF SOME LIQUIDS ON NON-ETCHED AND ETCHED GLASS

Liquid	Surface tension (dyne/cm)	Glass	
		Original	Etched
Chlorobenzene	33.1	0.945	0.990
Dichlorobenzene	41.4	0.906	0.974
Chloronaphthalene	41.8	0.809	0.915
Bromonaphthalene	44.6	0.755	0.900

TABLE III

VISCOSITIES AND SURFACE TENSIONS OF SOME SOLVENTS

Viscosities and surface tensions were measured at 20°, except those marked ^a (30°) and ^b (25°).

Solvent	Viscosity, η (Poise $\times 10^5$)	Surface tension, γ (dyne/cm)	$\eta/\gamma \times 10^5$
<i>n</i> -Pentane	240	16.0	15
<i>n</i> -Hexane	318	18.4	17.3
<i>n</i> -Heptane	403	20.4	19.8
<i>n</i> -Octane	548	21.8	25.2
Benzene	845	28.9	29.3
<i>o</i> -Xylene	693 ^a	29.1 ^a	23.8
Dichloromethane	437	28.1	15.6
Tetrachloromethane	845 ^a	25.6 ^a	33.0
Acetone	322	23.3	13.8
Methanol	592	22.6	26.1
Ethanol	1209	22.3	54.0
<i>n</i> -Propanol	1814 ^a	22.9 ^a	79.2
Di- <i>n</i> -propyl ether	398 ^b	20.0 ^b	19.9
Di- <i>n</i> -butyl ether	602 ^a	22.0 ^a	27.4
<i>n</i> -Propyl chloride	318 ^a	20.0 ^a	15.5
<i>n</i> -Amyl fluoride	372	20.0	18.6

solvent predominates with respect to low concentrations during the coating and thus the liquid with the lowest possible surface tension should be selected. As shown in Table III, from this viewpoint alkanes (C_6 to C_7), acetone, alcohols, ethers and some halogen derivatives are advantageous. Aromatic hydrocarbons, dichloromethane, etc., have higher surface tensions.

The contribution of the surface tension of the liquid film in the capillary increases with gradual evaporation of the solvent until only the film of the stationary liquid phase remains on the wall. If the film destruction is not to occur at this moment, the surface tension of the stationary phase must be lower than the critical surface tension of the capillary wall. If surface tensions of some stationary phases (Table IV) are compared with critical surface tensions of column materials (Table I), it can be seen that non-polar phases have the lowest values and that these values increase with increasing polarity. Solid materials form two groups according to the value of the critical surface tension: metals, polytetrafluoroethylene and unmodified glass, with critical surface tensions of 19–28 dyne/cm; and polyamides, polyethylene terephthalate and glass with an acid-washed surface, with critical surface tensions of 40–44 dyne/cm. In addition to this, the surface roughened by etching increases

TABLE IV

SURFACE TENSIONS OF SOME STATIONARY PHASES

Phase	Surface tension, γ (dyne/cm)
Squalane	30.0
Polypropylene glycol	31.3
Triton (polyether alcohol with polyoxyethylene chain)	34.0
Diglycerol	50.3

the critical surface tension by a factor of 1.1 so that the resulting value for an acid-etched glass surface may be approximately 48 dyne/cm, which gives a high probability of preparing capillary columns with high efficiency.

Film thickness is also a function of the ratio of viscosity, η , and surface tension, γ , according to eqn. 1. This ratio should not, according to previous work⁴, exceed the value 0.09. It is obvious from Table III that the ratio of the viscosity and surface tension does not reach this boundary value with most solvents. In spite of this, it is advantageous to select the solvent with the lowest viscosity as the expression for the concentration (%) in eqn. 1 expresses empirically its viscosity. *n*-Paraffins, acetone, *n*-propyl chloride, *n*-amyl fluoride and di-*n*-propyl ether appear to be the solvents with the lowest η/γ ratio. Alcohols and aromatic hydrocarbons have viscosities which are too high.

The thickness of the film on the capillary wall is thus influenced by several factors, of which the influence of the capillary radius and velocity of the flow of the coating solution have already been studied. The remaining factors, *viz.* surface tension and viscosity, which is a function of coating temperature, were therefore studied.

For experimental proof of these factors, a series of glass capillaries with etched surfaces was prepared and coated with (a) a solution of di-*n*-decyl phthalate in *o*-xylene at various temperatures; (b) a solution of di-*n*-decyl phthalate in *n*-hexane at one temperature; or (c) a solution of silicone phase SE-30 in a mixture of acetone and benzene at one temperature.

EXPERIMENTAL

Glass capillaries were drawn in the apparatus described by DESTY *et al.*⁷ from tubes of the Czechoslovak glass Unihost, the chemical composition of which is presented in Table V. The length of the capillaries was varied between 25 and 29 m and internal diameters were in the range 0.2-0.34 mm. The diameters were measured under the microscope and, in agreement with the previous tests⁸, the deviations were not greater than 3%. All the capillaries were etched in the gaseous phase⁹ and then activated. The following solutions were prepared for capillary coating: 15% of di-*n*-decyl phthalate in *o*-xylene; 15% of di-*n*-decyl phthalate in *n*-hexane; and 5% of SE-30 in a mixture of acetone and benzene (1:1). Viscosities of the solutions were

TABLE V

CHEMICAL COMPOSITION (%) OF UNIHOST AND PN GLASSES

Component	Glass	
	Unihost	PN
SiO ₂	68.6	67.0
B ₂ O ₃	—	2.0
Al ₂ O ₃	3.9	3.0
CaO	5.5	6.5
MgO	2.9	—
ZnO	—	8.0
Na ₂ O	17.8	13.5
K ₂ O	1.3	—

measured in a Hoepler viscosimeter and surface tensions by the capillary elevation method.

The capillaries were coated by the dynamic method¹. They were placed in a water ultrathermostat during the whole period of coating and nitrogen blowing and were then transferred to a hot-air thermostat at the same temperature and kept there until tested.

The efficiency of capillaries was proved in a C. Erba Model C gas chromatograph with flame-ionisation detection. Nitrogen carrier gas flow rate was varied from 0.15 to 0.42 ml/min according to the capillary diameter. The splitting ratio was 1:150.

RESULTS AND DISCUSSION

The measured values of viscosities and surface tensions of the solutions and the square root of their ratios are listed in Table VI. If the results are compared with the values tabulated for pure solvents, it appears that the di-*n*-decyl phthalate solution increases the viscosity by *ca.* 50% while the surface tension decreases slightly. The solution of *n*-hexane had a much lower viscosity, which at 25° was still over 10% less than that of the *o*-xylene solution at 90°. The solution with 5% of SE-30 had a viscosity almost five times greater than that of the solution of di-*n*-decyl phthalate in *o*-xylene and about twelve times greater than that of the solution of di-*n*-decyl phthalate in *n*-hexane.

The glass capillaries were coated at 30°, 60° and 90° and tested at 105° by the injection of a mixture of *n*-octane, *n*-nonane and *n*-decane. Adjusted retention times were determined; dead retention time was measured by the injection of methane.

TABLE VI

VISCOSITIES AND SURFACE TENSIONS OF COATING SOLUTIONS

Surface tension values for 15% DDP (di-*n*-decyl phthalate) in *n*-hexane and 5% SE-30 in the mixture of acetone and benzene were not measured since even for a five-fold increase in the viscosity of the solution the ratio η/γ was less than 0.3.

Solution	Temperature (°C)	Viscosity η (Poise $\times 10^5$)	Surface tension, γ (dyne/cm)	$\sqrt{\eta/\gamma} \times 10^2$
15% DDP in <i>o</i> -xylene	15	1430	23.9	2.5
	25	1220	23.7	2.3
	30	1150	23.1	2.2
	36	1020	22.8	2.2
	46	940	22.0	2.1
	60	790		
	90	580		
15% DDP in <i>n</i> -hexane	25	512		
	30.3	483		
	40.2	418		
	50.3	392		
	61.3	335		
5% SE-30 in acetone + benzene (1:1)	20	5410		
	25	5320		
	30	5100		
	40	4900		
	50	4790		

TABLE VII

DIMENSIONS AND PROPERTIES OF CAPILLARY COLUMNS USED

Capillary number	T_s (°C)	r (mm)	l (m)	k	$n \times 10^{-3}$	$n_{eff} \times 10^{-3}$	d_F (μm)
I 1	30	0.18	25	2.66	50	32	0.73
I 2	30	0.10	26	1.65	73	26	0.20
I 3	30	0.11	29.5	1.27	42	14	0.22
I 4	30	0.16	24	1.21	67	21	0.30
I 5	30	0.14	23	1.23	44	14	0.26
I 1	60	0.15	25.5	1.27	68	21	0.30
I 2	60	0.15	27	1.37	67	23	0.32
I 3	60	0.15	26	1.33	60	20	0.32
I 4	60	0.14	27	1.72	52	21	0.36
I 5	60	0.15	28	1.43	51	18	0.42
I 1	90	0.19	26.5	1.25	52	17	0.28
I 2	90	0.17	26.6	1.28	38	12	0.33
I 3	90	0.16	25.5	1.07	38	10	0.32
I 4	90	0.13	29	0.95	78	19	0.22
I 5	90	0.10	25.5	1.17	58	24	0.22
II 1	30	0.13	27	1.03	80	20	0.25
II 2	30	0.16	39.6	1.23	117	36	0.37
III 1	30	0.13	27	2.05	38	18	3.9
III 2	30	0.17	26	2.6	26	20	7.1

The number of theoretical plates and effective theoretical plates, capacity ratio and hypothetical film thickness were calculated from the curves for *n*-decane. The last value was calculated with the aid of the known relation¹:

$$V_{g^0} = \frac{kv_g}{v_1 \rho_1} \cdot \frac{273}{T} \quad (5)$$

where V_{g^0} is the specific retention volume, v_g and v_1 the volume of the gaseous and liquid phase in the column, respectively, ρ_1 the density of the stationary phase, T the operational temperature (°K) and k the capacity ratio. This relation may be transformed for capillaries into the form:

$$d_F = \frac{kr}{2 V_{g^0} \rho_1} \cdot \frac{273}{T} \quad (6)$$

where d_F is the film thickness and r the capillary radius.

The calculated values of all the mentioned quantities are listed in Table VII. The thickness of di-*n*-decyl phthalate films varies between 0.22×10^{-3} and 0.42×10^{-3} mm, and the thickness of SE-30 films varies between 3.9×10^{-3} and 7.1×10^{-3} mm.

The influence of the operational temperature, and thus the viscosity, is obvious from Fig. I where the dependence of film thickness on capillary radius is demonstrated graphically for various temperatures. The influence of the capillary radius decreases and the tangent of the straight line approaches zero at coating temperatures lying 40–50° below the boiling point of the solvent. A further increase in the coating temperature may create conditions under which the possibility arises of neglecting the influence of the capillary radius on the film thickness. This increase in temperature

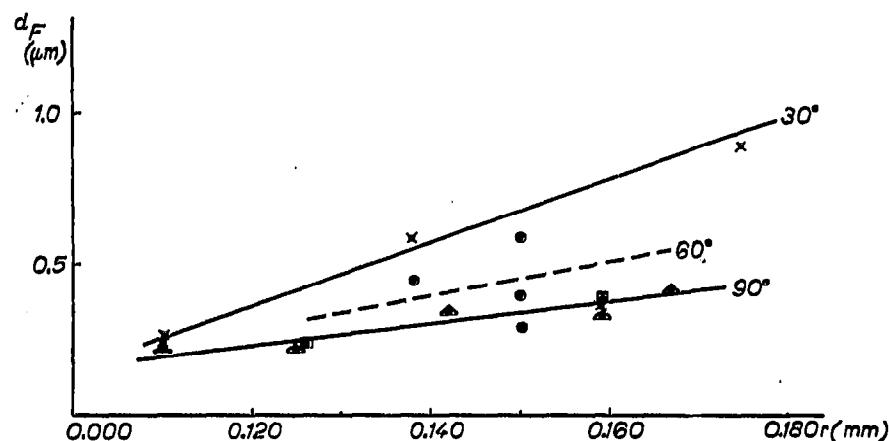


Fig. 1. Dependence of the film thickness on the capillary radius and operational temperature. Values for di-*n*-decyl phthalate at \times , 30° ; \circ , 60° and Δ , 90° .

is possible only up to temperatures *ca.* 15° lower than the boiling point of the solvent. In the vicinity of the boiling point repeated evaporation and condensation of the solvent occurs, which causes complete destruction of the stationary phase film.

The use of higher temperatures of the capillary coating is thus equivalent to the use of a solvent with a lower viscosity, as shown in Fig. 1 where the points for film thickness are plotted against capillary radius for a xylene solution of di-*n*-decyl phthalate at 90° and for a hexane solution of di-*n*-decyl phthalate at 30° . This information is utilized in the case of stationary phases which are needed for transfer into solutions in solvents with less suitable properties (e.g., Versamide 900 in a 1:1 mixture of chloroform and *n*-butanol) and the viscosities of which are the reason for films that are too thick. The viscosity of the coating solution is decreased and a thinner film is obtained by the use of a higher coating temperature.

The suitable coating temperature, derived from the boiling point of the solvent, can be expressed by a simple empirical relation:

$$T_c/T_b \approx 0.85-0.90 \quad (7)$$

where T_c is the coating temperature and T_b the boiling point ($^\circ$ K).

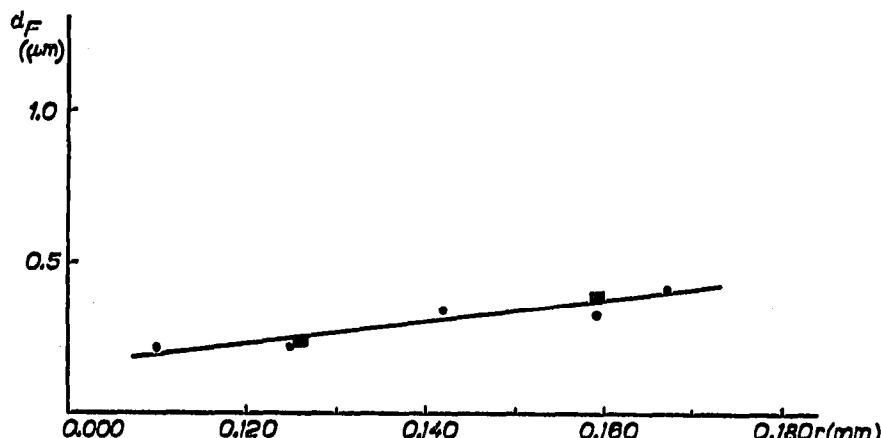


Fig. 2. Dependence of the film thickness on the capillary radius and viscosity of the coating solution. \bullet , Di-*n*-decyl phthalate in *n*-hexane at 90° ; \square , SE-30 in a mixture of acetone and benzene (1:1) at 30° .

CONCLUSIONS

The following conclusions can be drawn from the results obtained.

The film thickness is proportional to the viscosity of the coating solution and it may therefore be influenced by the selection of the solvent.

The film thickness is thus also a function of the coating temperature.

The film thickness is proportional to the capillary radius. This influence decreases with increase in the coating temperature. An operational temperature near the boiling point of the solvent permits the influence of the capillary radius to be neglected.

REFERENCES

- 1 L. S. ETTRE, *Open Tubular Columns in Gas Chromatography*, Plenum Press, New York, 1965, p. 80.
- 2 F. FAIRBROTHER AND A. E. STUBBS, *J. Chem. Soc.*, (1935) 527.
- 3 R. KAISER, *Gas Phase Chromatography, Vol. II, Capillary Chromatography*, Butterworths, London, 1963.
- 4 M. NOVOTNÝ, K. D. BARTLE AND L. BLOMBERG, *J. Chromatogr.*, 45 (1969) 469.
- 5 F. FARRÉ-RIUS, J. HENNIKER AND G. GUIOCHEON, *Nature*, 196 (1962) 63.
- 6 A. LIBERTI, in A. B. LITTLEWOOD (Editor), *Gas Chromatography*, Elsevier, Amsterdam, 1967, p. 95.
- 7 D. H. DESTY, J. N. HARESNAPE AND B. H. F. WHYMAN, *Anal. Chem.*, 32 (1960) 302.
- 8 K. TESAŘÍK AND M. NOVOTNÝ, *Chem. Listy*, 62 (1968) 1111.
- 9 K. TESAŘÍK AND M. NOVOTNÝ, in H. G. STRUPPE (Editor), *Gas Chromatography*, Akademie-Verlag, Berlin, 1968, p. 575.