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DETERMINATION OF SOLUTE DIFFUSION COEFFICIENTS IN CROSS-LINKED STATIONARY PHASES FOR FUSED-SILICA COLUMNS

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SUMMARY

Precise measurements of plate heights of fused-silica columns with either cross-linked or conventionally coated stationary liquids were used to determine solute diffusion coefficients in these media. Three different methods of calculating liquid diffusion coefficients from chromatographic data were evaluated. The most accurate results were obtained by combination of plate heights for two different carrier gases. Contrary to expectation, no significant differences were found between diffusion coefficients in conventional or *in situ* cross-linked stationary liquids. Solute diffusion coefficients are listed for *n*-alkanes in CP-Sil-5, OV-1, CP-Sil-5-CB and OV-1-CB.

INTRODUCTION

Procedures leading to enhanced stationary phase stability (*e.g.*, free-radical cross-linking) in capillary columns have received much attention in the literature. "Chemically bonded" phases will keep their efficiencies over a much longer period, as droplet formation and/or rearrangement of the film is impossible. It is even possible to wash the column with organic solvents to remove contaminants. Especially for splitless and on-column injection, chemically bonded phases are a good choice.

Generally, it is assumed that *in situ* cross-linked stationary phases are more viscous than conventionally coated liquids. This would cause a decreased solute diffusion in the liquid phase, resulting in less efficient columns. Very few data on solute diffusion in cross-linked phases are available.

Precise measurements of plate heights are necessary to allow the calculation of liquid diffusion coefficients. In this paper, different methods of determining diffusion coefficients in stationary liquids are evaluated. Comparisons are made of CP-Sil-5 and CP-Sil-5-CB and of OV-1 and OV-1-CB.

THEORETICAL

According to the Golay equation¹, extended by Giddings *et al.*², the plate height equation for capillary columns is

$$H = \left[2 \cdot \frac{D_{m,o}}{\bar{v}_0} + \frac{(11k^2 + 6k + 1)}{24(1 + k^2)} \cdot \frac{r^2 v_0}{D_{m,o}} \right] f_1 + \frac{2}{3} \cdot \frac{k}{(1 + k)^2} \cdot \frac{d_f^2 v_0 f_2}{D_s} \quad (1)$$

where v_0 is the linear gas velocity at the column outlet, $D_{m,o}$ is the diffusion coefficient of a solute in the mobile phase at the pressure of the column outlet, D_s is the diffusion coefficient of a component in the liquid stationary phase, r is the column radius, k is the capacity ratio of a solute ($= KV_s/V_m = Ka$), K is the partition coefficient of a solute, a is the volumetric phase ratio of stationary and mobile phase, d_f is the film thickness of the liquid stationary phase and f_1 and f_2 are factors correcting for the effect of pressure gradient on column efficiency:

$$f_1 = \frac{9}{8} \cdot \frac{(P^4 - 1)(P^2 - 1)}{(P^3 - 1)^2}$$

$$f_2 = \frac{3}{2} \cdot \frac{(P^2 - 1)}{(P^3 - 1)}$$

By definition, P is the ratio of inlet to outlet pressure $= p_i/p_o$. $v_0 f_2 = \bar{v}$ is the average carrier gas velocity.

Eqn. 1 can be written in simplified form as

$$\frac{H}{f_1} = \frac{B}{v_0} + \frac{C_{m,o} v_0}{D_{m,o}} + C_s v_0 \cdot \frac{f_2}{f_1} \quad (1a)$$

Determination of D_s

If C_s can be reliably calculated from plate-height data, D_s can be reduced from C_s (eqn. 1), provided the film thickness d_f is accurately known.

Assuming an even film of stationary liquid phase, d_f can be determined from

$$d_f = \frac{kr}{2V_g \varrho} \cdot \frac{273}{T} \quad (2)$$

where k and V_g are the capacity ratio and the specific retention volume of a solute at the column temperature T ($^{\circ}\text{K}$) and ϱ is the stationary phase density at the column temperature.

Determination of C_s

The term C_s , describing the resistance to mass exchange in the liquid phase, can be determined by three different methods:

(A) C_s is directly calculated from measured values of H using eqn. 1:

$$C_s = \frac{1}{f_2 v_0} \left(H - \frac{B f_1}{v_0} - C_{m,o} v_0 f_1 \right)$$

For this calculation, literature data of the gaseous diffusion coefficient $D_{m,o}$ must be used.

(B) Computer fitting of a large number of experimental H vs v_o data to the model given by eqn. 1a gives values for B , $C_{m,o}$ and C_s for the column under investigation.

(C) Measuring plate heights of a column with two different carrier gases³. For $x = v_o/D_{m,o}$, eqns. 1 and 1a can be rewritten as

$$\frac{H}{f_1} = \frac{2}{x} + C_{m,o}x + C_s D_{m,o} \cdot \frac{f_2}{f_1} \cdot x$$

or

$$\frac{H}{f_1} = F(x) + C_s D_{m,o} \cdot \frac{f_2}{f_1} \cdot x \quad (3)$$

By measuring the experimental plate heights H at identical values of $x = v_o/D_{m,o}$ in two different carrier gases, I and II, it follows from eqn. 3 that

$$\left(\frac{H}{f_{1I}} - \frac{H}{f_{1II}} \right) = C_s x \left(D_{m,o} \cdot \frac{f_2}{f_{1I}} - D_{m,o} \cdot \frac{f_2}{f_{1II}} \right)$$

or

$$C_s = \frac{\Delta \left(\frac{H}{f_1} \right)}{x \Delta \left(D_{m,o} \cdot \frac{f_2}{f_1} \right)}$$

Data on the gaseous diffusion constants of the solutes in the two carrier gases must be taken from literature or must be determined experimentally.

EXPERIMENTAL

Columns

Fused-silica columns were obtained from Chrompack (Middelburg, The Netherlands). The column properties are presented in Table I.

Gas chromatograph

All experiments were carried out on a Fractovap 4160 gas chromatograph (Carlo Erba, Milan, Italy) with the injector in the split mode. The column inlets were positioned in the centre of the 2-mm I.D. glass liner of the injector. The column outlets almost reached the tip of the flame-ionization detector. The column head pressure was measured with a precision manometer (Wallace and Tiernan, Gönzberg, F.R.G.). The time constant of the electrometer was 50 msec.

TABLE I
COLUMNS USED FOR D_s DETERMINATIONS

Column No.	Stationary phase*	Length (m)	Radius (mm)	Film thickness (μm)**
1	CP-Sil-5-CB	24.7	0.155	2.00
2	CP-Sil-5	27.0	0.158	2.35
3	CP-Sil-5-CB	24.5	0.157	1.13
4	CP-Sil-5	25.0	0.157	1.06
5	OV-1-CB	23.0	0.160	1.40
6	OV-1	23.5	0.157	1.86

* CB = "chemically bonded", *i.e.*, *in situ* cross-linked phase. CP-Sil-5 is a dimethylsilicone.

** d_t is calculated using eqn. 2 with V_g data obtained from packed columns.

Sample

A 0.1% solution of *n*-alkanes in cyclohexane was injected at a splitting ratio of 1:250.

Data acquisition and handling

All raw chromatographic data were first collected on a floppy disc (SP 4000, Spectra-Physics, Santa Clara, CA, U.S.A.). Using a laboratory computer (Nova 4/S Data General Company, Westboro, MA, U.S.A.) and modem the data were subsequently transferred for further calculation to a Burroughs B7700 mainframe computer. The retention time and standard deviation of each peak were calculated after a least-squares fit of a Gaussian curve to the data points by the minimization method of Marquart and Levensberg^{5,6}. Using data calculated according to ref. 4 for gaseous diffusion coefficients, values of C_s were calculated according to methods A and C. Values for B , $C_{m,o}$ and C_s were calculated by a least-squares fit of eqn. 1 to the H values.

RESULTS AND DISCUSSION

After curve fitting on the Burroughs B7700 computer, very precise data on the standard deviation, σ , of the peaks were obtained. The Gaussian model fits the data points very well; the relative standard deviation of the σ values obtained was 0.2%. The peaks appeared to be almost perfectly symmetrical.

Method A

Plate-height data were obtained with an average linear velocity of approximately 60 cm/sec for all columns. The inlet pressure was almost equal for all columns tested.

Values for the gas diffusion constants of *n*-alkanes were calculated following the method described by Fuller *et al.*⁴. From the obtained values of C_s (see Theoretical, method A) the values of the liquid diffusion coefficients were calculated. The results are given in Table II.

It may be concluded by comparison of D_s values at (almost) equal film thick-

TABLE II
LIQUID DIFFUSION COEFFICIENTS ($D_s \times 10^9 \text{ m}^2/\text{sec}$) OF *n*-ALKANES, CALCULATED BY METHOD A

Temperature (°C)	Carbon No.	CP-Sil 5 No. 2, $d_f = 2.35$	CP-Sil 5 CB No. 1, $d_f = 2.00$	OV-1 No. 6, $d_f = 1.86$	OV-1 CB No. 5, $d_f = 1.40$	CP-Sil 5 CB No. 3, $d_f = 1.13$	CP-Sil 5 No. 3, $d_f = 1.06$	SE-30 (Ref. 7)
75	9	0.51	0.59	0.52	0.48	—		
	10	0.38	0.47	0.42	0.35	0.32	0.24	
	11	0.26	0.37	0.34	0.25	0.14	0.15	
100	10	0.59	0.72	0.68	—	—	—	0.94
	11	0.49	0.51	0.44	0.43	0.36	0.33	0.80
	12	0.38	0.35	0.28	0.29	0.22	0.19	0.54
125	11	0.72	0.71	0.71	—	—	—	
	12	0.57	0.56	0.52	0.52	0.45	0.41	
	13	0.43	0.43	0.37	0.35	0.29	0.26	
	14	0.31	0.32	0.25	0.23	0.19	0.17	
150	13	0.76	0.86	0.80	—	—	—	1.22
	14	0.55	0.58	0.54	0.45	0.48	0.30	0.96
	15	0.39	0.39	0.36	0.29	0.24	0.22	
	16	0.27	0.26	0.24	0.18	0.13	0.16	0.58
175	15	0.71	0.71	0.75	—	—	—	
	16	0.53	0.57	0.51	0.43	0.37	0.36	
	17	0.39	0.45	0.35	0.28	0.26	0.23	
	18	0.28	0.35	0.24	0.18	0.18	0.15	
200	17	0.69	0.59	0.70	0.44	—	—	
	18	0.53	0.54	0.47	0.33	0.31	0.32	1.20
	19	0.40	0.48	0.33	0.25	0.23	0.21	
	20	0.30	0.43	0.23	0.18	0.17	0.14	0.43

ness that *in situ* cross-linking does not significantly alter the diffusion coefficient in silicone-type stationary phases.

A still unexplained phenomenon is the observation that the diffusion coefficients increase with increasing film thickness.

Method B

Using method B (see Theoretical), values of B , $C_{m,o}$ and C_s were calculated for columns 1 and 2 (Table II).

Although the fitted H vs. v_0 curves covered the experimental data points very well (Fig. 1), the discriminative power of the method was insufficient to distinguish the $C_{m,o}$ and C_s terms accurately (see Table III).

Method C

The gas diffusion coefficients for *n*-alkanes in nitrogen and helium were calculated by the method of Fuller *et al.*⁴. For the calculation of C_s , x was varied between $v_{o,opt}/D_{m,o}$ and $5 v_{o,opt}/D_{m,o}$ in both carrier gases.

In theory, the calculated value of C_s should be independent of x . In practice,

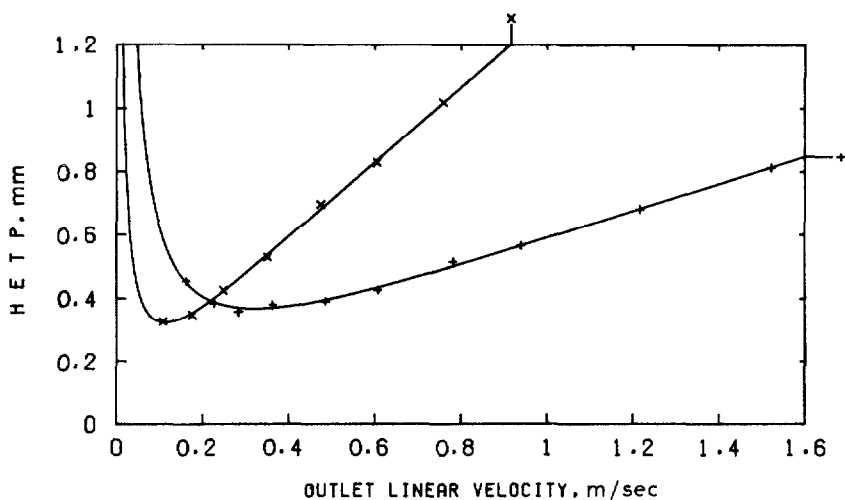


Fig. 1. Plate height of *n*-dodecane on column 1. Carrier gases: (+) helium; (x) nitrogen.

TABLE III

VALUES OF $C_{m,o}$ AND C_s CALCULATED BY METHOD B

Column temperature, 150°C. Values for *n*-C₉ and *n*-C₁₀ are omitted because of the large effect of extra-column contribution on the observed peak width of these early eluted peaks.

Compound	Column 1: CP-Sil 5 CB				Column 2: CP-Sil 5			
	He		N ₂		He		N ₂	
	$C_{m,o}$ (μsec)	C_s (μsec)	$C_{m,o}$ (μsec)	C_s (μsec)	$C_{m,o}$ (μsec)	C_s (μsec)	$C_{m,o}$ (μsec)	C_s (μsec)
<i>n</i> -C ₁₁	224	537	1060	338	264	591	1152	202
<i>n</i> -C ₁₂	314	350	830	687	349	395	1181	261
<i>n</i> -C ₁₃	277	409	1066	443	328	403	892	782

TABLE IV

CALCULATED VALUES OF C_s AND D_s USING CP-Sil-5 AND CP-Sil-5-CB

Column temperature, 150°C.

Compound	Column 1: CP-Sil-5-CB			Column 2: CP-Sil-5			z (ref. 2)	D_s (ref. 3)
	C_s (μsec)	z_{opt}	D_s (m^2/sec)	C_s (μsec)	z_{opt}	D_s (m^2/sec)		
<i>n</i> -C ₁₁	422	3.58	$1.06 \cdot 10^{-9}$	570	3.20	$0.953 \cdot 10^{-9}$	3.31	$1.79 \cdot 10^{-9}$
<i>n</i> -C ₁₂	244	3.11	$1.32 \cdot 10^{-9}$	409	3.13	$0.944 \cdot 10^{-9}$	3.31	$1.48 \cdot 10^{-9}$
<i>n</i> -C ₁₃	196	3.28	$1.13 \cdot 10^{-9}$	364	3.47	$0.719 \cdot 10^{-9}$	3.30	$1.22 \cdot 10^{-9}$

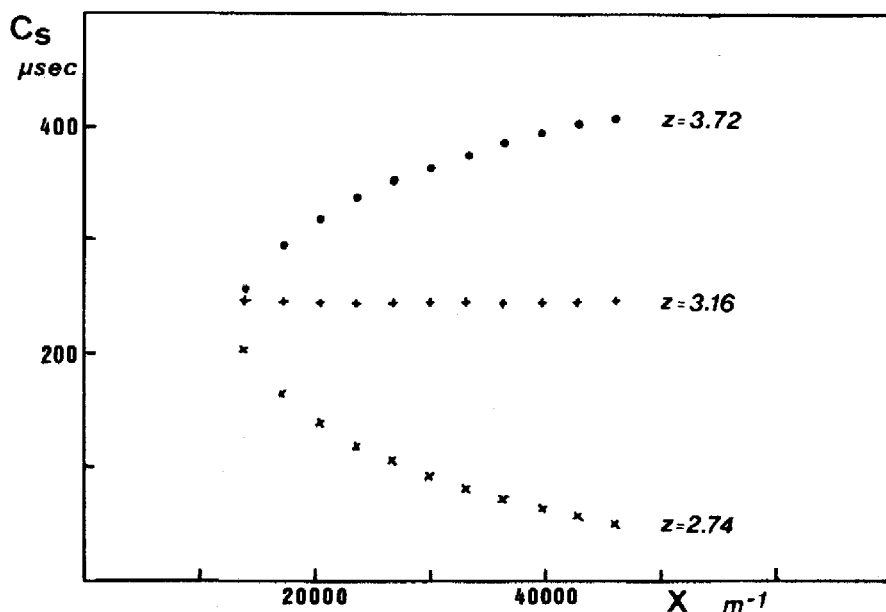


Fig. 2. Effect of the ratio of the solute gaseous diffusion coefficients in helium and nitrogen on the obtained value of C_s .

the value of C_s is very dependent on the ratio $z = D_{m,o}(\text{He})/D_{m,o}(\text{N}_2)$. The effect of values of z that are too large or too small is depicted in Fig. 2. In our experiments, the ideal situation was approached by small changes in z until an optimal value, z_{opt} , was found, producing a minimum of the function $\sum_i (C_{s,i} - \bar{C}_s)^2$, where \bar{C}_s is the average of the $C_{s,i}$ values calculated for a series of i evenly spaced values of x .

For the two thick-film columns 1 and 2 (Table I) the calculated values of C_s are listed in Table IV together with the accompanying values of D_s . Literature data from Millen and Hawkes⁷ for a silicone stationary phase are given for comparison.

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