Journal of Chromatography, 126 (1976) 87–95

CHROM. 9426

A STUDY OF COLUMN PERFORMANCES IN GAS CHROMATOGRAPHY

A C_{87} HYDROCARBON ON CHEMICALLY MODIFIED SUPPORTS

LÁSZLÓ BOKSÁNYI and E. sz. KOVÁTS
Laboratoire de Chimie Technique de l'École Polytechnique Fédérale de Lausanne, Lausanne (Switzerland)

SUMMARY

The surfaces of quartz plates and Chromosorb W were made to react with trimethylsilanol, docosyl-1-dimethylsilanol and 4,7-dioxaoctyl-1-dimethylsilanol. The density of the chemically bonded monomolecular layer is assumed to be maximal. One sample of Chromosorb W and one quartz plate were treated only by heating to 1250°. The modified support materials were used to prepare chromatographic columns with a C_{87} hydrocarbon stationary phase. Van Deemter plots of three substances were measured at each of the temperatures 60, 150 and 240°. The mass transfer terms of the calculated Van Deemter equations could be qualitatively related to wetting angles of the stationary phase, which were measured on the surface-modified vitreous quartz plates. The results indicate a method by which the column performances for the stationary phase used can be improved by suitable surface modification.

INTRODUCTION

The constant C in the Van Deemter equation

$$H = A + B/\bar{u} + C\bar{u} \tag{1}$$

where $\bar{u}$ is the linear gas velocity, accounting for the resistance to mass transfer of the solute across the gas–liquid interface and in the liquid phase is largely influenced by the effective or apparent film thickness. For a uniform film on the surface of the support put forward in the model of Van Deemter *et al.*[1], the value of this constant has been given as

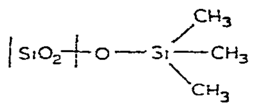
$$C = (2/\pi^2)\,[k'/(1+k')^2]\,(d_f^2/D_f) \tag{2}$$

where k' is the net retention given in units of the dead volume of the column, d_f is the film thickness and D_f is the diffusion coefficient of the solute in the stationary phase. In packed columns, uniform films are rarely encountered in practice, especially on surface-modified supports.

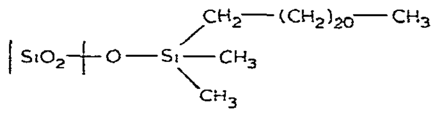
Surface modifications of supports are carried out in order to transform the heterogeneous high-energy surface of silicon dioxide into a uniform low-energy surface. By anchoring organic reagents on the surface hydroxyl groups, "completely" covered surfaces should lose all activity as strong adsorbents. Therefore, in our laboratory, the question of the optimal coverage was put forward[2] and a method was developed for attaining the densest layers of alkyldimethylsiloxy groups by reaction of alkyldimethylsilanols with the surface hydroxyl groups of the hydrated fume silica Cab-O-Sil[3]. We have also obtained results which suggest that dense layers can be prepared by the same method on the surface of acid-leached glass and on silica gels[4,5]. Consequently, an acid-washed diatomaceous earth should behave in an analogous manner.

We also considered the wetting properties of such modified surfaces. Following from ideas put forward by Novotny and Zlatkis[6], a good support should have a low-energy surface to be inactive as an adsorbent but should be wettable by the stationary phase. The commonly used modification by dimethyldichlorosilane, trimethylchlorosilane and hexamethyldisilazane results in surfaces with a critical surface energy of about 20–24 $\mathrm{erg \cdot cm^{-2}}$ (ref. 7). As the surface tension of most stationary phases exceeds this value, if complete wetting is achieved at all, it has to be attributed to surface roughness. Complete spreading would imply a thin uniform film with a low resistance to mass transfer, and the column packing would therefore be characterized by a small value of the constant C in the Van Deemter equation.

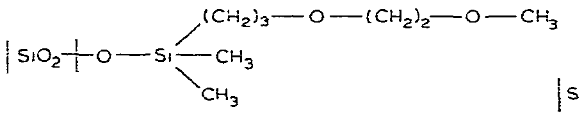
In this paper, we present preliminary results correlating the wettability of stationary phases and column performance, measured by the constant C in the Van Deemter equation. Three silanized supports were chosen as examples:



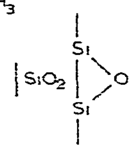
TM



DO



OO



HT

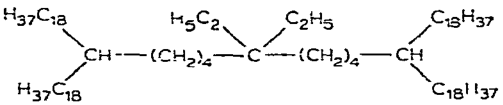
their surfaces being covered by trimethylsiloxy- (TM), docosyl-1-dimethylsiloxy (DO) and 4,7-dioxaoctyl-1-dimethylsiloxy (OO) groups; a fourth, thermally dehydrated, support (HT) was also included.

EXPERIMENTAL

An acid-washed diatomaceous support, Chromosorb WAW (Johns-Manville, Denver, Colo., U.S.A.; particle diameter 150–200 μm) was divided into four portions. One portion was heated at 1250° for 16 h: support HT (heat treated). Each of the other portions was made to react three times with an R-dimethylsilanol in an ampoule at 100° in an ammonia atmosphere. The amount of silanol applied in the reaction was 10 μmol for every square metre of surface to be treated (specific surface area of Chromosorb WAW ≈ 2 $m^2 \cdot g^{-1}$). Between successive reactions, the support was extracted with diethyl ether and dried under argon. This series of reactions gave support TM with trimethylsilanol, support DO with docosyl-1-dimethylsilanol and support OO with 4 7-dioxaoctyl-1-dimethylsilanol. For the preparation of the silanols, see ref. 8.

Small quartz plates were immersed in concentrated hydrochloric acid for 2 days to ensure complete surface hydration. One plate was heated to 1250°, and in every ampoule one plate was silanized together with the support.

The stationary phase used was a hydrocarbon of structure I, prepared in our laboratory[9] (for the properties of hydrocarbon I, see ref. 10):



I

For the preparation of the column packing, the support was impregnated with a solution of hydrocarbon I in pentane (ratio of support to hydrocarbon I = 94:6, w/w), then the solvent was evaporated. The columns were Pyrex glass tubes of length 225 cm and I.D. 0.4 cm, all columns having about the same filling volume. The ready-to-use columns with the four supports had the following weights of packings: HT, 11.2; TM, 9.8; DO, 8.3; and OO, 8.5 g. The column filling HT had a higher packing density because of sintering on heat treatment.

The wetting angles were measured at 40, 50 and 60 °C. The quartz plates were placed in a thermostated aluminium block. By means of a syringe small, 1–2-μl droplets of hydrocarbon I were placed on each plate, then photographs taken after 30 min.

The chromatographic work was carried out on a Packard-Becker (Delft, The Netherlands) Model 419 instrument, equipped with flame-ionization detectors. Helium was used as the carrier gas. In order to determine the Van Deemter plots at 60, 150 and 240°, 0.1 μl of a mixture of two *n*-alkanes and a 1-chloroalkane was injected. The linear gas velocity was calculated from the retention time of methane.

The constants *A*, *B* and *C* in the Van Deemter equation were calculated by the program CARLIN from the library of the Centre de Calcul de l'École Polytechnique Fédérale de Lausanne. This program allows the use of the least-squares method for functions with linear parameters.

RESULTS AND DISCUSSION

It was shown in a detailed investigation[2] that by treating the surface of the fume silica Cab-O-Sil (Cabot Corp., Boston, Mass., U.S.A.) with alkyl- and oxa-alkyldimethylsilanols, a surface layer of maximum density can be attained in two or three consecutive treatments. The surface concentration of the chemically bonded layer was highest when the reaction was conducted at low temperature (100°) in the presence of ammonia as catalyst. This reaction gave, on the surface of Cab-O-Sil, concentrations of 4.7 μmol·m^{-2} for trimethylsiloxy-, 4.1 μmol·m^{-2} for docosyl-1-dimethylsiloxy- and 3.5 μmol·m^{-2} for 4,7-dioxaoctyl-1-dimethylsiloxy groups. By applying the analogous treatment to acid-leached glass capillaries, a slight change of wettability was observed after the first and second consecutive treatment but further silanization did not have any effect[4]. We applied the same procedure to silanize the acid-washed Chromosorb W and the surface-hydrated vitreous quartz plates, assuming that the same surface concentrations were attained as on fume silica.

By heating fume silica to temperatures above 1100°, its surface is dehydrated completely with the formation of siloxane bridges[11,12]. After heat treatment, the surface is more or less deactivated as an adsorbent. We assume that the quartz plates and Chromosorb WAW were dehydrated in a similar manner by heating at 1250° for 16 h.

As described before, we assume that the surface concentration of organic substituents was the same on the quartz plates and on the silanized Chromosorb. Therefore, the wettability of the modified quartz plates is considered to be representative also for the surface-modified support. The results summarized in Table I show that the advancing wetting angle between the surface and hydrocarbon I is lowest on the plate treated with docosyl-1-dimethylsilanol. In the narrow experimental domain, the temperature had little or no effect on the wetting angle, variations being within the limit of experimental error (±2°). We therefore accepted the average to be characteristic of the wettability of the plates and the supports at lower temperatures.

TABLE I

WETTING ANGLES, θ, OF HYDROCARBON I ON SURFACE-MODIFIED VITREOUS QUARTZ

Averages of four measurements

Surface	*θ (°)*			*$\bar{\theta}$ (°)*
	40°	*50°*	*60°*	
Trimethylsiloxy (TM)	40	42	41	41
Docosyl-1-dimethylsiloxy (DO)	14	16	15	15
4,7-Dioxaoctyl-1-dimethylsiloxy (OO)	37	37	35	36
Siloxane bridges (heat treatment, HT)	29	30	28	29

In the Van Deemter equation, the constant *A* depends only on the geometry of the column and the column packing. The coefficient *B* shows a similar dependence, if the solute and temperature are kept constant. During column preparation, care was therefore taken to keep all geometrical factors and manipulations as similar as possible. The starting material used for preparation of the supports originated from the same batch, the temperature of the silanization was the same, all supports were prepared with the same relative amount of hydrocarbon I and on filling the columns care was taken to achieve about the same packing density. Of course, the heat-treated support showed slightly different packing properties.

Two *n*-alkanes and a chloroalkane were used to determine the Van Deemter plots at 60, 150 and 240°. The retention properties of the chosen substances are summarized in Table II.

For the evaluation of the results, we intended to use the least-squares method. Because of the strong heteroscedasticity in the experimental range, the value of *A*

TABLE II

RETENTION PROPERTIES OF THE SOLUTES USED FOR DETERMINATION OF VAN DEEMTER PLOTS

Retentions given as k values ($= 1 + k'$, see eqn. 2). T_c, column temperature.

T_c (°C)	*Substance*	*Column*			
		TM	*DO*	*OO*	*HT*
60	*n*-Pentane	1.77	1.70	1.79	2.12
	1-Chlorobutane	3.70	3.40	3.65	4.35
	n-Heptane	6.16	5.65	6.18	7.30
150	*n*-Decane	4.14	3.82	4.12	5.05
	1-Chlorononane	8.50	7.68	8.30	10.30
	n-Dodecane	10.80	9.80	10.70	13.12
240	*n*-Hexadecane	5.83	5.20	5.76	7.16
	1-Chlorotetradecane	7.35	6.61	7.18	9.10
	n-Octadecane	11.07	9.75	10.70	13.60

showed wide variations. Therefore, different weighting functions were examined. Among them, the weighting of the experimental points by $\log [\bar{u}/(\mathrm{cm \cdot sec^{-1}})]$ values for A were obtained which agreed satisfactorily with values obtained by visual inspection of the plots. The average of all results was 0.018 cm, in good agreement with the

TABLE III

CONSTANTS OF THE VAN DEEMTER EQUATIONS WITH THE ASSUMPTIONS DESCRIBED IN THE TEXT

Constant	*Temperature (°C)*	*Column*	*Value of constant*			
A (cm)			0.018			
B ($\mathrm{cm^2 \cdot sec^{-1}}$)	60		*Pentane*	*1-Chlorobutane*	*Heptane*	
			0.476	0.486	0.401	
	150		*Decane*	*1-Chlorononane*	*Dodecane*	
			0.478	0.443	0.382	
	240		*Hexadecane*	*1-Chlorotetradecane*	*Octadecane*	
			0.422	0.449	0.368	
$C \cdot 10^4$ (sec)	60		*Pentane*	*1-Chlorobutane*	*Heptane*	*Average*
		TM	108.8	116.4	109.2	111.5
		DO	46.9	51.5	50.2	49.5
		OO	101.2	105.1	111.5	105.9
		HT	158.0	138.1	130.7	142.3
	150		*Decane*	*1-Chlorononane*	*Dodecane*	*Average*
		TM	38.8	38.2	44.3	40.4
		DO	8.1	9.2	9.1	8.8
		OO	54.7	49.4	50.3	51.5
		HT	63.2	61.8	68.5	64.5
	240		*Hexadecane*	*1-Chlorotetradecane*	*Octadecane*	*Average*
		TM	30.7	25.9	33.6	30.1
		DO	8.0	4.0	7.5	6.5
		OO	51.3	45.3	49.0	48.5
		HT	63.7	57.2	70.1	63.7

value estimated from the particle diameter of the support with a form factor of 0.5 ($2\lambda d_p \approx$ 0.015–0.020 cm). After the constant A had been fixed at 0.018 cm, the values of the constants B and C were calculated by assuming that B is the same for different columns if the same solute was used at the same temperature. The results are summarized in Table III.

As an example, Fig. 1 shows the experimental points and the regression function. Systematic deviations of the experimental points occurred in most instances, but they nevertheless represent the best function if the above-mentioned assumptions concerning the constants A and B are accepted.

The results show that the resistance to mass transfer is about the same for different substances at constant temperature. In Fig. 2, their average value is plotted as a function of temperature. The column packing DO, deactivated by docosyl-1-dimethylsiloxy groups, gives the best performance over the whole temperature range.

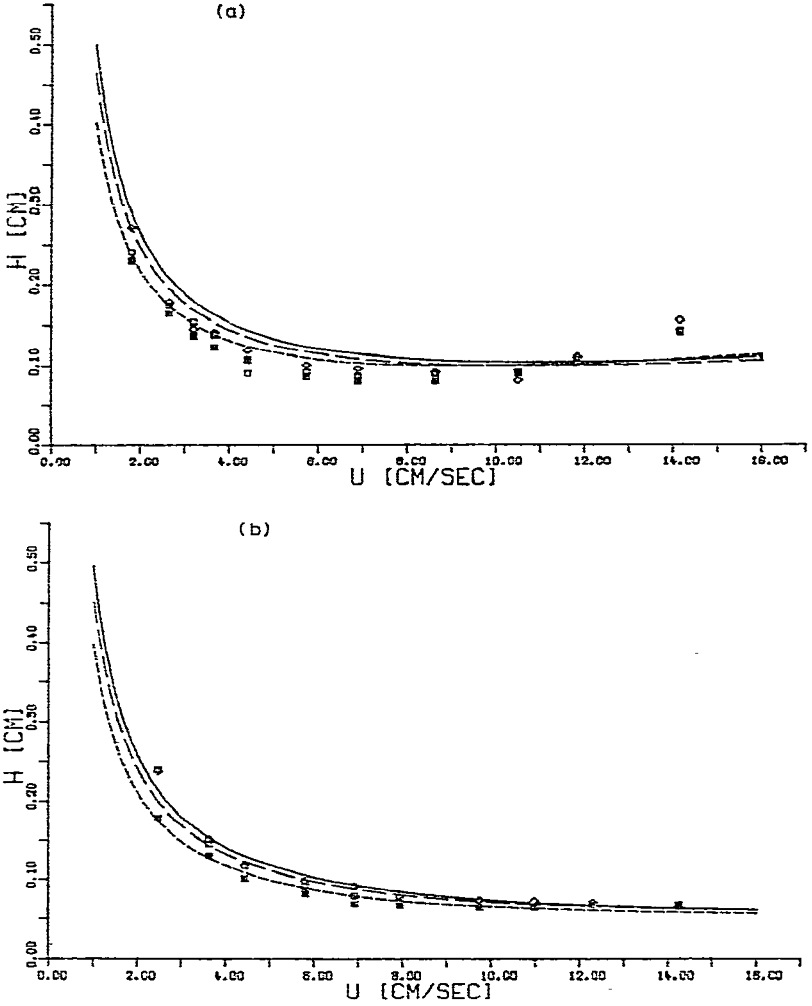


Fig. 1.

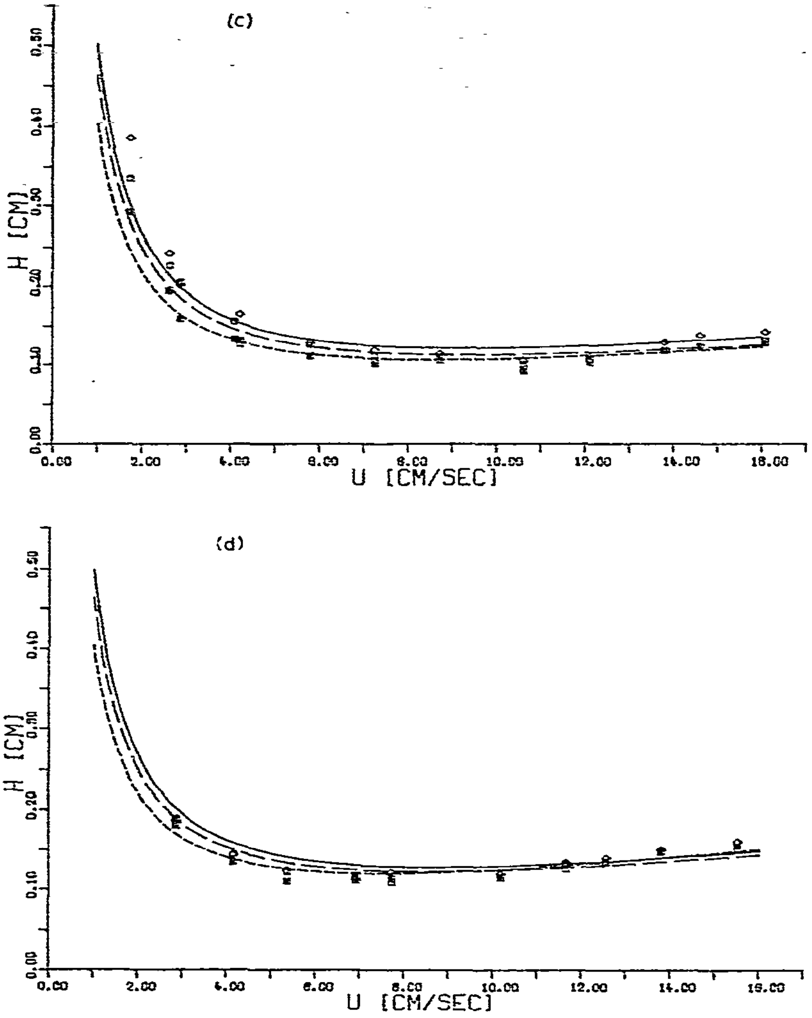


Fig. 1. Experimental values of theoretical plate height, H, on columns prepared with different surface-modified supports as a function of the linear gas velocity, u. Curves were calculated using the constants listed in Table III. Columns: (a) TM; (b) DO; (c) OO; (d) HT. Curves: ◇—◇, *n*-decane; □--□, 1-chlorononane; *---*, *n*-dodecane. All results at 150°.

It is interesting that the support covered with oxaalkyl chains shows a different temperature dependence compared with the other surfaces, having a relatively good performance at 60°, but resembles more the heat-treated surface at higher temperatures.

The wetting angles were measured at 40–60° and their average value is also shown in Fig. 2. For the results at 60° there is a linear relationship between the value of C and the wetting angle on the three silanized surfaces, but the support prepared by heat treatment is inferior, as would be expected from its wettability. In fact, we assumed that there is an analogy between the surface of quartz plates and that of the supports. However vitreous quartz is pure silicon dioxide and diatomaceous earth contains varying amounts of cations. Therefore, the thermally treated quartz and

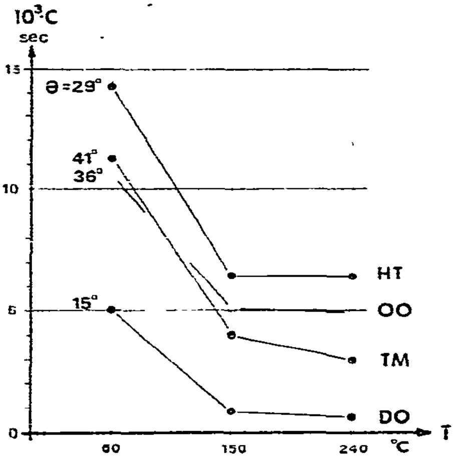


Fig. 2. Average values of the resistance to mass transfer expressed as the constant *C* as a function of the temperature on different columns.

Chromosorb must not have the same wettability. On the other hand, on surfaces covered by organic groups, the wettability is determined by the chemisorbed layer and so differences of the underlying surface will have little effect.

A small *C* value is not the only requirement of a support; it must also show a low activity on adsorption. Preliminary results[5] obtained on surface-modified silica gel have shown that for a maximally dense, chemically bonded monomolecular layer of R-dimethylsiloxy groups, the remaining surface activity depends upon the length and structure of the substituent. The activity decreases as a function of the substituent, R, as follows:

$$-CH_3 \gg -CH_2-(CH_2)_{20}-CH_3 > -CH_2(CH_2)_8-CH_3 \gg -CH_2-(CH_2)_3-O-CH_2- \\ -CH_2-O-CH_3$$

To show differences in adsorption, we injected primary alcohols onto the prepared columns capable of forming hydrogen bridges with surface hydroxyl groups. The chromatograms are shown in Fig. 3. Adsorption on the gas–liquid interface contributes to tailing, but differences must be the result of adsorbtion on the liquid–solid interface. The surface activity towards polar compounds is probably due to noncovered surface silanol groups. The alcohols are very strongly adsorbed on the chemically non-modified surface HT. Besides strong tailing, the appearance of ghost peaks on packing TM shows that the surface activity is higher than on packings DO and OO, where tailing is reduced on packing OO compared with packing DO. The ether groups of the deactivating agent 4,7-dioxaoctyl-1-dimethylsilyl groups on support OO can interact more strongly with the active sites of the surface than the longer alkyl chains bonded to the surface of support DO.

In conclusion, a better wettability of the support by the stationary phase will increase column efficiency. By extrapolation, the best results could be achieved if the contact angle of the pair stationary phase–support material is zero as a regular film thickness should result in the lowest minimal plate heights and the smallest increase

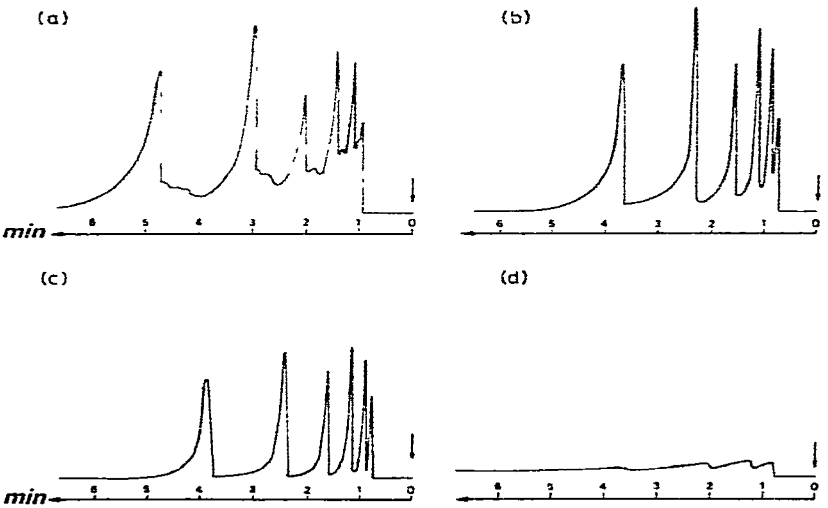


Fig. 3. Chromatograms showing separation of C_4–C_9 primary alcohols on different columns at 150°. Amount injected, 0.3 μl; different surface-treated supports with 6% of hydrocarbon I as stationary phase. Columns: (a) TM; (b) DO; (c) OO; (d) HT.

in the mass transfer term with gas velocity. The hydrocarbon stationary phase did not wet completely either of the supports, not even the surface modified by docosyl-1-dimethylsilanol. Further studies on wettability as well as adsorption characteristics are necessary in order to be able to choose the most appropriate treatment of the surface.

ACKNOWLEDGEMENTS

We thank F. Riedo for his advice and help in the execution of calculations. This work is part of a project supported by the Fonds National Suisse de la Recherche Scientifique.

REFERENCES

1 J. J. van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, 5 (1956) 271.
2 L. Boksányi, O. Liardon and E. sz. Kováts, *Advan. Colloid Interface Sci.*, 6 (1976) 95.
3 Booklet, Cabot Corp., Boston, Mass., U.S.A.
4 O. Liardon, *Doctoral Thesis*, École Polytechnique Fédérale de Lausanne, 1974.
5 L. Boksányi, *Doctoral Thesis*, École Polytechnique Fédérale de Lausanne, 1975.
6 M. Novotny and A. Zlatkis, *Chromatogr. Rev.*, 14 (1971) 1.
7 W. A. Zisman, *Ind. Eng. Chem.*, 55, No. 10 (1963) 19.
8 L. Boksányi, O. Liardon and E. sz. Kováts, *Helv. Chim. Acta*, 59 (1976) 717.
9 L. Boksányi, R. Peters, G. Tarján and E. sz. Kováts, to be published.
10 F. Riedo, D. Fritz, G. Tarján and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 63.
11 V. Ya. Davydov, A. V. Kiselev and L. T. Zhuravlev, *Trans. Faraday Soc.*, 60 (1964) 2254.
12 J. A. G. Taylor and J. A. Hockey, *J. Phys. Chem.*, 70 (1966) 2169.