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MIXED RETENTION MECHANISMS IN GAS–LIQUID CHROMATOGRAPHY

IV. COMPARISONS OF SILANIZED AND CARBOWAX-MODIFIED SUPPORTS*

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SUMMARY

The relative contributions of partition and adsorption to the retention volume were determined for polar solutes on a non-polar stationary phase (*n*-octadecane) coated on differently treated diatomaceous supports: acid-washed; cleaned with gaseous HCl at high temperatures; silanized; and polymer-coated with Carbowax 20M. Supports which were only cleaned with gaseous HCl showed high adsorption. The silanized support had intermediate adsorption and wettability properties. The extent of wetting was dependent on the procedure for cleaning the initial support. The Carbowax-modified support was very inert, the adsorption effects were negligible and the wettability by the stationary phase very poor.

Thus Carbowax-modified supports, owing to low adsorptivity and poor wetting (which in this case minimizes gas–liquid interface adsorption), are well suited to the analysis of polar compounds. Additionally, such supports should be of great value for physico-chemical measurements. The impairment of efficiency due to poor wetting seems to be of minor importance.

INTRODUCTION

Among several known methods for deactivation of diatomaceous supports for gas–liquid chromatography (GLC), silanization has been the most widely used. The common methods of silanization are well known and the literature concerning this problem is very rich. It has been found that, for steric reasons, the full blocking of silanol groups on a clean silica surface is not possible[1]. The silica skeletons of diatomites are the main components of diatomaceous supports, but they also contain aluminium silicates and some impurities, mainly metal oxides, which form electron donor–acceptor active sites not easily blocked by silanization[2]. To improve the silanization is still of vital importance.

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The method by Welsch et al.[3], used for glass capillary deactivation, seems to be the most effective. It is based on treatment with silane vapour at 300°C. Grob et al.[4] have adapted this method for their general procedure for glass capillary column preparation, which included exhaustive cleaning of the surface and a temperature of 400°C. Similar procedures could give a more effective silanization than common, commercial methods, also on diatomaceous supports. This has, to our knowledge, not yet been tried.

The siloxane layers formed by silanization are low-energy surfaces, which are poorly wetted by most liquids used as stationary phases in GLC. It has been argued that silanized supports are not wetted even by n-hydrocarbons, which have the lowest surface tensions of stationary phase liquids used[5].

So there seems to exist a conflict between the aims of getting a surface which is as inert as possible and a surface which is well wetted by the stationary phase. It is desirable that the latter should form a homogenous thin layer. The geometrical (porous) and crystallographic structure of the support can also be of a great importance to the ability of the liquid to cover the whole surface[6].

Aue and co-workers[7,8] developed a new method of deactivation of diatomaceous supports by Carbowax 20M, which was used to form a highly stable, non-extractable thin layer on the support surface. Such supports are now commercially available. Glass capillary columns are also deactivated by similar procedures[9,10]. The chromatographic properties of such supports are very good, but there is a lack of knowledge about the physicochemical bases for their unusual characteristics, owing to the lack of sufficiently precise methods for characterizing such thin polymer layers. It is assumed[7] that at least a part of the Carbowax molecule lies on the support surface, attached to it at many points by non-covalent forces. The layer is also assumed to be of about monolayer thickness.

If we accept this picture, the covering of solid surfaces with such layers should be more effective than silanization, thereby giving a higher degree of inertness. This is also in agreement with chromatographic experience.

To compare the properties of silanized supports and Carbowax-modified supports, a recently presented [11] procedure for the separation of different retention mechanisms has been used.

EXPERIMENTAL

Techniques

Retention volumes were measured with the automatic equipment described elsewhere[12] which enables direct measurement of retention volume, without involving the concept of retention time. Vapour samples of widely varying concentrations were injected under computer control. All calculated results[13] were stored on flexible discs for further processing. A semiempirical equation[11] was fitted to the retention data (retention volume vs. sample size). By this technique, the relative magnitudes of the different retention mechanisms, adsorption and partition, could be calculated.

Materials

Supports of Polish production were used in different modifications as follows. B1: Polsorb B, as received from factory (Permedia, Lublin, Poland). B2: B1 cleaned

with gaseous HCl at 850°C according to the procedure of Aue *et al.*[14]. B3: B2 modified with Carbowax 20M according to the procedure of Daniewski and Aue[8]. Elemental analysis of this material, stabilized in vacuum at 150°C for 4 h, yielded 0.07–0.08% carbon, approximately corresponding to monolayer coverage, in the agreement with Aue *et al.*[7]. The quality of the support was checked by the chromatographic method recommended by Aue *et al.*[14] B4: B2 silanized by vapours of dimethylchlorosilane at 80°C (10 g of support was packed in a glass column, mounted in a GC-oven kept at 80°C and the silanizing agent was injected in 15 portions, each of *ca.* 50 μl)[15]. B5: B1, acid-washed and silanized as described above. All supports were standardized before use by heating to 200°C overnight in a slow stream of oxygen-free nitrogen. The particle size was 0.125–0.25 mm. The specific surface areas are listed in Table I. The support material Polsorb B is very similar to Chromosorb G in mode of production and general characteristics[16].

TABLE I

SPECIFIC SURFACE AREAS OF THE SUPPORTS

Support type	$S\ (m^2/g)$
B1	0.46
B2	0.96
B3	1.05
B4	0.91
B5	0.77

n-Octadecane was used as stationary phase ($\geqslant 99\%$, F 28–30°C, Fluka, Buchs, Switzerland).

Samples were of p.a. grade (Merck, Darmstadt, G.F.R.).

Columns

Glass columns, V-shaped (800 × 2.5 mm I.D.) were used. The support was coated with liquid according to the method suggested by Conder and Young[17] and filled into the columns in small portions, between which the tube was carefully tapped.

All columns are listed in Table II. The column name indicates the support used and the approximate loading of liquid phase. The dead volume of all columns was *ca.* 2 ml and the weight of the packings *ca.* 1.5 g. The amount of stationary phase was determined from weighings during column preparation. Owing to bleeding of the liquid phase, this value decreased with the use of the column. This has been compensated for[18].

Experimental conditions

All runs were made at 60.0°C. The carrier gas was hydrogen and the flow-rate was *ca.* 20 ml/min. Dead volumes were measured by the injection of methane.

Surface area measurements

The surface areas of the different supports were measured with the nitrogen thermal-desorption method[19] first described by Nelsen and Eggertsen[20]. Absolute values of standards (one non-modified, one silanized, and one Carbowax-modified support) have been calculated from three points on the BET isotherm.

TABLE II

EXPERIMENTAL RESULTS

Column	Hexane V_N (ml)	Diisopropyl ether		Methanol	
		V_N^P (ml)	V_N^A (ml)	V_N^P (ml)	V_N^A (ml)
B2-0		22	12,000		.
0.3	0.37	16	655		
3	5.15	14	332		
8	12.23	14	321		
12	20.77	24	218		
B3-0				0.39	0.16
1	1.84	1.49	0	0.33	0.26
3	5.29	4.03	0	0.50	0.21
5	8.50	6.68	0	0.58	0.19
7	12.06	9.28	0	0.60	0.20
10	16.99	13.60	0	0.82	0.29
B4-0		0.003	6.20		
1		1.53	3.56		
3		3.35	1.94		
5		6.74	1.24		
7		8.75	1.91		
8		10.97	1.42		
10		13.44	1.51		
B5-0		−0.22	4.71		
1		0.75	3.26		
3		4.95	2.73		
5		6.16	4.23		
7		8.78	4.80		
10		12.93	2.44		
15		20.05	1.28	1.11	28.01

RESULTS AND DISCUSSION

The technique described in ref. 21, *i.e.* measuring net retention volume, V_N, as a function of sample size, n, varying over at least four decades, on columns with different loadings (0–*ca.* 15%, w/w) of n-octadecane, was carried out for all support types B2–B5. Samples were hexane, diisopropyl ether and, in some cases, methanol. A non-polar stationary phase and polar solutes are chosen, as in such systems a considerable gas–liquid surface adsorption appears, by which the size of the gas–liquid surface areas can be estimated. Also liquids such as n-octadecane are, owing to surface tension considerations, the only ones which have a chance to wet a surface ideally deactivated by silanization.

The contribution to V_N from partition, V_N^P, and adsorption, V_N^A, for diisopropyl ether and methanol, calculated by the procedure given in ref. 11 (where V_N^P and V_N^A are denoted A and C, respectively) are collected in Table II. All values are normalized to 1 g of column filling. When a zero appears in the table for V_N^A, no fitting was performed as the V_N values did not vary with n. In such cases, V_N^P is simply the mean of the values of V_N. For hexane, only the mean V_N values are given, for the same reason. The validity of the assumption that V_N^P is the contribution to V_N from partition is discussed below.

Adsorption and wetting on silanized supports

Plots of V_N^A versus liquid loading, λ', for diisopropyl ether on the silanized supports B4 and B5 (Fig. 1) are similar to those observed earlier on another type of silanized support, Supasorb AW DMCS (Fig. 4b in ref. 21); however, the magnitude
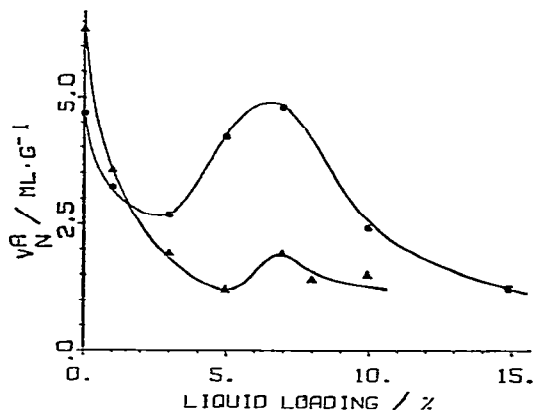

Fig. 1. Adsorption contribution to retention volume of diisopropyl ether *versus* liquid loading of *n*-octadecane for the supports B4 and B5 (HCl-gas treated, silanized and acid-washed, silanized) respectively. ▲, B4; ◉, B5.

of the maximum is considerably smaller for B5 and nearly insignificant for B4. This maximum must, as was discussed earlier[21], be attributed to adsorption on the liquid–gas interface (LGI). The adsorption on covered supports will additionally be the sum of the contributions from the gas–solid interface (GSI) and the liquid–solid interface (LSI). In the present context, the GSI adsorption (on uncovered parts of the support) is assumed to decrease continuously as λ' increases and the LSI adsorption is assumed to be negligibly small. To estimate the area of the LGI, the value of the adsorption coefficient, K_I, of diisopropyl ether on a *n*-octadecane surface is needed. This was measured[22] to $55 \cdot 10^{-6}$ m. If an upper estimate of the LGI adsorption is taken as the maximum value at λ' *ca.* 7%, and the lower estimate is found by subtracting the minimum value at λ' *ca.* 4%, the LGI areas will be 0.013–0.034 m^2/g for B4 and 0.038–0.087 m^2/g for B5, which means 1.4–3.7% and 5.0–11.3% of the support area for B4 and B5, respectively. Similar estimates for Supasorb (for which the specific surface area is 0.55 m^2/g, measured as described above) yield 0.27–0.31 m^2/g or 49–55% of the support area. Thus the silanized supports seem to be not completely wetted.

The adsorption coefficient K_A for GSI adsorption was calculated from the BET areas and V_N^A at zero coverage. The result is $6.8 \cdot 10^{-6}$ m and $6.1 \cdot 10^{-6}$ m for B4 and B5, respectively, and $10.8 \cdot 10^{-6}$ m for Supasorb AW DMS[21]. The more thorough cleaning and hydroxylation of the B4 support prior to silanization, which is assumed to result in a more effective silanization, does not seem to have appreciably influenced the adsorbing properties (probably more uncovered silanol groups exist on B4) of the uncoated support, but the liquid wetting properties are apparently different.

Adsorption and wetting on bare support

For the non-silanized support B2, the adsorption (Fig. 2) is initially very high but levels off to a fairly stable value. The GSI adsorption coefficients, K_A, can be calculated to about 10^{-2} m, but the very high value of V_N^A at $\lambda' = 0$ is for experimental reasons very uncertain. On this support, complete coverage is expected for values of λ' greater than 2% and the adsorption is accordingly much smaller for even low liquid loadings. If the area of the GLI is assumed to be the same as the BET area, which is true only at low liquid loadings, the contribution to V_N^A from GLI adsorption would be only *ca.* 50 ml. The LSI adsorption is assumed to be approximately constant, so the decrease in total adsorption for coverages greater than 2% must be attributed to some residual GSI adsorption, perhaps at pointed edges or other places which are difficult to cover.
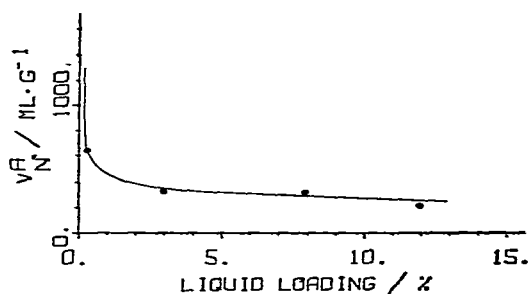

Fig. 2. Adsorption contribution to retention volume of diisopropyl ether *versus* liquid loading of *n*-octadecane for the support B2 (HCl-gas treated).

Adsorption and wetting on Carbowax-modified support

On B3 the adsorption of diisopropyl ether was not detectable. The corresponding results for methanol (Fig. 3) show a completely different picture from the previous ones in that the lowest adsorption is observed on the uncovered support and that the adsorption slowly increases as the liquid loading is increased. However, the small magnitude of these values makes this trend hardly reliable. K_A for methanol on uncovered B3 support is calculated to $0.16 \cdot 10^{-6}$ m. As the adsorption of methanol on another column (B5-15, see Table II) is 22 times greater than of diisopropyl ether, the K_A for the latter substance can be estimated to $7 \cdot 10^{-9}$ m, *i.e.* roughly 10^6 times less than on untreated B2 support and 10^3 times less than on silanized support.
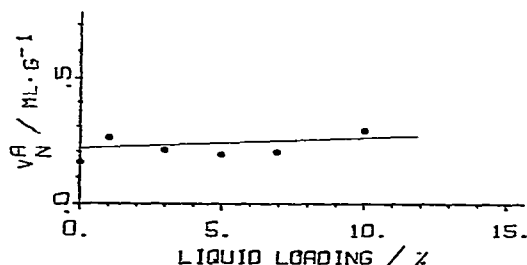

Fig. 3. Adsorption contribution to retention volume of methanol *versus* liquid loading of *n*-octadecane for support B3 (Carbowax-modified).

Furthermore, the area of the GLI is for these columns very small and difficult to estimate. The maximum probable magnitude at 10 % n-octadecane loading can be calculated from the V_N^A value of methanol for the B3-10 column, the conversion factor between methanol and diisopropyl ether, and K_I for diisopropyl ether. The result is $2.4 \cdot 10^{-4}$ m²/g or $ca.$ 0.02 % of the support area.

Apparently, the B3 support is very poorly wetted by n-octadecane which can be inferred from its very weak adsorption properties.

The very low adsorption effects on B3 are in agreement with the results found by Aue and Younker[23], who measured distribution ratio as a function of peak height for various solutes. They found a deviation from linearity only for very large sample sizes, (Fig. 5 in ref. 23), which supports the view that the retention mechanism on Carbowax-modified supports is similar to partition.

General discussion about wetting

The wetting properties of a solid are governed by the critical surface tension, γ_c, of the solid[24]. γ_c has been estimated to 22 dynes/cm for silanized supports by Serpinet[5], which is a lower value than the surface tensions of most liquids which consequently should not wet. To estimate a value of γ_c for a Carbowax-modified surface we can compare the γ_c for polyethylene (27–36 dynes/cm) and for poly(oxyethylene) (43 dynes/cm)[25]. Thus it does not seem probable that γ_c for the Carbowax-modified supports can be less than that for the silanized surface and, consequently, it does not seem to be a reason for less wetting on Carbowax-modified supports. A more probable reason would be less influence of non-bonded silanol groups and impurities which are more effectively covered by the Carbowax layer than by the silylation. The value of γ_c of the silanized layer was estimated for an ideally silanized surface, without consideration of non-bonded silanol groups and impurities. A true, average value for a real surface is certainly higher, and so are the possibilities of wetting. From the comparison between B4 and B5, with B4 being more thoroughly cleaned prior to silanization, this view can be substantiated, with the additional implication that mainly impurities will be responsible for the higher wetting of B5. As was seen above, B4 seems to have more uncovered silanol groups than B5, owing to more effective hydroxylation. The Supasorb support[21] is, in all the aspects studied here, inferior to both B4 and B5. It can also be remarked that although a completely silanized surface should have similar properties to the Carbowax-modified surface, with respect to critical surface tension and inertness, the common silanization of diatomaceous supports does not effectively cover the surface. The silanization techniques, however, might still be justified as they permit a higher working temperature of the chromatographic column than Carbowax modification, and thus could have a potential for development.

The highest efficiency of a chromatographic column is achieved if the thickness of the liquid phase is small, $i.e.$ the support is well wetted. On the other hand, considerable reduction of the liquid surface area in the case of deactivated supports causes a reduction of the LGI adsorption, together with a reduction of adsorption by the support itself. Also, taking into account that even on a wetted surface, according to the model of Giddings[26], the liquid is not spread out in a homogeneous layer, but mainly situated in pores, the disadvantage of bad wetting for highly deactivated supports seems to be of minor importance.

The partition contribution to V_N

The V_N values for hexane on B2 and B3 columns form straight lines when plotted against liquid volume, V_L (corrected for bleeding). The regression parameters are given in Table III and the results confirm the validity of the procedures for column preparation and measurement of retention volume. The slope of such a line is the partition coefficient K_L. The significant positive intercept for the B3 columns is expected, as the polymer layer of this modified support is assumed to contribute to partition retention[23].

For diisopropyl ether, the V_N^P values were plotted in the same way and regression lines were calculated (Table III). For B3, B4 and B5 supports, the slopes coincide well with each other and with previous similar measurements[11] and with static determinations[27] of the partition coefficient. The negative intercepts for B4 and B5 are not statistically significant. For B3 a positive, significant intercept approximately equal to that for hexane is observed. For the B2 support, no meaningful regression line can be calculated. The V_N^P values are in this case calculated in the presence of overwhelming adsorption effects and are not accurate; however, they are of the correct order of magnitude, especially for greater loadings.

TABLE III

REGRESSION PARAMETERS OF PARTITION RETENTION VOLUME *VERSUS* LIQUID LOADINGS

Solute	Column type	Intercept	Slope
Hexane	B2	−0.02	128.2
	B3	0.32	127.2
Diisopropyl ether	B3	0.28	99.8
	B4	−0.14	101.2
	B5	−0.32	101.4

The conclusions from these studies are the same as before[11]: V_N^P equals $V_L \cdot K_L$, the partition contribution to V_N, and thus the parameter V_N^A equals the adsorption contribution at infinite dilution.

CONCLUSIONS

Carbowax-modified supports with their great, near to ideal inertness seem to be promising materials for chromatographic analysis, especially of polar compounds. The possibility of using the support itself, which gives a highly efficient column with linear behaviour for most sample types, might be of great importance in the future. Also, such materials will be of a great interest for physico-chemical applications of gas chromatography, for example in the field of solution chemistry, where all adsorption effects have to be minimized.

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