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COMPARISON OF SUPPORTS CHEMICALLY MODIFIED BY ORGANOSILICON COMPOUNDS FOR GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The adsorption activities towards polar solutes of eight supports (including five commercial samples) coated with squalane were compared, taking into account different types of treatment. One of the best commercial supports was found to be about the same as a support treated with a siloxane tetramer reagent mixed with various substances. Possible modified support surfaces obtained when different silanization reagents are used for the modification are discussed. The best results seemed to be achieved when polymer chains were bound to the surface of the support.

INTRODUCTION

The adsorption activity of diatomaceous supports was reported in the earliest papers on chromatography[1,2]. Poor peak symmetry and dependence of retention on amount of sample are the results of non-linear adsorption isotherms on the liquid–solid interface in the chromatographic column. These effects have an adverse influence on reproducibility of retention data and the separation of polar solutes on non-polar or low-polar stationary phases[3]. Non-reproducibility of retention data reduces the value of these parameters in qualitative analysis. Any inhomogeneity of the support surface leads to non-linear adsorption isotherms, and therefore most efforts towards the development of ideal supports for gas–liquid chromatography (GLC) should be directed to homogenization of support surfaces.

Some treatment techniques have been reported[1,4–6] in which polar organic modifiers, polymers or Ag were added to the support in order to cover the surface with a homogeneous film. All of these attempts failed because of a lack of strong chemical interaction of the modifier with the support surface. Chemical treatment (silanization) was found to be a powerful technique for eliminating active adsorption sites from the support surface[7,8]. Dimethyldichlorosilane (DMCS) and hexamethyldisilazane (HMDS) solutions were found to be the best reagents for this purpose[9]. Silanization in solutions at high temperatures and pressures is the preferred procedure for the manufacture of commercial silanized supports; many other reagents have also been reported to be useful for this process. No details have been published

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about the preparation of new high-quality supports, for example, Chromosorb HP, Chromosorb 750 and Chromaton N Super.

Silanization in the vapour phase at room[10] or elevated temperatures[11,12] has been proposed by some workers as the best technique. Unfortunately, no reports have appeared on comparisons of the different silanization techniques, which makes it impossible to discuss further improvements to supports for use in GLC. This paper describes an evaluation of some silanization techniques for the treatment of supports.

EXPERIMENTAL

Gas chromatography

The retention data for the packings were determined by using a Chrom-41 gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) with a flame-ionization detector (FID). Argon was used as the carrier gas. Glass columns (1.2 m × 4 mm I.D.) were filled with the packing coated with 5% of squalane (Schuchardt, Munich, G.F.R.), which was purified by passage through a silica gel column. The freshly prepared packings were conditioned for 10 h at 90°C. Samples (0.1 ml) were injected as saturated vapours of the solutes with a gas-tight Hamilton syringe. Relative retentions were determined at column temperatures from 40 to 60°C. Retention times were measured with an electronic timer with an accuracy of about 0.1 sec.

Relative retentions and relative molar heats of solutions were calculated in the usual manner. The mean relative standard deviation of the relative retention (r) was about 0.5% and the mean standard deviation of the relative molar heat of solution (ΔH_s^0) was 0.05 kcal/mole. The standard column temperature was 50°C. *n*-Heptane was chosen as the standard.

When the retention time of a solute changes with the amount of sample, the following equation was used in order to give a linear relationship[13]:

$$r = (A/\log h) + B \tag{1}$$

where A and B are constants and h is peak height. Relative retentions for three or four different values of h were determined and then the r values were plotted against $1/\log h$. Peak heights were measured in centimetres on the 25-cm recorder scale and h values were recalculated to the full scale of the recorder (10^{-11} A). The isobaric relative retention for $1/\log h = 0.3$ was taken for the comparison of the packings. These values are reproducible for the instrument with a constant gas flow.

The degree of non-linearity of the sorption isotherm is related to the A value. The more representative function A^* is used for this purpose[13]:

$$A^* = \frac{r_{0.4} - r_{0.3}}{r_{0.3}} \tag{2}$$

where the subscripts 0.3 and 0.4 relate to the corresponding values of $1/\log h$.

Preparation of supports

Chromaton N AW (Lachema, Brno, Czechoslovakia) was chosen as the initial support for silanization[14]. The following reagents were used for treatment: poly-

methylsiloxane PMS-500, hexamethylcyclotrisiloxane D_3, octamethylcyclotetrasiloxane D_4, DMCS, trimethylchlorosilane (TMCS) (all manufactured in the U.S.S.R.; reagent grade). A mixture of D_4, DMCS and TMCS (2:1:1) was also used.

A liquid-phase process was used for PMS-500 and DMCS treatments. The initial support was heated to 400°C, then a 5% solution of PMS-500 or DMCS in carbon tetrachloride was mixed with the support for 30 min. The slurry was heated at 150°C for 2 h and then the residue was held in a vacuum at 250°C in order to evaporate all reagents and volatile substances. The DMCS-treated support was contacted with water vapour at 300°C for 2 h in order to eliminate Si–Cl groups, and the resulting product was heated at 250°C in a vacuum for 2–3 h.

The treatment with D_3 was carried out in the gaseous phase at 150°C for 1 h. The initial support was heated under vacuum and the product after silanization was held in a vacuum at 250°C for 2 h. The modification with the mixture of reagents was carried out at 350°C for 2 h with subsequent heating in a vacuum for 2 h.

The following supports were used for preparing the packings: (1) Chromaton N AW (Lachema); (2) Chromaton N AW DMCS (Lachema); (3) Chromaton N AW treated with D_3; (4) Chromaton N AW HMDS (Lachema); (5) Chromaton N Super (Lachema); (6) Chromosorb G AW DMCS (Johns-Manville, Denver, CO, U.S.A.); (7) Chromaton N AW treated with D_4–DMCS–TMCS (2:1:1); and (8) Chromaton N AW treated with PMS-500.

One volume of Chromosorb G is about 2.5 times heavier than one volume of Chromaton; therefore, the packing with Chromosorb G has only 2.5% of the weight of squalane.

Because the non-polar and low-polarity solutes have low adsorption on diatomaceous supports, two very polar solutes were used in order to demonstrate the adsorption ability of the supports: *n*-propanol, which forms strong hydrogen bonds, and methyl ethyl ketone, which has a very high dipole moment; A^* for *n*-heptane is zero.

RESULTS AND DISCUSSION

The relationship between the relative retention of *n*-propanol and $1/\log h$ is shown in Fig. 1. The numbers on the lines correspond to the numbers of the supports specified in the previous section. Line 1 for the initial support, Chromaton N AW, is curved for the range of concentrations examined. The dependence of r on $1/\log h$ tends to be non-linear for peak heights with $1/\log h > 0.45$. This range refers to Henry's law for the partition coefficient. When the vapour pressure of the solute is extremely small, each solute molecule is bound to active sites on the support surface. These sites seem to be identical from the energetic point of view, and therefore the adsorption isotherm is approximately linear. The nature of these adsorption sites may be suggested as hydroxyl groups chemically bonded to the surface.

Hydroxyl groups were etherified after the silanization procedure. This reaction eliminates the more active adsorption sites from the support surface, as many workers have claimed. However, no reports have considered the alternative aspect, *i.e.*, new hydrocarbon groups appear on the support surface after silanization. This should lead to an increase in the degree of inhomogeneity of the support surface. The experimental data for the silanized supports in Fig. 1 show that the curved adsorption

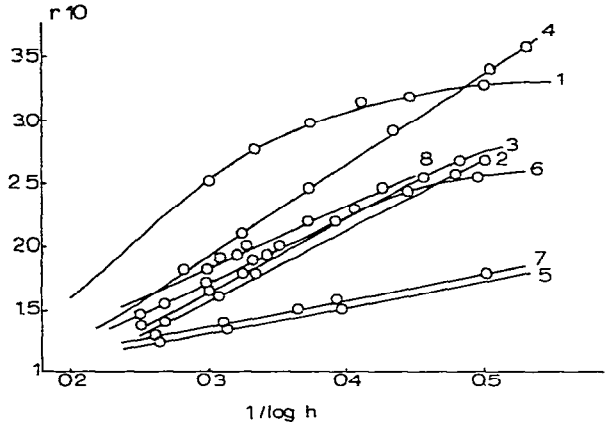

Fig. 1. Relationship between relative retention of *n*-propanol and 1/log *h* for the eight packings at 43.8°C.

isotherm for *n*-propanol extends over the whole range of vapour pressures for the solutes; no indication of the Henry's law region is observed for the silanized supports. Therefore, the relative retention of *n*-propanol is higher on silanized support No. 4 than on the initial support for extremely low vapour pressures.

The relationship in Fig. 1 gives two basic parameters for the sorption processes in the column: (i) the isobaric relative retention for any chosen filling of the interface surface and (ii) the slope of the relationship which indicates the degree of non-linearity of the sorption isotherm, A. The lower both values are, the better is the support.

The general picture for *n*-propanol also applies to the polar solute with a high dipole moment, methyl ethyl ketone (Fig. 2). The isobaric relative retentions at 1/log $h = 0.3$ and A^* values are presented in Table I, together with the relative isobaric heats of sorption for the solutes. A^* decreases when the column temperature increases (Fig. 3).

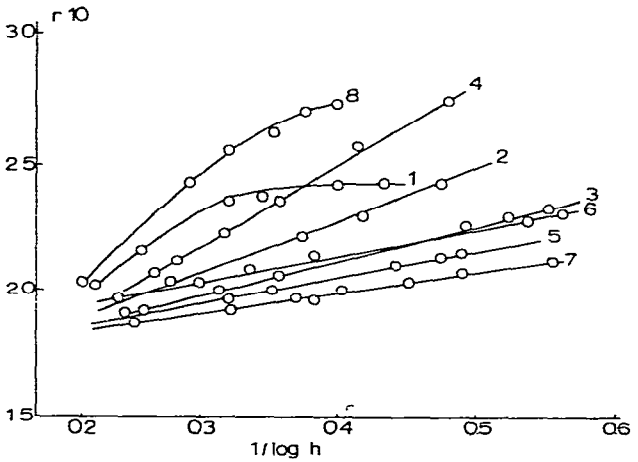

Fig. 2. Relationship between relative retention of methyl ethyl ketone and 1/log *h* for the eight packings at 43.8°C.

TABLE I

SORPTION PARAMETERS FOR THE EIGHT PACKINGS

Support No.	*n-Propanol*			*Methyl ethyl ketone*		
	A^*	ΔH_s^0 *(kcal/mole)*	r	A^*	ΔH_s^0 *(kcal/mole)*	r
1	3.55	0.25	0.252	1.70	1.25	0.240
2	3.50	0.85	0.170	1.16	1.50	0.216
3	3.57	0.90	0.172	0.90	1.35	0.207
4	3.68	0.30	0.193	1.50	1.35	0.230
5	1.55	1.20	0.137	0.68	1.60	0.200
6	3.08	0.75	0.176	0.74	1.55	0.214
7	1.55	1.20	0.143	0.42	1.60	0.189
8	2.69	0.25	0.184	2.10	0.60	0.251

Celite (Chromaton N AW is similar to Celite) has a surface covered by hydroxyl groups[15], which is the main reason for the high r values for n-propanol and low values of ΔH_s^0 on the packing with Chromaton N AW. The relative retention of n-propanol decreases markedly after silanization, which supports the theory of the elimination of hydroxyl groups from the surface. However, with different silanization techniques no linear isotherm resulted for n-propanol, which indicates the presence of different active sites on the support surface that can form hydrogen bonds. Elimination of hydroxyl groups from the support surface is insufficient for an ideal support to be obtained.

Treatment of the support with PMS-500 was tried in order to obtain the chemically bound layer of the stationary phase according to the principle of Aue and Younker[16]. When high temperatures are applied a chemically bound layer of the nonpolar liquid remains on the support surface, as was proved for polyethylene. Unfortunately, no such effects were observed on the support treated with PMS-500 at 250°C (line No. 8). This behaviour of PMS occurs with all stationary phases, and no improvements could be obtained for packings with this silicone.

Let us compare the packings by considering r and ΔH_s^0 values. According to these parameters, the hydrogen bonds are blocked to a minimum extent on packings 5 and 7. It is interesting to compare two silanizing agents (DMCS and HMDS) in order to understand the nature of the more effective deactivation of the support surface. ΔH_s^0 for n-propanol on packing 4 is 0.55 kcal/mole lower than that for packing 2. In general, both silanizing agents react with the surface hydroxyl groups, but DMCS has two active groups whereas HMDS has only one. This allows reaction with closely situated hydroxyl groups on the support surface when DMCS is used. It is surprising that ΔH_s^0 for n-propanol is about the same for the initial support Chromaton N AW and the HMDS-silanized support. This indicates that many hydroxyl groups are close together and some of them remain unsilanized with reagents such as HMDS.

It is interesting that two different types of supports treated with DMCS, Chromaton N AW and Chromosorb G, have similar sorption properties with respect to polar solutes. This shows the importance of the silanization procedure in spite of the nature of the support.

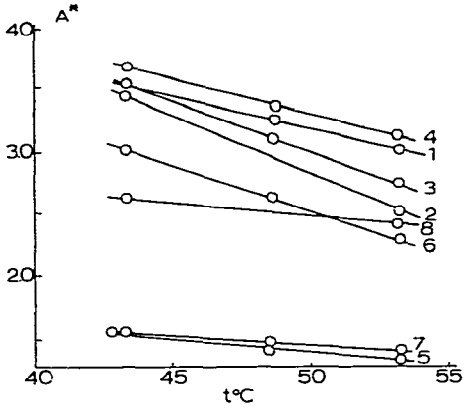

Fig. 3. Dependence of A^* values on column temperature with *n*-propanol as the solute.

When hydroxyl groups are eliminated by an effective silanization process, only other polar active sites remain on the support surface. The presence of these sites is the main reason for the selective adsorption of methyl ethyl ketone molecules. Supports 5 and 7 are the best for both polar solutes, but support 7 is better for methyl ethyl ketone. No great differences in ΔH_s^0 values for methyl ethyl ketone were observed for the different silanization processes, which indicates the relatively small importance of etherification of hydroxyl groups with respect to selective adsorption of methyl ethyl ketone.

The A^* values show the superiority of support 7 for methyl ethyl ketone (see also the temperature dependence of the A^* values). Support 7 therefore has the best homogeneity towards polar atomic groups.

Let us consider the ratio t_N/t_0 (where t_0 is the retention time of methane, which is assumed to be the non-sorbed solute, and t_N is the retention time of the solute) for pure supports in order to determine the hydrocarbon adsorption ability with respect to the surface. The t_N value is measured for an *n*-alkane. The data in Table II show that PMS-500 is the stationary phase rather than the modifier. Support 5 has a greater adsorption ability towards hydrocarbons than support 7, which indicates the different treatment processes used to prepare these supports. More hydrocarbon groups exist on the surface of support 2 (DMCS) than on support 4 (HMDS). It is

TABLE II

t_N/t_0 VALUES FOR DIFFERENT *n*-ALKANES ON THE SUPPORTS

Support No.	*Solute*			
	C_6	C_7	C_8	C_9
1	1.016	1.056	1.143	1.316
4	1.014	1.028	1.065	1.160
5	1.035	1.086	1.189	1.420
6	1.038	1.086	1.191	1.429
7	1.030	1.062	1.142	1.310
8	1.35	1.83	3.02	5.90

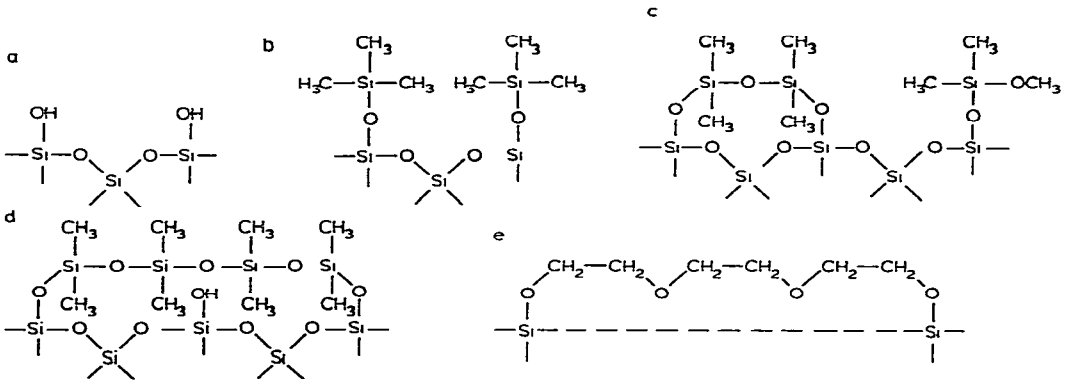

Fig. 4. Suggested structures of the support surface fragments (a) before and (b–e) after treatment with different reagents.

surprising that the sorption ability of hydrocarbons with respect to the HMDS-modified support is lower than that for the initial support, which indicates the complex nature of the modification process applied to the supports.

The possible explanations for the reactions with the different agents are illustrated in Fig. 4, where the silanization reagents bind with the support surface on hydroxyl group points. Fragment (a) shows a model for the support surface, and (b) shows the result of silanization with HMDS or TMCS. Fragment (c) is the support surface after treatment with DMCS and methanol vapour, and (d) and (e) show the supports after treatment with D_3 and D_4, respectively. This scheme shows that with increase in the part of the support surface shielded after the reaction, the more inert is the adsorption surface that results. This indicates the best means of developing an ideal support surface: treatment with a polymer which is chemically bound to the support surface and shielding of the whole surface by the polymer layer. An additional interesting point is the use of reagent mixtures, which are more effective than the individual reagents.

REFERENCES

1 A. T. James and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
2 R. A. Keller and G. H. Stewart, *J. Chromatogr.*, 9 (1962) 1.
3 A. Kwantes and G. W. A. Rijnders, in D. H. Desty (Editor), *Gas Chromatography*, Butterworths, London, 1958, p. 125.
4 A. A. Zhukhovitskii, M. L. Sazonov, M. Kh. Lunskii and V. S. Yusfin, *J. Chromatogr.*, 58 (1971) 87.
5 E. D. Ormerod and R. P. W. Scott, *J. Chromatogr.*, 2 (1959) 65.
6 V. G. Berezkin and L. S. Polak, *Dokl. Acad. Nauk S.S.S.R.*, 140 (1961) 115.
7 W. Supina, *Nasadochnye kolonki v gazovoy khromatographii*, Mir, Moscow, 1977.
8 R. A. Dewar and V. E. Maier, *J. Chromatogr.*, 11 (1963) 295.
9 J. Bohemen, S. H. Langer, R. H. Perrett and J. H. Purnell, *J. Chem. Soc.*, (1960) 2444.
10 A. Prevot, in J. Tranchant (Editor), *Practical Manual of Gas Chromatography*, Elsevier, Amsterdam, 1969, p. 100.
11 A. B. Littlewood, *Anal. Chem.*, 36 (1964) 1441.
12 Y. Takayama, *J. Chromatogr.*, 178 (1979) 63.
13 A. N. Korol, L. S. Lysyuk and G. V. Filonenko, *Teor. Eksp. Khim.*, 12 (1976) 796.
14 J. Viska, F. Kiss, M. Pollak and O. Pospíchal, *J. Chromatogr.*, 51 (1970) 103.
15 J. M. Bather and R. A. C. Gray, *J. Chromatogr.*, 122 (1976) 159.
16 W. A. Aue and D. R. Younker, *J. Chromatogr.*, 88 (1974) 7.