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SUPPORT TREATED WITH CARBOWAX FOR A STANDARD, NON-POLAR PACKING IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The molar heat of solutions, entropic selectivities of the packings and the relative retentions of many solutes of different polarity were determined for two non-polar packings with squalane: these packings were prepared by using silanized and modified supports. The modified support was shown to be the best for preparing non-polar packings for gas–liquid chromatography.

INTRODUCTION

Inter-laboratory reproducibility of retention data remains a problem in gas–liquid chromatography (GLC), especially for non-polar stationary phases and polar solutes. Interfacial adsorption on a solid–liquid surface is the main reason for the lack of reproducibility because of the poorly reproducible properties of chromatographic supports. Although tailor-made paraffinic stationary phase C_{87} seems to have become a standard non-polar stationary phase for GLC[1–3], no choice among the available support materials for the non-polar packing has yet been made. Demands for an ideal support have been reported earlier[4], but even the best modern commercially available support materials have marked adsorption activity towards polar solutes. This activity is non-reproducible from batch to batch of the support material, with two main disadvantages: (a) the retention data depend on the amount of stationary phase in the column; (b) because of a non-linear adsorption isotherm the retention data depend on the amount of sample and some peak tailing occurs on the chromatograms. Although the amount of the stationary phase in the column can be reproduced, injection of a reproducible liquid sample remains a serious technical problem for routine analysis. Also, the peak tailing decreases considerably the column performance.

Hence, the non-linearity of the adsorption isotherm seems to be a more deleterious effect for analytical GLC than the presence of interfacial adsorption itself. Moreover, it is impossible from a theoretical point of view to develop a support without any adsorption activity; therefore, the only real solution to the

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support problem is to develop a support with minimal adsorption activity and with a linear adsorption isotherm for all solutes.

The most widely used white supports are of diatomaceous origin; their surface has some different active centres, which lead to non-linear adsorption isotherms. Only one technique has been generally accepted after the evaluation of different treatments of diatomites, *viz.*, silanization of the supports with dimethyldichlorosilane, with subsequent special thermal treatment; this procedure allowed the development of supports such as Chromosorb W HP. Unfortunately, these supports seem to have non-silanized parts of the surface, which can be demonstrated by non-linear adsorption isotherms for polar solutes.

It seems that supports of the HP series are the best modifications for silanized supports, and it therefore seems necessary to search for new techniques of support treatments. Some techniques of support modification have been described[5–10]: the surface is covered with a non-extractable polymer layer which is formed on heating at high temperature. These supports seem to have a homogeneous surface, as demonstrated by the resolution of highly polar solutes: the alcohol peaks have a symmetrical form. The separating power of these supports has been investigated for many polar solutes, but only a few papers have reported applications of the modified support in GLC[10–13]. Many examples of almost linear sorption isotherms for highly polar solutes have been reported for supports modified by Carbowax[5–9]. When using this support for GLC some new properties may be observed, because the adsorption properties of the modified support–non-polar stationary phase interface are not the same as those for the support–gas interface. Adsorption properties of the modified support with a non-polar stationary phase have to be evaluated by using thermodynamic functions of sorption, which allow an interpretation of the intermolecular interactions with the solutes.

Comparison of the best silanized support with one modified by Carbowax allows a recommendation to be made for a standard support for a non-polar stationary phase.

EXPERIMENTAL

Materials

Chromaton N super (Lachema, Brno, Czechoslovakia), which is similar to Chromosorb W HP, was chosen as a silanized support. Chromaton N AW is the initial raw material for the preparation of Chromosorb N super, and therefore the same substance was chosen for the modification based on the Aue *et al.* technique[7]. The difference between the Aue *et al.* technique and our procedure is elimination of the methanol extraction step. We assume that the minimal amount of the modifier needed to cover the whole support surface (0.2% for the white supports) is bonded entirely with the support surface.

The modification procedure was as follows. Chromaton N AW was coated with 0.2% of Carbowax 15,000 and the resulting packing was conditioned at 260 °C for 4 h; the conditioning temperature was increased from room temperature to 260 °C at a rate of 1 °C/min. A commercial squalane sample was purified through a silica gel column in order to eliminate trace amounts of unsaturated hydrocarbons. A 5% coating of the stationary phase was used with both Chromaton N super (packing S)

and Chromaton N AW modified by Carbowax (packing M). These freshly prepared packings were conditioned at 100 °C for 8 h. Because the same amount of stationary phase was used on the supports, all differences in retention data for the two packings relate only to the differences in the supports.

Different standard solutes were used to evaluate the packings (Table I), which enabled the adsorption properties of the supports to be compared.

Apparatus and calculations

The experiments were carried out with Chrom-31 and Chrom-41 gas chromatographs (Laboratorni Pfistroje, Prague, Czechoslovakia) with flame-ionization detectors at column temperatures ranging from 40 to 80 °C. The samples were injected as vapours (100-μl Hamilton syringe) or as liquids (1-μl Hamilton syringe). Glass columns (1 m × 3 mm I.D.) were used. Helium was used as the carrier gas at a flow-rate of about 20 ml/min, which is about the optimal value in order to achieve the minimal HETP.

The following retention parameters were determined: relative retention (r), relative molar heat of solution* (ΔH_s^0) and the entropic selectivity (F^0)[14] (n-heptane was chosen as the standard). The last parameter was calculated by using the equation

$$F^\circ = R \ln r + \frac{0.565 \Delta H_s^0}{T}, \tag{1}$$

where ΔH_s^0 is in cal/mole, T is the column temperature (°K) and R is the gas constant.

We shall use the thermodynamic scale of ΔH_s^0, *i.e.*, the more negative the ΔH_s^0 value the stronger is the intermolecular interaction. We chose 50 °C as a standard temperature for entropy and relative retention calculations. The relative retention data were calculated from the relationship between ln r and $1/T$ at the standard temperature.

The entropic selectivity (F°) relates to the rotational entropy changes when the solute passes from the gas phase to the stationary phase, and this parameter expresses the entropic selectivity of the stationary phases. It should be noted that the experimental retention values relate to the whole sorption process, including solution in the stationary phase and adsorption on the solid–liquid interface. Adsorption on the gas–liquid interface is negligible for the systems under study.

When the sorption isotherm is non-linear, the retention volume depends on the amount of sample and the isobaric (for a fixed peak height, h) retention data are calculated as in ref. 15. The following equation is used in order to determine the relationship between the net retention volume, V_N, and h:

$$V_N = A/\log h + B \tag{2}$$

where A and B are constants. The slope of this line may be expressed as

$$\delta A^* = \frac{V_N' - V_N''}{V_N''} \tag{3}$$

* The difference between the molar heats of solution for the solute under study and the standard solute (n-heptane).

where the primes refer to the net retention volumes, which were determined for two different values of h (for $1/\log h = 0.4$ and $1/\log h = 0.3$; h is measured in millimetres on the 250-mm recorder chart, the full scale of the recorder being $1 \cdot 10^{-11}$A). The V_N value for $1/\log h = 0.3$ was chosen as the standard isobaric retention volume and the isobaric thermodynamic functions of sorption were calculated from the isobaric retention volumes; the thermodynamic functions depend on the peak height chosen for the determinations and these functions actually are differential thermodynamic functions. The δA^* term expresses non-linearity of the sorption isotherm; the greater the δA^* value, the greater is the non-linearity of the sorption isotherm. When comparing δA^* values for the same solute on different packings (S and M), it is possible to determine the non-linearity of the adsorption isotherm on the solid–liquid interface. As the retention volume depends on the amount of sample, solute samples in different amounts were injected into the column and the relationship between V_N or t_N (net retention time) and $1/\log h$ was plotted; all the necessary retention data were determined from this graph.

ΔH_s^0 was calculated by using the temperature dependence of $\log r$ for four or five different column temperatures. The mean standard deviation for ΔH_s^0 is 0.03 kcal/mole and the mean relative standard deviation for the r values is about 0.1%.

RESULTS AND DISCUSSION

The main results are given in Table I. These data show marked differences for polar solutes on the compared packings which are related to adsorption on the liquid–solid interface.

Linearity of adsorption isotherm (δA^*)

Dependence of the retention volume on the amount of sample was observed for only three solutes, ethyl acetate, methyl ethyl ketone and 1-propanol, on packing S. When using packing M, only 1-propanol showed a marked dependence of V_N on amount of sample (Fig. 1). The δA^* value for 1-propanol is about 10 times smaller on packing M than on packing S, which illustrates the better homogeneity of the support surface modified by Carbowax. The difference relates to the treatment techniques for the basic Chromaton N AW.

The diatomaceous surface has relatively small amounts of hydroxyl groups; these groups react with silanizing agents and are then shielded by trimethylsilyl groups. The latter groups cover only part of the support surface; therefore, dichlorodimethylsilane is used in order to form a dimer chain (with traces of water) on the support surface around the contact point on the hydroxyl group location. In our opinion, this process is the reason for the greater effectiveness of dimethyldichlorosilane than hexamethyldisilazane, because the latter agent does not dimerize. Unfortunately, the support surface is not covered entirely even with the best silanization procedures; the δA^* values confirm this assumption. Some additional evidence was obtained on modification of the silanized supports with Carbowax[16].

The modification process with Carbowax also occurs on hydroxyl groups[17,18], but the presence of C–O–Si bonds is not definitely established, because these bonds must be broken when the modified support is washed with methanol at high temperatures[18]. The long polymer molecules of Carbowax seem to be polymerized

TABLE I

RELATIVE RETENTIONS AND RELATIVE THERMODYNAMIC FUNCTIONS OF SOLUTIONS ON PACKINGS M AND S

Solute	*Packing M*			*Packing S*			*r*
	r	ΔH_s^0 *(kcal/mole)*	F° *(e.u.)*	*r*	ΔH_s^0 *(kcal/mole)*	F° *(e.u.)*	*(ref.19)*
n-Hexane	0.370	1.20	0.12	0.380	1.15	0.10	0.380
n-Octane	2.63	−1.20	−0.18	2.650	−1.20	−0.16	2.635
n-Nonane	7.02	−2.20	0.02	7.09	−2.20	0.04	7.03
Hexene-1	0.308	1.50	0.28	0.332	1.40	0.20	0.318
Cyclohexane	0.690	0.75	0.57	0.720	0.75	0.66	0.703
Benzene	0.550	1.15	0.83	0.572	1.25	1.08	0.556
Toluene	1.54	0	0.86	1.60	0.05	1.02	1.575
p-Xylene	4.25	−1.10	1.02	4.320	−1.05	1.12	4.31
Chloroform	0.311	1.45	−0.21	0.324	1.30	−0.02	—
1,2-Dichloroethane	0.386	1.10	0.03	0.398	1.00	−0.08	—
Carbon tetrachloride	0.574	1.15	0.91	0.607	1.15	1.02	—
Isoamyl chloride	0.916	0.40	0.53	0.930	0.40	0.56	—
Diisopropyl ether	0.307	0.85	−0.86	0.320	0.85	−0.78	—
Ethyl acetate	0.246	1.30	−0.57	0.257	1.25	−0.51	—
Methyl ethyl ketone	0.215	1.00	−1.31	0.231	1.65	−0.03	—
1-Propanol	0.160	0.90	−2.07	0.153	2.00	−0.25	—

additionally at high temperatures, and the non-extractable polymer layer covers the support with a homogeneous film. Hence, the experimental data show that the chromatographic properties of packing M are better than those of packing S, based on δA^* values.

The "self-modification" effect occurs in GLC when polar solutes are separated on a non-polar packing[16]: the long tail of the peak modifies the liquid–solid inter-

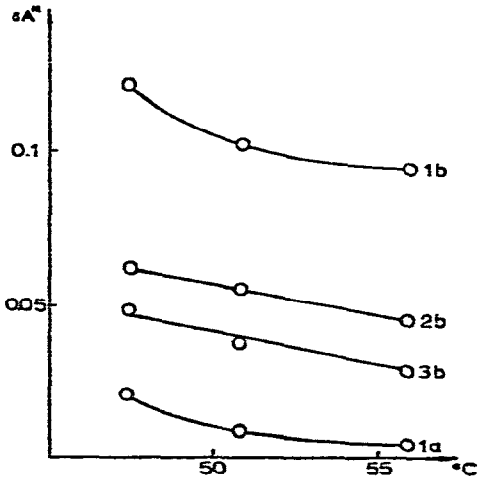

Fig. 1. Relationship between δA^* and column temperature on (a) packing M and (b) packing S: 1, 1-propanol; 2, methylethyl ketone; 3, ethyl acetate.

face and decreases the retention volume for polar solutes. This "self-modification" phenomenon is not reproducible and changes all of the retention parameters markedly. Because of this effect only pure solutes are needed in order to determine reproducible retention data for systems including a polar solute and a non-polar stationary phase. The length of the tail of the peak is proportional to the δA^* value, and therefore a decrease in the δA^* value on passing from packing S to packing M is preferable in the GLC of polar solutes. This phenomenon is illustrated in Fig. 2. The time between two injections of *n*-propanol is denoted T. r and δA^* were measured for the second injection (this relates to the influence of the first injection on the data for the second sample). The data show that the parameters change even with 20-min intervals between successive injections on packing S. Fig. 2 shows no "self-modification" effects for packing M, owing to the more polar nature of the interface. These data show that packing M is better for the determination of reproducible retention dat for mixtures with polar solutes; the column performance also seems to be better for packing M.

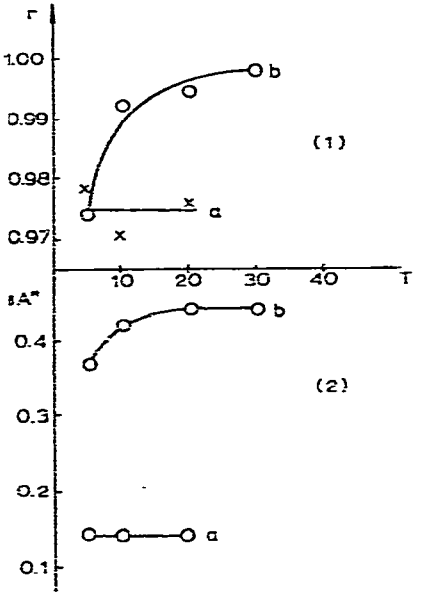

Fig. 2. Relationship between time of injection and (1) relative retention and (2) δA^* for 1-propanol on (a) packing M and (b) packing S.

Retention data

Because of the differences in the nature of the surfaces of the supports, a change in retention is observed when comparing packing S with packing M.

ΔH_2^0 values are related to the energy of intermolecular forces and allow one to evaluate the differences in intermolecular forces for the two types of supports. These values are virtually identical for *n*-paraffins for both packings, but the r values are lower for packing M than packing S. These small differences may be due to the hydrocarbon nature of the Chromaton N super support. The data in ref. 19 confirm

this explanation: these data were determined on the stainless-steel capillary column with a non-hydrocarbon nature. The r values determined on packing M are lower than those on the capillary column.

Some low-polar solutes have more positive ΔH_s^0 values on packing M than on packing S: this indicates a decrease in the intermolecular forces with the interface for packing M. Hexene-1, dichloroethane and chloroform belong to this group of solutes. In general, solutes of low and moderate polarity have nearly the same ΔH_s^0 values on both packings.

The aromatic hydrocarbons are high polarizable solutes, and therefore the intermolecular forces of these solutes with the interface are greater on the more polar packing M. Highly polar solutes (methyl ethyl ketone) have stronger intermolecular forces with packing M. The same effect was observed for solutes that can form hydrogen bonds (1-propanol). Hence, the polar nature of the modified support is observed only for highly polar solutes. This effect has to be taken into account when the thermodynamics of solution are determined by GLC. The silanized support allows one to determine more accurate thermodynamic values for highly polar solutes.

The r values on packing M are lower than those on packing S with only one exception (1-propanol). The r values for highly polarizable hydrocarbons on packing M are lower than those on the capillary column. The $F°$ values are the main reason for this difference. This may be explained by the differences in adsorption on homogeneous and non-homogeneous surfaces. The latter surface has active centres of different activity; the solute molecule bonds with the more active adsorption centre at one point. The remaining groups in the solute molecule bond with less active adsorption centres; rotation of the solute molecule is possible for the groups that bond with the less active centres. The adsorption centres on a homogeneous surface have the same activity and all groups in the solute molecule have the same degree of hindrance for rotation. Hindrance of rotation is greater for packing M (this can be seen from the $F°$ values). Hence, the adsorption entropy on a homogeneous surface is lower than that for a non-homogeneous surface.

When expressing the "polarity" term in Rohrschneider or McReynolds units, packing M is less polar than packing S. Actually, the intermolecular forces with polar solutes are greater for packing M and, therefore, this packing is more polar from the physico-chemical point of view.

The next point for comparison is the variation with temperature of the relative retentions, which is related to the ΔH_s^0 value. The difference between the ΔH_s^0 values for the two packings is small, except for very polar solutes. This causes a more rapid increase in the r values on packing M than on packing S when the column temperature is decreased.

Bleeding for support M is observed at 260 °C[9]; this is the upper limit for use of packing M, whereas the silanized packings may be used up to 350 °C. This restricts the application of the modified supports in high-temperature separations.

In conclusion, the results show that the Carbowax-modified support is the best for reproducible GLC analysis with non-polar stationary phases, and this support can be recommended as a standard for non-polar packings. Precautions are necessary when thermodynamic data are determined for highly polar solutes because of the polarity of the support surface modified with Carbowax.

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