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CALCULATION OF THE CHARACTERISTICS OF THE BONDED LAYERS OF REVERSED STATIONARY PHASES

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SUMMARY

A new stationary phase parameter, R , the percentage of rigid structure, was introduced. It will be determined by the structural characteristics of the initial support and the modifier employed. This parameter will permit the characterization of any reversed stationary phase more completely and its relation to other types of bonded layer structure. Reproducibility is expected only for stationary phases with similar structures of the bonded layer. The carbon content, bonding density and R were calculated for different stationary phases from data on the pore structure of the initial support and the modifier structure.

INTRODUCTION

Reversed stationary phases with bonded long chain hydrocarbon groups are the most widely used stationary phases for the separation of a large variety of mixtures by high-performance liquid chromatography (HPLC). More than half of all HPLC analyses are carried out in this way. The main drawback of commercially available stationary phases, is their poor reproducibility^{1,2}.

In spite of the apparent simplicity of the bonded layer structures of these stationary phases they are rather complicated systems. Therefore much attention has recently been paid to the structure of reversed stationary phases^{3–6}. The majority of suppliers give only the value of carbon content. Evidently, the description of stationary phases in this way is insufficient since this macrovalue enables only their capacity to be calculated. Stationary phases having similar values of the carbon contents may be quite different in their chromatographic characteristics.

The concept of bonding density (the number of bonded modifier groups per unit area) gives additional and essential information about reversed phases. The use of these parameters and structural data for the initial silicas (specific surface area, average pore diameter, pore size dispersion) allows any sample of modified silica to be characterized. In this context it could be of interest to introduce a new parameter which would include structural characteristics of both the initial support and of the bonded layer one. Such parameter can be obtained by structural-geometrical consid-

eration of a bonded layer of modified silica as described in our paper⁷. It was shown that there are three basic types of bonded layer structures of reversed stationary phases, namely: flexible, rigid and intermediate, the last consisting of both flexible and rigid structures in different ratios. Also that the bonded molecules in flexible and rigid structures have different conformational mobilities. In a rigid structure the conformation of the bonded hydrocarbon chains is practically independent of the external conditions, and under chromatographic conditions the adsorption retention mechanism is dominant. The conformation of the bonded chains in a flexible structure is determined by the temperature and solvent composition. The probe molecules can penetrate the bonded layer and a distribution retention mechanism is dominant.

We have introduced a parameter R (ref. 7), the percentage of rigid structure as the characteristics of a bonded layer which will be determined by the structural characteristics of initial support and modifier employed. We believe that this additional parameter will permit the characterization of any reversed stationary phase more completely and its relation to other types of bonded layer structure. Reproducibility should be expected only for stationary phases with similar structures of the bonded layer.

This paper deals with the calculation of the carbon content, bonding density, p and R from data on the pore structure of the initial support and the modifier structure.

RESULTS AND DISCUSSION

In the previous paper⁷ we offered a new calculation method for the characteristics of a bonded layer from data on the pore structure of the initial support (average pore diameter and pore size distribution) and the modifier structure (size of anchor group, the number of carbon atoms in the case of alkyl modifiers).

The following assumptions have been taken as a basis for the calculation of the characteristics of the modified surface:

- (i) support pores have a cylindrical form;
- (ii) bonded modifier molecules are evenly distributed throughout the surface;
- (iii) bonded chains adopt such a conformation which provides the maximum bonding density;
- (iv) pore diameters are distributed according to the normal law.

In the framework of this model, simple equations have been obtained which contain integrals easily calculable on a computer. The calculation data have been shown⁷ to be in good agreement with experimental data.

Effect of pore diameter and pore size distribution on carbon content for C_8 and C_{18} reversed stationary phases

The results of the calculations are given in Figs. 1 and 2. The carbon content remains constant for a number of silicas with the same pore volume when the average pore diameter is less than 10 nm for C_{18} bonded phases and 4 nm for C_8 bonded phases, but decrease linearly with increasing average pore diameter. Thus, we believe, it is wrong to use a narrow pore support to increase the carbon content owing to the increase in specific surface area, S , of the initial support. Indeed S increases with decreasing average pore diameter, simultaneously to the decrease in bonding density, that is why the carbon content remains unchanged and, hence, the maximum pos-

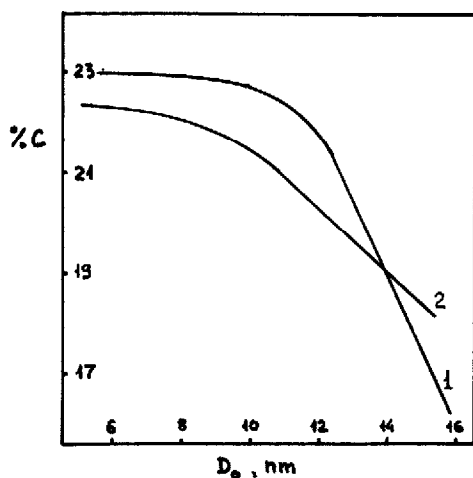


Fig. 1. Effect of the average pore diameter and dispersion of the pore size distribution, σ , on the carbon content for C_{18} reversed stationary phases. Pore volume = 0.75 ml/g. 1, $\sigma = 1$ nm; 2, $\sigma = 3$ nm.

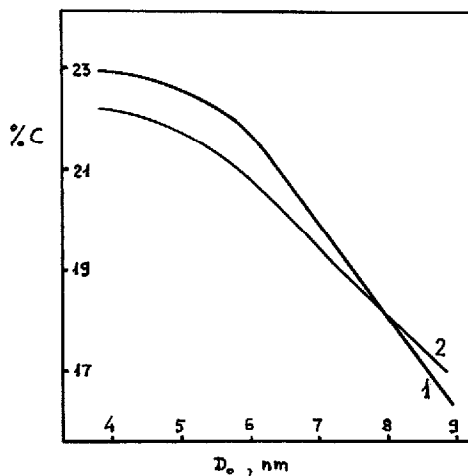


Fig. 2. Effect of the average pore diameter and dispersion of the pore size distribution, σ , on the carbon content for C_8 reversed stationary phases. Other details as in Fig. 1.

sible. For instance, for C_{18} bonded phases with pore volume 0.75 ml/g, the maximum carbon content is 23%.

The carbon content also depends upon the width of the pore size distribution. However, the calculations show that this dependence is fairly slight and one can conclude that the carbon content is practically independent of σ , the dispersion of the pore size distribution (Figs. 1 and 2).

Effect of chain length on carbon content at fixed pore diameter

The effect of the chain length of a bonded n -alkyl modifier for a support with an average pore diameter of 10 nm (the most frequently used support in HPLC) on the carbon content is presented in Fig. 3. Increasing the chain length to 18 carbon atoms (C_{18} stationary phase) leads to a linear increase in carbon content. It is interesting that the application of a longer chain modifier (C_{20} , C_{22} , etc.) does not result in further increases in the carbon content.

Bonding density: effect of average pore diameter and dispersion of pore size distribution

The results of the calculations are given in Fig. 4. In the case of alkyldimethyl- and alkyltrichlorosilanes, the bonding density for C_{18} stationary phases with an average pore diameter of more than 10 nm remains constant and equal to 2.3 groups per nm^2 . However, when employing stationary phases with an average pore diameter less than 10 nm, the bonding density reduces linearly with decreasing average pore diameter. For instance, in the case of C_{18} stationary phases with average pore diameter 6 nm and dispersion $\sigma = 1$ nm, the maximum possible bonding density of alkyl chains is about 55% from 2.3 groups per nm^2 .

Only stationary phases with the same bonding density can be reproducible

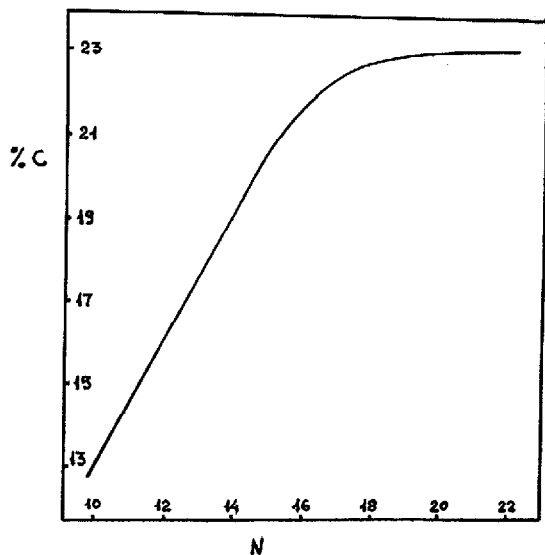


Fig. 3. Effect of the chain length of the modifier molecule on the carbon content. Average pore diameter = 10 nm; pore volume = 0.75 ml/g.

ones. It is preferred if $p = p_{\max} = 2.3$ groups per nm^2 , *i.e.*, remaining silanol groups on the surface are maximally shielded by modifier molecules. In the case of C_{18} stationary phases, these conditions will be realized for supports with $D_o \geq 12$ nm, *i.e.*, within sufficiently wide pores. For such supports even considerable changes in D_o from lot to lot do not result in large changes in p value (Fig. 4). Unfortunately, this is not true of commercially available C_{18} stationary phases, the majority of which have $D_o = 8\text{--}12$ nm and $p < p_{\max}$ and depends on D_o .

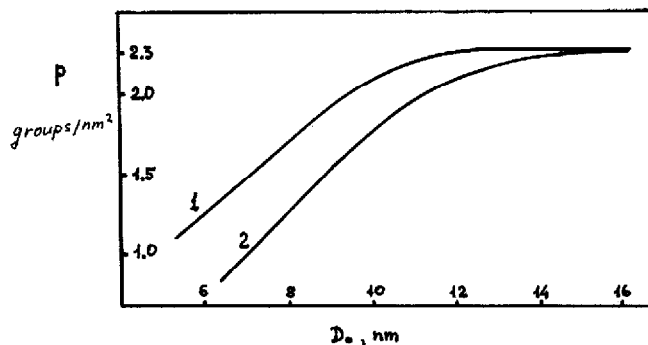


Fig. 4. Effect of the average pore diameter and dispersion of the pore size distribution, σ , on the bonding density for C_{18} reversed stationary phases. 1, $\sigma = 1$ nm; 2, $\sigma = 3$ nm.

Calculation of percentage of rigid structure: effect of D_o and σ for C_{18} stationary phases

The results of the calculations show (Fig. 5) that in the case of the support with a narrow pore size distribution ($\sigma = 1$ nm), the rigid structure is transformed into a flexible one within a narrow interval of D_o . Indeed, when $D_o = 8$ nm, R is 100% and if $D_o = 14$ nm, $R = 0$. For wide pore size distribution this interval is extended considerably (Fig. 5).

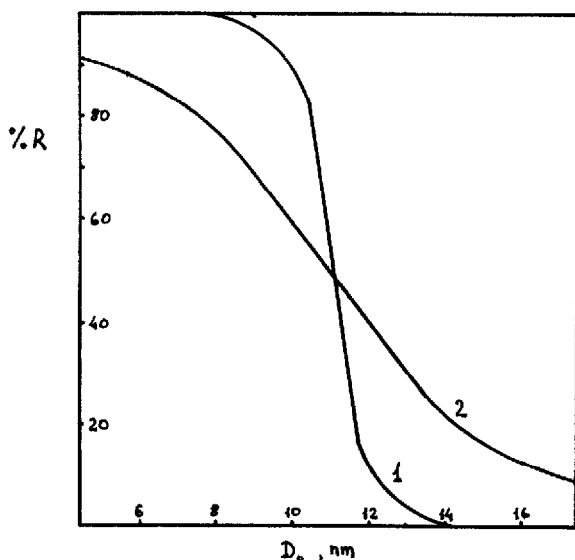


Fig. 5. Effect of the average pore diameter and dispersion of the pore size distribution, σ , on the percentage of rigid structure for C_{18} reversed stationary phases. Pore volume = 0.75 ml/g. 1, $\sigma = 1$ nm; 2, $\sigma = 3$ nm.

Reproducibility of chromatographic characteristics is expected where R is 0 or 100%. Then a negligible change in the average pore diameter of the initial support will not lead to a considerable change in the percentage of rigid structure.

To modify the silica surface chemically, one should choose the support with a narrow and symmetric pore size distribution in order to reduce the interval of the rigid-flexible transformation.

As mentioned above, the majority of commercial C_{18} stationary phases are manufactured on the basis of supports with average pore diameters of 8–12 nm. Comparing two samples of C_{18} stationary phases with $D_o = 11$ and 12 nm ($\sigma = 1$ nm in both cases), which differentiate insignificantly, both their carbon contents and bonding densities (Figs. 1 and 4), they can differ in four times by the percentage of rigid structure (R). The number of adsorption sites in the bonding layer is also different, hence, the adsorption and chromatographic characteristics will also be different.

Diagram of bonded layer state for reversed stationary phases

Finally we combined the results of the calculations for the bonded layer of reversed stationary phases into a state diagram (Fig. 6). This allows the kind of the

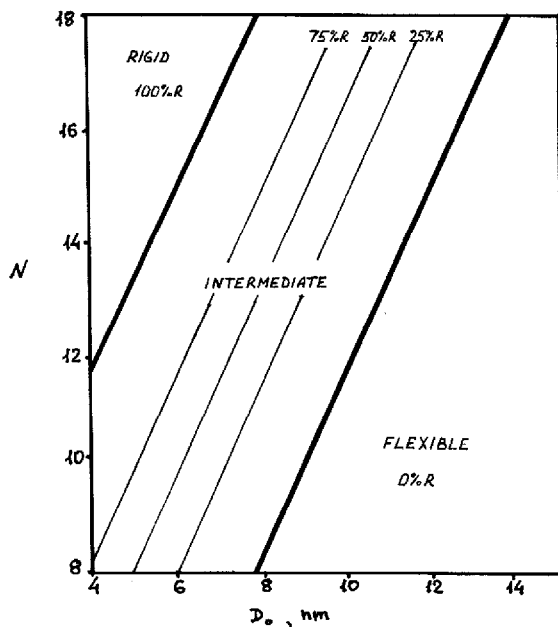


Fig. 6. Diagram of the bonded layer state for reversed stationary phases. Pore volume = 0.75 ml/g; $\sigma = 1$ nm.

bonded layer structure to be identified from the average pore diameter of the initial support and the number of carbon atoms in the bonded *n*-alkyl chain of the modifier.

The diagram contains three parts: rigid, intermediate and flexible structures. To employ the diagram it is necessary to raise a perpendicular from the value of the average pore diameter (*D*₀) on the abscissa to crossing with a perpendicular raised from the *N* value, the number of carbon atoms in the bonded *n*-alkyl chain of a modifier. The point of intersection will lie within the region, which demonstrates the state of the bonded layer, namely rigid, intermediate or flexible. For instance, supports with an average pore diameter of 10 nm with bonded octyl groups (C₈ stationary phases) have bonded layers with a flexible structure, and similar supports with bonded octadecyl groups (C₁₈ stationary phases) have bonded layers with intermediate structure comprising 75% rigid structure.

It is interesting that stationary phases corresponding to the intersection points, lying in the upper left part of the diagram (100% rigid structure), are characterized by identical carbon contents. These results additionally confirm that carbon percentage does not depend on *D*₀ for small pores. For stationary phases with a pore volume 0.75 ml/g this value of the carbon content is 23%, for stationary phases with a pore volume of 0.6 ml/g it is 18.4% and it is impossible to reach higher carbon contents for supports with the stated pore volume neither by increasing the specific surface nor by decreasing *D*₀.

The given diagram was constructed for narrow distributions of pore diameters (dispersion is 1 nm). In the case of wider distributions, the limits of the intermediate structure region will be essentially broadened (Fig. 7).

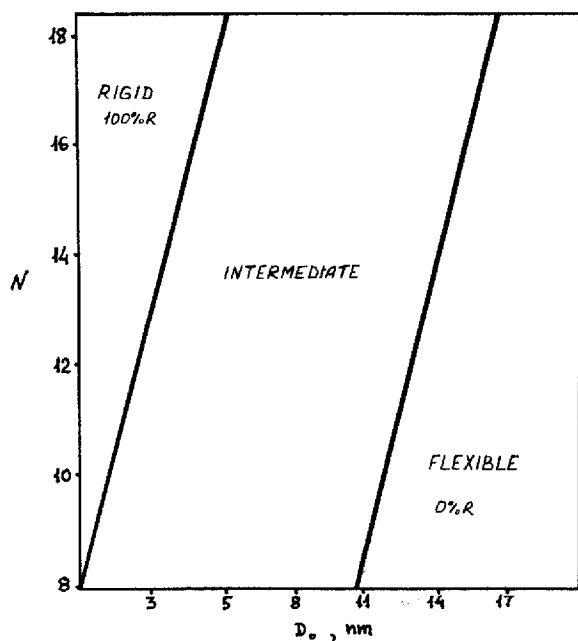


Fig. 7. Diagram of the bonded layer state for reversed stationary phases. Pore volume = 0.75 ml/g; $\sigma = 3$ nm.

CONCLUSIONS

The given results testify once more to the fact that to obtain reproducible reversed stationary phases one needs rigorous control of the porous structure of the initial support.

The introduction of a new parameter giving the percentage of rigid structure of a bonded layer permits the reversed stationary phases to be classified into three basic groups according to the structure of the bonded layer: rigid, flexible and intermediate. In our opinion, only stationary phases with rigid or flexible structures of the bonded layer can possess reproducible characteristics. Only the same lot of an initial support is likely to be able to reproduce the characteristics of a stationary phase with intermediate structure, since even negligible changes in the pore size distribution of the initial support can result in significant changes in the adsorption and chromatographic characteristics of the stationary phases. Unfortunately, the majority of commercially available stationary phases with bonded octadecyl groups are manufactured on the basis of silicas with average pore diameters ranging from 8 to 12 nm, which leads to bonded layers of intermediate structure. In our opinion, this is one of the main reasons why their characteristics are not reproducible.

The diagrams presented here reveal the trends in the basic parameters of the bonded layer depending on the porous structure of the initial support and the n -alkyl chain length of the modifier, as well as enable the choice of better support-modifier pair to make a stationary phase with the required characteristics.

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