SURFACE AREA AND VOLUME OF PORES AS CHARACTERISTICS OF SILICA SUPPORTS FOR GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

A comparison of porous silica gels of different origin was made. It was shown that there is no simple correlation between the mercury porosimetry curve and the corresponding chromatographic data.

The pore surface area was found to be an important parameter reflecting both the size and the shape of the pores. A linear dependence was established between log M_{infl} and log V/SA, where M_{infl} is the molecular weight at the inflection point of the chromatographic calibration curve, V is the total pore volume and SA the total pore surface area.

INTRODUCTION

One of the advantages of inorganic support materials for gel permeation chromatography (GPC) is their dimensional stability, resulting in the ability to characterise them by means of porosity data. The quantitative description of the separation (fractionation) ability of the gel in terms of both the shape and dimensions of its pores might permit the preparation of suitable gel mixtures which would be most effective over the given range of the molecular weights for polymer fractionation. Furthermore, such a description might lead to a universal calibration method for gel permeation chromatography, which — provided that the interaction of the solute with the support material is negligible — would include not only the parameters of the dissolved macromolecules, but also the characteristics of the gels. The establishment of a relationship between the size and shape of the gel pores and its fractionation ability may also be interesting from a theoretical point of view.

Several authors[1-3] have attempted to correlate the pore volume determined by mercury porosimetry with corresponding chromatographic data. Their results show a good agreement, at least qualitatively, between theory and experiments. However, they have to make assumptions about the shape of the pores, which means that the parameters obtained from simple mercury porosimetry data are not the only ones that

govern chromatographic separation. An important role may also be played by the surface of the pores, even if one assumes that there is no adsorption. In this work, it will be shown by comparing gels from different sources that mercury intrusion porosimetry is not the only method for characterising the separation ability of the columns and that a very simple parameter, the volume over surface area of the pores, can, at least in our case, describe the chromatographic behaviour of the columns.

EXPERIMENTAL

The silica beads studied were either products of Péchiney-Saint-Gobain, distributed under the name Sphérosil, or samples prepared at the Institute of Inorganic Chemistry of the SAV, Bratislava. (The letters A to F refer to the Sphérosil samples, HA and HC to the samples made in Bratislava.) The calibration curves, *i.e.*, the curves obtained by plotting the logarithm of polymer molecular weight (M) as function of elution volume (V_e), were determined on a Waters Model 200 gel permeation chromatograph under the following conditions:

Temperature: 20 ± 1°C
Column: length 120 cm, diameter 3/8 in.
Solvent: tetrahydrofuran
Polymer: Waters' and Pressure Chemical Co. "monodisperse" polystyrene samples and samples prepared and characterised in Strasbourg
Concentration: 2 mg/cc
Injection time: 2 min
Elution rate: 1 cc/min

The total surface area and the pore volume were measured for all the gels, the former being determined from argon adsorption at 77.3 °K by the BET method[4], the latter by means of either the Carlo Erba mercury intrusion porosimeter Model AG 65 or the differences between mercury and benzene pycnometry data.

RESULTS AND DISCUSSION

The calibration curves of the gels C, HA and HC are shown in Fig. 1. Instead of plotting the classical calibration curves which are difficult to compare due to slight chan
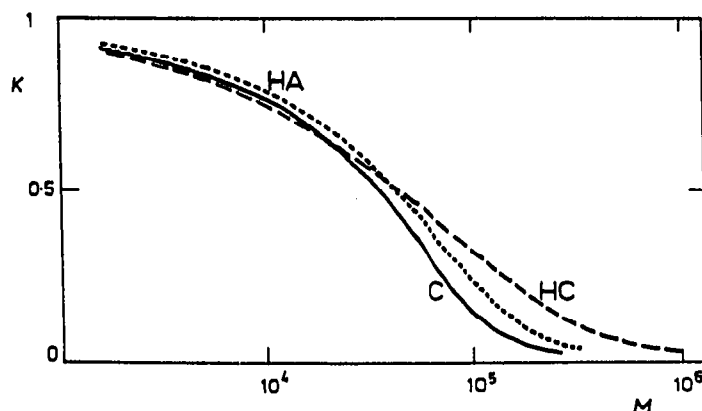

Fig. 1. The calibration curve for gels: Sphérosil C, HA and HC.

ges in total column volumes, the partition coefficients, $K = (V_e - V_0)/(V_t - V_0)$, were plotted as a function of log M. In this expression, V_e is the elution volume of the polymer, V_0 and V_t are respectively the interstitial volume (dead volume) and the total volume of the eluent, i.e. the elution volume of benzene. The cumulative pore size distribution obtained from mercury porosimetry is shown in Fig. 2.
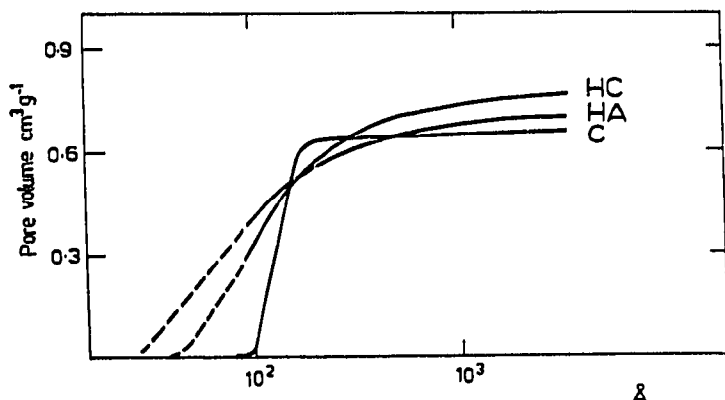

Fig. 2. The porosimetry curves for gels: Sphérosil C, HA and HC.

It is important to note that, despite the similarity of calibration curves for gels HA and C, their porosimetric curves do differ appreciably.

On the other hand, the HA and HC gels, whose partition coefficients behave differently as reflected by the slope of the "linear" part of the calibration curve, possess more similar porosimetric curves. These results show that there is no simple relation between the porosimetric curves and calibration curves. This is not surprising since there is no reason to assume that gels of different origins having the same pore size distribution will also have the same pore shape.

From an experimental point of view, it should also be stated that extremely high pressures ($>$ 1000 atm) are necessary for the determination of the volumes of pores with effective radii less than 75 Å. Due to this difficulty, the total pore volumes for HA and HC gels were calculated from the pycnometric data and the dashed portions of the porosimetric curves in Fig. 2 show the assumed courses. However, this fact does not affect the above-mentioned conclusion.

In addition to the pore size distribution, the surface area, SA, is also an important characteristic of the porous silica beads. The SA reflects the shape and the size of the pores (the bigger the pores, the smaller is the SA and vice versa) and is independent of the texture of the porous gel particles (their shape, irregularity etc....). Thus, the silica beads can be evaluated by a single parameter depending only on their pore structure. The pore surface also plays an important role in the presence of specific interaction forces between gel and solute molecules and governs the adsorption effects. The relative simplicity of the surface area determination is a further advantage of using this parameter. Since this factor is closely related to the nature of the gel, it was interesting to see whether or not it would be possible to establish a correlation between surface area and the chromatographic properties of these gels.

The calibration curve, V_e vs. log M, is a direct picture of the fractionation ability of a given gel. If one is interested only in the range of molecular weight in which the
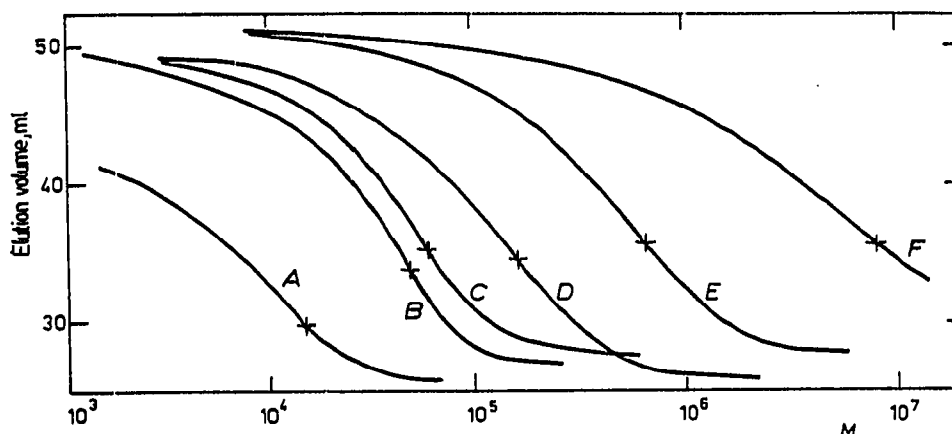
Fig. 3. The calibration curves for the series of Sphérosil gels.

TABLE I

PARAMETERS AT THE INFLECTION POINTS OF THE CALIBRATION CURVES GIVEN IN Fig. 4

Silica beads	Total surface area (m^2g^{-1})	Total pore volume (cm^3g^{-1})	M_{infl}
A	277.8	1.05[a]	1.5×10^4
B	155.0	1.14[a]	4.5×10^4
C	88.2	0.67	5.5×10^4
D	31.0	0.60	1.5×10^5
E	17.6	0.70	6.0×10^5
F	3.51	0.50	8.0×10^6
HA	91.2	0.70[a]	6.1×10^4
HC	76.5	0.79[a]	9.5×10^4

[a] Data calculated from the difference between mercury and benzene pycnometry determinations.

column is efficient, the value of the molecular weight at the inflection point is a very interesting parameter. As shown by our experiments, this parameter is insensitive to different practical aspects of the preparation of the columns (such as the dead volumes, the amount of gel in the column and the method of its filling etc....) and to the size and shape of the gel particles. In Fig. 3, the calibration curves V_e vs. log M are shown for the different Sphérosils. The corresponding inflection points, evaluated by means of auxiliary curves $\Delta V_e/\Delta \log M$ = f(log M) are marked. Such a determination is not very accurate owing to the shape of the calibration curves and to experimental errors. It can be used as a first approximation only. In order to determine M_{infl} more accurately, an analytical expression describing the calibration curves should be used.

The values of total surface area, total volume of pores and molecular weights at the inflection points of the calibration curves are summarised in Table I. The total volume of the pores (V) for individual gels changes only slightly. On the other hand, there is a good correlation between SA and M_{infl}. More precisely, if one plots log SA as function of log M_{infl}, the points lie on a straight line, regardless of the method of preparation of the gels. (See Fig. 4.)

The V/SA ratio seems to be a good parameter to describe the chromatographic behaviour of the gel; the straight line in Fig. 5 obeys the following equation:

$$M_{\text{infl}} = 1.61 \times 10^8 \left(\frac{V}{SA}\right)^{5/3}$$

Physically, the ratio V/SA represents an effective pore radius averaged over all the pores of different shapes and sizes. It is evident that the larger this value, the bigger the molecules which can enter into the gel. Since the V/SA ratio has the dimensions of length, it can be related to the diameters of molecules penetrating into the gel.
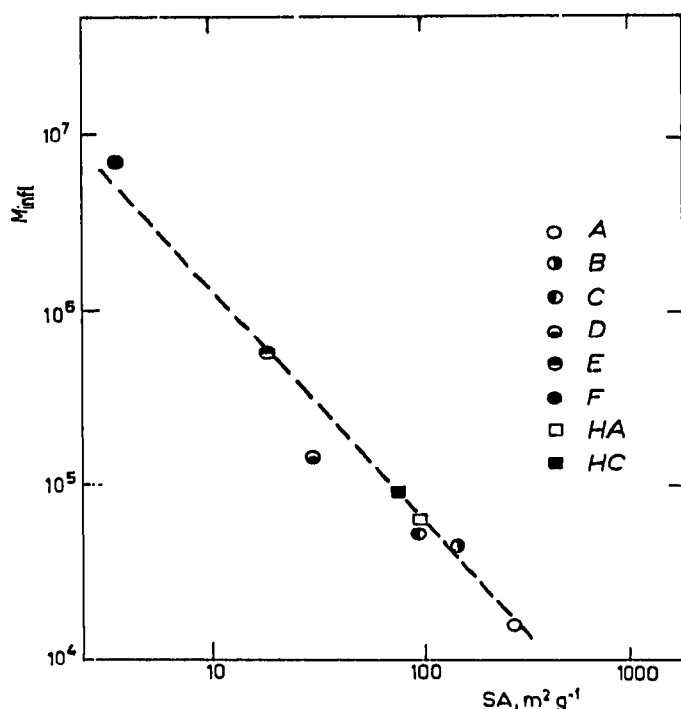

Fig. 4. The dependence of M_{infl} on the total pore surface area.

The corresponding results are to be found in Fig. 6. Values of the hydrodynamic diameters $2R\eta$ of the macromolecules were calculated from the M_{infl} data according to the relation

$$2R\eta = 2\left[\frac{[\eta]M}{\Phi_0 6^{3/2}}\right]^{1/3}$$

where $[\eta]$ is the limiting viscosity number, M the average molecular weight of polymer and Φ_0 Flory's universal constant. The limiting viscosity numbers were calculated for the M_{infl} values from the relation[5]:

$$[\eta] = 1.41 \times 10^{-2} M^{0.70}$$

From Fig. 6, where the $2R\eta$ values are plotted as a function of V/SA, it can be seen that there is a good correlation between these two quantities. More precisely, $2R\eta$ and V/SA are almost directly proportional and the $2R\eta$ values are numerically close to the values of the "effective pore size".
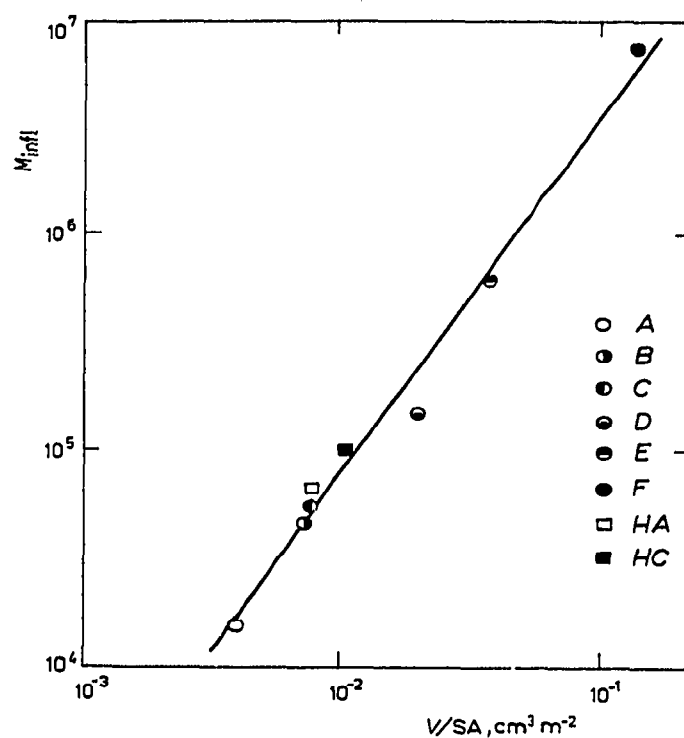
Fig. 5. The dependence of M_{infl} on the ratio: total pore volume (V) over total pore surface area (SA).
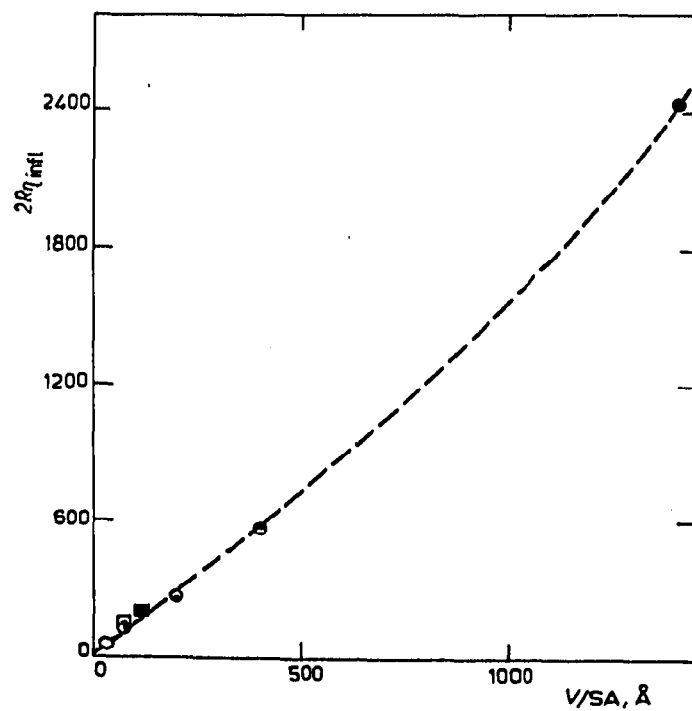

Fig. 6. The dependence of the hydrodynamic coil diameter, $2R\eta_{infl}$, on the ratio V/SA.

CONCLUSIONS

In this paper we have tried to compare porous silica gels from different sources for their use in gel permeation chromatography. We have shown that there is no simple correlation between the mercury intrusion porosimetry data and the GPC calibration curve. This fact can be explained by differences in the shape of pores and also by the limitation of the mercury porosimeter technique.

Further, we have tried to characterise a given gel by the range of molecular weights in which it is efficient. For this purpose, we have used the molecular weight M_{infl} for which the calibration curve exhibits an inflection point.

It is remarkable that the logarithm of M_{infl} depends linearly on the logarithm of the volume over surface ratio of the pores. If it can be shown that this law, already verified on two different kinds of gel, is general, it would be very helpful in the selection of an appropriate gel for studying a given polymeric material. Some work still in progress is attempting to extend these results and to show that the slope of the inflectional tangent, i.e., the selectivity of the column, can also be related directly to cumulative variation of volume and surface of the pores.

ACKNOWLEDGEMENT

REFERENCES

1 M. J. R. CANTOW AND J. F. JOHNSON, J. Polymer Sci., A-1, 5 (1967) 2835.
2 R. BEAU, M. LE PAGE AND A. J. DE VRIES, Appl. Polymer Symp., 8 (1969) 137.
3 Z. GRUBISIC-GALLOT AND H. BENOIT, Intern. Seminar GPC, Monte Carlo, 1969.
4 S. BRUNAUER, P. EMMETT AND E. TELLER, J. Am. Chem. Soc., 60 (1938) 309.
5 H. BENOIT, Z. GRUBISIC-GALLOT, P. REMPP, D. DECKER AND J. ZILLIOX, J. Chim. Phys., 63 (1966) 1507.