Can porosity properties of particles really be determined by inverse gel permeation chromatography?

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Inverse gel permeation chromatography can be fruitfully used for the texture determination of porous mineral beads. However for swelling macroporous gels the same procedure may lead to flagrant errors, which are pointed out on some examples. Thermodynamic considerations explain such results and some ways to take into account perturbing effects are suggested.

(Keywords: porosity; gel; gel permeation chromatography; swelling; beads)

INTRODUCTION

Mineral and organic gel beads are now currently used in various industrial fields such as ion-exchange, catalysis (or more generally supported reactions[1] and as packings in chromatography. In all cases the morphology (or texture) of the beads plays a major role, if not in the mechanism of the reaction involved, at least in its kinetics.

For rigid solids (mineral packings) the pore structure does not depend on the surrounding medium and structural data can be determined by classical procedures.

Gel permeation chromatography (g.p.c.), now frequently called size exclusion chromatography, is classically used for the characterization of the molecular weight parameters of polymers. The inverse problem, i.e. the determination of the porous structure of packings, may be expected to be solved by examining the retention data of macromolecules of known molecular weight. This idea appeared very soon[2] and has been progressively developed later[3-8]. Orignally used for mineral gels, the method was also claimed as being valuable for swelling gels. In this case, it appears as particularly attractive since it can be used with gels in their swollen state, contrary to classical tests which need the dry form. In fact we will show here, according to thermodynamic considerations supported by some typical experiments, that the 'inverse' g.p.c. may lead to flagrant errors for these kind of gels.

PRINCIPLE OF POROSITY DATA DETERMINATION

If we consider a column packed with porous beads, the total volume (V_T) of the column can be divided into three parts:

- the external (extrabed) volume V_o.
- the intrabed volume of pores, V_p, i.e. the volume of zones which are permanently filled by solvent molecules and always free of any chains of the framework when the swelling equilibrium is reached.
- the structural volume, V_s, occupied by the framework of the packing. If the packing is a gel it can be considered, to a first approximation, as close to a viscous liquid.

The porosity data are deduced from a calibration curve obtained by eluting a family of well known macromolecules (*Figure 1a*). Only the part of the pores larger than the probe are taken into account. Some refinements must be used, since flexible macromolecular solutes cannot be considered as equivalent to rigid spheres but to flexibles coils[9-11].

A correct picture of the pore size distribution can be obtained under two conditions:

- the flow rate is sufficiently low to allow the thermodynamic equilibrium of macromolecules between beads and eluent to be reached.
- the only retention mechanism involved is the size effect, i.e. a purely entropic phenomenon.

The first condition is not drastic since batch experiments can be performed if necessary. But the second condition is more difficult to verify as non-exclusive effects are well known in g.p.c. systems[12].

In the particular case of rigid gels, an adsorption of macromolecules may occur[6,12,13] or occasionally a repulsion[13,14]. But these drawbacks can be avoided by an appropriate choice of the pair macromolecule/eluent. However, owing to convenient precautions, a reasonable agreement is observed between inverse g.p.c. and classical methods[5,7,8] for such materials.

Unfortunately, the situation is not so favourable with swellable gels as these packings, besides possible adsorption, exhibit a complementary retention effect through a solute partition between eluent and swollen gel phases.

THERMODYNAMICAL ASPECTS OF SOLUTE PARTITION IN ELUENT/GEL SYSTEM

If we introduce a solute (macromolecular or not) into a solvent/homogeneous (not macroporous) gel system, a

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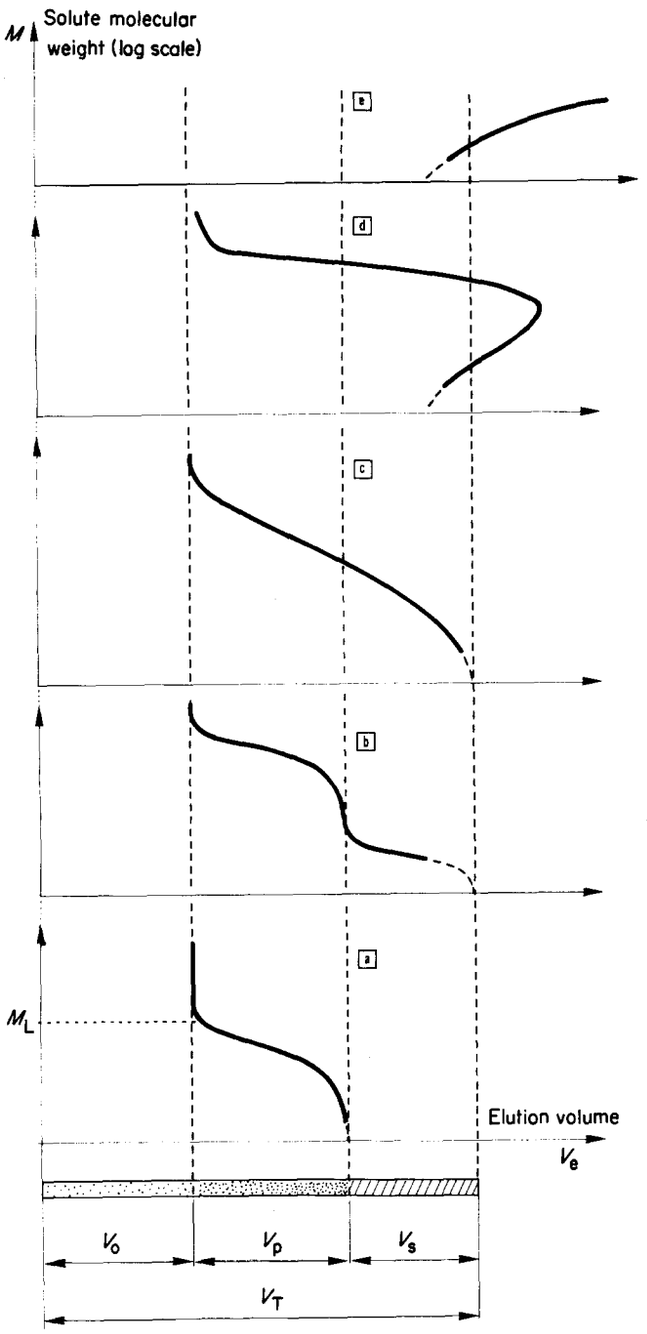

Figure 1 Typical retention data of a homologous series of solutes from a column packed with a swollen organic gel : the elution volume V_e is plotted *versus* the solute molecular weight (log scale). V_o is the intergranular volume; V_p the macroporous volume, V_s the volume of the swollen gel and $V_T = V_o + V_p + V_s$ is the total volume of the empty column

partition between the two phases can be predicted[16-21] and effectively observed[18,22-25].

If the gel is macroporous the size exclusion mechanism may occur in macropores at the same time as the partition effect in the swollen part of the gel. Consequently the shape of the global calibration curve is modified, to a first approximation, from *Figure 2a–e* with the increase of the partition mechanism[25-28].

Several predictions of the elution volume, V_e, were proposed for systems where the two mechanisms occurs simultaneously[23,29,30]. But assuming the successive equilibria:

Solute in bulk solution $\xrightleftharpoons{K_{g.p.c.}}$ Solute in a pore $\xrightleftharpoons{K_{g.p.c.}K_p}$ Solute in the structural swollen part of the gel

the elution volume can be expressed[25]:

$$V_e = V_o + K_{g.p.c.}V_p + K_{g.p.c.}K_pV_s \qquad (1)$$

$K_{g.p.c.}$ depicts the only size exclusion effect. K_p is the ratio of the solute concentration in the gel to the concentration of the solute in the bulk solution. It can be described in terms of interaction parameters, χ_{ij},[20,23-25] or of solubility parameters δ_i, more classically used in chromatography[23,30-33]. In any event, the two procedures are equivalent according to the relationship:

$$\chi_{ij} = \frac{v}{RT}(\delta_1 - \delta_j)^2$$

where v is the molar volume of the 'segment' defined as the volume unit in the lattice model[16] (practically the molar volume of the eluent). For instance, the K_p expression we proposed[20] may be rewritten:

$$\log K_p = r[\log(1-\phi) + \frac{2v\phi}{RT}(\delta_e - \delta_g)(\delta_e - \delta_s)] \qquad (2)$$

where ϕ is the volume fraction of the polymer in the swollen gel that is the ratio of the volume, V_D, the dry gel (structural part) to the volume of the swollen gel (V_s). The parameter r is the ratio of the molar volume of the solute to the molar volume of the eluent. The subscripts s, g, e, refer to solute gel and eluent respectively.

This K_p expression has the same form as those already published but takes into account the swelling of the gel. We present here some typical examples chosen to show its reliability and discussed from the point of view of the practical incidence in porosity measurements.

CHROMATOGRAPHIC EXPERIMENTS

Three types of packings were used: packings 1 and 2 were styrene/divinylbenzene macroporous gels (Styragel 10^6 and Styragel 10^3 Waters), packing 3 was a nitrated styrene/divinylbenzene gel obtained by nitration of a macroporous gel, according to Zenftman[34], (ES 861—Diaprosim[35]). The nitrogen content is 7.82% (degree of substitution: 0.9). The packing characteristics are given in *Table 1*.

Polar and non polar compounds (n-alcohols and n-alkanes, pure grade) were eluted in polar and non polar solvents (methanol and heptane, analytical grade). Experiments were performed on a ALC 201 Waters apparatus using a 18.5 cm × 0.47 cm i.d. column (total volume 3.3 cm^3) at 2 ml/min flow rate. Elution volumes, corrected for extra-column void volume are given in *Tables 2* and *3*.

ELUTION BEHAVIOUR

According to the steric exclusion point of view, the maximum volume accessible to a solute (V_{emax}) is defined as the total volume of the empty column minus the volume of the packing itself, i.e. its volume in the dry state, V_D):

Table 1 Packing characteristics

Packing	Dry bead size (μm)	Specific gravity (g cm^{-3})	Apparent density	Specific surface area* (m^2 g^{-1})	Porous volume in the dry state† (cm^{3}g^{-1})	Weight of dry packing (g)	
						Methanol as eluent	Heptane as eluent
1 (Styragel 10^6)	35–75	1.05	0.254	46	–	0.8	0.8
2 (Styragel 10^3)	20	1.05	0.439	480	0.58	1.15	0.95
3 (Nitrated ES 861)	10–28	1.4	0.33	460	0.42	1.65	1.45

* BET measurements in N_2

† From extrapolated BJT curves for $P_{N_2} \rightarrow P_{Atmos.}$. No significant values are obtained by this technique for very large pores beads (packing 1)

Table 2 Elution volume of n-alcohols (cm^3)

Packing	1		2		3	
	Eluent					
Solute	Methanol	Heptane	Methanol	Heptane	Methanol	Heptane*
Ethanol	2.5	–	2.4	12.8	2.3	
Propanol	2.6	14.2	2.4	11.1	2.3	
Butanol	2.6	8.8	2.5	10.3	2.3	
Pentanol	2.6	6.6	2.6	9.4		
Hexanol	2.7	5.4	2.7	9.4		> 20
Octanol	2.8	4.6	3.0	8.6	2.3	
Decanol	2.9	4.1	3.5			
Tetradecanol	3.2	3.1	5.7	7.3	2.3	
Octadecanol	3.4	2.9	10.4	6.5		
Docosanol	7.6	2.7	–	5.7		

* $V_e > 20$ cm^3 for all solutes

Table 3 Elution volume of n-alkanes

Packing	1		2		3	
	Eluent					
Solute	Methanol	Heptane	Methanol	Heptane	Methanol	Heptane
Methane	2.9	2.7	2.8	2.8	2.4	2.7
Ethane	3.2	2.7	3.2	2.8	2.4	2.6
Propane	3.4	2.6	3.4	2.6	2.4	2.5
Butane	3.6	2.5			2.4	2.3
Pentane	4.1	2.4	4.4	2.5	2.3	2.2
Hexane	4.6	2.4	4.7	2.5	2.4	2.2
Heptane	5.3	–	5.6	–	2.3	–
Octane	5.7	2.4	6.5	2.4	2.3	2.2
Nonane	–		7.6		2.3	–
Decane	7.6	2.3	–	2.6		2.1
Dodecane	10.2	2.3	12.6	2.4	2.3	
Hexadecane		2.3		2.3		2.0
Octadecane				2.3	2.3	
Eicosane		2.3			2.3	2.0
Docosane				2.2		

$$V_{e\,max} = V_T - V_D$$

$V_{e\,max}$ is given in *Table 4*. It must be close to but larger than the elution volume of the smallest solutes used. As depicted in *Table 4* there are serious discrepancies between this prediction and experimental results. Even for systems where no adsorption phenomenon can be put forward (elution of low molecular weight alkanes as solutes in heptane), the observed elution volumes are larger than $V_{e\,max}$.

In the partition hypothesis, relationship (2) takes a very simple form when the solute and the eluent have the same characteristics: $r = 1$ and $\delta_s = \delta_e$, then $K_p = 1 - \phi$. Moreover, when the packing is not macroporous or if it is macroporous but with very large pores with regard to the solute size, $K_{g.p.c.}$ is allowed to equal 1. In fact, this situation occurs with our three packings since their pore diameters are larger than 30 Å according to measurements based on adsorption/desorption BET curves performed with nitrogen.

Table 4 Observed and previously calculated elution volumes of (eluent in eluent'

Packing	Eluent	V_e max (cm^3)	Elution volume (cm^3) of the smallest solute (methane or ethanol) in methanol or n-heptane. ethanol	methane	Elution volume of 'eluent' in 'eluent' (cm^3)
1	Methanol	2.6	2.5	2.9	2.5
	Heptane	2.6	> 20	2.4	2.4
2	Methanol	2.2	2.4	2.8	2.3
	Heptane	2.4	≃ 13	2.8	2.4
3	Methanol	1.8	2.3	2.4	2.3
	Heptane	1	> 20	2.7	2.2

Table 5 Measurements of the porous volume

Packing	Swelling agent	Porous volume of the packing (cm^3) According to the only size exclusion effect: From ethanol retention	From methane retention	Taking into account the partition effect: From rention data of large size solute (normal phase systems)	From linearization of k' values (reverse phase systems)	V_p max (no swelling of the network)
1	Methanol	1.2	1.6	–	0.4	1.2
	Heptane	> 20	1.4	1.2	–	1.2
2	Methanol	1.1	1.5	–	0.8	0.9
	Heptane	≃ 13	1.5	0.9	–	1.1
3	Methanol	1.0	1.1	–	–	0.5
	Heptane	> 20	1.4	0.6	–	0.7

In these conditions the relationship (1) becomes:

$$V_e = V_o + V_p + (1-\phi)V_s$$

As $\phi = \frac{V_D}{V_s}$ and $V_T = V_I + V_p + V_s$

it becomes $$V_e = V_T - V_D$$

We obtain for such systems, an expression of the same form as above; the expected elution volume is the so called $V_{e\,max}$ already introduced. The retention volume of solutes identical to the solvent cannot be directly measured but it can be estimated from data of *Tables 2* and *3*: in the case of n-alkanes in heptane the elution volume of heptane is obtained by intrapolation; the elution volume of methanol in methanol is obtained by extrapolation from the elution volumes of n-alcohols in methanol. The observed elution volumes of 'eluent in eluent' are in fairly good agreement with those previously calculated (*Table 4*), which checks the reliability of relationship (2).

On the other hand this expression of V_e, using the tabulated δ values, justifies the influence of the solute molecular weight on their chromatographic behaviour depicted in *Tables 2* and 3. For instance, the classical increase of V_e with the size of solutes in reverse phase chromatography of non polar solutes is well observed, that is V_e increases with r if $(\delta_e - \delta_g)$ and $(\delta_e - \delta_s)$ are positive. But relationship (2) includes the swelling effect of the packing which as experimentally observed[26]: for instance the elution of a given family of solutes may increase for slightly crosslinked packings but may present the reverse order for packings of the same nature but highly crosslinked (in this last case $\phi \simeq 1$ and the first term in (2) becomes predominant).

POROSITY MEASUREMENTS

The porous volume can be estimated by a purely exclusive mechanism hypothesis, as the elution volume of low molecular weight solutes minus the void volume V_o. This void volume can be determined as the elution volume of a macromolecular solute excluded from the pores but it can be simply estimated by taking into account that, in chromatographic filling conditions, regular shaped beads occupied 62–63% of the total volume of the column ($V_o = 0.38\ V_T$)[36]. The porous volume values obtained are given in *Table 5*: they are completely aberrant, always larger than the possible maximum porous volume, also given in *Table 5* is $V_{p\,max} (= V_T - V_o - V_D)$.

Taking into account the partition phenomena, formulae (1) and (2) theoretically allow the calculation of ϕ and V_p from the retention data of all pairs of solutes. But in fact such a calculation requires various thermodynamic data which are not always available. More seriously formula (1) is obtained from the lattice solution theory which is valid only for regular solutions (practically systems of non-polar compounds), so it must be used very cautiously. However, if the K_p values can be quantitatively inaccurate their general evolution with r is correct. Especially K_p

tends to zero for large size solutes in normal phase systems, that is, according to formula (2), $\log K_p$ is negative and proportional to r. These conditions are observed with heptane as eluent and alkanes as solutes (see *Table 3*). The corresponding porous volumes are given (*Table 5*). The partition phenomenon takes a large part for systems in which the term $(\delta e - \delta s)$ is important (see formula (2)). But even if the eluent and the gel have the same characteristics ($\delta e = \delta g$), $\log K_p \neq 0$ because of the swelling term $(\log(1-\theta))$[24]. In all cases the partition effect vanishes for unswellable gels ($\theta = 0$).

The real dead volume V_o (then V_p) can be determined by another method according to the same principle as suggested[37] for bonded phases. For such packings used in reverse phase chromatography, it is assumed that the capacity factors, k', of homologous solutes in a series are in the form:

$$\log k' = a + bn$$

where n is the number of carbon atoms of the solute; a and b are constants and taking in account that:

$$k' = (V_e - V_o)/V_s$$

then:

$$\log(V_e - V_o) = (a + \log V_s) + bn$$

The V_o value is chosen as leading to the best linear fit of $\log(V_e - V_o)$ against n. This method is not precise, when the constant b is small and the theoretical basis of the linear variation of $\log k'$ with n is questionable. It can be noticed that such an evolution is consistent with formula (2) as long as δ_s is independent of n. This is practically observed for n-alkanes with $n > 5$ since δ, in $(\text{cal cm}^{-3})^{1/2}$, increases from 5.4 (methane) to 7.4 (hexane) and does not exceed 7.9 for polyethylene.

Using this method for the elution data of alkanes with mathanol as eluent we obtained, respectively for the 1 and 2 columns the V_o value of 1.7 cm^3 and 2.1 cm^3 which correspond to V_p of 0.4 cm^3 and 0.8 cm^3.

As shown in *Table 5*, the porous volumes obtained by taking in account the partition phenomenon are in a range compatible with the $V_{p\,max}$ value.

CONCLUSIONS

By taking precautions, inverse g.p.c. is a valuable technique for the morphology determination of rigid solids. But with swelling gels, if the retention is considered as only being due to a size exclusion mechanism of solutes, the porosity determined for the packing may be largely overestimated. This discrepancy is due to complementary retention by the swollen macromolecular substance. An expression of the corresponding partition coefficient is given. However, the proposed formula must be considered only as a first approach. Hence, it cannot be hoped to obtain with precision only the contribution of size exclusion mechanism in the pores by subtracting the partition effect from the global retention observed.

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