Non-exclusion effects in g.p.c.: a review

Roland Audebert
Laboratoire de Physico-Chimie Macromoléculaire de l'Université Pierre et Marie Curie (CNRS), E.S.P.C.I., 10, rue Vauquelin, 75231 Paris Cedex 05

Steric exclusion is generally the predominant separation mechanism in gel chromatography. However, adsorption on the gel and dissolution inside the gel also occur, greatly disturbing solute retention and especially hindering universal calibration for polymers. Some typical examples of such effects are given. The corresponding mechanisms are discussed and the bases of methods to present non-exclusion effects are given.

INTRODUCTION

Column chromatography, using porous packings such as mineral beads of soft and rigid organic gels, is commonly used for size fractionation of polymers and the separation of low molecular weight compounds. The chromatograms obtained are a 'fingerprint' of the injected sample and provide by an appropriate mathematical treatment, an accurate characterization of the polymer (molecular weight, dispersity, chain expansion, branching, etc.). This calculation is facilitated by the universal calibration, proposed by Benoit and al.[1,2]. A plot of $\log[\eta]M$ versus the elution volume, V_e, gives one calibraiton curve (*Figure 1*) ($[\eta]$ is the intrinsic viscosity, M the molecular weight of the solute). The plot does not depend on the eluant (at least for non-swelling gels) nor the nature and structure (rigidity, branching, etc.) of the injected polymer. These results, generally in good agreement with various experiments (see ref in [3]), are based upon the assumption that the size exclusion effect is a purely entropic phenomenon, due to the decreasing number of possible configurations of a given macromolecule when it transfers from the bulk dilute solution to the vicinity of a pore wall. This aspect has been studied from a thermodynamic point of view, especially by Casassa who justified the universal calibration[4–7] except perhaps, for macromolecules of very different structures[3,7]. Nevertheless, serious discrepancies with universal calibration are observed. The origin of these variations and the best choice of experimental conditions to remove this difficulty will be discussed.

ABNORMAL RETENTIONS IN G.P.C.

Observed anomalies are of three types. First, the unexpected elution volumes are observed for high molecular weight compounds. This is the classical example of the polymer retained in the column: here, only oligomers are eluted (see for instance *Figure 2*, pure silica). In other experiments the actual calibration curve, if compared with the 'universal' one, is globally shifted in the whole range of molecular weight (see *Figures 3–5*). The second case is more important for low molecular weight species. Such discrepancies are more specially observed when polymers are eluted in poor solvents but for all types of packings: Altgelt[8], Eenila[9], Dawkins[10–13] (see *Figure 3*), Ambler[3,14], Dubin[15,16], Otocka[17], Asche[18] and Krantz[19] used crosslinked polystyrene gels; Kuzaev[20], Berek[21,22] (*Figure 4*), Dawkins[23], Eltekov[24], Tannikov[25] and Campos[26], silica packings; Hope[27], Chitumbo[28], Berek[29], Belenkii[30,31] (*Figure 5*), Heitz[32], Sabbagh[33], Kissing[34,35] and Kuzaev[36] cellulose derivatives or other organic gels. In the third case, only the low molecular weight polymer range is affected. In the field of small molecules it was observed that the elution order was not governed only by the size of the solute[37–40]. Solid–liquid chromatography of solutes on high specific surface area mineral packings is well known, but anomalies are also observed with organic gels, especially swelling gels. The recent development of gel chromatography in the field of low molecular weight compounds[41–44] has pointed out the extra mechanisms involved in separation. For instance the elution volume has to decrease by increas-

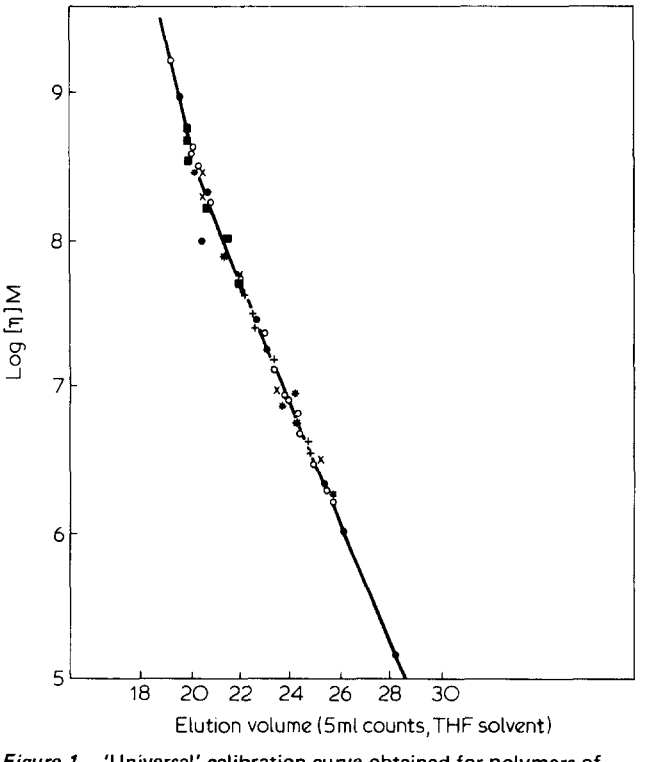

Figure 1 'Universal' calibration curve obtained for polymers of various nature and structure (from [2]) ● PS; ○ PS 'comb'; + PS 'star'; * hetero graft copol; x polymethylmethacrylate; ○ polyvinylchloride; ▲ graft copol. PS–PMMA; ■ polyphenylsiloxane; ■ polybutadiene

0032–3861/79/121561–06$02.00

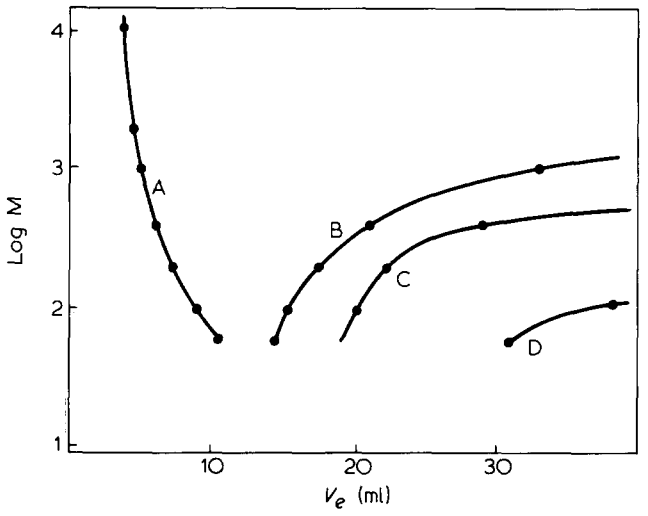

Figure 2 Elution of polyethyleneoxides by acetonitrile on pure silica (Si^{60}) and on silica grafted with polyethyleneoxide $\bar{M}$: 400 of various loading rates T from [59] A – T = 15%; B – 14%; C – 8%; D – 0%, pure silica

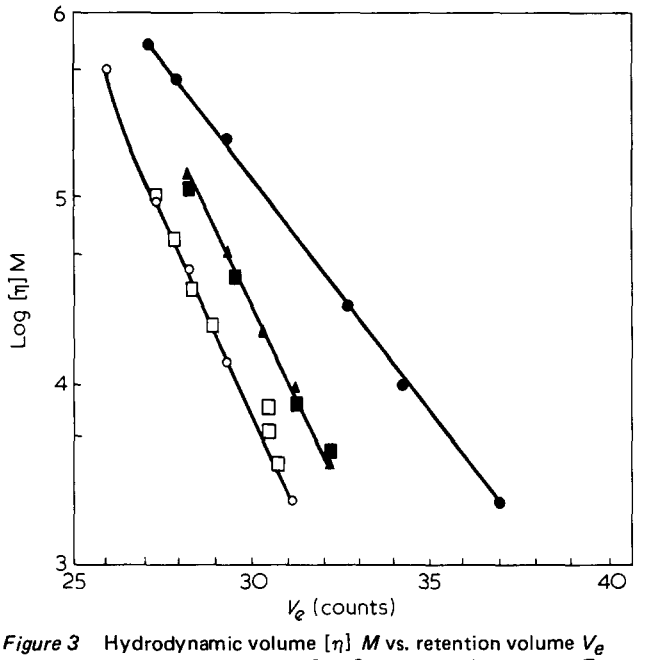

Figure 3 Hydrodynamic volume $[\eta]$ M vs. retention volume V_e calibration plots for polystyrene ○ or ●; polydimethylsiloxane □ or ■; polyisoprene ▲ in cyclohexane (filled symbols) and chloroform (open symbols) at 35°C ($[\eta]$ in dl mol^{-1}; 1 count = 5 ml) (from [10])

ing the solute molecular weight in classical g.p.c.: the opposite order may be observed in some cases with swelling gels[28–29,45–53]. A typical example is given in *Figure 6*: *n*–alkanes are eluted on a classical styrene–divinyl–benzene packing (Poragel 60 Å [54]). In tetrahydrofuran (THF) the g.p.c. expected elution order is observed. Nevertheless, the elution volume of small alkanes is surprisingly high and generally higher than the total volume of the column minus the bulk volume of the gel if the gel is supposed swelled. In dimethylformamide (DMF), a poor solvent for alkanes, the elution volume increases with the molecular weight of the solute.

SEPARATION MECHANISMS

Separation mechanisms in gel chromatography have been amply discussed[4,32,55–57,69]. In classical chromatographic conditions it is now considered that the solute is in equilibrium between the gel and the mobile phase. So transport properties like diffusion processes or hydrodynamic flow, which are also supposed to lead to fractionation, will not be taken in account here. Besides the size exclusion effect three mechanisms may explain the shape of actual calibration curves: solvation of solute species, adsorption on the pore walls of packings and, for swelling packings, partition between gel and whole phase.

Solvation of solutes

In the size exclusion separation of rigid molecules it was soon proved that the calibration curve had to be established not with the molar volume of the solute but with the volume of the solvated species. The difference of solvation between two compounds of closed bulkiness may be an element in their separation[83,84]. For polymers, solvation also occurs and is especially observed when the mobile phase is a liquid mixture. In that case a preferential solvation appears. It can be

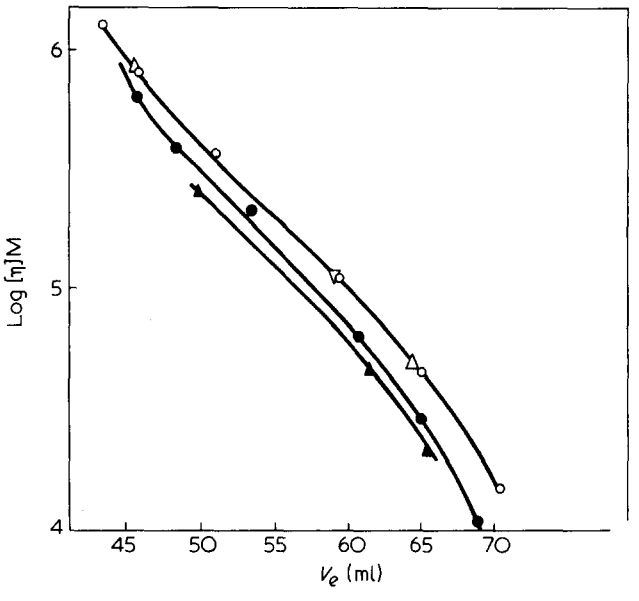

Figure 4 'Universal' calibration curves of polystyrene in benzene (○); chloroform (△); theta mixtures benzene/methanol (●); and chloroform/methanol (▲) (from [21])

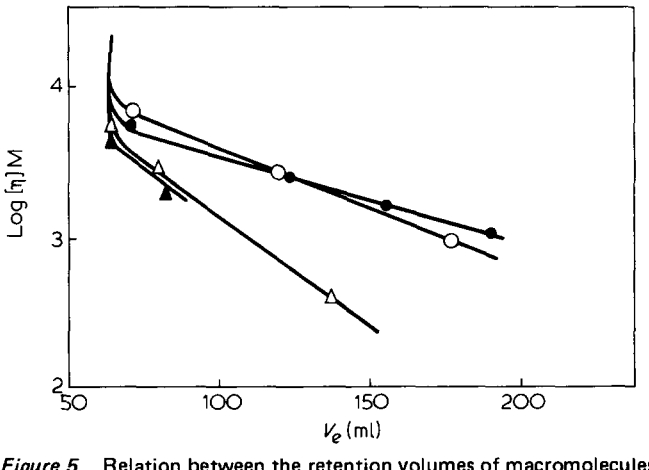

Figure 5 Relation between the retention volumes of macromolecules and their hydrodynamic dimensions using G-100 Sephadex (from [30]). ○ – dextran; ● – polyvinylpyrrolidone; △ – polyethyleneglycol; ▲ – polyvinylalcohol

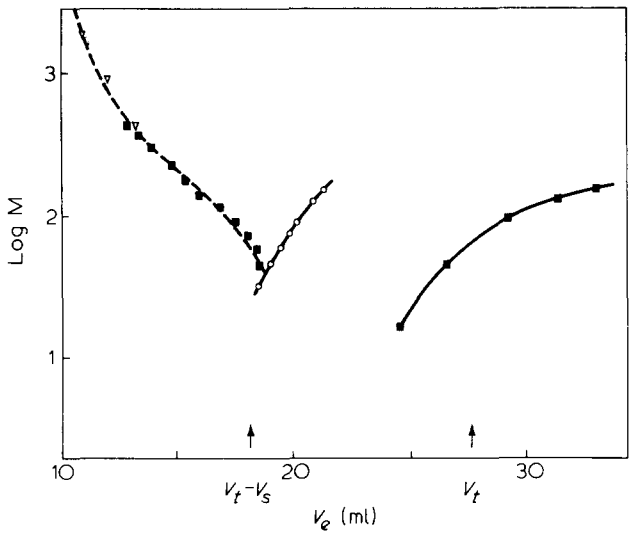

Figure 6 Relation between the retention volume of some solutes and their molecular weight in various eluents. Packing: cross-linked styrene–divinylbenzene gel (Poragel 60 Å). V_t: internal volume of the column. V_s: volume of the dry packing (from [54]). ——— – DMF; – – – – THF; ■ – alkane; ○ – n-alcohol; △ – POE

studied by g.p.c.[21,26,85–87,90]. If the solvation must always be taken into account it cannot explain the important discrepancies in calibration curves previously described.

Dissolution mechanism

In the case of the dissolution of alkanes in DMF, shown in *Figure 6*, the unexpected elution order cannot be governed by adsorption on styrene–divinylbenzene network because this elution order is not observed with a rigid gel of the same nature. In a general way a solute partition occurs with swelled gels and these act as a liquid phase as in classical liquid–liquid chromatography. Particularly with lipophilic gels (e.g. polystyrene gels) used with polar mobile phases, solutes are eluted according to the behaviour of reverse phase chromatography[28,29,45,53]. This partition was put forward to explain elution data on swelling gel[15,26,28,33,48–50,58,60,61]. It has to occur, of course, even with a non-macroporous gel and in this case the basic chromatographic law is:

$$V_e = V_o + K_D V_g$$

(V_o is the void volume, K_D the partition coefficient of the solute between the gel and the mobile phase and V_g the volume of the stationary phase, here the swelled gel). Experimental evidence of dissolution mechanism was clearly proposed by Benoit, Rempp *et al.*[62–64], who prepared 'tailor-made' non-macroporous polystyrene gels in which the distance between two cross-linking points is well defined. They studied the partition of linear polystyrene in various organic solvents between the swelled gel phase and the solvent. Batch experiments and also chromatographic essays are described. As indicated in *Figure 7*, a partition mechanism leading to fractionation occurs. In this case the elution volume (or K_D) increases when the molecular weight of the solute decreases. For a given solute K_D increases with the size of the gel segments between two cross-linking points. Motozato who studied the relationship between network structure and molecula size of permeable substances observed similar results[65]. A theory of macromolecule partition in a gel was proposed by De Ruvo[66], Belenkii *et al.*[31] and especially Lecourtier *et al.*[67,68]: by taking as size unity the molar volume of the solvent, K_D can be expressed in the simplified form

$$\log K_D = DP[\log(1 - \phi_g) + \phi_g(\chi_{gs} + \chi_{ps} - \chi_{pg})]$$

where ϕ_g is the volume fraction of the gel in the swollen gel, χ_{ij} the Flory interaction parameter related to segment interaction of gel (g) solute (p) and solvent (s) and DP has the dimension of the polymerization degree of the solute. This formula indicates that there is no dissolution effect for non-swelling gels (K_D is 0 for $\phi_g = 1$). For a given chemical nature of the eluting species (χ_{ij} constant) the partition coefficient increases with the swelling of the gel. For poor swelling K_D increases (from 0 to 1) when the molecular weight of the solute decreases. For increasing values of the swelling, if the solute–gel interactions are important ($\chi_{pg} < 0$) and the solute–eluent interactions are low ($\chi_{ps} > 0$), the term between brackets might be positive. Then, K_D increases with the molecular weight of the solute. For a given family of solutes $\log K_D$ is proportional to their molecular weight (at least when the χ_{ij} are independent of the molecular size); this is a typical behaviour observed in reverse phase chromatography. Experimental results previously described are correctly predicted, at least qualitatively, by these theoretical considerations.

Adsorption mechanism

If the dissolution mechanism affects only the low molecular weight range of the solutes (the larger the swelling, the larger is this range), adsorption (liquid–solid chromatography) may occur for any solute. It is sometimes difficult to pre-

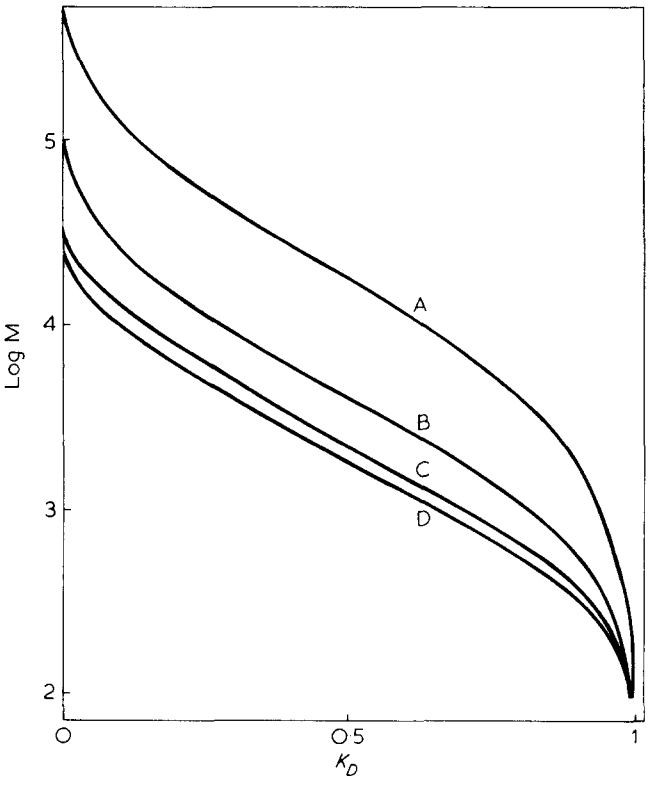

Figure 7 Partition coefficients in systems polystyrene–THF–gel. The various gels used are 'tailor made' gels characterized by the molecular weight of polystyrene precursor (size of the macromolecular chain between two cross-linking points (from [62]). A – 95 000; B – 45 000; C – 21 300; D – 10 600

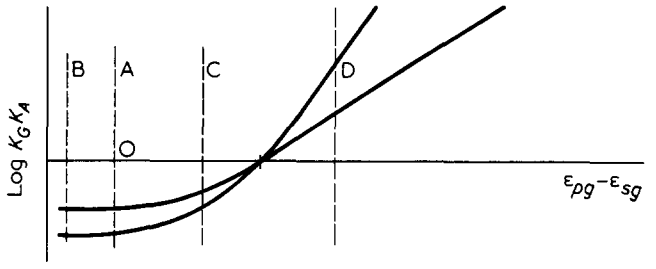

Figure 8 Relation between the global partition coefficient on a porous sorbent and the difference of interaction energy of solvent and polymer units towards the support (from [92]

dict the respective part of these two mechanisms, especially with modified gels leading to specific interactions with the solute[34,35,70–73]. With these 'reactive gels'[74–76] it is not clear if, in the chromatographic conditions, interactions occur either only onto the surface of the porous structure or inside the bulk of the bel. Different ways have been used to describe solute adsorption[77–79]. Klein's model is related to solutes with rigid molecules[80]. It takes into account the tortuosity of the porous structure[81] which prevents solute molecules from having access to the porous volume. When solute sizes are rather small if compared with pore dimensions the elution volume is given by a very simple relation:

$$V_e = V_o + (K_G + K_A)V_p$$

expressing the addivity of GPC (K_G) and adsorption (K_A) effects (V_p is the porous volume). In the general case K_A has to be modified by taking in account the relative loss of pore surface accessibility due to tortuosity. Predicted calibration curves look like those observed in *Figure 2*. The Dawkins' model is more convenient for macromolecular solutes[82]. When polymers are separated by steric exclusion alone the elution volume is given by

$$V_e = V_o + K_G V_p$$

If adsorption occurs, it can be characterized by an affinity coefficient related to the surface area unit. If it is assumed that the porous structure in beads is simple, the total surface area is directly proportional to the porous volume. If the two mechanisms are cumulative, the elution volume is then

$$V_e = V_o + K_G K_A V_p$$

where K_A is related to adsorption (positive adsorption or repulsion). This formula is fairly well verified for different experimental results[10–12,61,69,82].

A more complete view on the molecular scale is given by the studies of Tennikov and Belenkii *et al.*[25,91,92]. Let us consider a dilute solution of a flexible polymer in the vicinity of a pore. In a pure size exclusion mechanism, the concentration in polymer units gradually decreases from the bulk solution to the pore wall and becomes zero on the surface according to a law which may be calculated[93]. Concentration profiles are modified if other mechanisms occur. An overconcentration is observed for positive adsorption, and the contrary for repulsion. The free energy change when a polymer molecule transfers from the mobile phase to a pore within the gel not only depends on the size of the macromolecule but also on the difference of interaction energy of solvent and polymer segment towards the gel $\epsilon = (\epsilon_{pg} - \epsilon_{sg})$.

Calculations, based on the classical theory of polymer adsorption[94,95], lead to a general behaviour of flexible macromolecules in the vicinity of a rigid wall. A pure size exclusion mechanism has to be considered only as a particular case, where no enthalpic effect is operative. From this calculation the elution volume is given by the equation proposed by Dawkins. $K_G K_A$ is expressed *versus* $(\epsilon_{pg} - \epsilon_{sg})$ in *Figure 8*.

Below a critical value ϵ_c of the energy term ϵ, the loss of entropy resulting from adsorption is not balanced by the stability gain occurring from interactions with the surface and the resulting calibration curves are given in *Figure 9*: (A) without enthalpic effect; (B) there is a repulsion between the gel and macromolecular segments; (C) slightly positive interaction effect. For the value ϵ_c there is no segment concentration drop from the bulk solution to the pore wall, so all the solutes are eluted at the volume $V_o + V_p$. For $\epsilon > \epsilon_c$ adsorption predominates (D). These theoretical predications have been successfully compared with experimental results in column[25] and thin layer[91] chromatography. They explain other published data (see for instance *Figure 3, 4, 5*). Nevertheless, refinements will be probably necessary because the calculation does not take into account the polymer–solvent interactions which undoubtedly take a part in the adsorption phenomenon (as in gel partition).

PRACTICAL CONSEQUENCES

Extra exclusion effects need not be eliminated in a chromatographic procedure, especially in the case of low molecular weight solutes, because a complementary resolution is obtained.

Organic porous swelling gels appear to be very attractive packings for direct or reverse phase chromatography, especially in the preparative scale where they have reasonable efficiency and high capacity[96]. If universal calibration is the objective, experimental precautions must be taken into account. Unfortunately, in gel filtration, packings swell and a dissolution effect is always possible. In high pressure g.p.c. with organic gels, only the low molecular weight range fraction swells in practice. Their omission from the column set may save time and money, and improve the reliability of measurements if the sample has no fractions with molecular weight lower than 1000.

In a general way, to avoid both adsorption and dissolution, chromatographic conditions must be chosen with high polymer–solvent and gel–solvent interactions and poor polymer–gel affinity. This is generally obtained by a convenient choice of the eluent. A mixture of solvents, with a

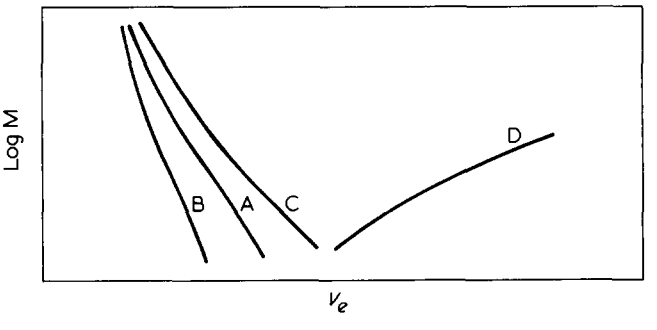

Figure 9 Calibration curves corresponding to various values of $\epsilon_{pg} - \epsilon_{sg}$ (see *Figure 8*)

minor constituent leading to strong interactions with the packing, and the major an adequate solubility of the sample, may give good results[15,25,97–99]. For drastic adsorptions only the gel surface change leads to a reduction in adsorption. These bonded gels have been widely used in g.p.c. and commercial packings of this type are now available[44,100]. The incidence of polyoxyethylene silica grafting ($\bar{M}$ = 400) on the calibration curve of linear polyoxyethylene in acetonitrile is given in *Figure 2*. The strong adsorption observed in pure silica progressively decreases when the rate of grafting increases. Finally the classical shape of calibration curve is recovered. Nevertheless if such a procedure eliminates, or at least strongly minimizes, the adsorption process, the grafted phase creates a dissolution effect[59,86,101] which may again disturb the exclusion size effects. Small grafts (no dissolution in the grafted phase) leading to total coverage of the packing surface are the most efficient.

ACKNOWLEDGEMENT

The author wishes to ahank Prof. Benoit for helpful discussion at the 6th French meeting on g.p.c. (Grenoble, June 1978). Thanks are also due to Prof. Belenkii and Dr. Dawkins for valuable discussions during the meeting 'Chromatography of polymers and polymers in chromatography' (Prague, June 1978).

REFERENCES

1 Benoit, H., Grubisic, Z., Rempp, P., Decker, D. and Zilliox, J. *J. Chim. Phys.* 1966, **63**, 1507
2 Grubisic, Z., Rempp, P., and Benoit, H. *J. Polym. Sci. B.* 1967, **5**, 573
3 Ambler, M. and McIntyre, D. *J. Polym. Sci. B.* 1975, **13**, 589
4 Casassa, E. *J. Phys. Chem.* 1971, **75**, 3929
5 Casassa, E. *J. Polym. Sci. B.* 1967, **5**, 773
6 Casassa, E. and Tagami, Y. *Macromolecules* 1969, **2**, 14
7 Casassa, E. *Macromolecules* 1976, **9**, 182
8 Altgelt, K. *Sep. Sci.* 1970, **5**, 777
9 Eenila, P. and Bredenberg, U. IUPAC, Macromolecular Symposium, Helsinki, 1972. Prep. II, 12 p 65
10 Dawkins, J. V. and Hemming, M. *Makromol. Chem.* 1975, **176**, 1777
11 Dawkins, J. V. and Hemming, M. *Makromol. Chem.* 1975, **176**, 1795
12 Dawkins, J. V. and Hemming, M. *Makromol. Chem.* 1975, **176**, 1815
13 Dawkins, J. V. *J. Chromatog.* 1977, **135**, 470
14 Ambler, M. J. *J. Polym. Sci., Polym. Lett. Ed.* 1976, **14**, 683
15 Dubin, P. *Ind. Res.* 1976, 57
16 Dubin, P., Koontz, S. and Wright, K. *J. Polym. Sci. Polym. Chem. Ed.* 1977, **15**, 2047
17 Otocka, E. and Hellman, M. *J. Polym. Sci. Polym. Lett. Ed.* 1974, **12**, 331
18 Asche, W. and Oelert, H. *J. Chromatogr.* 1975, **106**, 490
19 Krantz, D., Pohl, U. and Baumann, H. *Angew. Makromol. Chem.* 1972, **26**, 67
20 Kuzaev, A., Mirontseva, G., Olkova, O. and Entelis, S. *Zh. Fiz. Khim.* 1974, **48**, 1235
21 Berek, D., Bakoš, D., Dleha, T. and Šoltes, L. *Makromol. Chem.* 1975, **176**, 391
22 Berek, D., Bakoš, D., Šoltes, L. and Bleha, T. *J. Polym. Sci. Polym. Lett. Ed.* 1974, **12**, 277
23 Longman, G., Wignall, G., Hemming, M. and Dawkins, J. V. *Colloid Polym. Sci.* 1974, **252**, 298
24 Eltekov, Y. and Nazansky, A. *J. Chromatogr.* 1976, **99**
25 Tennikov, M., Nefedov, P., Lazareva, M. and Frenkel, S. *Vysokomol. Soedin Sec. A.*, 1977, **19**, 657
26 Campos, A. and Figueruelo, J. *Makromol. Chem.* 1977, **178**, 3249
27 Hope, P. *Angew. Makromol. Chem.* 1973, **33**, 191
28 Chitumbo, K. and Brown, W. *J. Chromatogr.* 1973, **80**, 187
29 Berek, D. and Bakoš, D. *J. Chromatogr.* 1974, **91**, 237
30 Belenkii, B., Vilenchik, L., Nesterov, V. and Shasina, T. *Vysokomol. Soedin., A*, 1973, **15**, 2164; *Polym. Sci. USSR* 1973, **15**, 2973
31 Belenkii, B., Vilenchik, L., Nesterov, V., Kolegov, V. and Frenkel, S. *J. Chromatogr.* 1975, **109**, 233
32 Heitz, W. and Fresenius, Z. *Anal. Chem.* 1975, **297**, 323
33 Sabbagh, N., Fagerson, I. *J. Chromatogr.* 1976, **120**, 55
34 Kissing, W. and Reiner, R. *Chromatographia* 1977, **10**, 129
35 Kissing, W. and Reiner, R. *Chromatographia* 1978, **11**, 83
36 Kuzaev, A., Afanasev, N. and Linde, V. *Zh. Fiz. Khim.* 1977, **51**, 2918
37 Lambert, A. *J. Appl. Chem.* 1970, **20**, 305
38 Lambert, A. *Anal. Chim. Acta.* 1971, **53**, 63
39 Aurenge, J., Gallot, Z., De Vries, A. and Benoit, H. *J. Polym. Sci. Polym. Symp. Ed.* 1975, **52**, 217
40 Shanks, R. *Aust. J. Chem.* 1975, **28**, 189
41 Pokorny, S. *Chem. Listy* 1974, **68**, 1027
42 Minarik, M. and Komers, R. *Chem. Listy* 1974, **68**, 696
43 Krishen, A. *J. Chromatog. Sci.* 1977, **15**, 434
44 Walton, H. *Anal. Chem.* 1978, **50**, 36 R
45 Marsden, N. *Ann. N. Y. Acad. Sci.* 1965, **125**, 428
46 Muto, G. and Nakae, A. *Chem. Lett.* 1974, **6**, 549
47 Takahagi, H. and Seno, S. *J. Chromatogr. Sci.* 1974, **12**, 507
48 Millot, M., Lesec, J., Audebert, R. and Quivoron, C. *Analusis* 1976, **4**, 410
49 Yamamoto, M. and Yamamoto, Y. *Anal. Chim. Acta.* 1976, **87**, 375
50 Nakae, A. and Muto, G. *J. Chromatogr.* 1976, **120**, 47
51 Popl, M., Dolansky, V. and Čoupek, J. *J. Chromatogr.* 1977, **130**, 195
52 Uchida, M. and Tanimura, T. *J. Chromatogr.* 1977, **138**, 17
53 Bergmann, J., Duffy, L. and Stevenson, R. *Anal. Chem.* 1971, **43**, 131
54 Lecourtier, J., Audebert, R. and Quivoron, C. *Pure Appl. Chem.* 1979, **51**, 1483
55 Yau, W., Malone, C. and Suchan, H. *Sep. Sci.* 1970, **5**, 259
56 Janca, J. and Kolinsky, M. *Chem. Listy* 1975, **69**, 228
57 Audebert, R. *Analusis* 1976, **4**, 399
58 Heitz, W. *Angew. Chem.* 1970, **9**, 689
59 Lecourtier, J., Audebert, R. and Quivoron, C. J. Liquid Chromatog., 1978, **1**, 367; *J. Liquid Chromatog.* 1978, **1**, 729
60 Minarik, M., Komers, R. and Čoupek, J. *J. Chromatogr.* 1978, **148**, 175
61 Freeman, D. and Killion, D. *J. Polym. Sci. Polym. Phys. Ed.* 1977, **15**, 2047
62 Weiss, P., Herz, J., Gallot, Z. and Benoit, H. *Makromol. Chem.* 1971, **145**, 105
63 Hild, G., Froelich, D., Rempp, P. and Benoit, H. *Makromol. Chem.* 1972, **151**, 59
64 Rempp, P. 'Reaction on Polymers' (Ed. J. Moore) Dreidel, Dordrecht, Holland; Boston USA, 1973 p 265
65 Motozato, Y., Kusumoto, N., Hirayama, C., Murakami, R. and Isozaki, H. *Polymer* 1965, **16**, 321
66 De Ruvo, A. *J. Polym. Sci. Polym. Ed.* 1973, **11**, 3017
67 Lecourtier, J., Audebert, R. and Quivoron, C. *J. Chromatogr.* 1976, **121**, 173
68 Lecourtier, J., Audebert, R. and Quivoron, C. 'Synthetic and Biological Polymers' Vol 1 (Ed. R. Epton) Ellis Horwood, Chichester, 1978, p 156
69 Dawkins, J. *J. Liquid Chromatogr.* 1978, **1**, 279
70 Hjerten, S. *J. Chromatogr.* 1973, **87**, 325
71 Ackers, G. *Methods Enzymol.* 1973, **27**, 441
72 Determan, H. and Lambert, K. *J. Chromatogr.* 1972, **69**, 123
73 Freeman, D. and Angeles, R. *J. Chromatogr.* 1974, **12**, 730
74 Freeman, D. *Anal. Chem.* 1971, **44**, 117
75 Freeman, D. *J. Chromatogr. Sci.* 1973, **11**, 175
76 Freeman, D., Angeles, R., Enagonio, D. and May, W. *Anal. Chem.* 1973, **45**, 768
77 Vilenchik, L. and Belenkii, B. *J. Polym. Sci. USSR* 1971, **13**, 2183 (Vysokomol. Soedin., Ser. A 1971, **13**, 1943)
78 Scott, R. and Kucera, P. *J. Chromatogr.* 1975, **112**, 425
79 Tager, A. and Tsilipotkina, M. Usp. Khim. 1978, **47**, 152
80 Klein, J. and Treichel, K. *Chromatographia* 1977, **10**, 604
81 Kubin, M. *J. Chromatogr.* 1975, **108**, 1
82 Dawkins, J. V. *J. Polym. Sci. Polym. Phys. Ed.* 1976, **14**, 569
83 Cazes, J. and Gaskill, D. Sep. Sci. 1967, **2**, 421
84 Cazes, J. and Herron, S. Sep. Sci. 1973, **8**, 395
85 Bakoš, D., Berek, D. and Bleha, T. *Eur. Polym. J.* 1976, **12**, 801

86 Lecourtier, J., Audebert, R. and Quivoron, C. *J. Liquid. Chromatog.* 1978, **1**, 479

87 Lindström, T., De Ruvo, A. and Söremark, C. *J. Polym. Sci., Polym. Chem. Ed.* 1977, **15**, 2029

88 Berek, D., Bleha, T. and Pevna, Z. *Polymer Lett. Ed.* 1976, **14**, 323; *J. Chromatogr. Sci.* 1976, **14**, 560

89 Campos, A., Borque, L. and Figueruelo, J. E. *J. Chromatogr.* 1977, **140**, 219

90 Chaufer, B., Lesec, J. and Quivoron, C. C. R. Acad. Sci., *Ser. C.* 1977, **284**, 881

91 Belenkii, B., Gankina, E., Tennikov, M. and Vilenchik, L. *J. Chromatogr.* 1978, **147**, 99

92 Skvortzov, A., Belenkii, B., Gankina, E. and Tennikov, M. *Vysokomol. Soedin. Ser. A.*, 1978, **20**, 678

93 Casassa, E. *Sep. Sci.* 1971, **6**, 305

94 Lipatov, Yu. and Sergeeva, L. 'Adsorption of Polymers' (Russian Ed. Slutzkin, D. 1972) Wiley, New York, Toronto, 1974

95 DiMarzio, E. and Rubin, R. *J. Chem. Phys.* 1971, **55**, 4318

96 Lesec, J. and Quivoron, C. *J. Liquid. Chromatog.* 1979, **2**, 467

97 Frenkel, M. and Blagrove, R. *J. Chromatogr.* 1975, **111**, 397

98 Mizutani, T. and Mizutani, A. *J. Chromatog.* 1975, **111**, 214

99 Minarik, M. and Čoupek, J. *Angew. Makromol. Chem.* 1977, **64**, 147

100 'Bonded Stationary Phases in Chromatography' (Ed. E. Grushka) Ann Arbor Sci. Pub., Michigan, USA, 1974

101 Lecourtier, J., Audebert, R. and Quivoron, C. *Macromolecules* 1979, **12**, 141