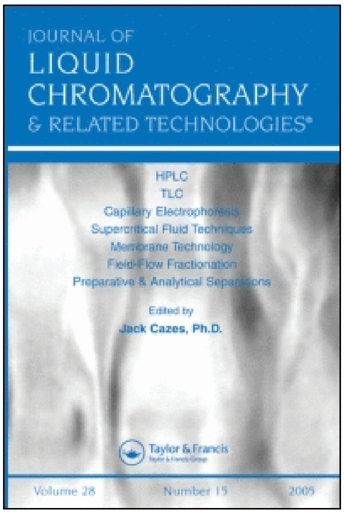


Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Experimental Study of Model Bonded Stationary Phases for Liquid Chromatography I. Silica/Polyethyleneoxide

J. Lecourtier[a b]; R. Audebert[a b]; C. Quivoron[a b]
[a] E.S.P.C.I. 10, Paris Cedex 05, France [b] Laboratoire de Physico-Chimie Macromoleculaire de 1'Universite, Pierre et Marie Curie

To cite this Article Lecourtier, J. , Audebert, R. and Quivoron, C.(1978) 'Experimental Study of Model Bonded Stationary Phases for Liquid Chromatography I. Silica/Polyethyleneoxide', Journal of Liquid Chromatography & Related Technologies, 1: 3, 367 — 384

To link to this Article: DOI: 10.1080/01483917808060005

URL: http://dx.doi.org/10.1080/01483917808060005

JOURNAL OF LIQUID CHROMATOGRAPHY, 1(3), 367-384 (1978)

EXPERIMENTAL STUDY OF MODEL BONDED STATIONARY PHASES FOR LIQUID CHROMATOGRAPHY

I. SILICA/POLYETHYLENEOXIDE

J. Lecourtier, R. Audebert and C. Quivoron

E.S.P.C.I. 10, rue Vauquelin 75231 - Paris Cedex 05, France
Laboratoire de Physico-Chimie Macromoleculaire
de l'Universite Pierre et Marie Curie

ABSTRACT

Model bonded phases have been prepared by reaction of polyethyleneoxide of various molecular weights ($200 < \bar{M} < 5.10^6$) on silica.

The retention behavior of solutes on these bonded stationary phases for liquid chromatography depends on silica loadings, grafted molecule length, solute size and solvent nature. Different mechanisms such as dissolution effect in the grafted phase, adsorption on mineral support and steric exclusion due to the residual porosity of silica, are involved in the observed separations. An expression of elution volumes in relation with these mechanisms is proposed.

Chromatographic data and thermodynamic predictions are in good agreement.

INTRODUCTION

In the past few years, chemically bonded stationary phases have gained increasing importance in H.P.L.C.[1-6]. This remarkable development is due, in great part, to high selectivities and to thermal and solvolytic stabilities of such phases. They can be used with a large range of solvents and are convenient for gradient elution.

Bonded phases are applied to a great variety of separation problems but few studies have been devoted to provide a mechanistic description of their operation.

Little[7], Grushka[8], Halasz[9], Kirkland[10,11] and Unger[12] showed the importance of the amount of organic grafted phase on the mineral support. Residual adsorption on these supports can greatly modify elution volumes. Several authors[8,13,14] observed that increasing the bonded molecule length from ethyl to octadecyl causes elution volumes to increase.

Locke[15], Scott[16] and Grushka[17] demonstrated that retention order is a function of the solute solubilities in the mobile phase. In other words, in reverse phase chromatography, hydrophobic interactions between the solute and the stationary phase play an important part in the separation[18,19].

Such results have little theoretical support and do not elucidate,completely,mechanisms of chromatographic separations on grafted phases. Adsorption on the mineral support, steric exclusion effect in the case of porous mineral support, and partition of the solute between the grafted phase and the solvent may simultaneously occur. The importance of this last mechanism we studied[20] depends upon the interactions between the molecules present in the solvent/solute/grafted molecules system and the sizes of these molecules.

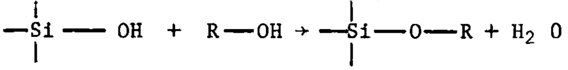
In order to better understand the chromatographic behavior of grafted phases, we prepared supports by bonding polyethyleneoxide of various molecular weights on silica and we have carried out a chromatographic study of these supports.

MATERIALS

Preparation and Characterization of Model Bonded Phases

The silica support used is Merck silica gel Si - 60 (40 - 60μ). Titration of hydroxyl groups gives 0.6 ± 0.05 OH groups per mg of silica gel[21]. ($1.7 \cdot 10^{-6}$ OH per m^2).

The terminal hydroxyl group of polyethyleneoxide reacts with a silanol function of the silica surface[22-24]:



$$-\overset{|}{\underset{|}{Si}}-OH + R-OH \rightarrow -\overset{|}{\underset{|}{Si}}-O-R + H_2O$$

Silica is heat treated at 200°C under vacuum for 12h. Then, it is mixed with an excess of polyethyleneoxide and heated at 400°c, under nitrogen, for 8h.

After cool-down to room temperature, the support is exhaustively extracted in a soxhlet with chloroform.

Polyethyleneoxide of various molecular weights (200, 400, 2.10^4, 5.10^6) were bonded to silica. These commercial samples were obtained from Omnium Scientific Industriel. The determination of the terminal hydroxyl groups of polyethyleneoxide gave an average value of 1,5 OH group per molecule[25].

A thermogravimetric study and an elemental analysis gave bonded silica loading τ. τ is the ratio of the weight of bonded polyethyleneoxide to the weight of grafted silica.

The specific surface s and the porous volume V_p of each prepared support were determined by adsorption of nitrogen[26]. Results are given in Table 1:

TABLE 1

Nature of Support	s m^2/g	V_p cm^3/g	τ
Si 60	345	0.58	0
Si 60-(POE 200)	300	0.50	12%
Si 60-(POE 400)	240	0.50	14%
Si 60-(POE 2.10^4)	200	0.40	22%
Si 60-(POE 5.10^6)	290	0.52	13%

Table 1: Specific surface s and Porous volume V_p of silica bonded with polyethyleneoxide.

Porous volume decrease with increasing loading and a diminution of 0.18 cm^3/g of porous volume is obtained for $\tau = 22\%$. In comparing with the polyethyleneoxide density ($d \simeq 1.1$), this indicates that polymer molecules are mainly grafted inside silica pores.

Apparatus and Experimental Conditions

A liquid chromatograph (Waters Assoc. Model 201) equipped with an M6000 pump and an R-401 differential refractometer as detector, was used throughout the experiments.

Silica bonded with polyethyleneoxide does not swell, even in good solvents for this polymer. Consequently, and according to the granulometric range of our supports, stainless steel columns (20 in x 1/4 in O.D.) were dry-packed. The flow rate of the solvent was adjusted to 1 ml/mn. Concentration of injected solutions was about 1g/1.

EXPERIMENTAL

Chromatographic Behavior of Pure Silica

Silica contains many surface silanol groups. So, it is not an inert chromatographic support, particularly for solutes such as polyethyleneoxides. In other words, this material is porous and separates solutes of various molecular weight by a steric exclusion mechanism. Consequently, we first studied the chromatographic behavior of pure silica for the different systems of solvent/solute used with the bonded phases themselves.

Chromatographic results show that polyethyleneoxides are adsorbed on the silica surface when acetonitrile, tetrahydrofuran (THF) or methanol is the solvent. In these cases, polyethyleneoxides are eluted in increasing order of molecular weight and retention is strong. The same holds true when polystyrene solutes are eluted by decalin.

For good solvents for the solutes, the elution order is opposite. The plot of the logarithm of the molecular weight of solute as a function of the elution volume is a classical GPC calibration curve. The average exclusion molecular weight of silica Si 60 is about 4,000 (see figure 3).

Chromatographic Behavior of Silica-Polyethyleneoxide Bonded Phases

Systems for which adsorption occurs on pure silica

On a silica bonded with polyethyleneoxide ($\bar{M}$ = 200), retention of polyethyleneoxide solutes in acetonitrile is weaker than on pure silica. For all loading levels studied, retention increased with solute size. (Trials were performed for $8\% < \tau < 12\%$). According to titrations, for τ maximum ($\tau = 12\%$), each silanol group of the silica surface is bonded with a polymer chain.

In the case of grafted polyethyleneoxide of molecular weight higher than 400, the elution order is a function of silica loading. In this way, for polyethyleneoxide 400, a variation of τ 8% to 15% leads to an inversion of the elution order of polyethyleneoxide (figure 1).

Similar results are obtained for elution of polyethyleneoxides by THF, but elution volumes are smaller (figure 2).

For a given molecular weight of grafted polymer, the τ value corresponding to the inversion of the elution order is also slightly over.

Mixed retention mechanisms such as adsorption, steric exclusion effect of silica, or dissolution of the solute into the grafted phase, seem to play a part in the observed phenomena.

On pure silica, steric exclusion effect occurs but adsorption predominates.

After grafting, adsorption decreases and curves $\log M_2=f(V_e)$ are non-linear. For an adequate amount of bonded stationary phase, an inversion of solute elution order is observed. Indeed, the silica surface which causes adsorption of solutes decreases as loading increases. Conversely, grafted phase volume becomes more important and the dissolution effect predominates.

The proportion of silica surface covered by polymer and chromatographic data may be correlated. A macromolecule of molecular weight M in a θ-solvent, occupies a spherical volume V proportion-

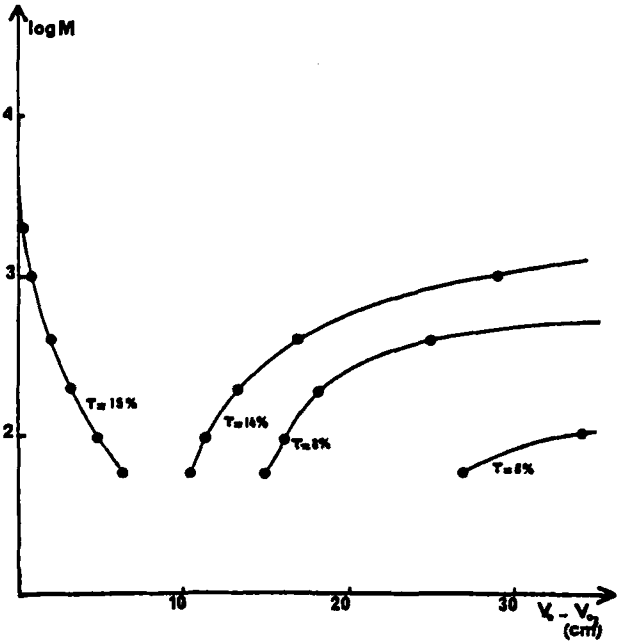


Figure 1. Elution of polyethyleneoxides by acetonitrile on pure silica Si 60 and silica bonded with polyethyleneoxide $\bar{M}$ = 400. (τ = 15%, 15%, 8%) (V_o = dead volume of the column).

al to $M^{3/2}$ 27. The surface S covered by such a molecule can be likened to the surface of a great circle of this sphere. Hence:

$$S = K.V^{2/3} = K'.M.$$

Considering 1 gram of silica, the number of grafted molecules is proportional to $\frac{\tau}{M}$. So, in a first approximation, the total surface of silica covered by these grafted molecules is proportional to τ and does not depend on M. Effectively, the inversion of the elution order of solutes is observed for loadings about 13% - 15%, whatever the molecular weight of grafts may be ($400 < \bar{M} < 5.10^6$). So, a critical amount of grafted phase, τ_c, is suggested and all chromatographic data are easily predicted. Dissolution effect predominates when no part of silica surface is available for adsorption of the solutes, i.e. when $\tau = \tau_c$.

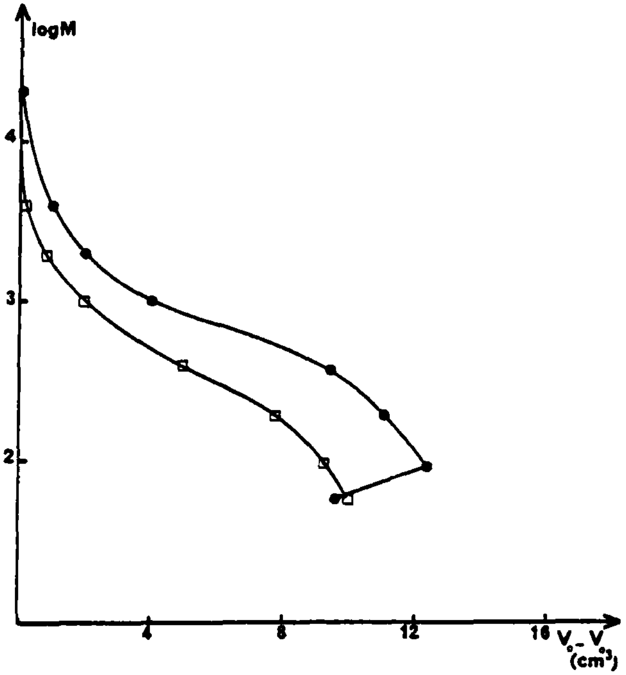


Figure 2. Elution of polyethyleneoxides by acetonitrile (o) and tetrahydrofuran ( ) on silica bonded with polyethyleneoxide M = 2.10^4 (τ = 22%).

In the case of grafted molecules of low molecular weight ($\bar{M}$ < 200), even when all silanol groups of the silica are substituted, τ_c is not reached and adsorption predominates.

Systems Leading to Adsorption on Pure Silica

When polyethyleneoxides are eluted by dimethylformamide on bonded silicas, whatever the molecular weight of grafted molecules may be, retention is lower than on pure silica. The elution volume of a given polyethyleneoxide decreases by increasing the molecular weight of the graft from 200 to 2.10^4. Then, for a grafted polymer of molecular weight 5.10^6, retention increases (see figure 3).

The same holds true for elution of polystyrenes, polyisobutenes and n-alkanes by THF or chloroform.

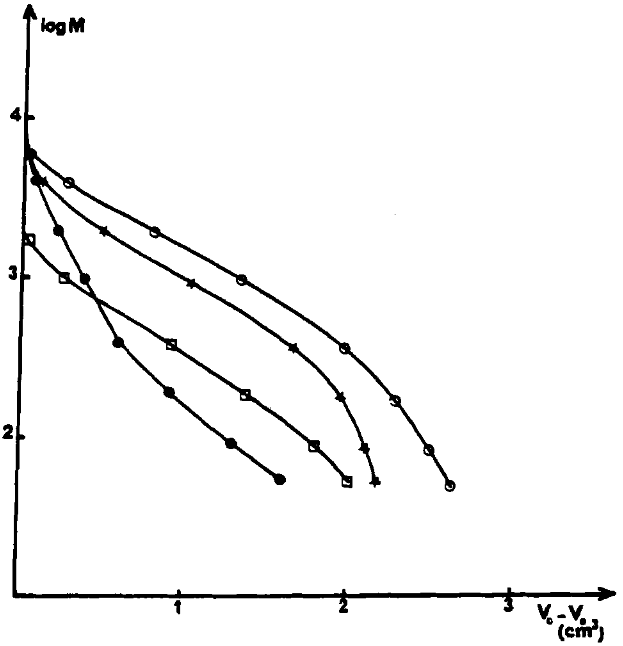


Figure 3. Elution of polyethyleneoxides by dimethylformamide on pure silica Si_60 ( ) and silicas bonded with polyethyleneoxides $\bar{M}$ = 200 ( ), $\bar{M}$ = 400 ( ), M = 2.10^4 (o) and $\bar{M}$ = 5.10^6 ( ).

The influence of the nature of the solvent on the retention characteristics of our supports depends on the molecular weights of grafted molecules. Thus, for a silica bonded with low molecular weight polyethyleneoxide ($\bar{M}$ = 400), retention of polystyrenes and n-alkanes becomes stronger when solvent is changed from chloroform to THF to dimethylformamide (figure 4). Elution volumes of polyisobutenes are also greater in dimethylformamide than in chloroform.

A reverse effect for solvent nature is observed (figure 5) when the molecular weight of the grafted polyethyleneoxide is 5.10^6.

Our experimental observations involving measurements of specific surface and porous volume, absence of swelling of the packings even in good solvent for polyethyleneoxide, and increasing weight

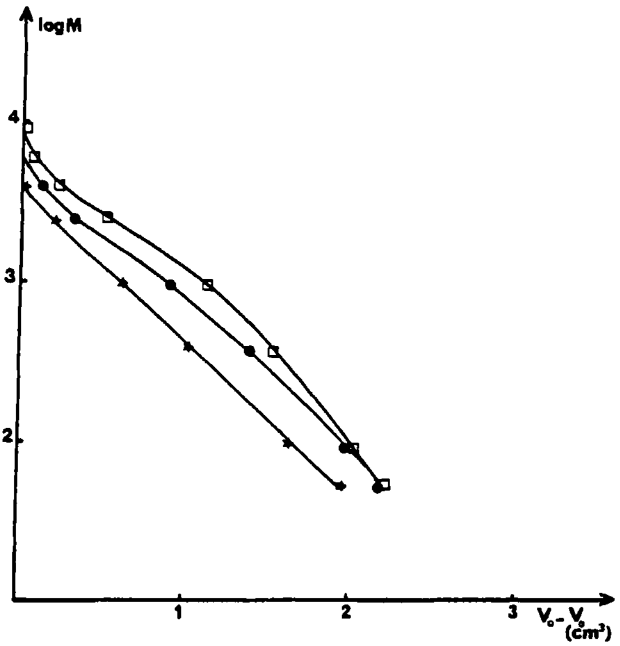


Figure 4._ Elution of polystyrenes on silica bonded with polyethyleneoxide $\bar{M}$ = 400 by tetrahydrofuran (o), chloroform ( ) and dimethylformamide ( ).

of a given volume of grafted silica with τ, show that polyethyleneoxide is mainly grafted inside the silica pores. This is not surprising in view of the method of bulk synthesis that was used.

As a result, a scheme of a support silica-polyethyleneoxide is depicted in figure 6. The initial porous volume V_p of the silica is partly occupied by the grafted swelled phase V_s (zone I). A porous volume (V_p - V_s) remains (zone II). Separation of solutes proceeds by steric exclusion effect and dissolution into the grafted phase.

When geometric characteristics of pores and grafted molecules are known, the relative importance of each mechanism involved may be evaluated and an average partition coefficient $\bar{K}$ may be expressed.

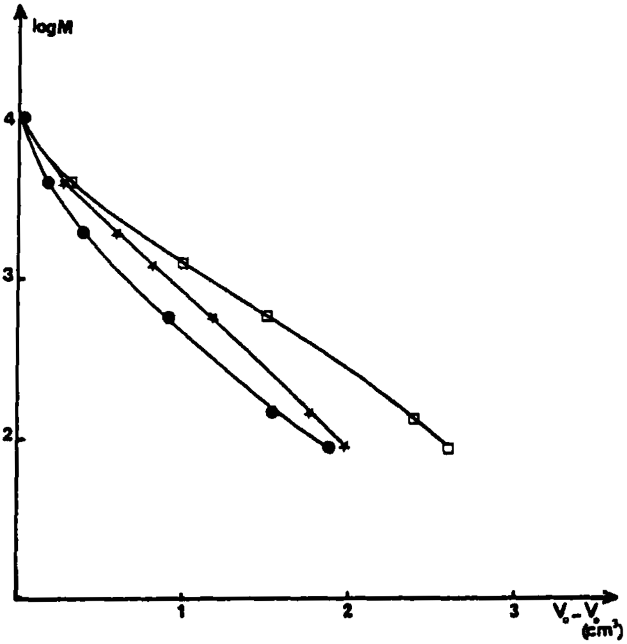


Figure 5._ Elution of polystyrenes on silica bonded with polyethyleneoxide $\bar{M} = 5.10^6$ by tetrahydrofuran (o), chloroform ( ), and dimethylformamide ( ).

Let - K_{GPC}^1 be the GPC partition coefficient in the total porous volume (zone I + II).

- K_{GPC}^2, the GPC partition coefficient in the porous volume containing only solvent (zone II).
- K_D, the partition coefficient of the solute between the mobile and the grafted phases.
- C_2^m, the concentration of the solute in the mobile phase.

First, we calculate the weight of solute molecules m_1, having at least one segment inside zone I. It is difficult to directly evaluate m_1, but it may be determined by difference. With the hypothesis of a porous volume (zone I + II) completely filled by grafted phase, the total weight of solute inside this volume would be:

$$m = K_{GPC}^{1}\ K_D\ V_p\ C_2^m$$

m can be artificially separated into two terms:

The first corresponds to solute molecules having at least a segment inside the zone I, i.e. m_1.

The second is composed of solute molecules having all segments inside zone II. This last quantity m_2, could be observed if a GPC effect and a dissolution inside the smaller pores corresponding with the zone III would occur. $(m = m_1 + m_2)$.

$$m_2 = K_{GPC}^{2}\ K_D\ (V_p - V_s)\ C_2^m$$

Hence:

$$m_1 = K_{GPC}^{1}\ K_D\ C_2^m\ V_p - K_{GPC}^{2}\ K_D\ (V_p - V_s)\ C_2^m$$

In fact, there are no grafted molecules inside zone II and the weight of solute inside this zone is m'_2 (not m_2). m'_2 depends upon the steric effect in the reduced porous volume, so:

$$m'_2 = K_{GPC}^{2}\ (V_p - V_s)\ c_2^m$$

The weight of solute molecules effectively present inside the internal volume of the support is:

$$m' = m_1 + m_2$$

Hence:

$$m' = K_{GPC}^{1}\ K_D\ V_p\ C_2^m - K_{GPC}^{2}\ K_D\ (V_p - V_s)\ C_2^m + K_{GPC}^{2}\ (V_p - V_s)\ C_2^m$$

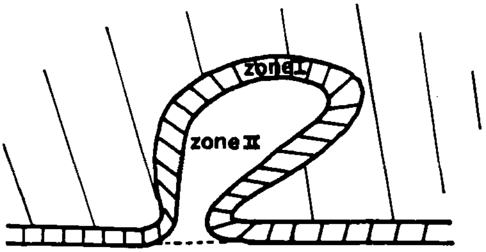


Figure 6. Scheme of a support silica - polyethyleneoxide.

The grafted phase behaves as a chromatographic support of average partition coefficient $\bar{K}$ with a V_p volume of stationary phase:

$$\bar{K} = \frac{\text{average concentration of solute inside pores}}{\text{average concentration of solute in the mobile phase}} = \frac{m'}{C_2^m V_p}$$

Consequently, the elution volume of solute must be:

(I)

$$V_e = V_o + \bar{K}V_p = V_o + K_{GPC}{}^1 K_D V_p + (1 - K_D) K_{GPC}{}^2 (V_p - V_s)$$

$K_{GPC}{}^1$ and $K_{GPC}{}^2$ were evaluated by means of the characteristics of the different grafted silicas. Assuming pores of silica to be a group of cylinders of average diameter a, the partition coefficient by steric exclusion effect is then[28]:

$$K_{GPC}{}^1 = (1 - \frac{R}{a})^2$$

where R is the radius of the equivalent hydrodynamic sphere occupied by a molecule of polyethyleneoxide in solution.

For a Θ-solvent of polyethyleneoxide:

$$R^3 = \frac{(\eta)\ .\ M}{\Phi'}{}^{27} \quad \text{with } \Phi' = 6^{3/2}\cdot 3.62\cdot 10^{21}$$

$$R \simeq 2.5\ (1.5\cdot 10^{-3}\cdot M^{1\cdot 5})^{1/3}$$

Pure silica Si 60 is a GPC packing which separates compounds of molecular weight lower than 4000 (i.e. a = 18 Å). This value of the average diameter of pores is in good agreement with our measurements of the pore distribution by nitrogen adsorption. The relationship given above leads to a theoretical GPC curve which agrees with the experimental curve obtained with silica Si 60.

Porous volume and average diameter of pores, a, of a grafted silica are smaller. The residual porous volume evaluated by means of τ gives the a value for each packing. Hence, $K_{GPC}{}^2$ is easily deduced.

TABLE 2

Molecular Weight of Grafted Molecules	τ	Residual Porous Volume per Gramme of Packing $(V_p - V_s)$. (cm^3)	a (Å)
Silica pure	0	0.45	18
200	12%	0.35	16
400	15%	0.25	13
$2 \cdot 10^4$	22%	0	--
$5 \cdot 10^6$	15%	0	--

Table 2: Residual porous volume and average diameter of pores of silica bonded with polyethyleneoxide.

A theoretical expression of K_D is obtained from our thermodynamic study[20] of the partition of a solute between a macromolecular phase and a solvent.

$$\mathrm{Log}\ K_D \simeq - r_2 \left(\frac{1}{r_1} - \frac{1}{r_3}\right)\phi_3 - \frac{(\phi_3^{1/3} - \phi_3)}{2}\frac{r_2}{r_3} + \mathrm{Log}\left(1 - \frac{r_1}{r_3}\phi_3\right) r_2 + \chi_{12}\frac{r_2}{r_1}\phi_3$$

$$+ \chi_{13}\frac{r_2}{r_1}\phi_1\ \phi_3 - \chi_{23} r_2 \phi_3 - \frac{\phi_3^{4/3}\sqrt{\frac{2}{3\pi}\frac{r_1 r_2^2}{r_3^3}}}{\mathrm{erf}\sqrt{\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}}}\, e^{-\left(\frac{3}{2}\frac{r_1}{r_3}\phi_3^{2/3}\right)} + \qquad \text{(II)}$$

$$\mathrm{Log}\left(\mathrm{erf}\left(\phi_3^{-1/3}\sqrt{\frac{r_3}{r_2}\frac{3}{2}}\right) + \sqrt{\frac{2}{3\pi}\frac{r_2}{r_3}}\ \phi_3^{1/3}\left(e^{-\left(\frac{3}{2}\frac{r_3}{r_2}\phi_3^{-2/3}\right)} - 1\right)\right)$$

and: (III)

$$\mathrm{Log}\ (1 - \phi_3) + \phi_3\left(1 - \frac{r_1}{r_3}\right) - \mathrm{Log}\left(1 - \phi_3\frac{r_1}{r_3}\right) + \frac{r_1}{2r_3}(\phi_3^{1/3} - \phi_3)$$

$$+\left(\operatorname{erf}\sqrt{\frac{3}{2}\frac{r_1}{r_3}\phi_3^{\;2/3}}\right)^{-1} e^{-\frac{3}{2}\frac{r_1}{r_3}\phi_3^{\;2/3}} \sqrt{\frac{2}{3\pi}\left(\frac{r_1}{r_3}\right)^3}\ \phi_3^{\;4/3} + \chi_{13}\phi_3^{\;2} = 0$$

r_1, r_2, r_3 are the number of segments of identical volume constituting a solvent, a solute and a grafted polymer molecule, respectively[27]. ϕ_3 is the volume fraction of grafted molecules in the stationary phase. χ_{ij} are Flory's interaction parameters[27] which may be expressed in terms of solubility parameters.

In this way, K_D was evaluated for each kind of grafted molecule we used. The application of equations I, II, and III gives the curves for $\bar{K} = \frac{Ve - Vo}{Vp}$ as a function of the logarithm of the molecular weight M_2 of the solute for each support we studied (figure 7).

These curves are qualitatively in good agreement with experiments. The residual steric exclusion effect and of dissolution effect are opposite. So, initially, by increasing molecular weight of grafted molecules, retention of solute begins to decrease, then, for high molecular weight grafts, it increases.

For a series of solvents, all having the same affinity towards the grafted polymer, Vs and $K_{GPC}{}^2$ remain constant. The equation (I) can be written as:

$$Ve = Vo + K_D\ ((K_{GPC}{}^1 - K_{GPC}{}^2)\ V_p + K_{GPC}{}^2\ Vs) + K_{GPC}{}^2\ (V_p - Vs)$$

Consequently, the dependence of Ve and K_D on solvent/solute interactions is the same.

Equation II shows that K_D is especially increased as the solute affinity for the solvent decreases. Effectively, polystyrene and n-alkanes are less retained in chloroform (good solvent) than in dimethylformamide (poor solvent) (figure 4 and 5).

Comparison of retention volumes of polystyrenes, polyisobutenes and n-alkanes in THF and in chloroform is more difficult to do for the grafted phases that are not swollen similarly by these

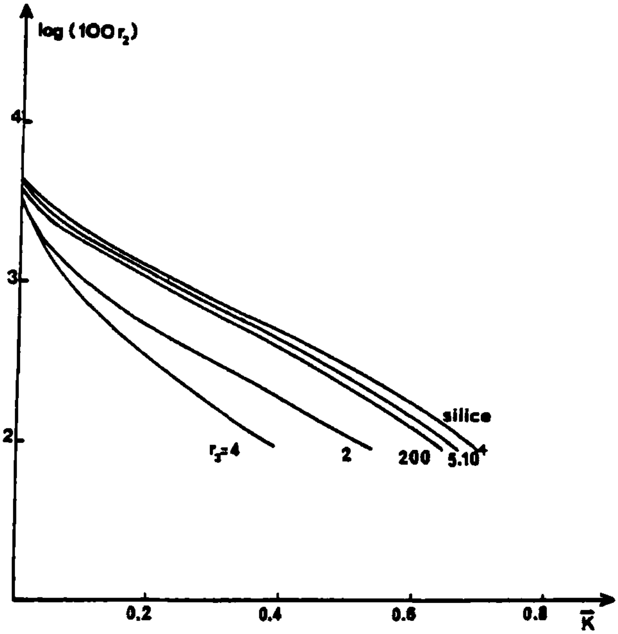


Figure 7. Theoretical curves log M_2 = f($\bar{K}$) for silicas bonded with polyethyleneoxides of various molecular weights ($\chi_{12}=\chi_{13}=\chi_{23}=0$).

solvents. For grafted polyethyleneoxide of low molecular weight, equations II and III show that:

$$K_D^{THF} \simeq K_D^{CHCl_3}$$

THF is a poor solvent for polyethyleneoxide: the swelling of the grafted phase is lower in this solvent than in chloroform. Hence the fraction of porous volume occupied by grafted molecules is greater in this latter solvent.

$$K_{GPC}^{2,THF} > K_{GPC}^{2,CHCl_3}$$

It follows that, whatever the solute may be:

$$Ve^{THF} > Ve^{CHCl_3}$$

Effectively, this is experimentally observed (figure 4).

For grafted polyethyleneoxide of high molecular weight, previous relationships show that $K_{GPC}^2 = 0$. Hence,

$$V_e = V_o + K_D\, K_{GPC}^1\, V_p$$

In this case, K_D varies to a high degree, with the affinity of solvent towards solutes.

Equations II and III give:

$$K_D^{CHCl_3} > K_D^{THF}$$

According to our experimental results (figure 5) polystyrenes and polyisobutenes have effectively larger elution volumes in chloroform than in THF on silica bonded with polyethyleneoxide ($\bar{M}$=5.6^6).

CONCLUSION

The choice of grafting conditions permits the experimental modification and study of the relative importance of the dissolution, adsorption and steric exclusion mechanisms.

In the case of low molecular weight solutes, for separations involving adsorption, a progressive modification of mineral support properties may be obtained by using short grafts and by adjusting the mineral support loadings.

Conversely, for separations requiring a dissolution mechanism (for instance, separations by reverse-phase chromatography) it may be interesting to graft high molecular weight molecules and to use high loading, in spite of the decrease in efficiency which results.

For polymers, fractionation by gel permeation chromatography, a steric exclusion effect must be the only mechanism involved. Recently, grafted GPC packings have been commercialized. In that case our results indicate that grafts could perturb calibration curves.

REFERENCES

1. Grushka, E., Bonded Stationary Phases in Chromatography, Ann. Arbor. Sci., Mick, 1974.

2. Locke, D.C., J. Chrom. Sci., 11, 120, 1973.
3. Majors, R., Analusis, 10, 549, 1975.
4. Pryde, A., J. Chrom. Sci., 12, 486, 1974.
5. Rehak, V., and Smolkova, E., Chromatogr., 9 (5), 219, 1976.
6. Rosset, R., Caude, M., and Jardy, A., Manuel Pratique de Chromatographie en Phase Liquide, Varian, Orsay, 1975.
7. Little, J.N., Dark, W.A., Farlinger, P.W., and Bombaugh, K., J. Chrom. Sci., 8, 647, 1970.
8. Grushka, E., and Kikta, E.J., Anal. Chem., 48, 1098, 1976.
9. Halasz, I., and Sebastian, J., J. Chrom. Sci., 12, 161, 1974.
10. Kirkland, J., J. Chrom. Sci., 9, 206, 1971.
11. Kirkland, J., Anal. Chem., 43, 36, 1971.
12. Unger, F.K., Becker, N., and Roomeliotis, P., J. Chrom., 125, 115, 1976.
13. Hemetsberger, H., Maasfield, W., and Ricken, H., Chromagr., 9, 303, 1976.
14. Gilpin, R.K., Korpi, J.A., and Janicki, G.A., Anal. Chem., 47, 1498, 1975.
15. Locke, D.C., J. Chrom. Sci., 12, 433, 1974.
16. Scott, W., and Kucera, P., J. Chrom., 112, 425, 1975.
17. Grushka, E., and Kikta, E.J., Anal. Chem., 46, 1370, 1974.
18. Karger, B.L., Gant, J.R., Hartkopp, A., and Weiner, P.H., J. Chrom., 128, 65, 1976.
19. Horvath, C., Melander, W., and Molnar, I., J. Chrom., 125, 129, 1976.
20. Lecourtier, J., Thesis of Doctorat, University P. et M. Curie, Paris, 1977.

    Lecourtier, J., Audebert, R., and Quivoron, C., Macromolecules, to be published.
21. Boechn, H.P., Schneider, N., and Arend, F., Zeit. Für An. and All. Chem., 43, 320, 1963.
22. Hastings, C.R., Augl, J.M., Kapila, S., and Aue, W.A., J. Chrom., 87, 49, 1973.

23. Vihlein, M., and Halasz, I., J. Chrom., <u>80</u>, 1, 1973.

24. Belenkii, B.G., Vilenchik, L., Nesterov, V., and Saashina, T. I., Polym. Sci., SSR, <u>11</u>, 2973, 1973.

25. Rempp, P., J. Chem. Phys., <u>54</u>, 432, 1957.

26. Gregg, S.J., and Swing, K., <u>Adsorption Surface Area and Porosity</u>, Acad. Press, London, 1967.

27. Flory, P., <u>Principle of Polymer Chemistry</u>, Cornell, Ithaca, NY, 1953.

28. Casassa, E., J. Phys. Chem., <u>75</u>, 3929, 1971.

29. Brandrup, J., and Immergut, E.H., <u>Polymers Handbook</u>, Interscience, 1965.