Factors influencing polybutadiene deposition within porous chromatographic zirconia

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Abstract

We have studied the effect of the conditions for the deposition of polymers in the preparation of polybutadiene-coated porous zirconia particles for reversed-phase chromatography. Chromatographic performance improves when the particle surface is pre-coated with elemental carbon by a chemical vapor deposition (CVD) process. Conversely, performance is significantly degraded when the solvent is removed very slowly during the deposition process. No improvement results when the particles are coated using small sequential loads of polymer. We hypothesize that the polymer deposition process is controlled by the rate at which the solvent meniscus recedes during solvent evaporation, by the affinity of the polymer for the zirconia surface, and by polymer–solvent and polymer–polymer interactions.   © 1997 Elsevier Science B.V.

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1. Introduction

The deposition and immobilization of nonpolar polymers [e.g., polybutadiene (PBD), polystyrene and perfluoropolymers] on silica gels has been used as the basis for making a variety of packing materials for reversed-phase liquid chromatography (LC) [1–4]. The goal of this approach is to enhance the chemical stability of the silica support and to eliminate the silanophillic interactions between the silanol groups on the silica surface and basic compounds such as pharmaceuticals [2]. As has been demonstrated [2,4–6], polymer-coated materials do indeed show enhanced pH stability and decreased silanophilic interactions, making these materials more useful for the separations of amino acids, peptides and proteins. Alumina coated with hydrophobic polymers by the same procedures as those tested on silica is even more stable (pH 3–12) in alkaline solution than are similarly coated silica supports [7,8], indicating that the chemical stability of the underlying material is still important.

While developing zirconia-based reversed-phase materials, we realized that it is very difficult to form chemically stable organosilane coatings on the surface of zirconia. Consequently, the approach taken in this laboratory has been to physically deposit nonpolar polymers such as PBD in the pores of the particles, and to then immobilize them using a cross-linking treatment [9,10]. This method combines the

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superior chemical and thermal stability of zirconia [11] and PBD, making PBD-coated zirconia a chemically and thermally stable reversed-phase material. This process is entirely analogous to that developed by Bien-Vogelsang et al. [7] for preparing reversed-phase alumina [7]. Rigney et al. [9] found that PBD-coated zirconia was stable in alkaline solution, there was no evidence for degradation of the support even after exposure to 1 M sodium hydroxide at 100°C. Recently, PBD-coated zirconia has been tested at 100°C for more than seven thousand column volumes with similar results [12]. The extreme thermal stability of this material allows it to be used for optimization of separation selectivity by varying the column temperature over a wide range [13].

As demonstrated in an earlier study [14], the absolute retention (k') (and presumably the column loading capacity) increases with the amount of polymer loaded on zirconia. Thus, from the standpoint of retention alone, it is desirable to have the PBD load as high as possible. However, chromatographic efficiency also depends on the amount of polymer. Our previous chromatographic studies [15] indicated that high loadings of PBD reduced the diffusion rate (as evaluated by the C term in the Knox equation [16]) within the stationary phase, lowering the column efficiency. Rigney [17] showed in early work that, at very high carbon loads (about 8% carbon), polymer depositions on the external surface were observed by scanning electron microscopy (SEM) and that such particles were glued together and unpackable in high-performance liquid chromatography (HPLC) columns. [We did take SEM micrographs at the highest loads used here and saw no evidence of aggregates or external deposits. In addition our particles were free flowing and readily packable.] It is hoped that a better coating procedure would produce materials with high polymer loads and better chromatographic performance. Although Kurganov et al. [18] reported some results on coating PBD on zirconia, a more detailed understanding of the coating process is certainly important.

In an earlier paper [19] we developed models to aid in interpreting experimental nitrogen adsorption data for PBD-coated porous chromatographic zirconia. Comparisons of measured pore size distributions with the predicted distributions suggested that

at low loadings (about 3% carbon by weight) the PBD deposits in thin layers on the surface with little preference for filling either large or small pores. At higher PBD loadings, our data showed that the polymer deposits preferentially in smaller pores. In this paper, we will examine the effects of changing a number of the parameters of the coating procedure with the hope of achieving higher polymer loads without reducing the chromatographic efficiency.

2. Experimental

2.1. Reagents

All reagents used were obtained from commercial sources and were reagent grade or better. Poly-butadiene of molecular mass 5000 (20% vinyl, 80% *cis*- and *trans*-1,4) and dicumyl peroxide (DCP) were from Aldrich (Milwaukee, WI, USA). Hexane (EM Sciences, Gibbstown, NJ, USA), toluene (Fisher, Fair Lawn, NJ, USA) and isopropanol (IPA) (Mallinckrodt, Paris, KY, USA) were all HPLC grade. HPLC-grade acetonitrile (Mallinckrodt) was used as the organic solvent in LC. Water was obtained through a Barnstead filter with an organic-free cartridge and boiled before use to remove dissolved carbon dioxide. Benzene (Aldrich) was used to measure column efficiency.

2.2. Zirconia particles and general coating procedure

The microparticulate porous zirconia support used in this study was the same as reported in previous investigations [12–15]. The particles were nominally 2.5 μm in diameter with pore diameters predominantly between 200–240 Å. Zirconia particles were synthesized in our laboratory by the polymerization-induced colloid aggregation process (batch PICA-7), as detailed elsewhere [14].

Our method for preparing PBD-coatings on chromatographic zirconia has also been described previously [20]. Particles were dried under vacuum for 16 h at 120°C and cooled over phosphorus pentoxide. Then about 200 ml of hexane was transferred to the particles, followed by a solution of molar mass 5000

PBD in hexane. The slurry was sonicated under vacuum for 10 min to displace the air within the pores with liquid; it was then gently rocked for at least 8 h. The cross-linking agent DCP was added to the slurry in a ratio of 2.5% (w/w) DCP/PBD. This mixture was sonicated and swirled for an additional hour, after which the solvent was evaporated over the course of 1 h (for about 200 ml of hexane) by applying a weak vacuum (about 24 Torr; 1 Torr= 133.322 Pa) at 35°C. The particles were dried at 110°C for 1 h in a vacuum oven, and then the polymer was thermally cross-linked at 120°C for 1 h and 160°C for 4 h. Finally, the particles were Soxhlet extracted with toluene (110°C for at least 8 h) and washed with hexane to remove any free polymer. This is considered the standard procedure. The carbon loading reproducibility (R.S.D.) of this "standard" procedure is usually about 7%. We note that about 70% of low-molecular-mass PBD offered to the zirconia is retained after cross-linking and Soxhlet extraction independent of the amount of offered.

2.3. Variations on the coating procedure

(1) Deposition was made sequentially (three times). Each time 2.5% (w/w) PBD was used relative to the mass of zirconia. That is, the above "standard" procedure was used with 2.5% PBD/ zirconia, cross-linked, extracted and the whole process repeated twice more.

(2) Solvent was slowly evaporated over a period of 24 h (by applying a vacuum of about 20 Torr at room temperature) instead of during the 1 h period in the "standard" procedure. 8% (w/w) of PBD/zir-conia was offered.

(3) To study the effects of surface wetting by the polymer, we also used zirconia particles which were pre-coated with elemental carbon by the CVD method [21]. 8% PBD was offered for deposition by the "standard" procedure.

2.4. Physical characterization of PDB-coated zirconia

The pore structures were characterized after heating the samples for 8 h at 150°C at 0.1 Pa to remove surface contaminants. Nitrogen sorption was performed using a Micromeritics ASAP 2000 sorptome-

ter (Micromeritics, Norcross, GA, USA). Pore size distributions were calculated from nitrogen adsorption and desorption data using the BJH method [22]. These are approximate since the method treats the pore structure as a collection of unconnected cylinders.

Carbon loads were determined by elemental analysis (M-H-W Laboratories, Phoenix, AZ, USA).

Particles were packed into columns (100×4.6 mm I.D.) via a packing procedure described elsewhere [20], but the slurry solvent was changed to 50% hexane and 50% IPA.

2.5. Chromatographic characterization of PBD-coated zirconia

Chromatographic experiments were performed on a HP1090 system with binary gradient pumps, autosampler, temperature control, filter photometric detector, and a HP 3396 integrator (Hewlett-Packard, Wilmington, DE, USA). For these experiments, the column temperature was maintained at 30.0 ± 0.2°C and detection was at 254 nm.

We performed column dynamic measurements using benzene in pure acetonitrile mobile phase. Because benzene is unretained ($k'=0$) under these conditions, the dependence of the reduced plate height on the reduced velocity of the solute in the mobile phase relates directly to the intraparticle diffusion rate without complications due to sorption kinetics [23,24]. Although the fluid film mass transport process may also contribute to reduced plate height, it is usually considered negligible [23,24], and will not affect our results. The flow-rate ranged from 0.1 to 5.0 ml/min. The solute concentration was about 2 mg/ml with an injection volume of 0.5 μl.

2.6. Data-processing

The plate count (N) of each peak was computed by:

$$N = 2\pi\left(\frac{t_{R}}{W_{A/H}}\right)^{2} \tag{1}$$

where t_{R} is the retention time, and $W_{A/H}$ is the peak width computed by the area-to-height ratio. The reduced plate height (h) was then computed by

$h = H/d_p = L/Nd_p$ (L = the length of the column). The reduced velocity (ν) was computed as:

$$\nu = \frac{F}{60\epsilon_e \pi R^2} \frac{d_p}{D_e} \qquad (2)$$

where F is the flow-rate (ml/min), ϵ_e is the external porosity (0.38 for our columns), R is the radius of the column (0.23 cm), and D_e is the diffusion coefficient of benzene ($3.73 \cdot 10^{-5}$ cm^2/s at 30°C) measured in a previous study [25]. The h vs. ν data obtained were fitted to the Knox equation [16]:

$$h = \frac{B}{\nu} + A\nu^{1/3} + C\nu \qquad (3)$$

where the B term characterizes axial diffusion, the A term denotes packing quality (non-homogeneity of the flow), and non-equilibrium effects (e.g., mass transfer limitations and retention kinetics) are accounted for by the C term [23,24]. Since we conducted our studies using an unretained solute, we will treat the C term as a measure of the mass transfer resistance due to diffusion in the stagnant mobile phase within the particle pores [23,24]. Although the peak widths at very high flow-rates may be affected by the relatively slow detection time constant (0.1 s), we did not correct for this [15] because the columns used had the same dimensions, any effect would be consistent between materials. Accordingly, the conclusions will not be affected. Curve-fitting was performed with commercial software package Origin (MicroCal Software, Northampton, MA, USA).

3. Results and discussion

3.1. Sequential coating

In our previous study of polymer coating we observed a qualitative change in the polymer deposition process at polymer loads above 2–3% carbon by weight; this was indicated both by nitrogen sorption data and by the C term of the Knox equation [15,19]. At polymer loads of more than the 2–3% level, the C term increases rather abruptly for species with the same k' and even for unretained species. Since the sorptometry data suggested a more homogeneous

coating at the low levels of polymer [14,19], we hypothesized that polymer–polymer interactions at high loads were leading to aggregation of polymer in microdroplets, through which diffusion would be slow. We hypothesized then that sequential deposition and immobilization of small amounts of polymer (e.g., three time 2.5% w/w to total 7.5%) might provide a highly loaded phase with greater chromatographic efficiency since this procedure might reduce polymer–polymer aggregation before immobilization. Table 1 summarizes the physical characterization of the materials, and Fig. 1 shows the pore size distributions for the three materials (along with bare zirconia) calculated from nitrogen adsorption data.

Surprisingly, the change in pore size distribution (Fig. 1) upon sequential coating is no different from that found with single step coating [14,19]. With lower polymer loads (2.2% carbon, first loading), the distribution remains similar to that of the un-coated material, except for a slight shift in peaks towards smaller pore diameters. At higher loadings (4.1 and 6.1% carbon, second and third loadings), the volume contribution of smaller pores decreases more rapidly than the contribution of larger pores. More importantly, the pore size distribution after the third coating (total carbon load 6.1%) is very similar to that obtained in a single step coating with a large amount of polymer (5.6%, dotted line) [14]. The pores are only slightly smaller and the distribution is slightly broader. This similarity indicates that the immobilized polymer layers do not significantly alter the interaction of polymer with the surface or with itself. This suggests that the weak polymer–surface interactions result in a tendency for polymer to form droplets in the narrower parts of the pores regardless of how much is coated at any given stage. Fig. 2 illustrates schematically a simplified representation of the result of drying in a porous particle. Mass transfer limitations and capillary forces due to the pore structures cause solvent to evaporate most rapidly from large pores at the gas–liquid interfaces. This can lead to the formation of isolated liquid clusters.

In order to further evaluate the coating homogeneity, we also conducted column dynamic measurements with an unretained test solute (benzene). Fig. 3 shows the data with curves fitted to the Knox equation. The Knox coefficients are summarized in

Table 1
Summary of physical characterization[a]

Material[b]	Polymer load[c] (%Carbon)	Pore volume[d] (V, ml/g)	PBD volume[e] (ml/g)	PBD volume[f] (ml/g)	Surface area[d] (A, m²/g)	Pore diameter[d,g] (Å)
Bare[h]	0	0.174	0.000	0.00	34.1	198
"Standard"[h]	5.6	0.094	0.076	0.073	21.4	256
Sequential 1[i]	2.2	0.153	0.021	0.029	25.9	237
Sequential 2[j]	4.1	0.126	0.048	0.054	20.5	246
Sequential 3[k]	6.1	0.099	0.075	0.080	15.0	266
Carbon/PBD[l]	5.9	0.099	0.075	0.077	15.2	276
Slow evaporation[m]	5.1	0.044	0.130	0.068	7.5	233

[a] BET nitrogen adsorption and elemental analysis data.

[b] Materials obtained by different coating procedures.

[c] Polymer load measured as the relative amount of carbon on zirconia (percent by weight) obtained by elemental analysis.

[d] BET results.

[e] PBD volume computed as the difference in pore volume between bare and coated zirconia.

[f] PBD volume calculated from the amount of immobilized PBD, assuming no change in PBD density (0.89 g/ml) as a result of immobilization and cross-linking [14].

[g] Average pore diameter determined by BET ($4V/A$, V is the volume and A is the surface area).

[h] Obtained by the "standard" coating procedure [14].

[i] Obtained by the first sequential coating (2.5% PBD).

[j] Obtained by second sequential coating on the first coating (2.5% PBD).

[k] Obtained by the third sequential coating on the second coating (2.5% PBD).

[l] Obtained by coating PBD on carbon-clad zirconia.

[m] Obtained by very slow evaporation of hexane.

Table 2. We can observe from both Fig. 3 and Table 2 that, similar to that obtained for bare zirconia [15], there is no evidence of internal mass transfer limitation for the first and second coatings (the C term is negligible at these velocities and statistically zero). After the third coating, though, even at these low
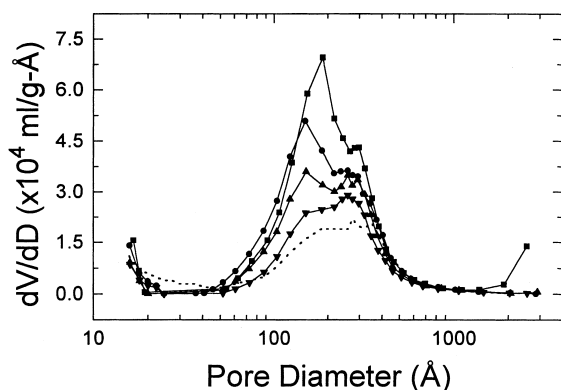

Fig. 1. Pore volume distribution of PBD-coated zirconia obtained by the "standard" and sequential coating procedures. Samples/symbols: (■) bare zirconia; (●) first loading; (▲) second loading; (▼) third loading; (– · –) standard, 5.6% carbon [14].
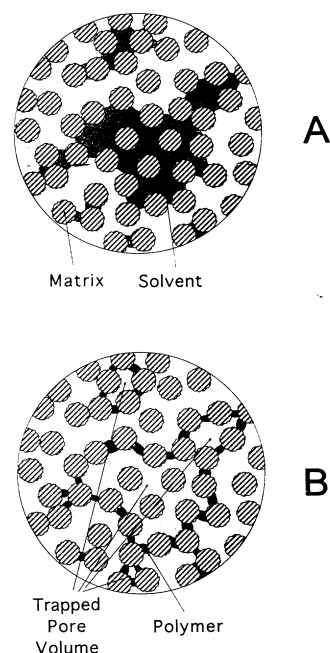

Fig. 2. Schematic illustrations of PBD distribution within porous zirconia resulting from different coating conditions. (A) "Standard" coating procedure; (B) very slow evaporation procedure.
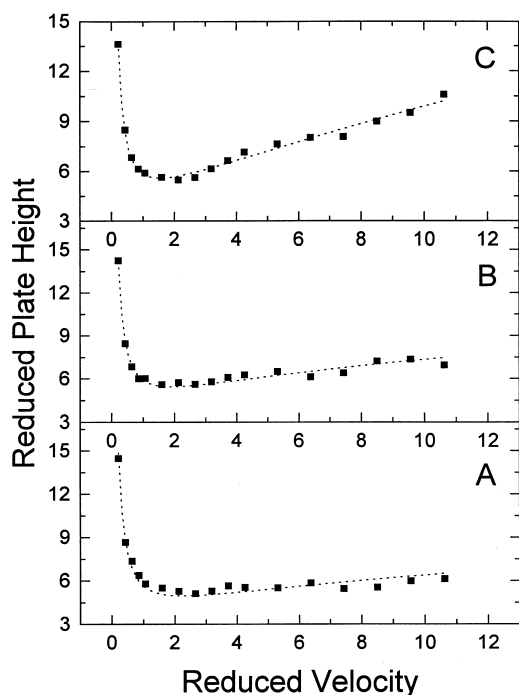
Fig. 3. Plot of reduced plate height against reduced velocity for sequentially coated samples. Symbols: (A) first loading; (B) second loading; (C) third loading; (– · –) fitted curves.

velocities the C term contribution has increased. This is very much as we observed for the same polymer load obtained with the "standard" coating method (see Table 2) [15].

Table 2
Effect of coating procedure on column efficiency[a]

Material[b]	Knox coefficients			$(\chi^2)^c$
	A	B	C	
Bare[d]	2.3±0.2	3.7±0.1	0.00±0.04	0.08
"Standard"[d]	2.4±0.1	2.3±0.0	0.39±0.02	0.03
Sequential 1	2.8±0.2	2.8±0.1	0.00±0.06	0.15
Sequential 2	3.3±0.2	2.6±0.1	0.00±0.04	0.08
Sequential 3	3.0±0.1	2.5±0.1	0.32±0.04	0.06
Carbon/PBD	2.8±0.2	2.3±0.1	0.07±0.05	0.10

[a] Results of fitting Knox equation to experimental data.
[b] See Table 1 for explanation.
[c] Chi-square of the fit.
[d] Obtained from previously published data [15].

3.2. Slow evaporation of solvent

We also hypothesized that the coating might become more homogeneous if we allowed more time for polymer–wall interactions to more fully equilibrate. We will see that our hypothesis is clearly wrong. When the "standard" coating procedure is used, the decrease in pore volume as measured by nitrogen sorptometry is in good agreement with the volume of PBD deposited (assuming no change in the density of the polymer upon deposition) [14] (see also Table 1). This indicates that the deposited polymer is not blocking the access of nitrogen to any pores. However, as shown in Table 1, when the solvent is intentionally very slowly removed (polymer load 5.1% carbon by weight), the pore volume and surface area are dramatically lower than those observed for materials with quite similar polymer loads prepared by the "standard" coating method (see "slow evaporation" data in the last row of Table 1).

Fig. 4 clarifies this point, showing the full pore size distribution of these materials. For comparison, we also show the distribution of a "standard" material with a similar polymer load (5.6%, dotted line). Although the polymer loads are very similar, there is a significant difference in the magnitude of the pore size distributions. During the drying process
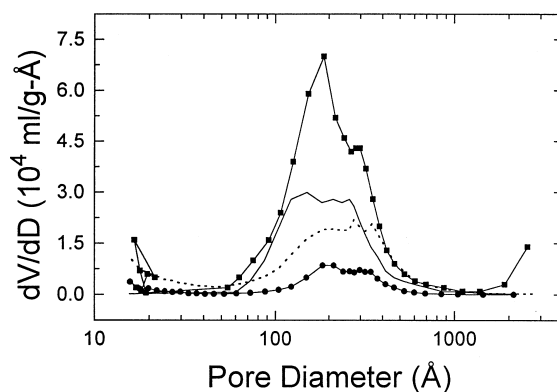

Fig. 4. Pore volume distribution of PBD-coated zirconia obtained by slow evaporation. Samples/symbols: (■) bare zirconia; (—) PBD-coated carbon-clad zirconia (carbon load, 5.9%); (– · –) "standard" coating procedure (carbon load, 5.6%) [14]; (●) slow evaporation (carbon load, 5.1%).

the formation of isolated liquid clusters is common and expected, and the dramatic reduction in measured pore volume and surface area is likely due to polymer collecting in and plugging the smallest pores, preventing access to the interior volume within the clusters. We believe that these distributions indicate that we have only succeeded at providing more time for equilibration of polymer–polymer interactions which favor polymer clustering. Given sufficient time, the polymer avoids unfavorable deposition at the walls until the meniscus has receded to the smaller pores, where they concentrate in and plug the pore constrictions. Fig. 2B illustrates schematically a simplified representation of the PBD distribution within the porous zirconia made by slow evaporation of the organic solvent. The increased time for polymer diffusion and existence of favorable polymer–solvent interactions result in a higher concentration of polymer in the small pores. Droplet formation in pore constrictions, due to favorable polymer–polymer interactions, blocks access to some of the unfilled pore volume. Owing to its very low surface area and pore volume, we did not test the chromatographic behavior of this material.

3.3. PBD coating on carbon-clad zirconia

Enhancing the affinity of the polymer for the walls ought to improve deposition homogeneity [1,4]. We tested this by modifying the walls with CVD carbon [21]. Polybutadiene is a nonpolar polymer, hence, its use in reversed-phase chromatography. The native zirconia surface, by contrast, is extremely polar. Prior work has shown that PBD does not adsorb at all on zirconia when hexane is used as the solvent at room temperature. This indicates that the polymer–solvent interactions are much stronger than the polymer–surface interactions. Others have achieved relatively uniform coatings of polar (siloxane) polymer on silica; this surface was demonstrated by the decrease in the tailing of amine peaks [4]. We hypothesized then that the strength of polymer–surface interactions could be increased by use of a nonpolar surface. PBD has been shown to remain strongly bound to carbon surfaces, even in the presence of good solvents [26]. Thus, our motivation in depositing PBD on a nonpolar surface such as

carbon was to examine the role of interfacial energies between the polymer, the solvent and the pore surface. Fig. 4 shows the pore volume distribution results. It is seen in Fig. 4 that at similar polymer loading (see Table 1), coating on the hydrophobic surface allows a larger proportion of smaller pores to remain unblocked, resulting in much better diffusion. Fig. 5 shows the column dynamic measurement data for the two materials. The C term of PBD-coated carbon-clad zirconia is 0.07, while the C term for a conventional bare zirconia loaded with the same amount of PBD is about 0.4 (see Table 2). Although the data in Fig. 5 were obtained at somewhat different temperatures, the small difference in temperature can not account for the significant difference in the C term. The chromatographic results here indicate that we have kept the pore space more accessible, resulting in better mass transfer. This suggests that the favorable polymer–surface interactions make it less likely that the polymer will follow
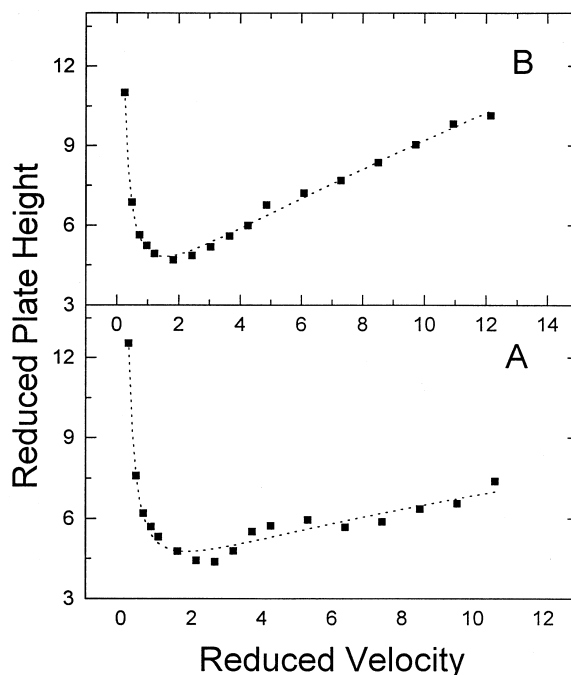
Fig. 5. Plot of reduced plate height against reduced velocity for PBD-coated carbon-clad zirconia. Symbols: (A) PBD on carbon-clad zirconia (temperature 30°C); (B) "standard" coating procedure (column temperature 25°C; [15]); (– · –) fitted curves.

the solvent meniscus into the smallest pores and less likely that polymer microdroplets will form.

4. Conclusions

We have tried variations on a "standard" method of preparing PBD-coated porous zirconia particles for reversed-phase chromatography. Chromatographic performance improves when the surface is made to be nonpolar by pre-coating with elemental carbon. Contrary to our hypothesis, performance worsens very appreciably when the solvent is removed slowly. No significant advantage is observed using stepwise coating of the particle. These results lead us to hypothesize that a homogeneous coating is favored by a gentle receding meniscus and/or high affinity of polymer for the particle surface.

Acknowledgements

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