Resolution in Column Chromatography of Polymer Latexes. II. A Comparison of Porous and Nonporous Packing Systems

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Synopsis

Data are presented to compare the size separation capabilities of several porous packing systems for latex particle chromatography. Material balance problems as well as nonequilibrium behavior encountered with small-pore systems (pores less than 1 μm) lead to the conclusion that larger pore systems (diameter 2 μm or greater) are superior from an operational viewpoint. The separation mechanism for a large-pore Fractosil system is shown to be predominantly hydrodynamic in nature with flow separation occurring in both the pores and packing interstices. The name Hydrodynamic Permeation Chromatography, or HDPC, is used to describe the process. The effects of calibration slope and band broadening on peak resolution are compared for an HDC system and the Fractosil system indicating the superior resolving power of the HDC system. Qualitative and semiquantitative considerations are made with regard to improved porous packing characteristics for an ideal HDPC system which would improve separation efficiency and resolution.

INTRODUCTION

In part I, the effects of output signal characteristics on resolution in Hydrodynamic Chromatography (HDC) were discussed. In this article, attention will be addressed to questions concerning the effects of packing porosity on separation mechanisms and column resolution. Results will be presented to compare the peak separation and band broadening characteristics of porous and nonporous packing systems. We begin with a background discussion of porous column chromatography and a review of previous studies.

POROUS PARTICLE CHROMATOGRAPHY

Particle fractionation in HDC, using nonporous packing, results from a size-dependent interaction between the electrostatically stabilized colloidal particles and eluant velocity gradients in the packing interstices.[1–3] Particles are excluded from regions near the packing surface because of their finite size and electrostatic repulsion forces. Since eluant velocities are lowest in this region, the particles attain an average velocity which exceeds that of the eluant, and this velocity difference increases with particle size. Porous packed systems represent, in addition to the hydrodynamic effect, the possibility for size separation owing

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to steric exclusion from the pores. The latter mechanism is the principal basis for size separation in gel permeation and gel filtration chromatography of dissolved macromolecules.[4,5] Results presented here, however, indicate that a clear distinction between a size exclusion and a flow-separation mechanism may not be possible with particle chromatography.

In line with liquid exclusion chromatography practice, the particle elution volume V_R can be written as

$$V_R = V_0 + kV_i \tag{1}$$

where V_0 is the interstitial void volume, V_i is the packing pore volume, and k represents the fraction of the pore volume accessible to the solute particle. Values of k range from zero to 1. In the literature on size exclusion chromatography, considerable attention has been given to the precise meaning of k (often written as K_{sec}) and its interpretation as an equilibrium distribution coefficient (see for example refs. 6 and 7 for reviews). From a fundamental viewpoint, mathematical solutions of the rate equations for the chromatography process can be used to establish the conditions under which eq. (1) results as a limiting solution. From an experimental viewpoint, k has been established as an equilibrium coefficient on the basis of several observations. These are (1) the good agreement found between statically determined and chromatographically measured k values; (2) the general shape of the chromatographic peaks; and (3) the independence of peak elution volumes (as determined by either peak maxima or first moments) with flow rate. Similar complete studies of particle chromatography have not, to our knowledge, been published.

Obvious similarities with treatments developed for the liquid exclusion separation mechanism of rigid macromolecules[8] might lead to the expectation that colloidal particle separation in a porous system involves the same equilibrium process. These calculations, however, involve solute species with maximum sizes on the order of hundreds of angstroms, whereas in particle chromatography latex diameters range from several hundred to several thousand angstroms. Reduced diffusivities and increased hydrodynamic wall effects, in combination with electrochemical parameters involved in the stabilization of the particles, point to the expectation that, in fact, different mechanisms should be dominant. Thus, eq. (1) should be viewed as an experimental definition of k which gives a measure of the pore exclusion and/or hydrodynamic flow separation. Values of k greater than unity would indicate adsorption effects, while excessive diffusion effects would most likely show up in a flow rate dependence. Some of the results to be presented from this study indicate that further experimentation will be needed to establish whether an LEC-type exclusion process can occur with colloidal-sized particles.

REVIEW OF PREVIOUS INVESTIGATIONS WITH LEC

The first reported fractionation of colloidal latexes within a porous matrix of wide pore-size distribution was that of Krebs and Wunderlich.[9] They investigated the effect of silica gel packings with pore sizes ranging from 500 to 50,000 Å for the separation of polystyrene and poly(methyl methacrylate) latexes. The observed linearity of the calibration curve—log (particle diameter) versus elution volume—was strikingly similar to that seen for GPC of polymer solutions. The

possibility of computing a particle size distribution of an unknown mixture through use of the calibration curve was an obvious conclusion.

Gaylor and James[10] investigated the fractionation of monodisperse polystyrene, butadiene copolymers of acrylonitrile or styrene, and colloidal silica on porous silica glass. Experimental parameters such as resolution, percent recoveries, peak height reproducibility, and ionic strength of the solvent were examined. Investigations into the use of a differential refractometer showed the signal response to be highly dependent on both chemical composition and particle size and the need for quantitative interpretation of the chromatogram into the corresponding particle size distribution.

Coll and Fague's work with an LEC system[11] employed the use of Controlled-Pore Glass (CPG) with the following pore sizes: 500, 1000, 2000, and 3000 Å. CPG is a rigid silica glass, irregularly shaped with a high degree of porosity, and having a size range of 74–120 μm. The mobile-phase eluting solution consisted of 1.0 g Aerosol OT/l. and 0.01M KNO_3 for a total ionic strength of 0.012M.

They found k values ranging from 0.68 for 250-Å colloidal silica particles to 0.03 for a 3120-Å polystyrene standard. Above a 1000-Å particle diam, their k values showed a dramatic decrease, indicating exclusion from the porous matrix. This effect was also reflected in the magnitudes of their separation factors R_F, which were considerably larger than those normally found in HDC. These R_F values are essentially an artifact of the definition (i.e., marker elution volume divided by particle elution volume) since most of the latex particles are only sampling a small portion of the pore volume V_i, while the marker species samples essentially the total column void volume ($V_0 + V_i$). Increasing the mobile-phase ionic strength by addition of KNO_3 caused a significant shift in their calibration curves, presumably the result of reduction in electrostatic double-layer forces between the particles and packing leading to an increase in accessible pore volume. The use of only Triton X-100 (a nonionic surfactant) in the mobile phase resulted in the latex particles emerging from the columns near the interstitial void volume V_0, indicating virtual exclusion from all the pores due to expanded double-layer forces. Thus, as in HDC, ionic strength plays a major role in determining the nature of the separation process.

Material balance data were not reported; however, it was indicated that their chromatographic peaks showed considerable skewing, possibly indicating particle entrapment within the pores. Peak broadening observed with the polystyrene latexes was extensive, and the resolution of the system did not approach that normally observed with GPC.

The LEC system investigated by Singh and Hamielec[12] employed a much wider distribution of pore sizes, ranging from 100 to 30,000 Å. This system was basically developed as an off-line monitor to follow the growth of polymer particles in emulsion polymerization. Linear behavior of the semilogarithmic calibration plot was also seen.

The extent of axial dispersion of the latexes investigated (such as polystyrene) was reported to be considerably greater than that for HDC. It was observed that the variance decreased with increasing particle size. Similar results were reported for a vinyl acetate latex, and no investigations into column efficiency or resolution were reported for the determination of particle size distributions.

Several of the features of porous chromatography seen in these studies are

similar to what has been observed for nonporous HDC, and several show distinct differences. There are, however, fundamental questions which have not been addressed in these studies, principal among them being whether material recoveries are good or bad with a small-pore system and whether porous particle chromatography can be modeled with the same success as HDC. The following sections describe the experimental investigations we have carried out to address these points. Some of the data have been reported elsewhere[14,16] in somewhat abbreviated form and are further referenced here to present a more cohesive picture of what we feel are the most critical points we have learned. For more detail, particularly concerning the modeling calculations for the large-pore packing system used in the study, ref. 16 should be consulted. The latex system we have been using is the Dow monodisperse polystyrenes.

EXPERIMENTAL

The experimental set up for the small pore LEC studies was virtually identical with the HDC system described previously,[1,13] with the exception of the columns, which were stainless steel 4.6 mm i.d. and 100 cm in length. The packing material was Controlled-Pore Glass (CPG) from Electronucleonics, Fairfield, NJ, with pore diameters ranging from 500 to 1000 Å. Column packing procedures are given in ref. 14.

For the large-pore porous studies, Fractosil 25,000 silica glass was used (EM Laboratories, #9395-3E) having a particle size ranging from 63 to 125 μm and a nominal pore size of 2.5 μm. Fractosil has a highly irregular geometry and an extremely high porosity, as shown by the scanning electron micrograph of Figure 1. The pores can be considered to be essentially open and flow-through, with little, if any, dead spaces. A single glass column (9.0 mm i.d. × 110 cm) was used in the study, and details of packing procedure are also given in ref. 14.

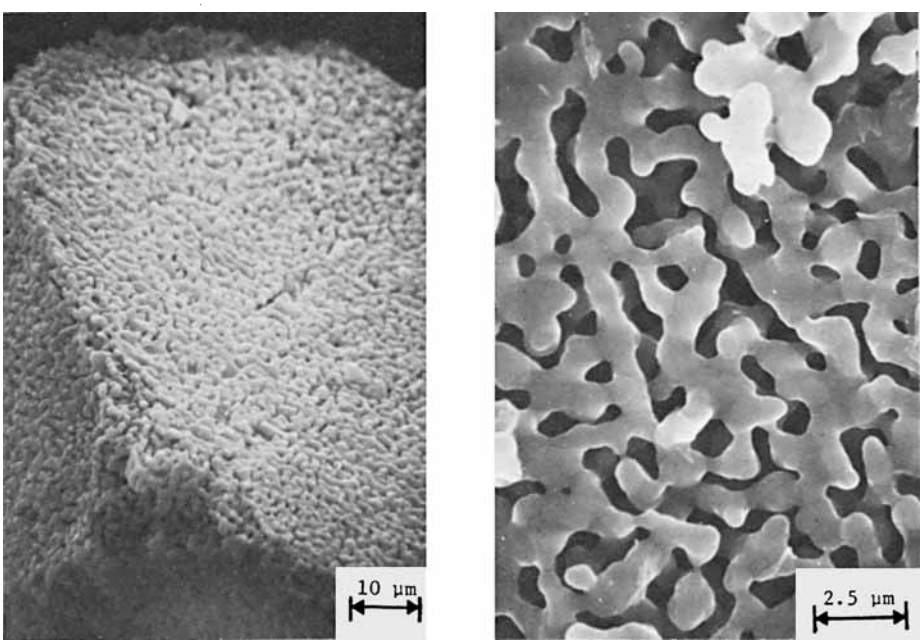

Fig. 1. Scanning electron micrographs of porous silica Fractosil, 2.5 μm pore size.

TABLE I
Column Packing Distribution

	Set I	Set II	Set III
Column A	500	1000	10,000
Column B	1000	2000	—
Column C	2000	3000	—

The mobile phase consisted of either sodium lauryl sulfate (SLS) or sodium dihexylsulfosuccinate (AMA) with no added salt. Preparation of all the polystyrene monodisperse (Dow) latex samples was identical to that in HDC, as described in ref. 1.

LEC RESULTS

Experimentation with Controlled-Pore Glass (CPG) involved the use of several column sets packed with different pore diameters in angstrom units as defined in Table I. Each set of columns was run with AMA as the surfactant in the mobile phase at a concentration of $5.2 \times 10^{-3}M$, and R_F-vs.-D_p data were obtained using the polystyrene standards. Separation factors were determined from the ratio of elution volumes corresponding to the marker and particle, respectively. These results are shown in Figure 2 and illustrate the effect of pore size distribution on the values of R_F. Figure 3, the corresponding calibration curve for set I, shows two distinct linear regions: that for 880-, 910-, and 1090-Å-diam particles and that for 1760, 2340, and 3570 Å. The changed slopes indicate that smaller particles may be penetrating the porous matrix and that larger particles are being totally excluded from the pores for this particular pore size distribution. This sharp distinction between penetration and exclusion

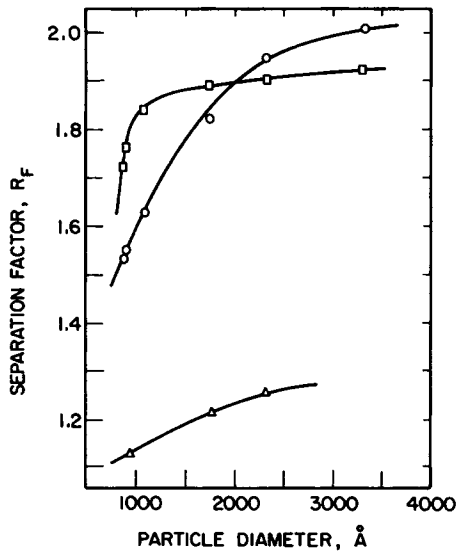

Fig. 2. Effect of pore size distribution on R_F of polystyrene standards for various LEC packing systems at $0.0052M$ AMA ionic strength: (□) column set I; (○) column set II; (△) column set III.

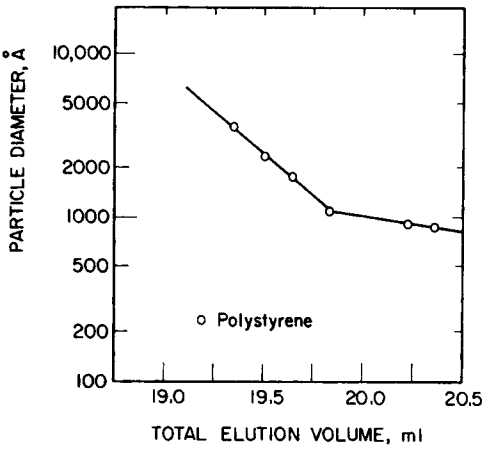

Fig. 3. Polystyrene standards calibration curve for LEC system of set I (Table I).

regions of the calibration curve points to an upper limit on the diameter of the particles which can penetrate the pores. Pore diameters must be two to three times greater than the particles to be fractionated for significant pore penetration to occur. Freeman and Poinescu[15] have found that maximum GPC selectivity is obtained when the solute size is one-fourth the pore size. A much less dramatic effect is seen for the R_F curve of set II, where pores of up to 3000 Å in size were used, resulting in a greater availability for pore penetration by all the particles. For set III, where only pores of 10,000 Å were used, all particles can pass through all the pores, resulting in a nearly linear dependence of R_F on D_p.

The values of R_F using the small pore diameters of CPG packing such as for sets I and II are considerably larger than those found for HDC. As with Coll's work, this is due to the fact that the marker species ($Na_2Cr_2O_7$) can sample the total column volume, while the latex particles sample only a small fraction, if any, of V_i. However, when pores of 10,000 Å are used, R_F values are much lower (nearer to those of HDC), indicating that both latex and marker are sampling a significant fraction of the pore volume.

Material balances were determined by comparison of turbidity peaks for samples passed through the columns and injected directly into the detector. Percent recoveries of polystyrene latexes at 254-nm detector wavelength for the columns of set II are given in Table II. The small particle sizes (<1000 Å) are completely recovered, while significant loss of sample is seen for the larger particle sizes. Possible causes for particle retention in the columns are particle entrap-

TABLE II
Percent Recoveries of Polystyrene Latexes Using Column Set II

D_p, Å	%
880	100
910	91
1090	100
1760	45
2340	24
3570	2

ment within the porous matrix and/or irreversible adsorption onto the surface of the silica glass. Since silica glass is strongly charged in aqueous media owing to ionization of surface hydroxyl groups at pH $\geq$ 3, significant electrostatic repulsion should be imparted between the particle and the glass packing, especially at low ionic strength. Thus, particle adsorption was not considered to be a significant cause of sample loss through the columns.

Peak skewing or tailing of the latex chromatographic peaks exhibited a general increase with increasing particle size, as also noted by Coll and Fague.[11] This was attributed to steric exclusion from the pores as the particle diameters approached the upper limit of the pore size distribution.[11] However, increasing skewness with increasing particle size, as well as the corresponding decrease in percent recoveries of sample, is a strong indication of particle entrapment within the porous bed and nonequilibrium behavior. It points to the necessity of using a more uniform, larger pore size.

RESULTS USING FRACTOSIL PACKING

The rate of particle transport using Fractosil packing with a nominal pore size of 2.5 μm is considerably different from that of the previously described LEC systems. Since the specified pore size of the Fractosil packing is almost an order of magnitude larger than the particle diameters to be fractionated, virtually complete penetration of the pores by all the particle diameters is to be expected. The k factors measured for the polystyrene latexes with the Fractosil system compared to values obtained using the LEC system of set II at an ionic strength of $5.15 \times 10^{-3}M$ are shown in Table III. A significant increase in the degree of pore penetration occurs with the Fractosil system. This system, in fact, might be more accurately described as an example of permeation chromatography; and, for reasons to be discussed shortly, we believe enhanced hydrodynamic effects within the pores leads to increased rates of particle transport through the bed. For the LEC packing system, it is not clear whether separation is being controlled by hydrodynamic or by exclusion effects. On one hand, the relative differences between k values for the various particle sizes with the LEC system indicates superior peak separation compared to the Fractosil. It seems tempting to ascribe size separation on this basis to an exclusion process similar to that for classical LEC. On the other hand, the very low k values for the CPG system would in-

TABLE III
Partition Coefficients for CPG and Fractosil Packings

D_p, Å	CPG[a]	Fractosil[b]
$Na_2Cr_2O_7$	1.00	1.00
880	0.25	0.84
910	0.23	0.83
1090	0.16	0.81
1760	0.02	0.75
2340	0	0.69
3570	0	0.59

[a] Three columns: pore sizes of 1000, 2000, and 3000 Å (set II).
[b] One column: pore size of 25,000 Å.

dicate that a hydrodynamic mechanism in the interstitial regions is controlling the separation process, much the same as in HDC. In any case, the relative increase in peak separation over the Fractosil system needs to be balanced against the fact that material recoveries are poor, and therefore size distribution analyses for such systems would be essentially useless. For this reason we felt the Fractosil system would be a more practically useful system for experimental and theoretical study.

Figure 4 shows the results of a series of experiments to determine the dependence of the separation factor R_F as a function of eluant ionic strength for the Fractosil system. Here, the ionic strength ranges from $2.2 \times 10^{-4}M$ to $0.342M$ and includes only surfactant at concentrations above and below the CMC. As in HDC, the particles move with an average velocity greater than that of the fluid stream, and the R_F values are up to 10% greater than those observed for the corresponding ionic strengths in HDC. This fact indicates the significant role played by the 2.5-μm pores in the enhancement of the rate of particle transport through the bed, even though the packing size of the silica glass ranges from 63 to 120 μm. According to Small,[13] as the packing size increases, R_F will decrease; however, we see the opposite effect due to the presence of the porous matrix. It appears that the hydrodynamic effects exhibited within the interstitial void regions are significantly less than those within the pores.

Several of the concentrations in Figure 4 were run using SLS above the CMC, and the contribution of the anionically charged micelles was included in the calculation of the total ionic strength.[16,17] Values of $m = 80$ and $Q = 23$ for the aggregation number and effective charge, respectively, were used for SLS to calculate the total ionic strength as given by eq. (2):

$$I = \tfrac{1}{2}\{[Na^+](+1)^2 + [SL^-](-1)^2 + [SLS]_m(Q)^2\} \quad (2)$$

Equation (2) has been discussed elsewhere.[16,17] The ionic strength dependence is similar to that seen in HDC.[13,17] At moderate to high ionic strengths, a bending of the curves is seen, indicating that double-layer repulsive forces have been sufficiently compressed to retard the movement of larger particles through

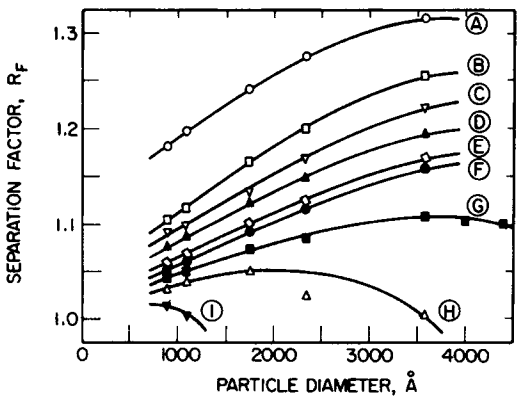

Fig. 4. Separation factor vs. particle diameter for various ionic strengths. Values in parenthesis represent calculations from eq. (2): A = 0.00022M SLS; B = 0.00055M SLS; C = 0.00103M SLS; D = 0.00129M AMA; E = 0.00515M AMA; F = 0.0101M AMA; G = 0.0210M SLS; (I = 0.053M); H = 0.035M SLS (I = 0.101M); I = 0.105M SLS (I = 0.342M).

the column. Typical values for the Hamaker constant A_{132} between polystyrene/water/silica lie in the range of 0.5–(10×10^{-14}) erg[18] and are of the same relative magnitude for A_{131} of polystyrene/water/polystyrene, as seen in HDC.

Earlier experimental work with HDC had shown that the use of only added salt to increase the ionic strength of the mobile phase leads to poor recoveries of latex from the column, perhaps because of flocculation and adsorption of the particles onto the packing.[13,17] Overall material recoveries for the Fractosil system were likewise significantly increased by use of only emulsifier. Table IV compares recovery data at various ionic strengths using SLS and AMA. It is interesting to note that a moderate to high ionic strengths (>50 mM) the recovery of latex from the column is as good as the HDC system and that the porous matrix and highly irregular packing geometry probably contribute little to material loss. Also, the symmetrical nature of the Fractosil peaks for polystyrene, although non-Gaussian,[23] tends to support complete penetration of the pores with no significant particle entrapment and an equilibrium or steady-state process. The separation factor has been shown also to be independent of the flow rate over an order of magnitude range of the flow changes.[16]

The separation behavior of this system has been modeled in terms of the parallel capillary HDC model,[16] and agreement between theory and experiment has led us to conclude that the size fractionation mechanism is basically that of nonporous HDC, with the added influence of fractionation by flow through the packing pores. Thus, we would describe this process as Hydrodynamic Permeation Chromatography (HDPC), to differentiate it from the exclusion process which might be occurring with the smaller-pore packing systems. In addition to explaining the nature of the enhanced flow separation, the HDPC model has been used to discuss packing characteristics for optimal separation.[16]

Comparison of the calibration curves (ln D_p vs. ΔV) for the HDC and porous Fractosil systems at an ionic strength of $1.29 \times 10^{-3}M$ showed that the range of Δv (the difference in elution volumes between latex peak and marker peak) for the Fractosil system for particle diameters of 880 and 3570 Å is almost 75% greater than that of HDC, even though total column volumes for the Fractosil and HDC systems are 50 and 68 cm^3, respectively.[14,16] The effective elution range of these particle diameters has been increased using the Fractosil, and this behavior is reflected in the magnitude of the separation factor.

The slopes of the calibration curves for the HDC and Fractosil systems are 0.512 and 0.289, respectively,[16] and indicate that the "resolution of the peak separation" for the Fractosil system is superior to that of HDC.[19] As shown in the next section, however, axial dispersion effects need also to be considered in the evaluation of overall resolution.

TABLE IV
Percent Recovery Data for Fractosil at Various Ionic Strengths
(Ionic Strengths in Millimolar, mM)

D_p, Å	1.0(SLS)	1.29(AMA)	5.15(AMA)	10.3(AMA)	57(SLS)	110(SLS)
880	100	99	100	100	100	97
1090	100	95	100	86	100	95
1760	96	90	100	90	100	89
2340	89	88	94	83	100	66
3570	68	77	89	66	84	3

OVERALL RESOLUTION ANALYSIS

The high efficiency of the HDC system is typified by the large number of theoretical plates in contrast to that of the porous Fractosil system. Taking the number of theoretical plates as 16 (V_R^2/W), where V_R and W are the elution volume and peak width, respectively, for the dichromate marker, the three-column, HDC system normally exhibits a theoretical plate count of about 20,000, compared to 600 for the Fractosil. This behavior is reflected when a comparison of the specific resolution R_S is made between the two systems.

From GPC theory, the specific resolution between two particle populations[20–22] is

$$R_S = \frac{(V_{R,p_2} - V_{R,p_1})}{\frac{1}{2}(W_1 + W_2)} = \frac{(V_{R,p_2} - V_{R,p_1})}{W_a} \tag{3}$$

where W_a is the peak arithmetic width average and V_{R,p_1} and V_{R,p_2} are the elution volumes of particle populations 1 and 2, respectively. The resolution can be expressed in a number of ways. From the definition of R_F, we have

$$R_S = \frac{V_c\{(1/R_{F,p_2}) - (1/R_{F,p_1})\}}{W_a} \tag{4}$$

where V_c is the total column void volume and R_{F,p_1} and P_{F,p_2} are the separation factors for populations 1 and 2. Since R_F is independent of column volume and length,[17,23] the resolution is a function of the bed volume and peak dispersion. The difference in the elution volumes of the two particle populations may be expressed from the slopes m of the ln D_p–elution volume calibration curve. Thus,

$$R_S = \frac{\ln(D_{p_2}/D_{p_1})}{mW_a} \tag{5}$$

Equation (5) shows that, for maximum resolution, a low degree of axial dispersion combined with a small value for the magnitude of the calibration slope is indicated. This also implies that some degree of peak broadening may be tolerated if particle peak separation is adequate, i.e., if the slope of the calibration curve is sufficiently small. When the value for R_S is 1.5, separation between adjacent bands is almost complete and the overlap is less than 1% (6σ separation). When R_S is 1, the overlap between bands is readily discernible. However, as R_S diminishes, the presence of the two bands becomes difficult to distinguish, especially if the bands are of unequal intensity.[20] Usually, R_S must be ≥ 0.5 to have particle peaks partially distinguishable.

The data of Table V show values for the specific resolution calculated for various particle populations between the HDC and Fractosil systems. The resolution of the Fractosil is significantly less than that shown by the HDC, even for the single column HDC system. Although the slope of the Fractosil calibration curve at any particular ionic strength is less than that of the HDC at the same ionic strength, axial dispersion is considerably greater, resulting in poorer resolution. Comparison of the axial dispersion of these two systems is shown in Table VI shows that the improved range of elution volume for the Fractosil system is overshadowed by the large increase in peak broadening. A larger degree of axial dispersion could be tolerated for a large pore system owing to this extended range, but not to the extent presently exhibited by the Fractosil. Similar behavior using Fractosil has been reported in ref. 12.

TABLE V
Resolution: HDC Versus Fractosil

Particle populations	R_s, HDC		R_s, Fractosil
	Three columns	One column	One column
880/1760	0.62	0.41	0.14
880/2340	0.91	0.61	0.24
880/3570	1.45	0.94	0.41
1090/2340	0.71	0.49	0.23
380/880	0.33	0.23	0.11
380/1090	0.51	0.36	0.12
380/1760	0.95	0.64	0.26
380/2340	1.23	0.83	0.36
380/3570	1.78	1.17	0.54

As discussed in part I, the ultimate test of column resolution efficiency is in the ease and accuracy with which the entire size distribution can be determined from the output chromatogram for a polydisperse system. In line with the R_S results shown here, size distribution calculations for a synthetically mixed bimodal distribution[14] show that the HDC system is capable of resolving two distinct particle populations, while the Fractosil chromatogram analysis yields a single broad distribution.

Numerous studies of macromolecular LEC have shown that the efficiency of a chromatographic system depends on factors such as column packing geometry, packing size, and column diameter. Detailed studies of band broadening have demonstrated that packing particle mass transfer effects play a controlling role. Such considerations have in fact led to a clear understanding of the conditions for high-performance operation which characterize current LEC operation.[6] Since in HDC, and in what we are calling here Hydrodynamic Permeation Chromatography (HDPC), fractionation results from velocity gradient effects, one would expect mobile-phase transverse diffusion to be the dominant dispersion mechanism. Modeling of band broadening, based on transverse diffusion calculations, has been reported for HDC data[1,24]; however, more complete studies involving variables such as packing diameter and column diameter, among others, need to be carried to more fully establish the dispersion behavior. Based on LEC studies,[20] one would expect a reduction in transverse diffusion effects and eddy diffusion (stream splitting), as compared to the Fractosil system, with spherical, monodisperse packing in the diameter range of 20–30 μm. For theoretical as

TABLE VI
Axial Dispersion: HDC vs. Fractosil

D_p, Å	W, HDC[a]		W, Fractosil
	Three columns	One column	One column
Marker	1.93	1.06	8.45
380	2.48	1.16	12.03
880	2.36	1.13	12.85
1090	2.36	1.07	12.67
1760	2.16	1.07	12.34
2340	2.12	1.04	11.85
3570	1.88	1.02	11.75

[a] $W = 4\sigma$, the width of the chromatographic peak at the baseline, ml.

well as practical reasons, more complete studies of porous and nonporous geometries need to be carried out to determine the limits of resolution for both systems and to determine more fully whether a true size exclusion process is possible with a colloidal particles.

The optimization of particle size analysis by HDC must be considered from the viewpoint of signal resolution and column efficiency. In part I, we showed the improvement in resolution which can occur for broad, continuous mixtures using absorbance to improve overall signal detection. In terms of column resolution, the HDC is a fairly efficient system. We feel that improvements in porous packing and our understanding of separation mechanisms can inevitably lead to even better column resolution, a necessary prerequisite for improved PSD analysis, and high performance operation on a par with macromolecular LEC.

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