An Analysis of Flow Separation in Hydrodynamic Chromatography of Polymer Latexes

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An analysis is presented for the flow separation process in hydrodynamic chromatography along with comparisons to experimental data. The flow separation model is based on calculations for the convected Brownian motion of colloidal particles in a capillary tube in the presence of a force field. The results indicate the role of the relevant experimental parameters in the separation process.

SCOPE

Hydrodynamic chromatography, or HDC, is a new method for obtaining particle size distributions in the colloid size range. The method is similar to gel permeation chromatography, or GPC, but differs in several important respects. Particle suspensions (as opposed to molecular solutions in GPC) are pumped through a series of columns packed with nonporous beads. Separation occurs by size, with larger particles eluting before smaller ones over a range of eluant ionic conditions. The process has been described before in the literature and shows great promise as an efficient and rapid means for determining particle size distributions for polymer latexes in the colloid size range.

The purpose of this paper is to present for the first time a detailed and, we believe, complete analysis to account for the separation phenomenon. The analysis is based on a fundamental model for the convected Brownian motion of the particles through an equivalent array of parallel capillaries and accounts explicitly for all the important parameters. These results along with a companion paper analyzing dispersion methods for obtaining particle size distributions directly from the optical density chromatogram offer an analysis of HDC which enables direct use of the technique as an analytic tool.

CONCLUSIONS AND SIGNIFICANCE

The model presented in this paper enables calculation of the column separation factor R_F in terms of the relevant experimental parameters. The good agreement between measured and calculated R_F values for a range of polymer latex particle sizes and eluant ionic concentrations indicates that HDC can be explained on the basis of a phenomenological approach. At low ionic strength, particle separation is shown to be insensitive to change in the Hamaker constant and surface charge within the range commonly observed for polymer latexes, enabling the development of universal calibration curves based on well-characterized latex systems such as monodisperse polystyrene. With increased ionic strength, particle residence time and separation become highly sensitive to the material parameters, and the separation begins to reverse; that is, larger particles elute later than smaller ones. The competitive mechanisms of HDC and PBC (potential barrier chromatography) also begin to favor PBC as shown both in calculations and adsorption-desorption experiments discussed in this paper. In addition, column resolution is shown to increase with decreased packing size in line with measurements by Small (1974). The model discussed in this paper will have application in quantifying our understanding of the separation mechanisms involved in HDC.

The application of chromatographic techniques to the determination of particle size distributions in the colloid size range is a relatively new concept. Krebs and Wunderlich (1971) reported a technique utilizing columns packed with a porous gel. More recently, Small (1974) presented a detailed experimental report utilizing columns packed with nonporous beads. Since particle separation appears to be derived from forces arising during flow through the interstitial regions, the term hydrodynamic chromatography has been coined for the process. Small's work did not entail any quantitative analysis for the separation, although a qualitative discussion was given

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based on calculations by DiMarzio and Guttman (1970) for separation by flow of polymer molecules in capillary tubes. In addition, Small discussed in a qualitative fashion the effects of ionic concentration on separation behavior.

We have been pursuing the development of HDC as an analytical tool for colloid particle size distribution for the last 2 yr in our labs. The use of HDC as an efficient means for determining unknown particle size distributions for a variety of latex systems with optimum resolution and reliability is one of our principal objectives. Our approach has been essentially twofold; from a fundamental viewpoint, we have been interested in quantifying a mechanism for the flow separation process in terms of the relevant experimental parameters which are known to affect the process. These are ionic strength and species in solution in the eluant phase, surfactant species and concentration, eluant flow rate, packing diameter, and latex particle size. Some of the results which we have been generating have been reported in previous publications (Stoisits et al., 1976; McHugh et al., 1976, 1977). Results from these studies will be briefly summarized along with more recent data which we have been quantifying in terms of a flow separation model to be developed in detail in this paper. We have also been testing column conditions for optimum resolution and evaluating various techniques for the determination of particle size distribution directly from the chromatogram. The results of these studies will be reported in a later publication (Silebi and McHugh, to be published).

BACKGROUND AND DATA

The experimental details of our instrument have been described elsewhere (Stoisits et al., 1976). The instrument consists of three 9 mm ID by 110 cm glass columns packed with uniform diameter nonporous styrene-divinylbenzene copolymer beads, 20 μm nominal diameter. Eluant consisting of deionized water, added ions, and surfactant is continuously pumped. A small amount of diluted latex, 0.01 wt %, suspended in eluant of the same composition is injected into the column along with a trace amount of sodium dichromate which acts as a marker. The particles elute through the three columns and pass through a flow-through cell which measures the turbidity at 254 nm and registers a peak for both the marker and the particles. Over a range of ionic strengths, the particles elute from the column with a residence time less than that of the marker, and the residence time decreases with increasing particle diameter, serving as the basis for the separation.

Tables 1 and 2 summarize the conditions which have been tested in our columns. The latex diameters are number average diameters and are given as nominal values for the polydisperse latexes as determined by electron microscopy. A variety of ionic strengths and surfactant concentrations were used. Below, we summarize the facts concerning column behavior as determined in our studies and Small's which are to be quantified by the flow separation model. The data to be discussed are limited to the monodisperse polystyrene and polyvinylchloride latexes, since these are the most well characterized systems studied.

TABLE 1. SUMMARY OF POLYMER LATEX SYSTEMS ANALYZED

Latex	Particle diameter range (nm)	Comments
Polystyrene	88-3570	6 monodisperse sizes
	138 and 150	Nominal diameters of polydisperse broad distributions
Polyvinyl chloride	37-145	4 monodisperse samples
	116-214	3 polydisperse samples
Butadiene-styrene copolymer	89	Relatively narrow size distribution
Carboxylated 70:30 styrene-butadiene copolymer	700 and 230	2 monodisperse samples
Carboxylated 55:45 styrene-butadiene copolymer	122-173	4 polydisperse samples
Polybutadiene	132-290	3 polydisperse samples
Neoprene	160	Polydisperse
Acrylate ester copolymer	417	Polydisperse

TABLE 2. SUMMARY OF HDC COLUMN CONDITIONS TESTED

Surfactants	Sodium dihexylsulfosuccinate (AMA) Sodium lauryl sulfate (SLS)
Ionic species	Disodium hydrogen phosphate Sodium chloride
Eluant flow rates	0.40-0.60 ml/min

SUMMARY OF EFFECTS

Particle Size, Ionic Species, and Concentration

Over a range of ionic strengths, the logarithm of the latex particle diameter varies linearly with ΔV, the elution volume difference between particle and marker turbidity peaks (McHugh et al., 1976; Scolere, 1977); a series of parallel lines results when the plots are made at different ionic concentrations (Figure 1). With the exception of the ionic effect, this behavior is similar to that often seen in GPC of polymer molecules. Since column resolution varies as the inverse of the slopes of

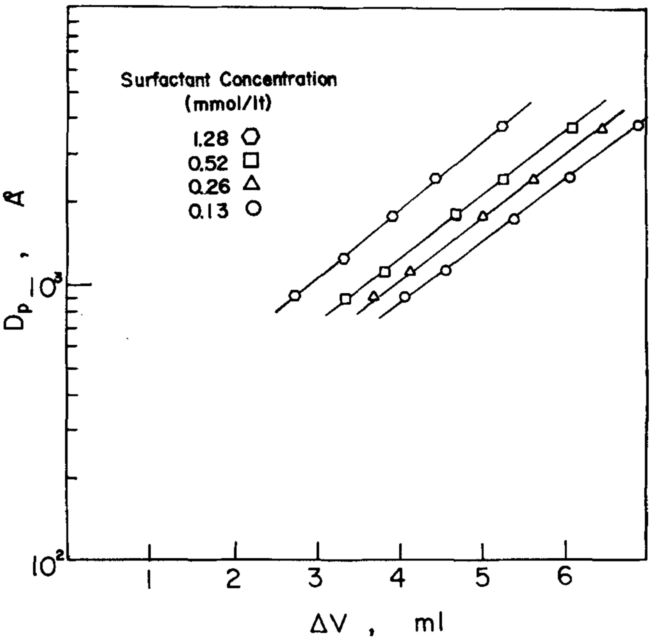

Fig. 1. Effect of surfactant concentration upon the difference in elution volume for different monodisperse polystyrene samples. Added 2×10^{-4}M sodium chloride at all different surfactant concentration.

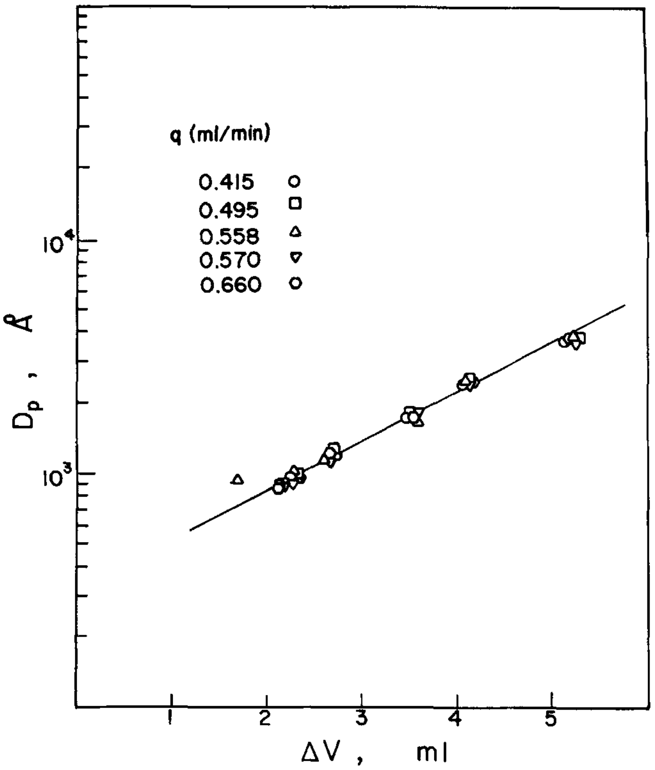

Fig. 2. Effect of flow rate upon the difference in elution volume for different polystyrene standards. Eluant concentration: 2.5 × 10^{-3}M AMA, 1.5 × 10^{-3}M Na_2 HPO_4.

these calibration curves (Friis and Hamielic, 1975), the resolution of particle separation will be independent of ionic strength over this range. At higher ionic strengths, the data begin to show a nonlinear behavior and an eventual reversal of particle residence times; that is, smaller particles begin to elute ahead of larger ones (McHugh et al., 1976). At each ionic strength, a maximum is found in the particle size that will elute from the columns which decreases with increasing ionic strength. This effect has been attributed to an irreversible adsorption of the latex onto the packing surfaces (Small, 1974; McHugh et al., 1976). The effect of surfactant is shown in Figure 1 which shows the ΔV-D_p behavior at various surfactant concentrations holding the added ion concentration (sodium chloride) constant. Similar behavior is seen for the sodium lauryl sulfate surfactant (Scolere, 1977), indicating that for polystyrene and polyvinylchloride latexes the surfactant, when present in amounts less than its critical micelle concentration (C.M.C.), acts merely as another ionic species. Curves of ΔV vs. D_p for total ionic strength, including surfactant concentration, show a perfect overlap when compared at the equivalent total ionic concentration which would give the same double-layer thickness (Silebi, 1977).

Eluant Flow Rate

The range of eluant flow rates available in our current system is somewhat limited, however, as Figure 2 shows. For the polystyrene latexes, the ΔV-D_p curves are independent of flow rate. Similar results occur with the polyvinylchloride latexes (Scolere, 1977). These results indicate that particle residence time decreases in inverse proportion to the increased flow rate, an effect also seen in GPC (Moore, 1964; Cantow et al., 1967).

Packing Type and Size

The effects of packing type and size have been fully discussed in Small's work which shows that the maximum particle size which will elute at a given ionic strength increases with increased packing size, and, conversely, column resolution decreases (that is, slopes of log D_p vs. ΔV increase). For the range of packing materials and geometries used, Small's data indicate particle separation to be independent of packing type.

Particle separation has been quantified in terms of the separation factor R_F which is the ratio of eluant marker and particle elution volumes, (Small, 1974) or, equivalently, the difference in elution volume between particle and eluant marker turbidity peaks (McHugh et al., 1976). The two are related by

$$\Delta V = V_m\left(1 - \frac{1}{R_F}\right) \tag{1}$$

with V_m the elution volume associated with the marker peak. Since the marker is a charged species ($Cr_2O_7^{-2}$), electrostatic repulsive forces between the ionic double layers surrounding the packing and the marker will prohibit it from completely sampling all of the bed void space. Thus, V_m will, in general, be less than V_c, the total void volume of the columns, and will also be a function of ionic strength of the eluant. This effect must be accounted for in the residence time calculation for the marker. Care also needs to be taken in relating Equation (1) to average velocities. In the next section, we will show, as a result of the fundamental calculations of Brenner and Gaydos (1977), that once an equivalent geometry is chosen for the interstitial regions accessible to the eluant, the volumetric flow rate of a charged Brownian species i, marker or colloid, through the interstices is given by

$$q = \int_{A_i} v_i P dA \tag{2}$$

where P represents the probability that i will occupy the given streamline. Owing either to the finite size of the colloidal particle or the ionic force field, the cross section of the equivalent duct available for flow will be lessened. Equation (2) can be written in terms of an average velocity by the mean value theorem

$$q = [v_i]A_i \tag{3}$$

A combination of Equation (3) with the definition of R_F leads directly to the equivalent expression

$$R_F = \frac{[v_p]}{[v_m]} \tag{4}$$

Equation (4) was used earlier by Stoisits et al. (1976) and McHugh et al. (1976). From Equations (1) and (4)

$$\Delta V = V_m\left(1 - \frac{[v_m]}{[v_p]}\right) \tag{5}$$

The calculation of ΔV from first principles thus resolves to the assumption of an equivalent interstitial geometry and the evaluation of the probability averaged velocity in such a geometry.

The calculations by Brenner and Gaydos (1977) for capillary geometry demonstrated that, in the absence of potential field effects, particle separation in HDC can be rationalized on the basis of the finite size of the colloidal particles and the presence of a velocity gradient. Since particles can, at best, only sample streamlines a distance R_p from the wall, their average velocity will exceed that of the fluid stream by an amount which increases with particle size. This excluded streamline effect they found to exceed the wall effect which acts in the opposite direction. Calculations by McHugh et al. (1976) attempted to account for ionic effects by essentially treating the probability function P as unity up to a distance a (distance of closest approach) and zero to the wall. The value of a was determined by a balance of van der Waal's attraction forces and electrostatic double-layer repulsive forces calculated as a function of ionic strength. Their results offered an explanation for the low ionic strength behavior but did not adequately describe $\Delta V\text{-}R_p$ data in the high ionic strength range. Interaction potential calculations for the high ionic strengths indicated the possibility (owing to well-developed secondary minima) of a reversible adsorption-desorption mechanism. The present analysis will indicate that accounting for ionic effects by the Brenner and Gaydos expression offers an explanation from a purely phenomenological view. In what follows, we shall assume the bed interstitial geometry can be modeled as a parallel array of capillaries.

ELUTION VOLUME CALCULATIONS

The principal result of the analysis by Brenner anl Gaydos (1977) predicts that a Brownian particle suspended in laminar, eluant flow in a capillary for several diffusion times (that is, values of R_o^2/D_∞) will achieve a trajectory resulting in the following expression for the average velocity:

$$[v_p] = \frac{\int_o^{R_o-R_p} v_p(r)e^{-\phi(r)/kT}rdr}{\int_o^{R_o-R_p} e^{-\phi(r)/kT}rdr} \tag{6}$$

The exponential function contains, in addition to the Boltzmann constant and temperature, the total energy of interaction between the particle and the capillary wall force fields and represents the probability weighting function. The particle streamline velocity at r is given by

$$v_p(r) = v_o\left(1 - \frac{r^2}{R_o^2}\right) - \gamma v_o\left(\frac{R_p}{R_o}\right)^2 \tag{7}$$

The wall effect parameter γ can be fit to the data of Goldsmith and Mason (1962) in the core region and calculated from the expressions obtained by Goldman et al. (1967) in the wall region:

$$\gamma = \begin{cases} \frac{2}{3}\left(1 + 3\frac{r}{R_o}\right) & \text{core region} \quad (8a) \\ \frac{5}{8}\frac{\frac{R_p}{R_o}}{\left(1 - \frac{r}{R_o}\right)^2} & \text{wall region} \quad (8b) \\ \frac{0.7431\left[1 - \left(\frac{r}{R_o}\right)^2\right]}{0.6376 - 0.2\ln\left(\frac{R_o}{a} - \frac{r}{a} - 1\right)} & \\ & \text{close to the wall} \quad (8c) \end{cases}$$

Integrations from the tube center line towards the wall begin with Equation (8*a*) and switch to (8*b*) when the γ values predicted by (8*a*) fall below those from (8*b*) and likewise for (8*c*). The total energy term is given by the superposition of the repulsive potentials arising from the double-layer and Born repulsive forces and the van der Waal's attractive potential. Thus

$$\phi = \phi_{DL} + \phi_B + \phi_{VW} \tag{9}$$

Surfaces immersed in polar solvents can develop electrostatic charges by dissociation of surface ionogenic groups and/or adsorption of species bearing an ionic group, resulting in double-layer forces. The particle-wall interaction can be calculated by assuming a sphere-plane interaction, an assumption justified by the small ratio of particle and packing radii. From Equation (6), we are interested in calculating energies of interaction in the range from small to large particle-wall separations. Approximate expressions covering this range as well as the range from large to small surface potentials have been developed by Bell et al. (1970). These generalized forms are

$$\phi_{DL} = \epsilon\left(\frac{kT}{e}\right)^2 Y_1 Y_2 R_p \exp(-\kappa a) \tag{10a}$$

$$Y_1 = 4\tanh\left(\frac{\Phi_1}{4}\right) \tag{10b}$$

$$Y_2 = Y_2(\Phi_2, \kappa R_p) \tag{10c}$$

$$\Phi_i = \frac{e\psi_{oi}}{kT} \tag{10d}$$

These expressions are appropriate for symmetrical electrolyte solutions when $\kappa R_p \geqq 5$. Values of κR_p depend on both ionic concentration and particle size, and for the small particle size and low ionic strength range considered in some of our calculations, values less than five result. In this region, the tabular values of Y_2 given by Bell et al. (1970) and obtained from the numerical solution of the nonlinear Poisson equation by Loeb et al. (1961) can be used. The latex surface potential depends on surface charge density and ionic concentration and is given by

$$\sigma = \sqrt{\frac{\epsilon kTc_o}{2\pi}}\left\{\sum_k \sum_j |z_{j,k}{}^*| \left[\exp\left(-\frac{z_{j,k}e\psi_{o2}}{kT}\right) - 1\right]\right\}^{1/2} \tag{11}$$

Equation (11) is a generalized form (Silebi, 1977) which for one symmetric electrolyte reduces to (Verwey and Overbeck, 1948)

$$\sigma = \sqrt{\frac{2\epsilon kTc_o}{\pi}}\sinh\left(\frac{ze\psi_{o2}}{2kT}\right) \tag{12}$$

Equations (11) and (12) are based on the flat plate approximation for the particle which is perhaps good for $\kappa R_p > 5$. As stated before, at very low electrolyte concentrations, where the above limitation is violated, we must use the numerical evaluation of the surface charge density as a function of the reduced potential and double-layer thickness (Loeb et al., 1961). The total surface charge density in the presence of surfactant can be evaluated from measurement of the zeta potential (which we equate to the surface potential) at a given total electrolyte concentration.

Born repulsion is a short-range atomic interaction considered necessary to explain the reversibility of such phenomena as repetization of colloidal agglomerates and adsorption-desorption of colloids from collectors as discussed by Prieve and Ruckenstein (1976). In our calculation, Born repulsion turns out to be of negligible importance since we are not directly concerned with adsorption-desorption rates. Variations between 1 and 15Å in the atomic collision diameter did not sensibly change the separation factor. A value of 5Å was used in the calculations to be reported here. The van der Waal's interaction energy between a sphere and wall was originally estimated by Hamaker (1937) based on the unretarded attraction energy between two atoms. This re-

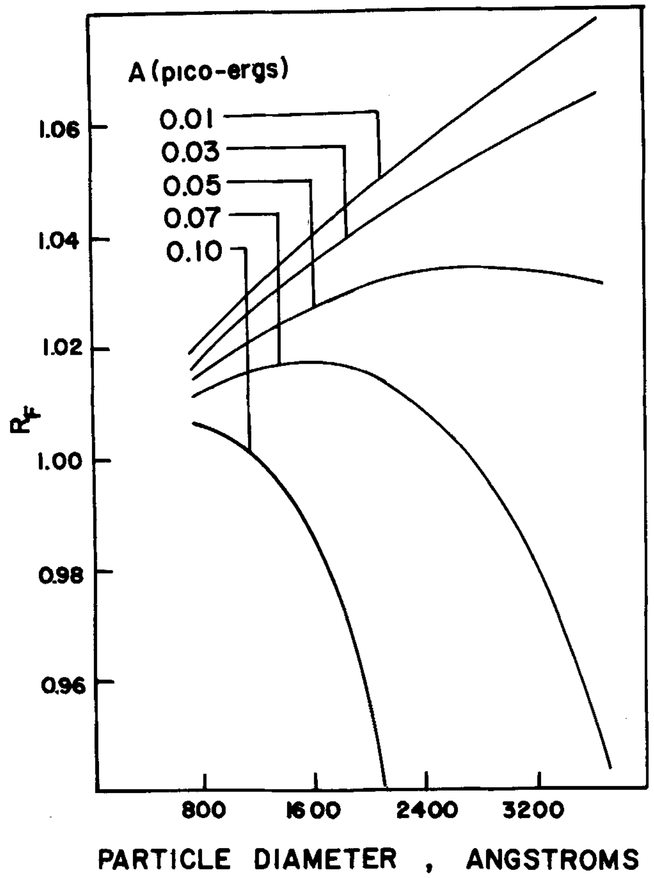

Fig. 3. Theoretical computation showing the effect of Hamaker constant on the separation factor at a high ionic strength, 0.1M in 1:1 electrolyte. Unless otherwise indicated $\psi_{o1} = 90$ mV, $\psi_{o2} = 30$ mV, $\epsilon = 74.3$, $T = 300°$K, $R_o = 3.72$ μm.

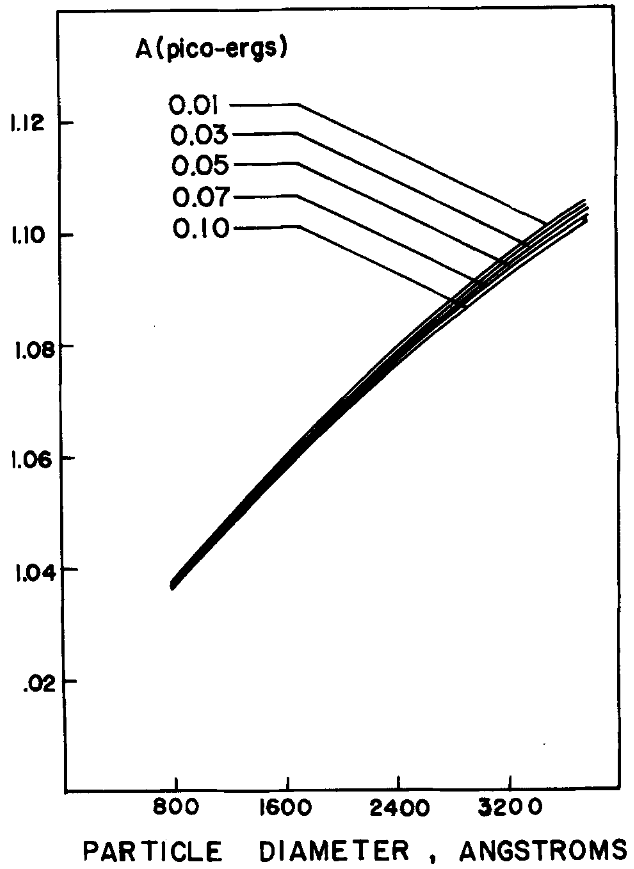

Fig. 4. Theoretical computation showing the effect of Hamaker constant on the separation factor at a moderate ionic strength, 0.01M in 1:1 electrolyte.

sult holds for the case of small separations where the retardation effect can be neglected. More recently, Clayfield and Lumb (1966) derived an analytical approximation accounting for this retardation effect using the Schenkel and Kitchener (1960) simplification of the Casimir and Polder (1948) equation for the retarded dispersion energy between two atoms. The Clayfield and Lumb expressions are

$$\phi_{VW} = -\frac{AR_p}{6a}\,\frac{1}{1+1.77p} \quad 0 < p < 2 \qquad (13a)$$

and

$$\phi_{VW} = -\frac{2AR_p}{a}\Bigg[\frac{0.04083}{p}\left(\frac{4a+R_p}{a} - \frac{a(4a+7R_p)}{(a+2R_p)^2} - \frac{10R_p}{(a+2R_p)}\right) - \frac{0.01206}{p^2}\left(\frac{R_p(5a+R_p)}{a^2} - \frac{aR_p(5a+9R_p)}{(a+2R_p)^3} - \frac{22{R_p}^2(a+R_p)}{a(a+2R_p)^2}\right) + \frac{0.000468}{p^3}\left(\frac{{R_p}^2(18a+3R_p)}{a^3} - \frac{{R_p}^2a(18a+33R_p)}{(2R_p+a)^4} - \frac{38{R_p}^3(3a^2+6aR_p+4{R_p}^2)}{a^2(a+2R_p)^3}\right)\Bigg] \quad 0.5 < p < \infty \qquad (13b)$$

Equation (13*a*) is an extension of the treatment suggested by Schenkel and Kitchener (1960) given by Wiese and Healy (1970). The maximum difference between the two expressions occurs near $p = 0.5$; thus, Equation (13*a*) is used for values of p less than 1.0.

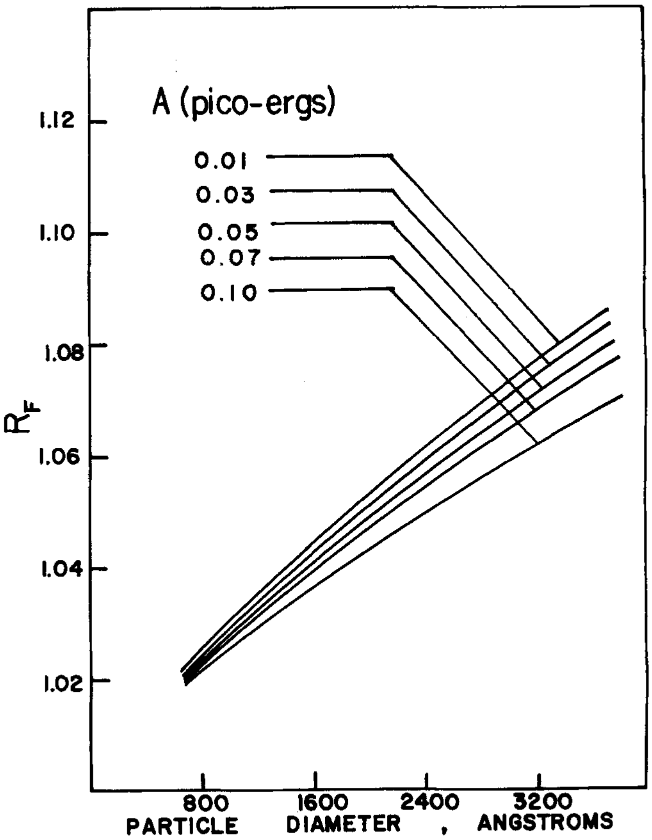

Fig. 5. Theoretical computation showing the effect of Hamaker constant on the separation factor at a low ionic strength, 0.001M in 1:1 electrolyte.

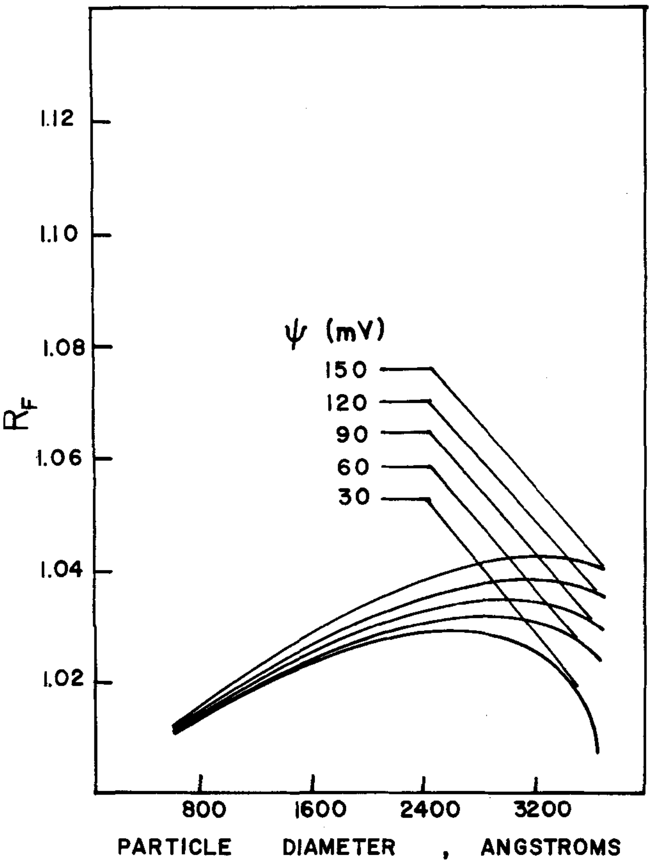

Fig. 6. Theoretical computation showing the effect of the electric surface potential of the particle on the separation factor at high ionic strength; 0.1M of 1:1 electrolyte, A = 5 × 10^{-14} erg. Other parameters have the same value as in Figure 3.

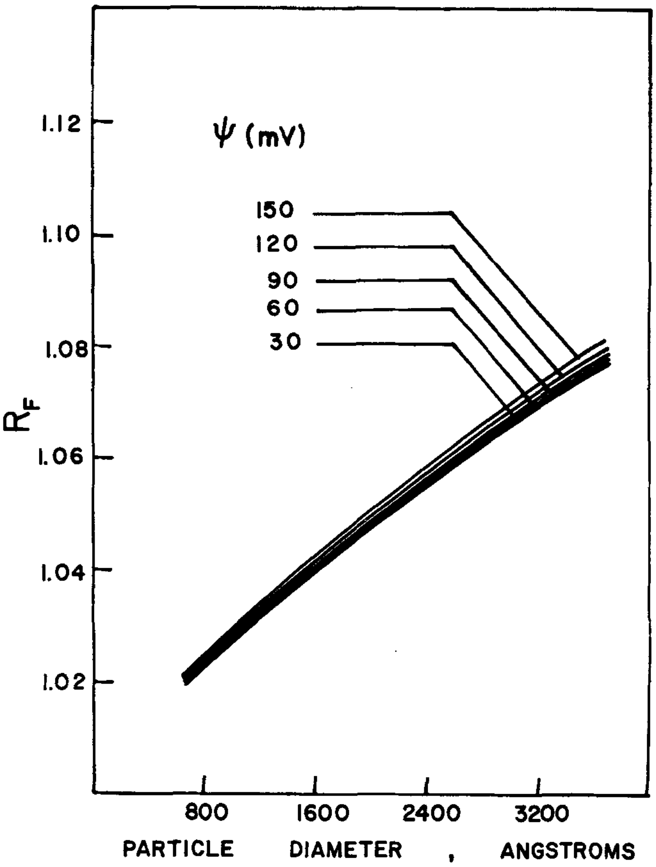

Fig. 7. Theoretical computation showing the effect of the electric surface potential of the particle on the separation factor at moderate ionic strength; 0.01M of a 1:1 electrolyte. Other parameters have the same value as in Figure 6.

In the case of a noninteracting tracer, $[v_m]$ would be given by one half the capillary center-line velocity. For the ionic marker, the London and Born contributions are negligible, and if we take the limit as $R_p \to 0$, Equations (10*b*) and (10*c*) approach the following limits (Bell et al., 1970): $Y_2 \to 2e^2/kT\epsilon R_p$. For the low surface potential of the packing, $Y_1 \to \Phi_1$; thus the tracer velocity expression becomes

$$[v_m] = \frac{\int_0^{R_o} v_o\left(1 - \frac{r^2}{R_o^2}\right)\exp\left[-\frac{2e\psi_{o1}}{kT}\exp(-\kappa a)\right] rdr}{\int_0^{R_o}\exp\left[-\frac{2e\psi_{o1}}{kT}\exp(-\kappa a)\right] rdr} \tag{14}$$

Combinations of the above equations were used with Equations (4) and (5) to compute latex particle transport as a function of the experimentally measured parameters: ionic strength and particle size, packing diameter and bed void volume, and the material parameters: Hamaker constant, surface charge density, and/or surface potential.

PARAMETER EVALUATION

1. Hamaker constant. Typical values of A lie in the range 0.5 to 10 × 10^{-14} erg for polymer latex particles such as polystyrene, polystyrene-acrylonitrile, styrene-butadiene polymethylmethacrylate, etc. (Visser, 1972).

2. Surface potential. Values reported for the zeta potential of polymer latexes are generally within the range 20 to 150 mV and usually display an ionic strength dependence indicative of the constancy of the surface charge density (Schaller and Humprey, 1966).

3. Capillary radius. The equivalent capillary radius can be computed from the bed hydraulic radius as (Bird et al., 1960)

$$R_o = \frac{D_{PK}\epsilon_V}{3(1-\epsilon_V)} \tag{15}$$

An internal check on the consistency of this calculation is available from an earlier analysis (Stoisits et al., 1976) which indicates that in the absence of wall effects and negligible ionic forces, a linear relationship between ΔV and D_p results in the small particle range, with the slope inversely proportional to R_o. Values of R_o from these data were found to agree well with predictions from Equation (15) (McHugh et al., 1976).

RESULTS AND DISCUSSIONS

Effect of Parameters in HDC

A series of calculations was made to determine the effects of parameter variations as predicted by the capillary model. Integrations of Equations (6) and (14) were done numerically using Simpson's rule, and results are illustrated in Figures 3 to 8. Figures 3 to 7 show the critical role of ionic strength both in controlling particle separation and parameter sensitivity of the separation. Figures 3 to 5 illustrate the effect of ionic strength on the sensitivity of the separation factor to the value of the Hamaker constant. Figures 6 to 8 show the similar effect of ionic strength on the sensitivity of the calculation to surface potential. Both sets of calculations demonstrate a feature which has important practical as well as

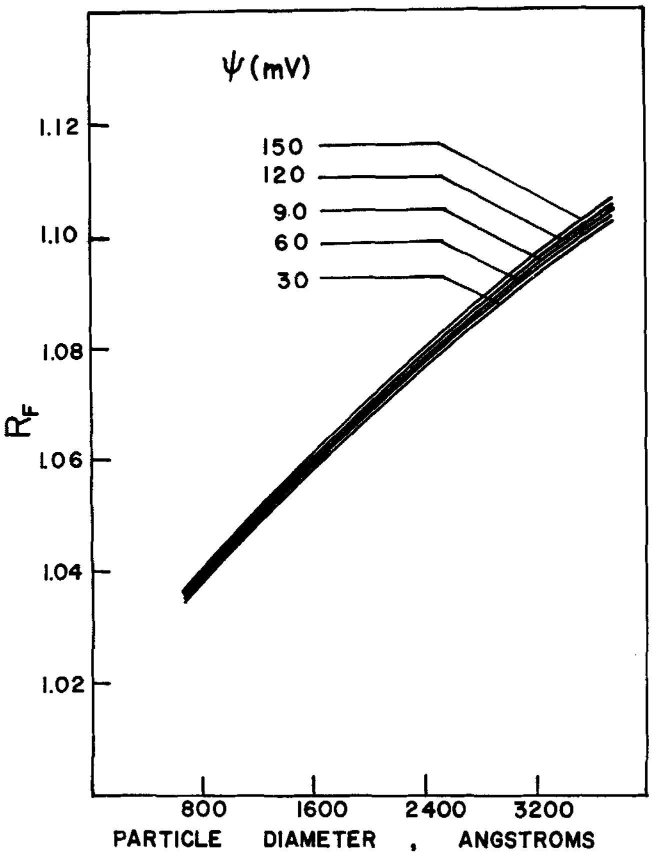

Fig. 8. Theoretical computation showing the effect of the electric surface potential of the particle on the separation factor at low ionic strength; 0.001M of a 1:1 electrolyte. Other parameters have the same value as in Figure 6.

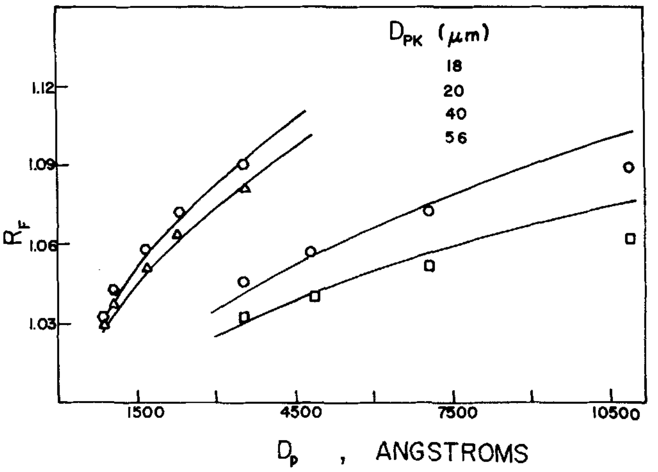

Fig. 9. Theoretical computation showing the effect of the equivalent capillary radius (computed from packing size and void volume fraction data) on the separation factor. Experimental data for different packing size from Small (1974). $A = 5 \times 110^{-14}$ erg, $\psi_{o1} = 125$ mV, $\psi_{o2} = 30$ mV, 4.6×10^{-3}M sodium chloride.

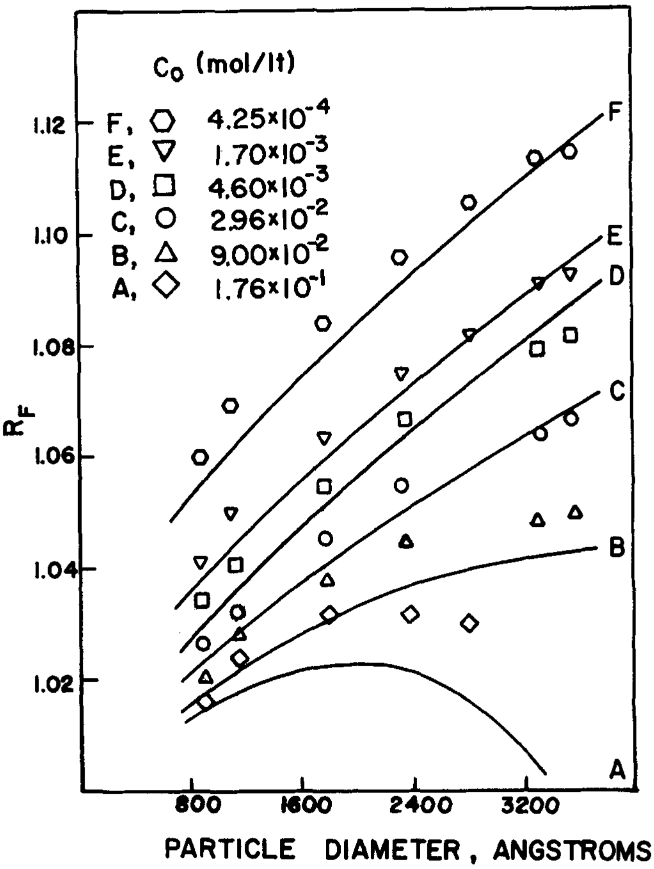

Fig. 10. Comparison between mathematical model and experimental data of Small (1974) for polystyrene. $A = 5 \times 10^{-14}$ erg, $\psi_{o2} = 30$ mV, $\sigma = 1.5 \times 10^4$ stc/cm², $D_{PK} = 20$ μm, $\epsilon_V = 0.358$.

theoretical significance. At low ionic strength, the essential independence of R_F to material parameters associated with the latex system indicates the feasibility of universal calibration curves. Calibration data on a well-characterized system such as monodisperse polystyrene latexes can be used to analyze particle size distribution data for different latex systems run at the same low ionic concentration (Silebi and McHugh, to be published). At higher ionic strengths one finds, owing to the reduced double-layer repulsion, a predominance of van der Waal's attraction and thus an increasing sensitivity of the separation factor-particle size relationship to values of A and/or ψ_{o2}. As shown, at high ionic strength a reversal in the particle size-residence time trend results. The particle size-residence time behavior in fact becomes controlled by material parameters. It may be more appropriate to analyze the separation process in this regime on the basis of adsorption-desorption effects as opposed to hydrodynamic effects. This approach has been discussed before and referred to as potential barrier chromatography (Prieve and Ruckenstein, 1976).

Figure 9 shows the dependence of the separation factor on packing diameter for the range of sizes reported by Small (1974). The good comparison to Small's data offers an explanation for the increased resolution seen with decreased packing size (Small, 1974; McHugh et al., 1976).

Polystyrene Results

In order to demonstrate the efficacy of the model, Figure 10 shows a comparison between measured and calculated values of the R_F-D_p behavior for column data of Small (1974) for a range of ionic strengths. The ionic concentration is in total equivalent sodium chloride including surfactant which in all cases is below the critical micelle concentration. Similar good agreement was obtained with data from our columns although, at present, we have not run at ionic concentrations above 0.05M (Scolere, 1977). There are several striking features to be emphasized concerning the fit seen in Figure 10, most especially the fact that it is a zero free parameter fit. Values for the material parameters which were used in the calculations were obtained from the literature. Following Fowkes (1964), the value for the Hamaker constant for polystyrene in water, 5×10^{-14} erg, was used. Values of the zeta potential were used based on measurements of the electrophoretic mobility in the presence of sodium lauryl sulfate surfactant (Schaller and Humprey, 1966).

Values of the zeta potential at a particular electrolyte concentration were used to evaluate the surface charge density from Equation (12). This value was used with aid of the tabular values in Loeb et al. (1961) to calculate the surface potential of the latex at other electrolyte concentrations. The characteristic wavelength of the dispersion interaction for polystyrene particles was obtained from the dispersion frequency reported by Ottewill and Shaw (1966); the value used was 1 460Å. The equivalent capillary radius is calculated from Equation (15) using the experimentally measured values of 20 μm and 0.358 for D_{PK} and ϵ_V, respectively. The fit at high ionic strength can be improved by using a value of R_o adjusted to ~4 μm [a value more closely associated with that determined by the previously mentioned extrapolation of data (McHugh et al., 1976)] and a value of 3×10^{-14} erg for the Hamaker constant typical of the experimental range (Visser, 1972). With these slight adjustments, the agreement can be made more dramatic (McHugh et al., 1977). However, we wish to illustrate here the fit which results with no parameter adjustments. The good agreement in the low ionic string range, that is, up to 4.6×10^{-3} etc., however, the fit to the behavior at high ionic strength with the present calculations is striking and we feel offers an excellent phenomenological explanation. These calculations indicate that at the higher ionic strengths, due to reduced double-layer repulsion, latex particles will preferentially sample streamlines close to the packing in their trajectory through the bed, resulting in increased residence time. This effect increases with increased particle size as indicated in both the data and calculations. The good agreement between calculated and measured R_F values indicates further that one need not necessarily resort to an adsorption-desorption mechanism to explain the increased time as suggested earlier (Small, 1974; Ruckenstein and Prieve, 1976; McHugh et al., 1976). Calculations in the high ionic strength range by McHugh et al. (1976) do show, however, the development of well-defined secondary minima in the potential energy profiles greater than 6 kT. One is tempted to conclude that a reversible adsorption-desorption on the packing surfaces may at least be possible. We have run controlled experiments to consider this effect (Gee, 1976). Packing particles attached to rotating stirrers were immersed in dilute polystyrene latex suspensions of total ionic concentration corresponding to the delayed residence time region of Figure 9. Packing particles were viewed under scanning electron microscopy after removal from the stirred suspensions both with and without prior dilution of the supernatant eluant. Comparison of micrographs for the rinsed and unrinsed packing showed a definite and near complete removal of latex particles. Further details will be presented in a future publication, but in terms of the calculations shown in this paper, it is worthwhile to emphasize that an adsorption-desorption mechanism, as such, may not be necessary to explain the behavior from a phenomenological view. Our adsorption-desorption experiments may, however, have a strong bearing on the application of the concept of potential barrier chromatography mentioned earlier. In addition, we feel it may be appropriate to regard the principal mechanism and/or mechanisms of separation in HDC to be separated into either a hydrodynamic regime or an adsorption-desorption regime on the basis of ionic concentration.

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NOTATION

a = minimum separation distance between wall and particle surface, cm
A = Hamaker's constant, erg
A_i = duct cross section available for flow to species i, cm^2
c_o = total electrolyte concentration of bulk solution, ions/cm^3
D_p = particle diameter, cm
D_{PK} = packing diameter, cm
D_∞ = particle diffusion coefficient, cm^2/s
e = protonic charge, statcoul
k = Boltzmann's constant, erg/°K
p = $2\pi\, a/\lambda$
P = probability density function
q = volumetric flow rate, cm^3/s
r = distance of particle center from cylinder axis, cm
R_F = separation factor for rate of transport
R_o = capillary radius, cm
R_p = particle radius, cm
T = absolute temperature, °K
v_i = axial velocity of marker or particle, cm/s
v_o = velocity at tube center line
$[v_p]$ = average velocity of particle as defined by Equation (6), cm/s
$[v_m]$ = average velocity of marker as defined by Equation (14), cm/s
ΔV = difference between marker and particle elution volume, ml
$z_{j,k}$ = valence of ion j of electrolyte k
$z_{j,k}^*$ = $z_{j,k}/\mathrm{lcm}\{z_{1,k}; z_{2,k} \ldots\}$
lcm refers to least common multiple

Greek Letters

γ = wall effect parameter
ϵ = fluid dielectric constant
ϵ_V = bed fractional void volume
ϕ_{DL} = double-layer energy of interaction, erg
ϕ_{VW} = van der Waal's energy of interaction, erg
ϕ_B = Born energy of interaction, erg
Φ_1 = reduced surface potential of wall
Φ_2 = reduced surface potential of particle
κ = $(8\pi c_o e^2/\epsilon kT)^{1/2}$, cm^{-1}
λ = wavelength of intrinsic electronic oscillation of atoms, cm
σ = electrostatic surface charge density, statcoul/cm^2
ψ_{o1} = electric surface potential of wall, statvolt
ψ_{o2} = electric surface potential of particle, statvolt

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Kinetic, Transport, and Deactivation Rate Interactions on Steady State and Transient Responses in Heterogeneous Catalysis

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The classical theory of diffusion and heterogeneous catalytic reaction has been primarily concerned with the interaction between chemical and physical rate processes in a time invariant system. In practice, however, various mechanisms act to alter activity and selectivity patterns, and one should append to the analysis yet another rate process, that of deactivation.

The present research is an experimental and modeling study of the effects of impurity poisoning on the steady state and transient behavior of a diffusionally influenced, exothermic, catalytic reaction. Major factors included in

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