Influence of bulk and surface composition on the retention of colloidal particles in thermal field-flow fractionation

Paul M. Shiundu[1], J. Calvin Giddings*

Field-Flow Fractionation Research Center, Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA

Abstract

In this paper we report a wide range of cases in which the retention of colloidal particles in thermal field-flow fractionation (FFF) shows a strong dependence on the chemical composition of the particles or of the particle surfaces. These results are observed among similar particles (such as different latexes) or between dissimilar particles (including latexes as well as inorganic and metallic colloids). These compositional effects are observed for particles suspended in both aqueous and nonaqueous carrier liquids. The dependence of retention on composition is complementary to its dependence on particle size, which has been amply demonstrated in previous studies. The compositional effect is attributed to the dependence of the thermal diffusion coefficient on compositional factors.

A number of cases are presented here where compositional effects are significant. Examples include the baseline resolution of 0.30-μm silica particles and 0.300-μm polystyrene (PS) particles and a large difference in retention times between 0.232-μm PS and 0.229-μm polymethylmethacrylate (PMMA) latexes in aqueous suspensions. Also, metallic particles (e.g., palladium) were less retained than silica particles, with latex particles most retained. The resolution of equal-size particles in the nonaqueous carrier liquid acetonitrile is also demonstrated.

Surface compositional effects have also been found in this study. These effects suggest the possibility of colloidal surface analysis by thermal FFF. The potential for performing both bulk and surface compositional analysis of particles by thermal FFF makes this FFF technique complementary to both sedimentation FFF and flow FFF techniques for the analysis of complex particulate materials.

1. Introduction

The capabilities of the field-flow fractionation (FFF) family of techniques to separate and characterize a broad range of macromolecular, colloidal, and particulate materials has now been well established [1]. For over two decades one of the FFF techniques, thermal field-flow fractiona-

tion (ThFFF), was used exclusively for the separation and characterization of synthetic polymers [2–16]. The molecular mass range studied has been wide, extending to ultra-high molecular mass polymers of mass ca. $20 \cdot 10^6$ [17]. Recently, however, the applications of ThFFF have expanded to include the retention and fractionation of particulate materials suspended in both aqueous and nonaqueous carrier liquids [18–20]. The technique has been applied both to colloidal particles (those under 1 μm diameter) and micrometer-size particles up to 20 μm diameter.

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* Corresponding author.
[1] Present address: Department of Chemistry, University of Nairobi, PO Box 30197, Nairobi, Kenya.

Particles are separated selectively according to size in both diameter ranges. However, these initial studies have demonstrated that retention also depends on the composition of the particles. The compositional dependence of retention is the focus of this study. If compositional effects are found to be sufficiently selective, ThFFF could become a valuable tool for the compositional analysis of particulate materials.

By examining the theory of ThFFF, it can be shown that compositional effects derived from the compositional dependence of the thermal diffusion coefficient D_T, a basic transport coefficient describing the movement of matter under an applied temperature gradient. In order to understand compositional effects in ThFFF, the compositional dependence of D_T must be known. Unfortunately, the fundamental basis of D_T is not well understood. However, ThFFF can be used to rapidly accumulate data on the compositional dependence of D_T. Accordingly, D_T measurements of several types of latex particles as well as silica particles have been made using ThFFF [18,19].

The compositional dependence of the retention of particles in ThFFF appears to be analogous to compositional effects for polymers. Many studies have shown that polymer retention depends on the chemical nature of the polymer as well as on its molecular mass [21–24]. The possibility for using ThFFF for the analysis of polymer composition as well as molecular mass has been under consideration for some time [21].

According to theory, the retention of sample materials (either polymeric or particulate) in ThFFF is controlled by two transport processes: ordinary concentration diffusion, coefficient D, and thermal diffusion, coefficient D_T [21]. Of the two parameters, only D is well understood. According to the Stokes–Einstein expression ($D = kT/3\pi\eta d$, where k = Boltzmann's constant, T = absolute temperature, η = solvent viscosity, and d = hydrodynamic diameter), D can be readily calculated if the hydrodynamic diameter d of the polymeric molecule or particle is known. Because the use of sample materials with well-characterized D values simplifies the examination of D_T, standard spherical particles of known

sizes were used in our experiments in order to improve the measurement process and eventually arrive at a better understanding of the thermal diffusion phenomenon in ThFFF.

Specific factors that influence D_T (and thus control retention) are not yet fully understood. However, some interesting characteristics of D_T have been determined that are applicable to both polymeric and particulate sample materials. For instance, D_T has been found to be sensitive not only to the chemical nature of the retained components but also to the solvent used [19,22]. However, it has been established that D_T for specific polymer classes is essentially constant, independent of both the molecular mass and the form of branching of the polymer molecule [23]. This is in sharp contrast with the behavior of particles in which D_T shows a significant dependence on diameter d [18]. In a recent publication, we reported opposite trends in the dependence of D_T on d for aqueous and nonaqueous carrier liquids (i.e., positive and negative slopes in the plots of D_T versus d, respectively), with the latter media showing a relatively smaller dependence [19].

The dual size–composition dependence of retention in ThFFF has the potential to provide particle compositional analysis, thereby making ThFFF a technique that could complement both sedimentation FFF and flow FFF for the characterization of complex sample materials. The possibility of doing a composition-based separation and analysis of particles was first suggested in an earlier publication [18]. However, in order to realize this goal, a better understanding of the influence of particle composition on D_T is required. For instance, we need to know whether the observed compositional effects are surface- or bulk-driven phenomena.

In this paper, we demonstrate that ThFFF can separate various particles of the same or similar size (or size distribution) that have different chemical compositions. We also report that modifying the surface of submicron particles has an effect on retention behavior, hence showing the influence of surface properties on observed compositional effects. Thus, based on the apparent sensitivity of the retention of colloidal par-

ticles on the particle surface, we demonstrate the potential of ThFFF to determine the chemical composition of particle surfaces.

2. Theory

According to the standard retention theory for normal-mode FFF, retention time t_R is related to the dimensionless retention parameter λ of a retained component by the expression [25,26]

$$\frac{t_R}{t^o} = \frac{1}{6\lambda[coth(1/2\lambda) - 2\lambda]} \qquad (1)$$

where t^o is the void time (the time needed to elute a nonretained component) and $\lambda = l/w$, where w is the channel thickness or distance between the hot and cold walls and l is the distance from the cold wall to the center of gravity of the component zone. The parameter λ is a measure of the extent of interaction between the external field or gradient and the sample component. From Eq. 1, it is clear that each experimental measurement of t_R yields a unique value of λ. Eq. 1 is, however, an approximation for ThFFF since it is based on a parabolic flow profile model which assumes uniform viscosity across the channel. Therefore, this expression needs to be corrected to account for distortions due to viscosity changes caused by the temperature gradient applied across the channel [27]. Such corrections have been made for all the calculated results provided in this paper.

For purposes of better understanding the relationships among t_R, λ, and the underlying transport coefficient D_T, we use several approximations that result in simple, but still reasonably accurate, mathematical forms. First of all, we begin with Eq. 1 despite perturbations caused by viscosity gradients. Second, for highly retained species (i.e., $\lambda \to 0$), we use the limiting form of Eq. 1

$$\frac{t_R}{t^o} = \frac{1}{6\lambda} \qquad (2)$$

We next need the relationship between the retention parameter λ and the coefficients D and D_T. This dependence is expressed by

$$\frac{1}{\lambda} = \frac{wD_T}{D}\frac{dT}{dx} \qquad (3)$$

where dT/dx is the temperature gradient applied across the component band in the channel. By assuming a linear temperature gradient across the channel thickness, the product $w \, dT/dx$ can be approximated as the temperature drop ΔT applied between the cold and hot walls. Thus, Eq. 3 is approximated by

$$\frac{1}{\lambda} = \frac{D_T\Delta T}{D} \qquad (4)$$

Combining Eqs. 2 and 4, we get

$$\frac{t_R}{t^o} = \frac{D_T\Delta T}{6D} \qquad (5)$$

From Eq. 5 it is evident that at constant ΔT, variations in t_R for different particles suspended in the same carrier solution can be attributed to differences in both D and D_T. Using the Stokes–Einstein expression ($D = kT/3\pi\eta d$), we can obtain the value of D for particles of known d. By substituting the Stokes–Einstein expression for D into Eq. 5, we get

$$\frac{t_R}{t^o} = \frac{\pi\eta dD_T\Delta T}{2kT} \qquad (6)$$

Because particles having the same size distribution are expected to have equivalent values of d and D, this equation shows that significant differences in their retention times can only be attributed to variations in D_T.

3. Experimental

The ThFFF system used for this work is similar in design to the Model T100 polymer fractionator from FFFractionation (Salt Lake City, UT, USA). Details are provided elsewhere [18]. The channel spacer was confined between two chrome-plated copper bars, with the top bar heated using rods controlled by relay switches with cycle times activated by a microprocessor. The cold wall was cooled using continuously flowing tap water. The temperatures of the hot and cold walls were monitored through three

thermal sensors that were inserted (two in the hot and one in the cold wall) into wells drilled into both the top and bottom bars.

The thickness of the mylar channel spacer used here was 76 μm, unless stated otherwise. The channel had a breadth of 2.0 cm and a tip-to-tip length of 46 cm. The ΔT used was 45 K unless indicated otherwise. Both acetonitrile (ACN) and aqueous carrier liquids were used in this study. They were delivered using a Model M-6000A pump from Waters Associates (Milford, MA, USA). The spectrograde ACN was obtained from EM Science (Cherry Hill, NJ, USA); its ionic strength was modified by 0.10 mM tetrabutylammonium perchlorate (TBAP). The aqueous carriers were either a phosphate buffer of ionic strength 0.01 M and pH 4.52 (or 9.68) or consisted of doubly distilled water containing 0.1% FL-70 surfactant plus 0.02% sodium azide. The flow-rate used was 0.20 ml/min unless noted otherwise. A Model UV-106 detector from Cole Scientific (Calasabas, CA, USA) operating at 254 nm wavelength was used to detect particles eluting from the ThFFF channel. Data acquisition of the detector signal was accomplished using a PC-AT compatible computer. The detector signal was also recorded using an OmniScribe chart recorder from Houston Instruments (Austin, TX, USA). Samples were injected via a 20-μl loop injection valve.

Several types of particles from different sources were used in this work. Silica particles of nominal diameters 0.15 and 0.25 μm were obtained from E. Merck (Darmstadt, Germany) while particles of 0.30 μm were obtained from Bangs Laboratories (Carmel, IN, USA). Polybutadiene (PB) and polystyrene (PS) latex particles were obtained from Dow Chemical (Midland, NJ, USA) and Duke Scientific (Palo Alto, CA, USA), respectively. Polymethylmethacrylate (PMMA) and 0.230-μm polystyrene-polymethylmethacrylate (PS/PMMA) core–shell latex particles were obtained from Seradyn (Indianapolis, IN, USA) and Bangs Laboratories. The core–shell latex particles consist of a PS core and a PMMA shell. Also obtained from Bangs Laboratories were 0.210-μm PS/acrylamide + hydrazine particles (containing 10 μeq/g of

particles with–NHNH$_2$ surface functional groups), 0.091-μm styrene–14% vinylbenzylchloride (VBC) having–CH$_2$Cl surface groups, and 0.098-μm styrene–34% vinylbenzylchloride (VBC) copolymer latex particles.

The surface of the 0.30-μm silica particles was modified by derivatization of the silanol groups using the process reported by Little et al. [28]. The silanization reagent used was octadecyl trichlorosilane and some of the unreacted silanol groups were "capped" using trimethylchlorosilane.

4. Results and discussion

Fig. 1a shows plots of $t_R/t°$ (retention time relative to void time) versus d for PS, PB, PMMA, and silica particles suspended in ACN carrier liquid. The concentration of tetrabutylammonium perchlorate (TBAP) used was 0.10 mM. (The importance of using a salt in nonaqueous carrier liquids was established in a previous publication [3].) Other experimental conditions entailed a channel flow-rate of 0.30 ml/min, a ΔT of 30 K, and a corresponding cold wall temperature of 287 K. It is evident from the figure that retention in ThFFF is not only dependent on particle size but also on the particle chemical composition. The dependence of particle retention on composition is reflected in the different retention levels for the various particle types. The figure shows that silica particles are the least retained compared to the three types of latex particles and that the retention levels varied between the different latexes. This variation among latexes is also found in aqueous carrier suspensions, as shown in Fig. 1b. The carrier liquid in this case was doubly distilled water containing 0.10 mM concentration of TBAP, with the other experimental conditions the same as in Fig. 1a. These results show that latex particles are retained somewhat longer in an aqueous carrier suspension than in the nonaqueous carrier liquid. It is also significant to note that the order of retention of the PMMA particles has been reversed in the two carrier
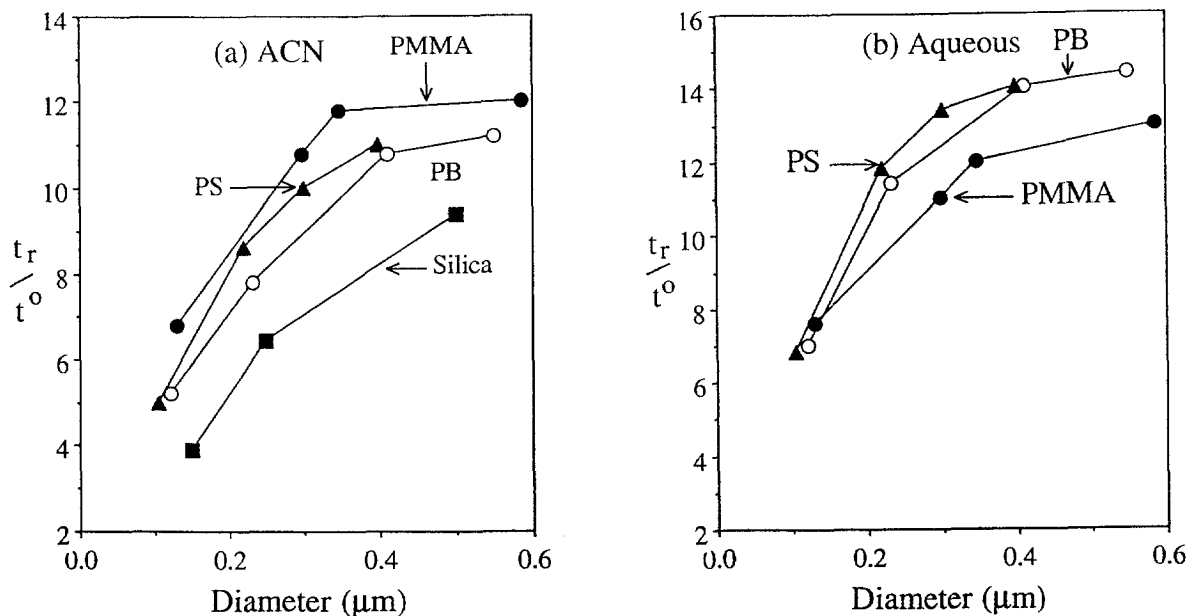
Fig. 1. Plots of retention time t_R (relative to void time t^o) versus particle diameter for (a) PS, PB, PMMA, and silica particles suspended in ACN, and (b) PS, PB, and PMMA particles suspended in an aqueous medium. Experimental conditions: flow-rate = 0.30 ml/min, [TBAP] = 0.10 mM, $\Delta T = 30$ K, $T_c = 287$ K.

liquids relative to both PS and PB (i.e., PMMA is the most retained latex in ACN and least retained in the aqueous carrier liquid). These observations further illustrate the dependence of particle retention in ThFFF on the composition of both the particle and the carrier solution.

Additional results showing compositional effects on latex particle retention in an aqueous carrier suspension are shown in Fig. 2. The figure shows elution profiles of different types of latexes of similar size distributions suspended in a phosphate buffer of pH 9.68 and ionic strength of 0.01 M. It is clear that the 0.232-μm PS particles are retained the most, followed by 0.230-μm PB latex beads. The 0.229-μm PMMA shows comparable retention with the 0.230-μm PS/PMMA core–shell latex particles. Two interesting observations can be made from this figure: (1) It is possible to separate equal sizes of PS from PB or PS from PS/PMMA, and (2) modification of the surface of latex particles can have a dramatic effect on retention behavior. For instance, despite the similar size distribution of the core–shell PS/PMMA and the PS latexes,
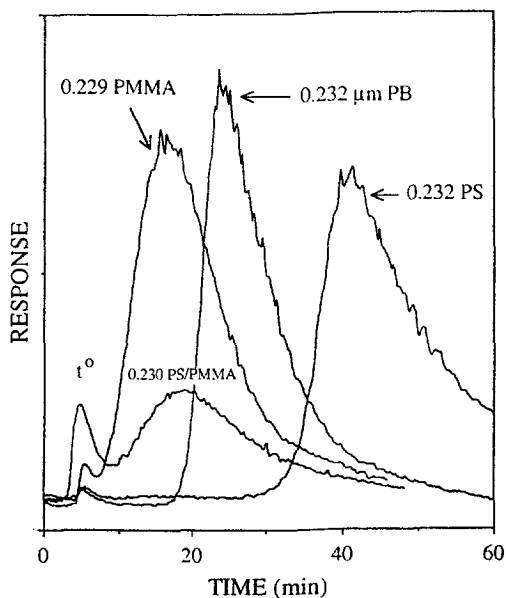

Fig. 2. Superimposed elution profiles of 0.229-μm PMMA, 0.230-μm PS/PMMA (core–shell), 0.232-μm PB, and 0.232-μm PS latex beads in a 0.01 M ionic strength phosphate buffer at pH 9.68. Experimental conditions: flow-rate = 0.20 ml/min, $\Delta T = 45$ K, and $T_c = 288$ K.

different retention times were observed for these samples. This illustrates the potential influence of surface properties on particle retention behavior in ThFFF. Of additional significance is the order and magnitude of the elution times for the PS and PB particles in the phosphate buffer carrier liquid. The elution order is similar to that reported for ACN in Fig. 1; however, the degree of separation is much higher in an aqueous carrier medium than was previously reported with ACN as a carrier liquid [19].

As mentioned earlier, the contribution of D to retention time in ThFFF should be the same for particles having the same or comparable size distributions. Thus, the observed differences in the retention times shown in Fig. 2 are attributable to the differences in their thermal diffusion coefficients, reflecting the dependence of D_T on particle chemical composition. This explanation is consistent with Eqs. 5 and 6.

The dual dependence of retention on both size and chemical composition promises to make ThFFF complementary to both sedimentation FFF, which separates samples according to density and size, and flow FFF, which separates sample materials only according to their hydrodynamic size (and hence would not distinguish between chemically unlike samples having similar size distributions).

Retention dependence on chemical composition between dissimilar types of particles (e.g., latexes versus inorganic or metallic particles) is widely observed. Such compositional effects are shown clearly in Fig. 3. Fig. 3a shows the separation of 0.25-μm silica particles from 0.232-μm PS latex particles in an aqueous carrier solution containing 0.1% FL-70 surfactant plus 0.02% sodium azide (as electrolyte and bactericide). In spite of the somewhat larger mean size of silica particles compared to PS particles, the silica particles are much less retained. This observation is consistent with the results shown in Fig. 1a. Fig. 3b similarly shows the near-baseline resolution between 0.30-μm silica particles and 0.300-μm PS latex beads. The experimental conditions were similar to those reported for Fig. 3a, except that the flow-rate was 0.30 instead of 0.20 ml/min.
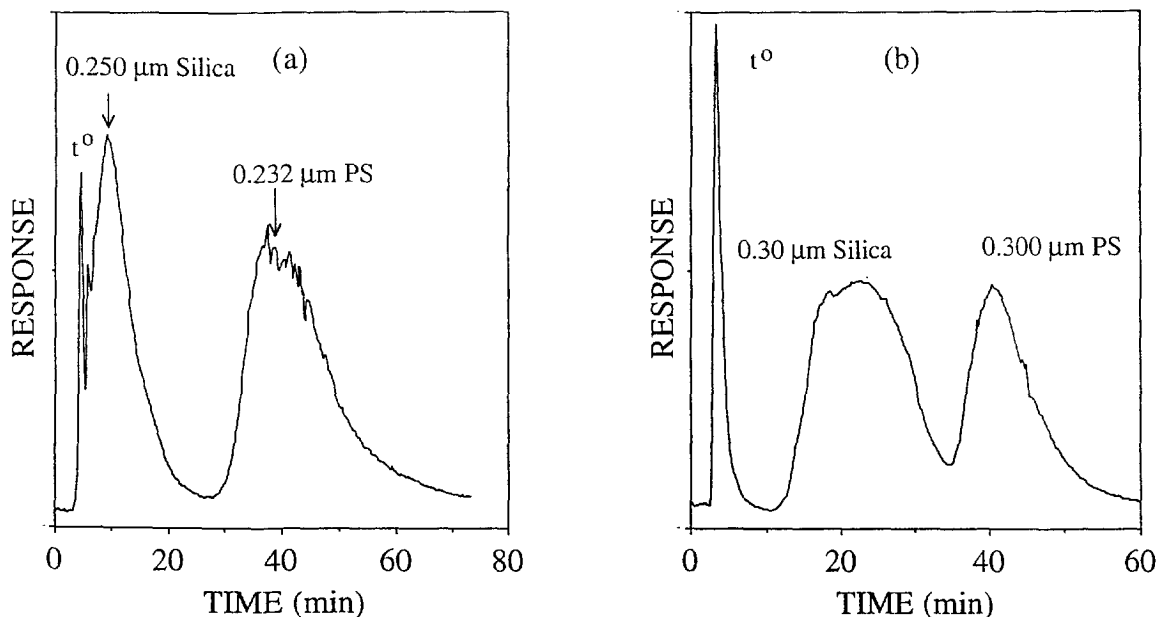

Fig. 3. Separation of submicrometer populations of silica and PS particles suspended in an aqueous carrier medium: (a) 0.25-μm silica and 0.232-μm PS particles and (b) 0.30-μm silica and 0.300-μm PS particles. Experimental conditions: flow-rate = 0.20 ml/min for (a) and 0.30 ml/min for (b), and $\Delta T = 45$ K, and $T_c = 288$ K.

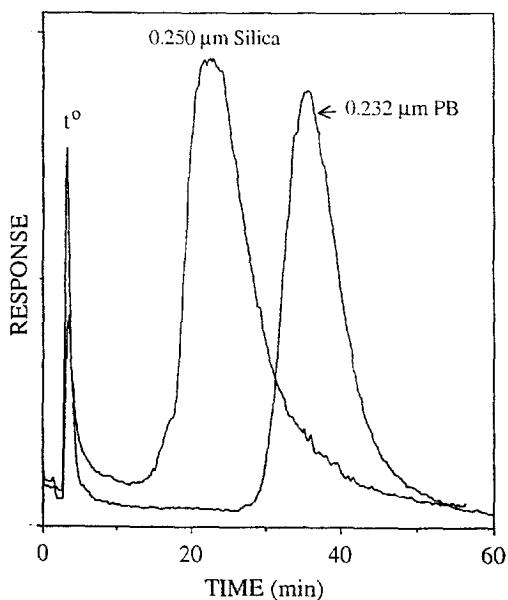Fig. 4. Superimposed elution profiles of 0.232-μm PB and 0.250-μm silica particles suspended in ACN. Experimental conditions: flow-rate = 0.30 ml/min, [TBAP] = 0.10 mM, ΔT = 45 K, and T_c = 288.5 K.

Fig. 5. Superimposed elution profiles of 0.198-μm PS and 0.2 ± 0.1-μm Pd metal particles suspended in ACN. Experimental conditions: flow-rate = 0.70 ml/min, [TBAP] = 0.10 mM, ΔT = 40 K, and T_c = 286 K.

Similar compositional effects are observed in nonaqueous carrier suspensions. Fig. 4 shows superimposed elution profiles of 0.232-μm PB and 0.25-μm silica particles obtained with ACN as the carrier liquid in a channel with a flow-rate of 0.30 ml/min, a ΔT of 20 K, and a cold wall temperature T_c of 288.5 K. The 0.25-μm silica particles were retained less than the PB latex beads, demonstrating the weaker thermal diffusivity of silica particles.

Fig. 5 shows superimposed elution profiles of 0.197-μm PS particles and 0.2 ± 0.1-μm palladium (Pd) metal particles obtained using ACN as carrier liquid in a channel with a flow-rate of 0.50 ml/min, a ΔT of 40 K, a cold wall temperature of 286 K, and a concentration of TBAP of 0.10 mM. (The channel thickness in this case was 127 μm.) Here again the retention time (measured at peak maxima) of the smaller PS latex particles is over twice as long as that of the Pd particles, showing the much weaker thermal diffusivity of metal particles relative to latexes. This is the first report on the use of ThFFF to retain metal particles.
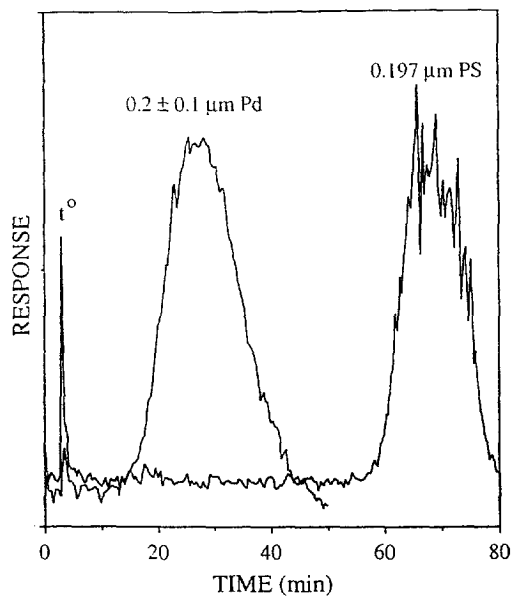
Despite the accumulation of evidence that D_T has a dependence on the chemical composition of particulate materials, most data do not indicate whether surface or bulk properties dominate these compositional effects. However, one of the retention experiments reported above suggests that surface composition effects are dominant in determining retention. This suggestion arises from Fig. 2, which shows that the retention of the PS/PMMA core–shell latex (in which the shell is composed of PMMA) is very close to that of equal-sized PMMA particles but substantially less than the observed retention of PS latex particles. This provocative result requires further substantiation.

In an attempt to further determine the relative contributions of bulk and surface composition, experiments were conducted using particles whose surfaces were either modified chemically or that had different compositions. First, we examine 0.30-μm silica particles, some untreated and some of whose surfaces were chemically derivatized by silanization using octadecyl trichlorosilane reagent. Fig. 6 shows the elution
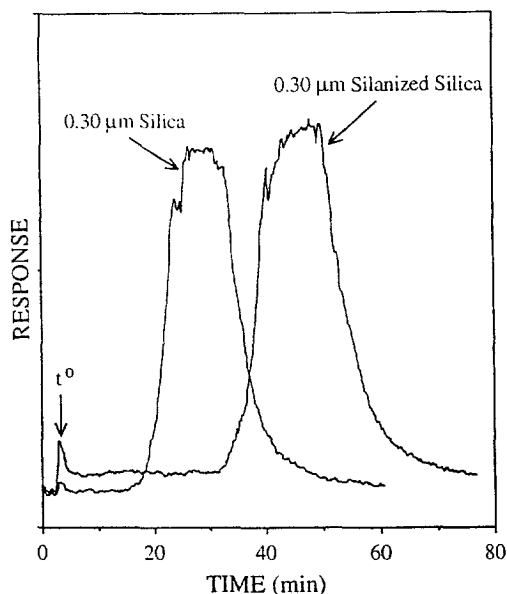
Fig. 6. Superimposed elution profiles of equal-size (0.30-μm) silanized and unsilanized silica particles in an aqueous carrier liquid. Experimental conditions: flow-rate = 0.30 ml/min, $\Delta T = 45$ K, and $T_c = 289$ K.

Fig. 7. Superimposed elution profiles of 0.300-μm PS latex beads and 0.30-μm silanized silica particles in an aqueous carrier liquid. Experimental conditions: flow-rate = 0.30 ml/min, $\Delta T = 45$ K, and $T_c = 289$ K.

profiles of the two forms of silica particles obtained under identical experimental conditions. The aqueous carrier contained 0.1% FL-70 and 0.02% sodium azide, the flow-rate was 0.30 ml/min, and ΔT was 45 K. From the two profiles, it is evident that the surface-derivatized silica particles were retained much longer than their underivatized counterparts, despite their equal size distributions. (It should be possible to baseline resolve any two monodisperse components.)

The above results further illustrate the sensitivity of particle retention in ThFFF to the chemical composition of the particle surface. While our understanding of the nature of this dependence is still limited, it may be related in part to the hydrophobicity or hydrophilicity of the particle surface. This hypothesis is substantiated by Fig. 7, which shows superimposed elution profiles of 0.300-μm PS latex particles and the 0.30-μm silanized silica particles. The two profiles almost coelute, in contrast with the earlier results shown in Fig. 3b where the unsilanized 0.30-μm silica was nearly baseline re-

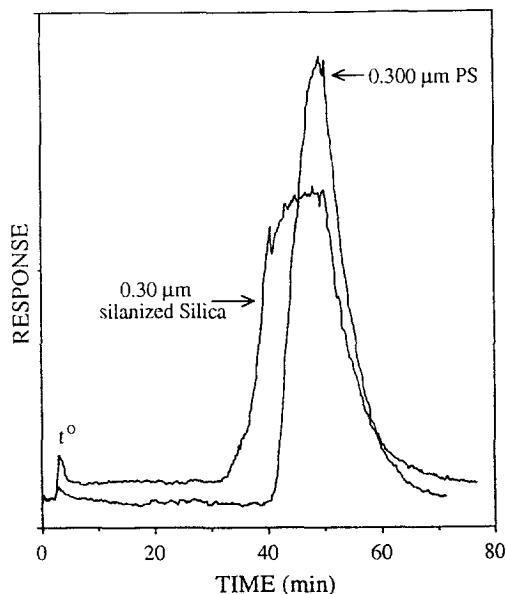solved from the 0.300-μm PS particles. The transformation of the silica surface from a hydrophilic surface (containing predominantly silanol groups) to a more hydrophobic surface comprised of long-chain hydrocarbons may account for the similarity in retention behavior of the silanized silica and the PS latex particles. (We assume that the relatively low-density coverage of the PS surface by sulfonate groups and the presence of some nonderivatized silanol groups on the silica surface only weakly affect retention.)

Additional experiments performed using PS latexes having comparable or equal size distributions and having different surface functional groups (generally at low density) such as carboxylates, sulfonates, hydroxylates, and so on, showed no significant differences in retention times. These results are omitted here for reasons of brevity. However, a significant difference in retention times was observed between the 0.198-μm PS and 0.210-μm PS/acrylamide + hydrazine particles. These results are shown in Fig. 8a. An aqueous carrier solution made up of
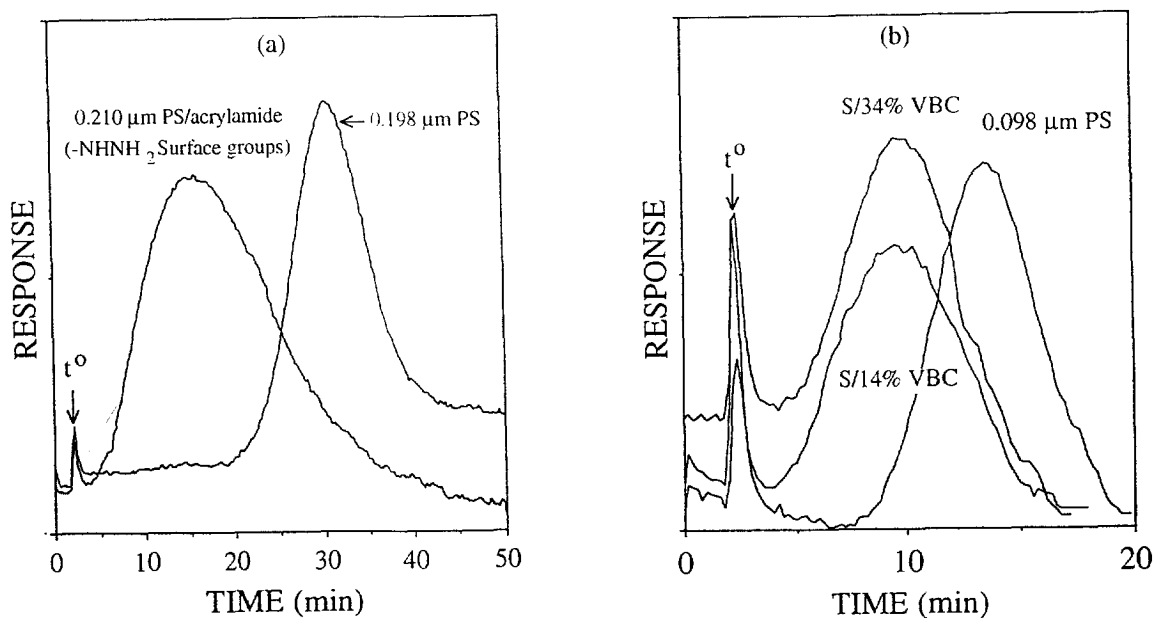
Fig. 8. (a) Elution profiles of 0.198-μm PS particles and 0.210-μm PS/acrylamide + hydrazine (–NHNH$_2$ surface groups) suspended in an aqueous carrier liquid containing 0.1% FL-70 surfactant and 0.02% sodium azide. Experimental conditions: flow-rate = 0.30 ml/min, ΔT = 40 K, and T_c = 286 K. (b) Elution profiles of 0.098-μm PS particles, 0.098-μm S/34%VBC (–CH$_2$Cl surface groups), and 0.091-μm S/14% VBC (–CH$_2$Cl surface groups). The carrier solution and experimental conditions are the same as in (a).

0.1% FL-70 surfactant and 0.02% sodium azide (as a bactericide) was used. The channel flow-rate was 0.30 ml/min and ΔT was 40 K with a corresponding cold wall temperature of 311 K. These results further illustrate a tendency toward a weaker retention for the more hydrophilic surface.

In Fig. 8b, the retention profile of 0.098-μm PS is compared with the profiles of both 0.091-μm S/14% VBC and 0.098-μm S/34% VBC, both having–CH$_2$Cl surface groups. The retention times of the two S/VBC copolymer particles appear to be independent of the ratio of styrene (S) to vinylbenzylchloride (VBC), but neither is retained as long as the 0.098-μm PS particles. Unfortunately, it is not clear whether the difference in retention time between the PS and the S/VBC particles is due to their different surface groups or to the fact that S/VBC is a copolymer whereas PS is not. Additional latex samples with well-defined bulk and surface properties would have to be studied to resolve this question.

5. Conclusions

In this paper we demonstrate that the effects of chemical composition on retention are sufficiently strong that the separation of equal-size particles in a variety of compositional classes (latex, inorganic, metallic) can be readily achieved. We thereby open up possibilities for compositional separations and analysis by ThFFF. This prospect is intriguing because field-flow fractionation techniques are generally considered to be physical separation methods that have only a secondary dependence on chemical composition. The results of this study show that the effects of composition might be quite subtle. Furthermore, the prospect that colloidal materials can be differentiated according to their surface composition not only has significant implications in utilizing ThFFF as a new surface analysis tool but is also suggestive of the enormous complexity of the chemical composition effects that underlie ThFFF retention.

Although this study has primarily focused on the intricate effects of changes in particle composition, the potential role of the carrier liquid composition is similarly promising. Once the thermal diffusion process is better understood, it may be possible to alter the composition of the carrier liquid in order to generate differential retention shifts. These shifts might be engineered to enhance resolution based on particle compositional factors of interest while suppressing resolution based on unimportant compositional differences. A great deal more work is needed to define and exploit these intricate compositional effects.

Acknowledgements

Symbols

d	particle diameter
dT/dx	temperature gradient in channel
D	ordinary diffusion coefficient
D_T	thermal diffusion coefficient
k	Boltzmann's constant
l	mean thickness of sample zone
R	retention ratio
t_R	retention time
t^o	channel void time
T	absolute temperature
T_c	cold wall temperature
w	channel thickness
ΔT	temperature drop across channel
η	viscosity
λ	dimensionless retention parameter

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