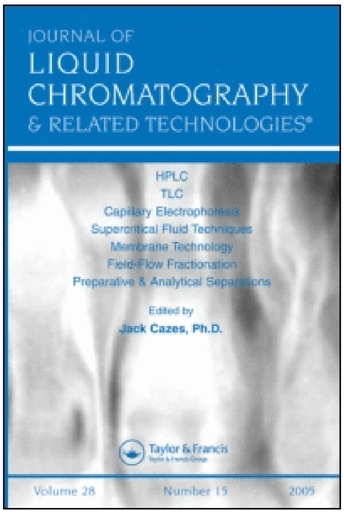

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FRACTIONATION AND SIZE DISTRIBUTION OF WATER SOLUBLE POLYMERS BY FLOW FIELD-FLOW FRACTIONATION

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ABSTRACT

Flow field-flow fractionation (flow FFF) is introduced as a chromatographic-like method with a potential for separating and characterizing water soluble polymers. The theory of the method is summarized, showing that one gets a size distribution curve based on the Stokes diameter, d. Problems in interpreting the elution profile in both flow FFF and gel permeation chromatography are discussed in the light of complications arising from electrostatic chain expansion in polyelectrolytes.

The experimental approach is described using a channel of 2.00 ml volume. Sulfonated polystyrenes of three different molecular weights are separated from one another with and without added salts. The dependence of retention on sample size is shown to be least in the salt solution, indicating that this is most suitable for analytical work.

The sodium salts of polyacrylic acid are also investigated. Distinct elution profiles are noted for two of these polydisperse polymers. Size distribution curves for the 2,000,000 MW sample curves are obtained from the elution profiles and are shown to be independent of experimental variations. Finally, fractions are collected after separation and rerun through the column, showing a reasonable confirmation of the expected fractionation effect.

INTRODUCTION

Water soluble polymers, already important in many areas of technology, have been the subject of accelerated study recently because of the prospect that they can substantially aid in the recovery of petroleum from underground formations. They serve even at considerable dilution to multiply the viscosity of aqueous solutions pumped into the formation. They have thus become an integral part of plans for extensive tertiary recovery (1,2,3).

The optimum use of water soluble polymers requires tools for the measurement of their molecular weight or size distributions. Rheological properties will depend on these distributions, and aspects of potential environmental impact will hinge on the degradation pattern of the polymer chains. Thus it is important to develop technologies which are capable of providing the relevant distributions.

Gel permeation chromatography (GPC) provides one avenue for the study of size distribution. However, there have been some difficulties in eliminating interactions between the solid surface and the polymer. These interactions include the ion exclusion effect in which a residual charge on the gel will influence the distribution of polymer. While progress has been made in reducing these interactions and thus producing good results (4,5), it is felt that other potential technologies should be simultaneously explored for their capabilities in yielding size distributions.

Field-flow fractionation, (FFF), which may also be called one-phase chromatography, is an alternate technology which we consider here for water soluble polymers. It has a number of advantages relative to GPC including external retention control, programmability, low surface area, large inherent range and peak capacity, and mathematically predictable elution (6,7). Perhaps the most important of these characteristics from the viewpoint of water soluble polymers is the intrinsically low surface area, which should act to minimize the multiplicity of interactions that can affect retention (7). The low surface area stems directly from the nature of the FFF process.

The FFF methodology has been explained and described in a number of publications (8,9,10,11,12,13). The method is based on the application of a lateral field or other influence across an unobstructed, ribbon-like channel. The field pushes the solutes into exponential layers against the lower channel wall. The layer thickness varies in a predictable way with molecular mass or size. Parabolic flow down the axis of the channel then sweeps the solutes forward selectively, giving each a mean velocity that can be predicted rather precisely in terms of layer thickness and thus the physicochemical properties that determine layer thickness. In overall characteristics, then, the methodology resembles chromatography, except that it is executed in one phase with retention induced by external fields.

In the work reported in this paper we use the subclass of FFF called flow FFF. Here the layer-forming influence is a cross-flow of solvent moving gradually across the width of the channel as a result of pressure applied across two semipermeable membranes which constitute the channel faces. Flow FFF has been successfully applied to other water soluble or dispersible materials including proteins (12,14,15), polystyrene latex beads (12,14), colloidal silica (16) and viruses (12,17).

We have employed two polyelectrolytes in order to study the applicability of flow FFF to water soluble polymers. First we used sulfonated polystyrenes, which can be prepared as narrow fractions of varying molecular weight from available polystyrene fractions. These help establish the properties of the system. Second we employed salts of polyacrylic acids whose broad weight distributions are more characteristic of water soluble polymers encountered in practical situations.

THEORY

In flow FFF the experimental solute layer established at one wall is of mean thickness

$$\ell = D/U \tag{1}$$

where D is the diffusion coefficient and U the velocity of the cross flow. If we express U in terms of the directly observable volumetric cross flow rate, $\dot{V}_c$, we have (14)

$$\ell = DaL/\dot{V}_c \qquad (2)$$

where a and L are channel breadth and length, respectively. It is useful to recast this equation into dimensionless layer thickness, $\lambda = \ell/w$, which expresses the ratio of ℓ to channel width w. Using the fact that the channel void volume is $V° = awL$, we can write equation 2 as

$$\lambda = DV°/\dot{V}_c w^2 \qquad (3)$$

which is a more convenient form.

Diffusion coefficient D is responsible for the selectivity that exists between solutes of different molecular weights in flow FFF. This parameter is a function of the effective "size" of the polymer. It can be expressed by the Stokes-Einstein equation

$$D = kT/3\Pi\eta d \qquad (4)$$

where k = the Boltzmann constant, T = temperature, η = viscosity and d = the Stokes diameter of the particle. The Stokes diameter, of course, is the diameter of a rigid sphere having the same friction coefficient as the polymer molecule in question. It is a diameter that increases with chain length (molecular weight) according to physico-chemical laws.

With equation 4 substituted into equation 3 we have

$$\lambda = \left(\frac{1}{3\Pi}\right)\frac{V°kT}{\dot{V}_c w^2 \eta d} = \frac{d_F}{d} \qquad (5)$$

where d_F is a parameter controllable by $\dot{V}_c$ and having the dimension of a length.

$$d_F = \left(\frac{1}{3\Pi}\right)\frac{V°kT}{\dot{V}_c w^2 \eta} \qquad (6)$$

The retention volume V_r of solute peaks in FFF relative to channel volume V^o is a function of λ that assumes the following forms:

$$\frac{V_r}{V°} = \frac{1}{6\lambda[\coth(1/2\lambda)-2\lambda]} \cong \frac{1}{6\lambda} + \frac{1}{3} \qquad (7)$$

The latter expression is an approximation valid at high retention, but in practice is valid within 6% at $V_r = 2V^o$ (16). The substitution of equation 5 into equation 7 yields

$$\frac{V_r}{V^\circ} = \frac{d}{6d_F[\coth(d/2d_F)-2d_F/d]} \simeq \frac{d}{6d_F} + \frac{1}{3} \qquad (8)$$

The approximate form here exhibits a linearity between retention volume V_r and the Stokes diameter d of the particle or molecule. This is a convenient relationship because one can interpret an elution diagram at all points beyond $V_r = 2V^\circ$ as directly representing a particle size distribution curve, m(d) (16).

It has been shown elsewhere that the complete particle size distribution curve that is accurate down to $V_r = V^\circ$, but not allowing for instrumental spreading, is given by (16)

$$m(d) = c(V_r)[dV_r/dd] \qquad (9)$$

The theory outlined above yields polymer distribution curves in terms of Stokes diameter d. It remains to relate chain length or molecular weight to d so that a molecular weight distribution can be obtained. This connection is complicated in polyelectrolytes because charge repulsion significantly expands the chain beyond its random configuration. The expansion is dependent on the concentration of salts in solution, from which counterions are provided. There are also severe concentration dependent effects even at extreme dilutions. These characteristics are summarized by Morawetz (18).

One should note that, purely at a calculational level, problems of equal or worse severity exist with GPC when applied to polyelectrolytes. Not only does one have all the difficulties of relating chain dimensions to molecular weight, as with FFF, but one has the added difficulty of determining which dimensional parameter controls retention, and the precise mathematical relationship by which it does so. Empirical correlations have worked well in handling the latter difficulty in the past, but whether they have much validity with new and unusual materials is open to doubt. This is always the limitation of empirical correlations.

More specifically, it is often assumed that the hydrodynamic radius of a particle controls its retention (19,20). Yet a general theory of retention which accounts for all the complications of pore shape in real GPC systems has never been developed. The theory of simple model systems illustrates that hydrodynamic volume is not the sole retention parameter (21, 22). In some cases a dimensional parameter that we have termed mean external length controls retention, but this is not universal either (21). In short no truly universal dimensional parameter can be identified that will work in all model GPC systems, let alone within the complex pores of real systems.

In flow FFF, by contrast, retention is at least rather rigorously related to parameter d, the Stokes diameter, for the model system which consists of a uniform channel of flat surfaces which have no attractive interactions with the polymer chains. Significant interactions, of course, must be absent both in GPC and FFF systems. Here FFF has the advantage, as noted before, because of the smaller surface area.

In that an unambiguous connection between molecular weight and d does not yet exist for polyelectrolytes, we will report the results of this paper directly in terms of distributions in d.

EXPERIMENTAL

The configuration of the flow FFF column and the method of operation used in this study have been described previously (14, 15). In the present case, channel dimensions were 10 x 0.44 x 450 mm. The channel had a void volume of 2.00 ml as measured by the elution of a void peak. Width w, rather than being measured directly, is calculated from the void volume because some deformation of the membrane walls can occur in column assembly.

The polystyrenes were obtained from Pressure Chemical Company, and had molecular weights of 20,000, 200,000 and 498,000. They were converted to the potassium salts of polystyrenesulfonic acid by a modification of the method of Carroll and Eisenberg (23). We refer to them by the molecular weights of the parent compounds as PS 20,000, PS 200,000 and PS 498,000, respectively.

The polyacrylic acids, reportedly of molecular weights 150,000 and 2,000,000, were obtained from Polysciences Inc. They were converted to their respective sodium salts by titration to pH 8.5 with 1 N sodium hydroxide. We refer to them as PAA 150,000 and PAA 2,000,000 respectively.

The concentrations of sulfonated polystyrene in each sample solution were determined by placing about 500 mg of the solution in a preweighed bottle in an oven at 95°C. After four days the bottle was weighed, returned to the oven for another four days and then reweighed. The weight percentage of the sulfonated polymer in the sample prepared from the 200,000 MW polystyrene was found to be 1.69% and that of the sample prepared from the 498,000 MW polystyrene was 1.60%. We use an average value of 1.645% to calculate μg of polymer per injected sample.

Two solvents were used in this study. The first was 0.02 M triethanolamine in distilled water, adjusted to pH 8.5 with nitric acid. The second solvent was the same as the first with the addition of 0.1 M potassium chloride. These solutions were fed into the system as both carrier and cross flow streams, using two Cheminert metering pumps with adjustable pumping rates from Chromatronix.

All experiments were carried out at ambient temperature of 22 ± 1°C. Peaks were monitored with a U.V. detector from Laboratory Data Control. The fractograms were recorded with an Omniscribe recorder from Houston Instruments. The eluate was collected in fractions when necessary by a Golden Retriever Pup model 1100 from Instrumentation Specialties.

RESULTS AND DISCUSSION

Sulfonated Polystyrenes. Figure 1 illustrates the success of flow FFF in separating three sulfonated polystyrene fractions in a solution of water containing only the 0.02 M triethanolamine.

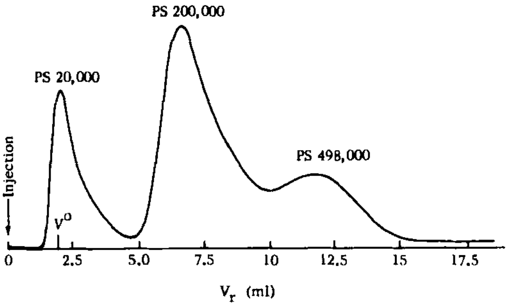

FIGURE 1
Separation of three sulfonated polystyrenes in 0.02 M triethanolamine without added salt. Sample size was 12 μl of each polymer. The void volume V^o was 2.00 ml, $\dot{V}$ was 3.44 ml/h and $\dot{V}_c$ was 14.9 ml/h. The numbers on the figure identify the polystyrene by its molecular weight prior to sulfonation.

The three distinct peaks are seen to be clearly identifiable, and in the expected sequence of molecular weights, from low to high as elution proceeds. Despite the success of the fractionation, peak shifts were observed to occur with changes in sample size in spite of the small sample (4 μl, ~66 μg of polymer) used. In analytical situations these retention shifts would hinder indentification and make impossible the acquisition of size distribution curves. It is well known that the strong concentration dependence of polyelectrolyte behavior can be ameliorated by the addition of salt (18). Therefore retention and fractionation were attempted in a salt-containing solution.

Figure 2 illustrates a fractionation of the same three samples in a solution containing 0.1 M KCl, along with the 0.02 M triethanolamine. The overall resolution is roughly comparable although it is evident that relative peak shifts have improved the separation of the last two peaks and worsened the resolution of the first two. However, the two fractograms are not directly comparable because of different experimental flow conditions. It is therefore instructive to look at the relative size distribu-

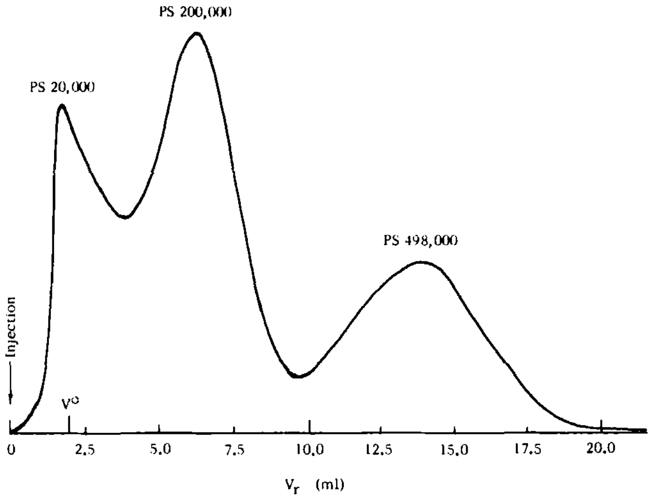

FIGURE 2
Separation of three sulfonated polystyrenes in 0.02 M triethanolamine with 0.1 M potassium chloride added. Sample size was 15 μl of each polymer. $\dot{V}$ was 2.90 ml/h and $\dot{V}_c$ was 10.0 ml/h.

tion curves produced by the two fractograms using equation 9. If the polymer chains in the two cases retained the same dimensions, the size distribution curves (with respect to Stokes diameter d) would superimpose.

Figure 3 shows the two size distribution curves taken from figures 1 and 2. The failure of superposition shows that important dimensional changes have indeed occurred with the addition of salt.

For analytical purposes it is important to establish the concentration ranges in which the chain dimensions stay essentially constant and therefore in which elution volumes are roughly independent of small changes in concentration. To this end we have run both 200,000 and 498,000 MW polystyrenes with a range of different injected sample sizes. Peak retention volumes and shifts in retention volumes were noted and the corresponding Stokes diameter was calculated for each peak. The results are shown in figure 4.

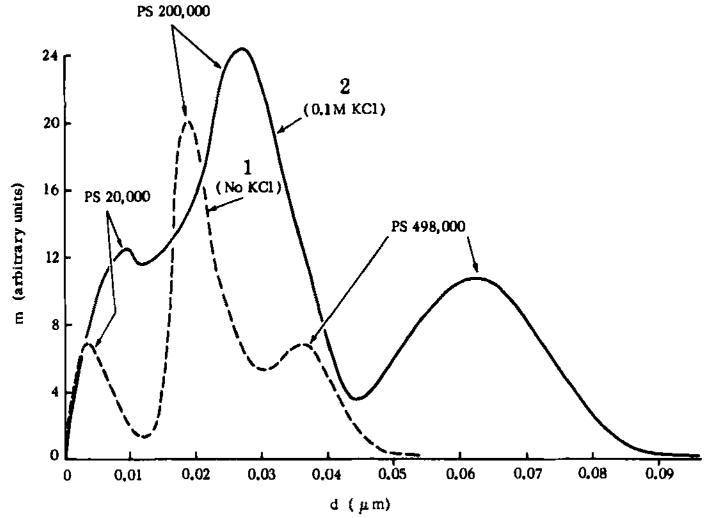

FIGURE 3
Comparison of size distribution curves in terms of Stokes diameter d for the fractograms of Figures 1 and 2. Curves 1 and 2 identify with Figures 1 and 2, respectively.

Figure 4 shows that chain dimensions and elution characteristics remain nearly static with increasing sample size in the 0.1 M KCl solution over the large range from 0-800 μg (~0-50 μl of injected polyelectrolyte). However, these properties change drastically with sample size when salt is omitted. In this case the Stokes diameter is seen to shrink two- to three-fold as the sample size is increased to 800 μg (~50 μl). This change is intolerable for practical purposes. Working in salt is therefore the only reasonable approach consistent with these results.

The data of figure 4 are largely consistent with the known behavior of polyelectrolytes. The addition of salt has been observed to reduce the concentration dependence of chain dimensions at low concentrations. However, we do note an apparent anomaly in our observation in that added salt has led to an increased d at all except the lowest concentrations. It is well established that the addition of salt to polyelectrolytes re-

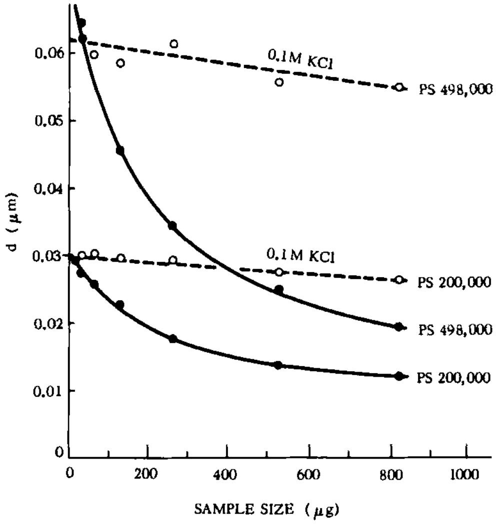

FIGURE 4
Effect of sample size on apparent values of Stokes diameter d for two different sulfonated polystyrenes. Solid lines show the effect in 0.02 M triethanolamine alone and dashed lines show the effect in 0.02 M triethanolamine plus 0.1 M potassium chloride.

duces the chain expansion resulting from charge repulsion within the polyion (18). This is not in accord with our results. Whether this unexpected result reflects a property of polyelectrolyte behavior or some unexpected interaction unique to our flow FFF system is not presently clear. More work in search of the roots of this phenomenon is certainly required. However our results in the salt solution are self-consistent and show that at the very least an empirical calibration curve relating molecular weight to Stokes diameter could be established for analytical purposes up until such a time that the theory and underlying phenomena are better understood.

As an added remark on the effects of the concentration dependence of salt-free polyelectrolyte, we note that this dependence causes a shift in the λ versus $1/\dot{V}_c$ plots so that the experimental lines fail to intercept the origin. This is shown in figure 5. In that interception of the origin is commonly

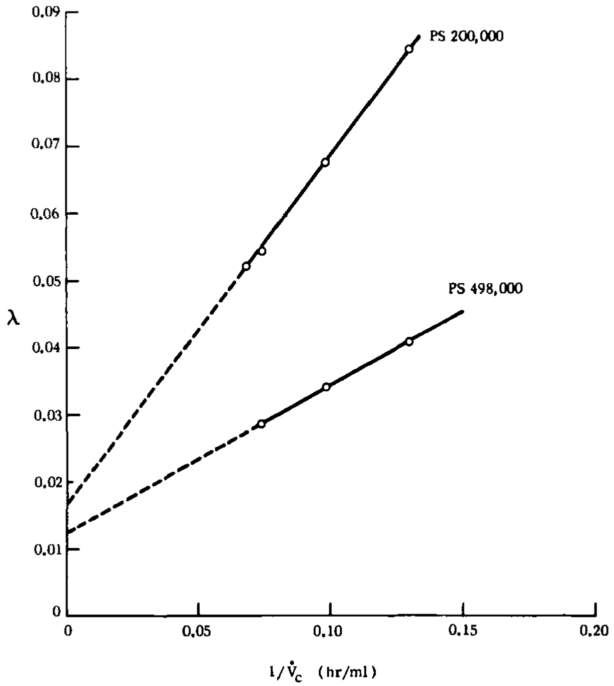

FIGURE 5
Plot of λ versus 1/$\dot{V}_c$ for two polystyrenes in triethanolamine without potassium chloride. The dashed portions represent extrapolated values. The channel flow rate $\dot{V}$ was approximately 3.2 in all cases and sample size was 4 μl or ∿ 66 μg.

taken as a test of proper behavior in flow FFF systems (14), the origin of this departure is important to establish. It stems, quite simply, from the fact that increased cross flow causes additional compression of the solute layer, concentrating it. This decreases the overall d, in accord with figure 4, and accordingly increases diffusivity. The enhanced diffusivity increases λ in accord with equation 3. Thus λ in figure 5 is expected to be anomalously high (above the origin) as $\dot{V}_c$ approaches infinity and thus as one approaches zero along the 1/$\dot{V}_c$ axis of the figure. This is confirmed by the positive intercepts of figure 5.

We should note that the above concentration effects are difficult to interpret quantitatively even barring complications in the polyelectrolyte systems themselves. In an FFF solute zone, concentration varies continuously with time as well as over two channel dimensions, width and length. Thus FFF behavior in the presence of concentration-dependent transport is extremely complicated, and has not been worked out theoretically.

Despite the above incompleteness in theory, it is useful to provide at least a "characteristic" concentration associated with the experiments so that the concentration effects can be put in better perspective. We take for this characteristic concentration the value existing at the bottom of the solute layer (where it touches the wall) and at the center of its extension along the channel axis at the time when the peak is eluting from the channel (11). We note that both higher and lower concentrations exist at different times and places in a zone during a run, but that this characteristic concentration is relatively high with respect to all the existing concentration levels.

Table 1 shows values of the characteristic concentration, labeled c_{oo}^L, in the channel. These values have been calculated from an equation (number 30) that appears elsewhere (11). We also show the apparent polymer diffusivity, D, obtained from experimental retention values. The association of D with C_{oo}^L is not exact because of the concentration variations noted, but because D is almost constant in the salt-containing solution, it provides a first approximation to a D versus concentration dependency.

In addition to the above considerations, some degree of peak distortion is expected from the concentration-dependent chain dimensions and resultant diffusivity. This is especially true, of course, for the salt-free solutions. In this case the lower diffusivity and thus the lower migration velocity at the dilute front and back edges of the zone will cause the center to overrun the front and thereby tend to create peak tailing. This expectation is generally borne out by the peaks shown in figure 1.

TABLE 1

Characteristic zone concentrations, c_{oo}^L, calculated by equation 30 of reference 11, for different concentrations of the two sulfonated polystyrenes with added KCl. Values of λ and diffusivity D are calculated from observed retention values using equations 7 and 3, respectively. The data are those of figure 4.

PS 200,000

sample size		λ	$<v>$	D	c_{oo}^L
µl	µg		mm/sec	$(cm^2/sec)x10^7$	%
4	65.8	0.0838	00.195	1.44	0.054%
8	131.6	0.0854	00.195	1.48	0.111%
16	263.2	0.0860	00.195	1.49	0.223%
32	526.4	0.0844	00.186	1.58	0.457%
50	822.5	0.0928	00.186	1.66	0.651%
PS 498,000					
8	131.6	0.0412	00.179	0.748	0.202%
16	263.2	0.0395	00.191	0.714	0.502%
32	526.4	0.0423	00.181	0.783	0.931%
50	822.5	0.0455	00.188	0.797	1.34%

Polyacrylic Acids. We turn now to the sodium salts of high molecular weight polyacrylic acid in order to investigate the operation of flow FFF with polydisperse materials of large chain length. Figure 6 illustrates the appearance of the elution curves for the polymers whose molecular weights prior to salt formation were reported as 150,000 (PAA 150,000) and 2,000,000 (PAA 2,000,000). The higher molecular weight material, PAA 2,000,000, extends further along the elution volume axis, as expected. Each principal peak is preceded by a small, sharp peak representing a fraction of lower molecular weight. We are assured that this early peak is not a foreign solvent or low molecular weight contaminant by the fact that the flow FFF

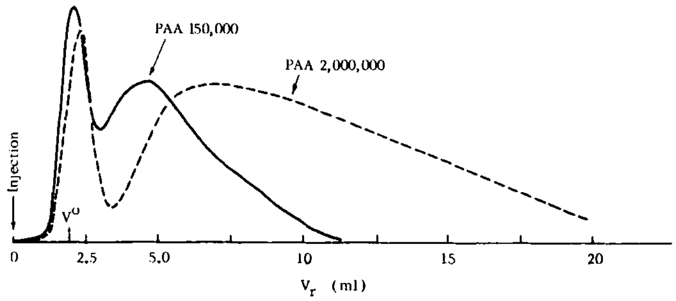

FIGURE 6
Comparison of fractograms of sodium salts of two polyacrylic acids in 0.02 M triethanolamine with 0.1 M potassium chloride added. For PAA 150,000, $\dot{V}$ was 3.10 ml/h, $\dot{V}_c$ was 6.84 ml/h and the sample size was 5 µl. For PAA 2,000,000, $\dot{V}$ was 3.04 ml/h, $\dot{V}_c$ was 6.84 ml/h and the sample size was 10 µl.

system acts simultaneously as a pressure dialysis cell, sweeping out through the lower membrane all species of a molecular weight below that of the membrane cutoff (24).

In the theory section we noted that the elution curves beyond about 2V° represent size distribution curves within a scale factor. In the case of figure 6, then, the principal peaks for each polymer are effectively size distribution curves whereas the early peaks are distorted because of their low elution volume. Direct inspection shows, therefore, that the curve maximum for PAA 2,000,000 corresponds to a Stokes diameter d roughly 1.55 times larger than that for PAA 150,000. Other similar comparisons can be made. For important numerical details, however, it is more useful to exhibit the size distribution curves directly on a d-scale plot using linear equation 8 for $V>2V°$ and a numerical solution of equation 9 for $V<2V°$. Figure 7 shows such curves for PAA 2,000,000.

The objectives of figure 7 are twofold. One purpose is to show the nature of the distribution curve as made available by flow FFF. Another purpose is to illustrate an important method for checking the validity of the results in terms of their inter-

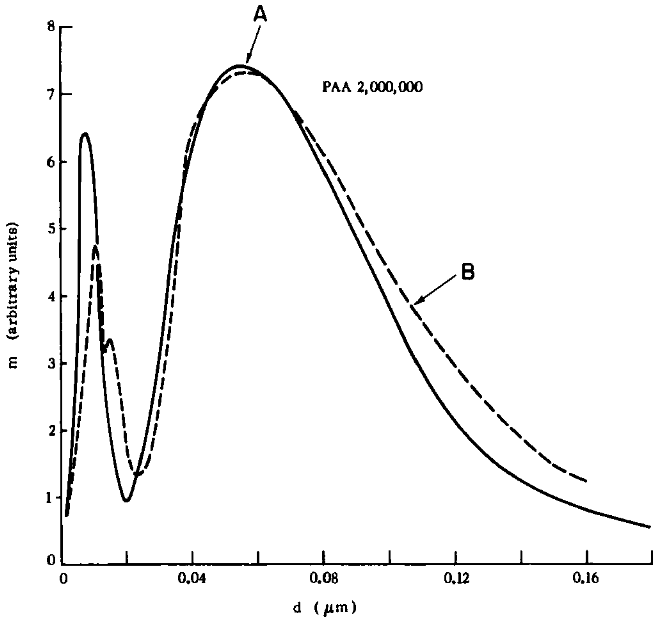

FIGURE 7
Comparison of two size distribution curves (in Stokes diameter d) for PAA 2,000,000 obtained under different cross flow conditions. The experiments were run in distilled water with 0.02 M triethanolamine with 0.1 M KCl added. In case A, $\dot{V}$ was 3.64 ml/h, $\dot{V}_c$ was 9.36 ml/h, and the sample size was 20 μl. In case B, $\dot{V}$ was 2.99 ml/h, $\dot{V}_c$ was 6.51 ml/h and the sample size was 20 μl.

nal self-consistency under different experimental conditions. This approach is applicable with all the FFF methods.

Briefly, self-consistency in FFF is checked by running elution curves under different field strength (cross flow) conditions. As the theory section makes clear, a change in cross flow alters the observed elution volume pattern, but it should leave the size distribution curve immutable. Any perturbation caused by adsorption or other unknown or unexpected factors will ordinarily create a divergence in the respective size distribution curves, thus revealing their presence and alerting the experimenter to take precautions.

The two size distribution curves in figure 7 were obtained at respective cross flows of 9.36 ml/hr (curve A) and 6.51 ml/hr (curve B). The reproducibility of the curves is excellent except in the vicinity of the minor peaks representing species of short chain length. This suggests that the size distribution curve is for the most part a valid one. Ideally this test should be applied over even greater extremes of cross flow, but the present range illustrates how the approach is applied.

A similar result was obtained for the lower molecular weight material, PAA 150,000, but the reproducibility was not as good, probably as a result of poor flow control in one of the two experiments.

We note that the accuracy of the size distribution curves is expected to be better for the major peaks than for the minor peaks consisting of the small chains. The minor peaks are both sharper and closer to the void peak, which impair the accuracy of analysis. Our results suggest that the minor peaks consist of components with d ~0.01 μm, a value that must be considered tentative until confirmed by additional studies.

A further analysis of figure 7 and similar data for PAA 150,000 has been carried out in order to derive the mean d value for each of the two polymers. Our result for PAA 150,000 is $\bar{d}$ = 0.029 μm and for PAA 200,000 is $\bar{d}$ = 0.058 μm.

Finally, we have attempted to collect elution samples from various parts of the polydisperse PAA 150,000 peak and rerun them in order to check the underlying fractionation process. Some difficulties are inherent in this process when solute properties are concentration dependent because the parent sample must be much larger than the derivative samples. Nonetheless reasonable success has been achieved as illustrated in figure 8. Sample A-1 should contain only the small chain component of the large parent peak. This is borne out by the small peak labeled A-1 in the figure. Sample A-2 should contain both the short chains and some of the larger chains of less than average length.

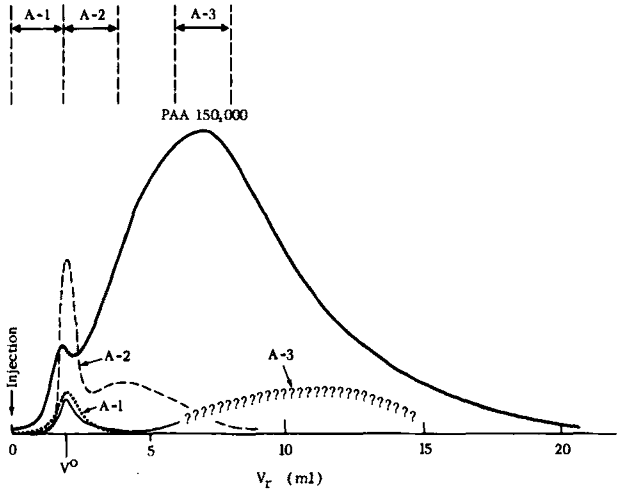

FIGURE 8
Elution curve for PAA 150,000 with superimposed peaks obtained from cuts from the parent material. The A-1, A-2, and A-3 labelled regions at the top show where the cuts were made from the parent curve.

This, too, is borne out. Sample A-3 should contain only long chains but for some unexplained reason it possessed a small short-chain peak as well. The details of A-3 were made somewhat unclear by slight baseline drift, as indicated by the question-mark line shown in the figure. Despite the latter uncertainties, the results, taken together, confirm our general expectations of the fractionation process.

CONCLUSIONS

The results presented above show clearly the existence of fractionation based on the effective size (Stokes diameter) of polyelectrolyte chains. This fractionation makes possible the generation of size distribution curves for the polymers. While the complications of polyelectrolyte behavior cloud the transformation of these curves into molecular weight distribution curves, the acquisition of the latter is clearly possible using realistic theoretical relationships between polyelectrolyte chain dimensions and molecular weight. Lacking these, empirical correlations would be possible as a temporary expedient. The acquisition of such correlations would be a useful objective for additional work.

Altogether our results tend to confirm that the small surface area, the theoretical simplicity and rigor, and the precise external retention control of FFF make this tool one of outstanding promise in the challenging field of water soluble polymer analysis.

ACKNOWLEDGMENT

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