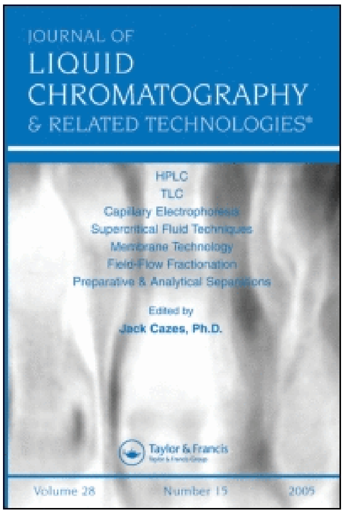

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Salt Effect on Separation of Polyvinylpyridines by Thermal Field-Flow Fractionation

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ABSTRACT

A mechanism for the separation of polymers under the influence of salt is proposed to account for experimental observations made on polyvinylpyridines subjected to thermal field-flow fractionation.

Key Words: Polymer separation; Polyelectrolyte; Salt effect.

INTRODUCTION

To date, the separation of polymers using thermal field-flow fractionation in aqueous solutions has not been very successful. This has greatly impeded

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the applications of the technology to the so-called water-soluble polymers. In a separate study in a commercial cationic starch polymer that was dissolved in dimethylsulfoxide, we discovered for the first time that, adding a salt, lithium nitrate, was having a great impact on the separation.[1] A better understanding of the science behind the salt influence is much desired in order to further develop the separation technology and its applications.

The influence of a salt, in a polymer solution has long been recognized in polymer science.[2] Salt causes electrostatic interference with a dissolved polymer chain that is either highly polarized or charged. A polymer that is subject to this type of salt effect often contains side groups that may be polarized or charged, under certain conditions. Many biologically important polymers, such as DNAs, proteins, and polysaccharides, as well as those synthetic industrial polymers like polyacrylamide and polyethylene oxide belong to this group. Therefore, the understanding of salt effects in polymer solutions is of great commercial interests.

It is unfortunate that the knowledge of the salt effect in its electrostatic context is rarely available. The polarization and charges on a polymer chain will affect both the short-range, e.g., the persistence length or Kuhn step, and the long-range, e.g., the excluded volume, interactions and will create unique solution behaviors. The deformable nature of a polymer chain adds many more uncertainties in the charge distribution on the polymer chains, and makes it extremely difficult to calculate the electrostatic potential in order to predict equilibrium properties of the polymer system. In aqueous systems, the hydrogen bonds make the situation even more complicated. It is a general strategy to study the salt influences first in a polar solvent, in which hydrogen bonds are not present.

The salt influence on polymer solutions is probably best understood for the so-called screening effect. By screening, one means that the charges on the smaller salt molecules form a loose and mobile layer in between the charged chain segments, which shields the electrostatic potential. The added salt also affects the polymer–solvent interactions and changes parameters like the second virial coefficient. Consequently, adding a salt may change the segment–segment interaction energies and the segment–solvent interactions as well. Thus, the quality of the solvent is affected. The screening effect is the basis of the recent developments in the scaling theories that predict the dimensional changes of charged polymer chains in response to the changes in electrostatic interactions caused by a salt.[3,4] For instance, the hydrodynamic volume of a polymer chain is scaled to the intrinsic viscosity times the molecular weight. Because of the screening effect, a charged polymer chain is less expanded in the presence of an added salt, than the chain without an added salt which experiences stronger segment–segment repulsion. As a result, the intrinsic viscosity of a charged polymer

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in a solution with an added salt is expected to be lower than the one without the salt.

We learned, that an adequate quantitative interpretation for the salt effect we observed in field-flow fractionation[1] is difficult to obtain. We have to start with the construction of a qualitative scheme or mechanism to describe the polymer properties under the influence of the salt. This mechanism must be proposed on the basis of broad and accurate experimental evidence. As many experiment tests as possible, need to be conducted through accurately designed experiments to gain insights into the mechanism. This work is confined to the understanding of the mechanisms of the salt influence in field-flow fractionation. A set of well characterized polyvinylpyridine standards with a quaternizer were subjected to separation in a polar solvent in thermal field-flow fractionation. A salt, lithium nitrate, is added to the carrier. Experimental observations were made at varied salt concentrations. At the same time, we have proposed a theory, based on a wall-exclusion hypothesis and scaling argument, in an attempt to impart the mysteries involved in the polymer separation process.

THEORY

The well-known, worm-like model is suitable for describing a linear polymer chain. Two parameters are used in the worm-like chain: the contour length L and the persistence length P. The contour length is defined as the maximum extension of a linear chain and is, thus, proportional to the degree of polymerization, DP, or the molecular weight, M. The persistence length is a measure of the local stiffness of the chain. It is the distance over which the short-range interactions between the chain segments are significant. The mean square radius of gyration of a worm-like chain is the function of these two parameters:

$$\langle r_g^2 \rangle = \frac{1}{3}\alpha^2 PL\left[1 - 3\left(\frac{P}{L}\right) + 6\left(\frac{P}{L}\right)^2 + 6\left(\frac{P}{L}\right)^3\left(1 - e^{-L/P}\right)\right] \tag{1}$$

where α is called the Flory expansion factor. It is noted, that the two limiting cases of this model are the random coil at $P \ll L$ and the rod at $P \gg L$.

The Debye-Huckel treatment of the diffuse double layer formed on the liquid side of a charged solid–liquid interface, can be used to describe the screening effect on the electrostatic interactions between the charges.[5]

In the Debye-Huckel treatment, a parameter called the Debye screening length $1/\kappa$; is defined as follows:

$$1/\kappa \equiv \frac{\varepsilon kT}{e^2}\left(\sum_{i=1}^{n} z_i^2 c_i\right)^{-1/2} \tag{2}$$

where ε stands for the dielectric constant of the liquid, k the Boltzmann constant, T the absolute temperature, e the elementary charge, z_i and c_i the charge valence and the mole concentration of species i, respectively. It is important to notice that the Debye screening length is only a function of the solvent dielectric constant and the so-called ionic strength. It is independent of the surface characteristics. The ionic strength is defined as follows:

$$I \equiv \frac{1}{2}\sum_{i=1}^{n} z_i^2 c_i \tag{3}$$

In order to simplify the problem so that we could accomplish something, we have chosen to involve only one kind of salt and let the salt be monovalent. Therefore, the ionic strength is scaled to the concentration of the salt:

$$I \sim c_s \tag{4}$$

The Debye screening length is, thus, scaled to reciprocal square root of the salt concentration:

$$\left(\frac{1}{\kappa}\right) \sim c_s^{-1/2} \tag{5}$$

According to de Gennes,[3] the radius of gyration of a charged chain can be scaled the following way:

$$\langle r_g \rangle \sim L^{3/5} P^{1/5} \left(\frac{1}{\kappa}\right)^{1/5} \tag{6}$$

According to Odijk,[4] the persistence length P can be scaled to the second or lower power of the screening length, with the second power being valid for high charge density and lower power for lower charge density:

$$P \sim \left(\frac{1}{\kappa}\right)^2 \tag{7}$$

Combining Eqs. (6) and (7), we obtain that,

$$\langle r_g \rangle \sim L^{3/5}\left(\frac{1}{\kappa}\right)^{3/5} \tag{8}$$

According to the worm-like model mentioned above, the contour length *L*, is scaled to the degree of polymerization or the molecular weight:

$$L \sim M \tag{9}$$

Therefore, the linear dimension, in terms of radius of gyration, of a charged polymer chain is finally scaled to the following relation:

$$\langle r_g \rangle \sim M^{3/5}\left(\frac{1}{\kappa}\right)^{3/5} \tag{10}$$

This relation is consistent to the theory derived by Flory for a random coil in a good solvent.[6]

Substituting Eq. 5 to Eq. 10, we can get

$$\langle r_g \rangle \sim M^{3/5} c_s^{-3/10} \tag{11}$$

According to the Stokes–Einstein relation, the diffusion coefficient of a particle is scaled to the reciprocal hydrodynamic radius. Therefore, we come to a conclusion,

$$D \sim \frac{c_s^{3/10}}{M^{3/5}} \tag{12}$$

The above scaling argument predicts that the diffusion coefficient of a charged polymer chain will increase with the increase in the salt concentration; and it will decrease with molecular weight.

In field-flow fractionation, as described in the literature,[1] the parameters that govern the retention are the diffusion coefficient, *D* and the field response parameter, such as the thermal diffusion coefficient, D_T for thermal field. The retention time t_R is essentially the reciprocal mean elevation *l*.[1]

$$t_R \sim \frac{1}{l} \tag{13}$$

Note, that the mean elevation, *l* is the distance of center of the equilibrium position of the polymer chains from the accumulation wall. In the absence of the salt, the unperturbed mean elevation of the polymer molecules, l_o, is scaled to the following relations:

$$l_o \sim \frac{D}{D_T \Delta T} \tag{14}$$

$$l_o \sim \frac{c_s^{3/10}}{M^{3/5} D_T \Delta T} \tag{15}$$

where ΔT is the temperature drop in the separation channel. We assume that there is a wall-exclusion layer, with a thickness of l_w, in addition to the unperturbed mean evaluation above the accumulation wall. In this excluded region, the long-range electrostatic repulsion is sufficiently strong to exclude the charged polymer chains. The wall-exclusion layer is elastic, such that the thickness of this layer varies as a result of the force between the electrostatic repulsion and the field force. We assume the thickness of the wall-exclusion layer has the same dependence on the salt concentration as the Debye screening length, a factor of K is added to stand for any scaling differences between the exclusion layer thickness and the "unperturbed" elevation l_o:

$$l_w \sim K c_s^{-1/2} \tag{16}$$

and the resulting mean elevation of the polymer chains in the field-flow fractionation channel is, thus, the sum of the "unperturbed" elevation plus the thickness of the wall-exclusion layer:

$$l \sim l_o + l_w \tag{17}$$

$$l \sim \frac{c_s^{3/10}}{M^{3/5} D_T \Delta T} + \frac{K}{c_s^{1/2}} \tag{18}$$

This relation is based on the assumption of a structure of the two additive layers in the force balance under the field: an unperturbed mean elevation on the top of an excluded vacant layer. This derivation suggests that the increase in the salt concentration has a two-fold effect on the retention of polymer in field-flow fractionation. The increase in the salt concentration makes the polymer molecules assume a more compact conformation in the carrier, which translates into higher diffusion coefficient and shorter retention. At the same time, the increase in the salt concentration reduces the exclusion layer on the accumulation wall, which contributes to the increase in the retention time of the polymer molecules. Therefore, between the two competing effects of the salt on retention, there should be a maximum point of retention as a function of the salt concentration if that concentration is accessible without causing the polymer to precipitate. When the effect on the exclusion layer dominates, the increase in salt concentration will result in an increase in retention. This can be used to explain the reason for our earlier observation, that the retention of the cationic starch increased after a salt was added to the carrier.[1]

EXPERIMENTAL

The thermal field-flow fractionation apparatus used in this work was of conventional design. The surfaces of the copper bars enclosing the channel were chrome plated and finely polished. Four one-kilowatt cartridge heaters were installed inside the hot bar. Water passages were drilled through the cold bar to allow tap water to cool the cold bar. The temperature drop was controlled precisely between the two bars by computer. A 76 μm thick spacer made of Mylar polyester was clamped tightly between the bars by twenty-two evenly spaced bolts. The center of the spacer was cut out to leave behind a ribbon-like flow channel measuring 2 cm in breadth and 47.3 cm in tip-to-tip length.

A Spectra-Physics (San Jose, CA) Model IsoChrom LC pump was used to deliver chromatographic grade tetrahydrofuran mixed with 0.01% (w/v) *n*-butylbromide, as the carrier, to a Rheodyne (Cotati, CA) sample injector. The injector was connected to the inlet of the separation channel, with a 0.007″-I.D. stainless steel tubing. The dead volume between the injector and the channel was 25 μL. The stop flow for sample relaxation was 30 s. The polymer was detected by an Applied Biosystems (Foster City, CA) Model 757 UV/Vis absorbance detector set at 260 nm.

Four polyvinylpyridine standards were used for this study. The nominal molecular weight ranged from 100,000 to 1,420,000 daltons. They are listed in Table 1.

Table 1. Polyvinylpyridine standards.

Sample #	Nominal *M*	*MW*/*Mn*	Supplier
1	100,000	1.05	Polysciences
2	240,000	—	Pressure Chemical
3	600,000	1.10	Lyle Bowman
4	1,420,000	1.40	American Polymer Standards

The samples were prepared with the carrier solvent with 0.15% (w/v) *n*-butylbromide in sealed vials. The polymer was dissolved while the vials were placed on a custom-built tilted rotor. The concentration of the polymer in the solution for injection was 0.1% (w/v), which was below the overlap concentration of the polymer.[3]

RESULTS AND DISCUSSION

All the four polymer standards were well retained in the thermal field-flow fractionation tests at a relatively high temperature drop, about 50°C. The peaks of the lower molecular weight samples (#1 and #2) were narrow, whereas those of #3 and #4 were much wider, suggesting that the high molecular weight standards were more polydispersed. A typical fractogram is shown for the runs without adding the salt, in Fig. 1 and the runs with added salt, in Fig. 2.

Once again, we found that the influence of adding the salt was well noticeable on the retention in the field-flow fractionation. It can be seen from the fractograms, that the increase in the salt concentration caused the retention to increase markedly for all the four polyvinylpyridine samples under the experimental conditions. This observation resembled the one we made on the commercial cationic starch.[1] Therefore, the effect on the wall exclusion layer [the second term in Eq. (18)] is seen as the one that dominates.

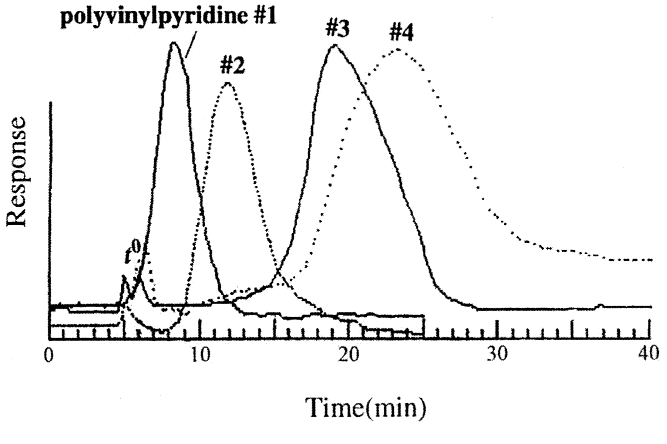

Figure 1. Fractograms of polyvinylpyridine samples in thermal field-flow fractionation. Experimental conditions: flow rate 0.1 mL/ min, temperature drop 50°C, cold wall temperature 30°C, salt concentration 0.

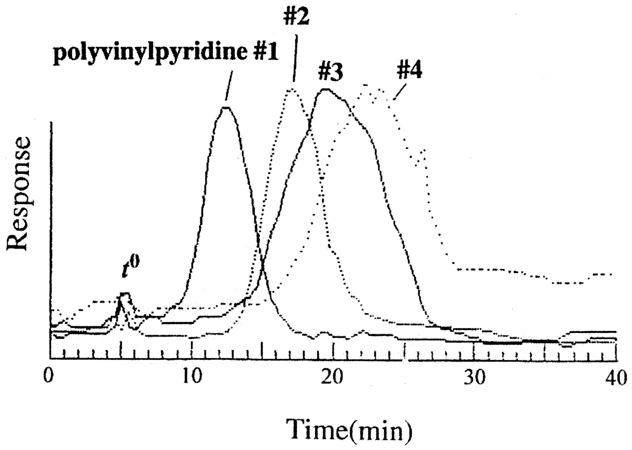

Figure 2. Fractograms of polyvinylpyridine samples in thermal field-flow fractionation. Experimental conditions: flow rate 0.1 mL/min, temperature drop 50°C, cold wall temperature 30°C, salt concentration 0.0001 M.

Most abnormalities observed in field-flow fractionation are related to the effect near the wall region. The fundamental retention equations for the field-flow fractionation did not consider any mass transfer from the channel wall.[1]

During the course of this study, as the salt concentration was increased, not only the peak shape and the retention time started to lose reproducibility, but the size of the peak also seemed to shrink slightly. It was not successful to demonstrate the existence of a maximum retention by simply increasing the salt concentration, beyond which we also expect the retention to decrease with the further increase in salt concentration. When the lithium nitrate concentration was increased to 0.01 M in the carrier, the peak areas were noticeably small, indicating sample lost due to possible adsorption on the channel wall. In a recovery test, a sample is injected at varied amounts and the peak areas are integrated and plotted against the sample amount injected to the channel. The recovery problem was noticed earlier in our cationic starch study. In this study, we estimated the peak area by weighing the paper weight of the peak cut out from the fractogram chart paper. We modified the recovery test slightly to reflect our interest in whether the peak size was affected by various experimental conditions. Figure 3 shows a test of peak area as a function of the salt concentration for sample #2. Apparently, the increase in either the salt concentration, or in the field force, had caused more polymer sample to be lost in the channel. This implies, that when the equilibrium elevation l of the polymer chains was closer to the wall, the recovery was lower. Sample loss

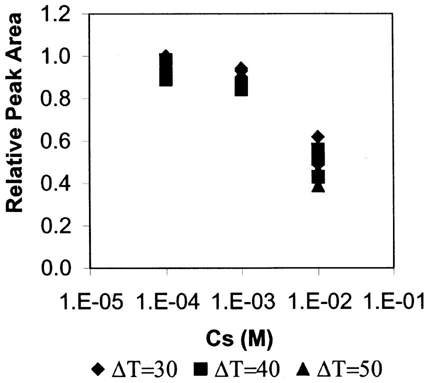

Figure 3. Peak area as a function of salt concentration in carrier for sample #2. Experimental conditions: flow rate 0.1 mL/min, temperature drop from 30 to 50°C, cold wall temperature held constant at 30°C.

appears to be an issue in the experiment, which prevented us from getting decent peaks at higher salt concentration. Future work is needed to deal with this problem.

CONCLUSION

In summary, we have proposed a mechanism based on the scaling argument for the effects of salt on the retention behavior of polymers in thermal field-flow fractionation. The hypothesis of the wall-exclusion layer has successfully provided an account for the fact that the retention increased with an increase in the salt concentration in a low salt regime.

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