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A Computational Investigation of the Critical Condition Used in the Liquid Chromatography of Polymers

Scott Orelli, Wenhua Jiang, and Yongmei Wang*

Department of Chemistry, The University of Memphis, Memphis, Tennessee 38152-3550

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ABSTRACT: The partitioning of a self-avoiding walk chain into a square channel with different surface interaction ϵ_w has been examined using lattice Monte Carlo simulation in order to have a better understanding of the critical condition used in the liquid chromatography. The partition coefficient, K, of the self-avoiding walk chain in a square channel at the critical adsorption point determined earlier was found to vary dramatically with the chain length when the channel width is comparable to or smaller than the chain sizes. As a result, the critical condition point relevant to the experiments cannot be defined as the critical adsorption point. Instead, the critical condition point, which is best defined as the point at which K varies least with the chain length, in the same spirit of experimental studies, can be identified clearly when the standard deviation of ln K, $\sigma(\ln K)$ for the given range of chain length, is plotted against the ϵ_w. The critical condition point thus found, ϵ_w^{cc}, was more attractive than the critical adsorption point in the channel. The narrower the channel is, the more attractive the surface interaction would be at the critical condition point. In a slit pore, however, the critical condition point does not shift and remains at the critical adsorption point regardless of the slit width. The phenomenon observed in the square channel is found to be consistent with earlier experimental results.

I. Introduction

The separation and characterization of polymers with complex architecture and chemical composition has led to the development of new chromatography methods such as thermal gradient interaction chromatography[1] and liquid chromatography at the limiting condition[2] or at the critical adsorption point.[1,3−6] Despite different names used in the literature, a common feature of these new chromatography methods is to find a condition called the “critical condition” where the elution time of a homopolymer becomes independent of the molecular weight. Then at this “critical condition” separation of polymers according to characteristics other than the molecular weight of the polymer or the “block” can be achieved. These new chromatography methods have found interesting applications in the separation and characterization of block polymers, ring polymers, stereoregular polymers, and so on.[3−13]

The current theoretical understanding of this critical condition is based on the Gaussian chain model,[14−16] where the excluded-volume interaction within the polymers is ignored. With this gross simplification, the understanding of the critical condition becomes relatively simple. Polymers in general will not stick to a solid surface because of the configurational entropy loss near a solid impenetrable surface. Only when there is certain attractive interaction between the monomers and the solid surface, ϵ_w, will the polymers possibly be adsorbed on the surface. Moreover, this monomeric surface interaction ϵ_w has to be large enough such that the enthalpic gain by the polymer overcomes the configurational entropy loss. For a polymer chain with no excluded-volume interaction, there is a well-defined, and chain length independent, critical adsorption point, ϵ_w^{cr}, at which polymers may approach a solid surface from the bulk solution without any penalty.[17] However, in liquid chromatography, it is not the polymer adsorption on solid surfaces from the mobile phase, but the partitioning of polymers between the mobile unconfined solution and the stationary confined pores in the column that primarily govern the elution time of polymers in the separation column.[18] The two processes, adsorption on a solid surface and partitioning between a bulk solution and a pore, nevertheless, are related to each other. According to the Gaussian chain theory, when the polymer/pore surface interaction is at the critical adsorption point, ϵ_w^{ca}, the partition coefficient $K = 1$ and is independent of the chain length.[14,16] Hence, the critical adsorption point is understood to be the critical condition in many of these liquid chromatography separations.

The presence of the excluded-volume interaction in a real polymeric chain modifies the simplicity of the above situation. First of all, the critical adsorption point of a homopolymer chain with excluded-volume interaction near a solid surface is believed to be chain length dependent, although this relationship is not well understood.[17] Nevertheless, this chain length dependence of the critical adsorption point is weak and may be ignored for a given range of the chain length, as we have shown recently through lattice Monte Carlo simulations.[19] The partitioning of a chain with the excluded-volume interaction into a slit pore at the determined critical adsorption point, however, significantly deviates from the theoretical prediction based on the Gaussian chain theory.[20,21] We have previously shown that in narrow slits the partition coefficient at the critical adsorption point, K^{cr}, is greater than one and still has a weak chain length dependence.[19] In the previous study, this chain length dependence is not very strong and is only seen in the narrowest slit examined there. We therefore concluded previously that the critical condition in the liquid chromatography was the critical adsorption point of homopolymers near the solid surface, even for the self-avoiding walks.

The pore in the liquid chromatography is probably better represented by a channel, not a slit. Compared with a slit, the confinement in a square channel is much

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Table 1. Size of Polymer Chains Studied in the Simulation[a]

N	25	50	100	200	300	400
$2R_{g0}$	5.84	8.68	13.07	19.75	24.95	29.74

[a] N is the chain length, and R_{g0} is the unconfined radius gyration of the chain in the bulk solution at infinite dilution. The error in R_{g0} is in the last digit.

stronger. In the former, the confinement is only in one direction, but in the latter the confinement is in two directions. Hence, the excluded-volume interaction in a chain can have much stronger manifestation in a channel than in a slit pore. An excellent illustration of the difference in the confinement effect on polymer chains by different pore geometries is seen in refs 22 and 23, where properties of an athermal polymer solution confined to a slit and to a channel pore are examined and compared. Here we report an examination of the partitioning of excluded-volume chains into a square channel using the same Monte Carlo method. We find striking difference in the critical condition between a slit and a channel pore. The critical condition in a channel does not correspond to the critical adsorption point in the common range of pore width utilized in the liquid chromatography. We show how one can identify the critical condition point and how this point varies with channel width. We also show clearly that only when the channel width becomes much larger will the critical condition point approach the critical adsorption point. In contrast, the critical condition point in a slit does not shift with the slit width. The difference in the two is ascribed to the difference in the geometry of the pore.

II. Simulation Method

All simulations are performed on a simple cubic lattice. The polymer chains studied are self-avoiding walks on the lattice. A square channel is represented by a tetragonal box with dimensions $(D + 1) \times (D + 1) \times L$ along the x, y, and z directions. Four solid walls located at $x = 1$, $x = D + 1$, $y = 1$, and $y = D + 1$ prohibit any occupancy of polymer beads on the walls. A reduced polymer/wall interaction, ϵ_w, is applied whenever a bead is in direct contact with the walls. No other interactions are applied. A periodic boundary condition is applied along the z direction where $L = 250a$, which is much longer than the linear dimension of the chain examined in this study, and a is the lattice unit. The chain lengths studied are $N = 25$, 50, 100, 200, 300, and 400. Their unconfined radius gyrations in the bulk solution are presented in Table 1.

The partition coefficient K is determined through the equation $-\ln K = \beta(\mu_{\mathrm{conf}} - \mu_{\mathrm{bulk}})$, where μ_{conf} and μ_{bulk} are the chemical potentials of a polymer chain in the square channel and in the bulk solution, respectively. The bulk solution is represented by a cubic lattice of size L^3 with periodic boundary conditions applied in all three directions. The chemical potential of the polymer chain is evaluated using a biased chain insertion method.[24,25] Briefly, a chain is inserted on the lattice bead by bead via a biased insertion and the Rosenbluth weighting factor, W, for the chain is determined. The chemical potential of the chain μ is related to the Rosenbluth weighting factor $\beta\mu = -\ln\langle W\rangle$.

The partition coefficient determined in theory or in simulation can be related to the retention volume of polymers V_R in the column through the following equation: $V_R = V_0 + KV_p$, where V_0 is the volume of the mobile phase and V_p is the volume of the pore region in the column. This is termed as the "quasi-equilibrium" condition, which is generally believed to be reached in the liquid chromatography separation using porous beads.[26] The elution volume of the solvent V_s in the experiment is used as a marker that defines whether the eluent is less likely or more likely to enter the pore. When $V_R < V_s$, polymers are less likely to enter the pore, which would imply $K < 1$; when $V_R > V_s$, polymers are more likely to enter the pore and $K > 1$. These correspondences between experimental observables and the theoretically determined K will be used in the discussion of our results.

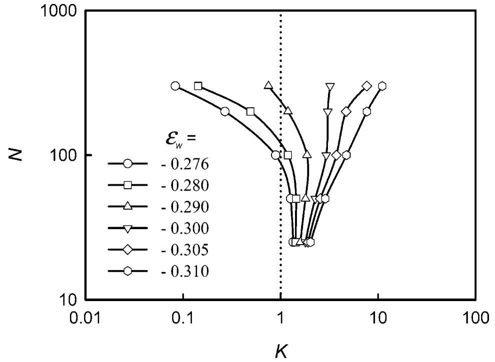

Figure 1. Variation in the partition coefficient K with the chain length N of a self-avoiding walk chain partitioning into a square channel with width $D = 10$ at different polymer/surface interaction ϵ_w.

III. Results and Discussion

The critical adsorption point of our self-avoiding walk chains near a single solid surface was determined earlier[19] to be −0.276. We will use the symbol $\epsilon_w^{ca} = -0.276$ to represent this point. Figure 1 presents the familiar plot of N vs K as used frequently in experiments of a polymer chain partitioning into a square channel of width $D = 10$ at different ϵ_w; all are more attractive than ϵ_w^{ca}. This pore width compared to the sizes of chains used here is relatively narrow, probably not a typical pore size used in experiments. These data, however, clearly illustrate the behavior of polymers in the channel pore. At $D = 10$, only chains with $N = 25$ and 50 have sizes smaller than the pore width. The vertical dotted line in the figure shows the location of $K = 1$. One immediately notes that at the critical adsorption point, ϵ_w^{ca}, K varies dramatically with N, and the overall elution in this range of chain length is mostly exclusion. Only chains with $N = 25$ and 50 have $K > 1$. All other chains with larger N are excluded from the pore ($K < 1$). Obviously, the critical adsorption point ϵ_w^{ca} in this case would not be the "critical condition" used in experiments. We also note that Figure 1 is remarkably similar to the reported experimental results (Figure 2 in ref 5). We may conclude that the same physical mechanism is responsible for the observed phenomena in simulation and in experiments.

One, therefore, wonders whether there is a "critical condition" used in experiments. If we visually examine the plot in Figure 1, we may identify that K varies least with the chain length when $\epsilon_w = -0.290$ to -0.300, and this would be the point deemed as the critical condition point in experiments. But is this critical condition well-defined? We therefore computed standard deviation in $\ln K$, $\sigma(\ln K)$, for each set of data in Figure 1. Certainly

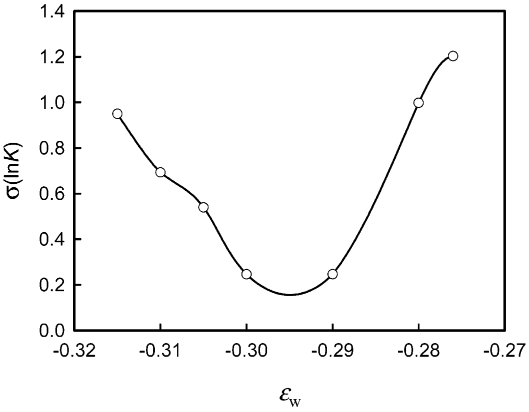

Figure 2. Plot of the standard deviation in ln K, $\sigma(\ln K)$, vs ϵ_w for the data sets presented in Figure 1. The chain length used in computing $\sigma(\ln K)$ was from $N = 25$ to $N = 400$.

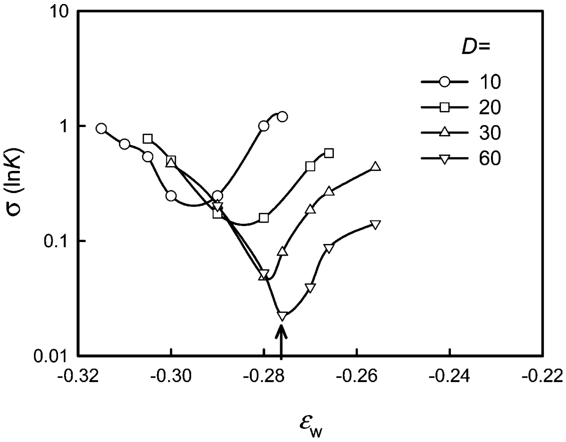

Figure 3. Plot of $\sigma(\ln K)$ vs ϵ_w for a self-avoiding walk chain partitioning into a square channel with different width D. The arrow in the plot indicates the location of the critical adsorption point, $\epsilon_w{}^{ca} = -0.276$. The ratio of the slit width D indicated in the figure over the largest R_{g0} of the chain examined are 0.674, 1.34, 2.02, and 4.03.

the computed standard deviation will depend on the range of chain length examined, but the latter will be fixed in our analysis. Figure 2 presents the plot of $\sigma(\ln K)$ as a function of ϵ_w for the data sets presented in Figure 1. The plot has a well-defined minimum at $\epsilon_w \cong -0.295$, which could be associated with the "critical condition" point in experiments, since this would also be the point at which there is a least variation of the partition coefficient due to the changes in the molecular weight of polymers. We note that if we use the standard deviation in K instead of ln K, the plot does not yield a well-defined minimum, especially at ϵ_w far away from the critical condition. We will refer to this point as the "critical condition" point. Note the point at which $\sigma(\ln K)$ reaches the minimum is equivalent to the location of the condition at which the partition coefficients form a straight line vertical to the K-axis in Figure 1. If a true vertical line is obtained, then $\sigma(\ln K) = 0$. This operational location of the critical condition is most appropriate and is in line with the experimental location of the critical condition.

Figure 3 presents $\sigma(\ln K)$ vs ϵ_w in a channel with different widths. At each channel width, there is a well-defined minimum in $\sigma(\ln K)$ vs ϵ_w, and the minimum shifts to the right and approaches $\epsilon_w{}^{ca}$ as D increases. Also, the minimum $\sigma(\ln K)$ decreases as D increases. We located the critical condition point approximately from the plots in Figure 3 and designated these points as $\epsilon_w{}^{cc}$, bearing in mind that $\epsilon_w{}^{cc}$ varies with D. Figure 4 presents how the critical condition point, $\epsilon_w{}^{cc}$, and the average partition coefficient at $\epsilon_w{}^{cc}$, noted as K^{cc}, varies with the slit width D. K^{cc} varies approximately as $1/D$ at small D and approaches unity at large D. The critical condition point $\epsilon_w{}^{cc}$ decreases (becomes more attractive) with the decrease in D and approaches the critical adsorption point $\epsilon_w{}^{ca}$ above a single solid wall at large D.

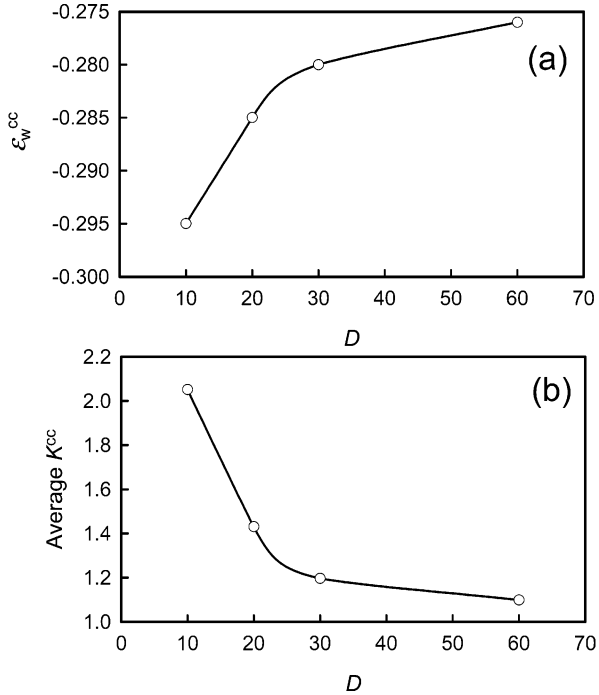

Figure 4. Variation of critical condition point $\epsilon_w{}^{cc}$ (panel a) and the average partition coefficient at the critical condition K^{cc} (panel b) as a function of channel width D.

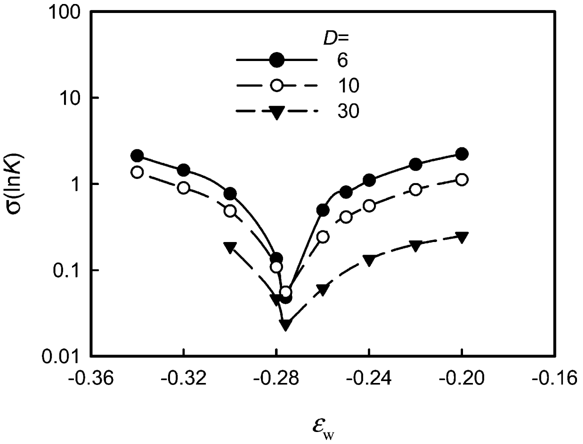

Figure 5. Plot of standard deviation $\sigma(\ln K)$ vs ϵ_w for a self-avoiding walk chain partitioning into a slit with different width D. The chain length used in computing $\sigma(\ln K)$ was from $N = 25$ to $N = 200$.

These results appeared to be different from what we obtained earlier for the partitioning of a self-avoiding walk chains into a slit (a confined space between two solid walls).[19] Hence, we reexamined the earlier results. Figure 5 presents the $\sigma(\ln K)$ vs ϵ_w for a self-avoiding walk chain partitioning into a slit with different width D. From $D = 6$ to $D = 30$, the minimum did not shift in the x axis and was at the critical adsorption point, $\epsilon_w{}^{ca} = -0.276$. The range of chain length examined in

Figure 5 ($N = 25-200$) is slightly smaller than in the channel pore ($N = 25-400$); however, the qualitative difference seen between Figure 5 and Figure 3 is not affected even after we corrected the difference in the chain length examined.

This comparison between the results in a slit pore and in a channel therefore suggests that the shift in the critical condition is likely a result of difference in the geometry of the pore. The interaction parameter, ϵ_w, used in the simulation characterizes the local interaction between polymer repeating units with the surface site of the pore. This parameter depends on many factors, such as the solvent strength, surface moiety of the pore, and chemical nature of the polymers. However, it is a short-ranged interaction, and it does not depend on the geometry of the pore surface. When the pore geometry changes from the planar surface to square channel, this local interaction parameter would not be expected to change if the chemical nature of the system remains the same. Hence, the intrinsic interactions between polymer beads and the surface of the pores, whether in the slit or in the square channel, are the same at the same ϵ_w in the simulation. The shift in the defined "critical condition" is not due to the intrinsic difference in the surface interaction of the pores with the polymer beads but is due to the difference in how a polymer chain interacts with a confining pore over a long-range scale.

A slit is a two-dimensional confining pore whereas a channel is a one-dimensional confining pore. Our results suggest that in a two-dimensional confining pore the critical condition, defined as the point at which K varies least with the chain length, is still at the critical adsorption point. However, in a one-dimensional confining pore, the critical condition shifts with the pore width and continually increases (becomes more attractive) as the pore width narrows. This qualitative difference is conceivable. Adsorption of a chain on a solid surface involves a change in the chain conformation from a three-dimensional state to a quasi-two-dimensional state. Adsorption in a slit still involves a similar change from a three-dimensional state to a two-dimensional state. Adsorption into a channel pore, however, involves a conformational change from a three-dimensional state to a one-dimensional state. The critical adsorption point is defined as the point at which the enthalpic interaction somehow compensates the entropic conformational loss during the adsorption. So in a slit, this critical point did not shift because a similar conformational entropy loss is encountered. But in a channel, this critical point shifts because now the entropic conformational loss is significantly different from that of the adsorption on a solid surface.

We have also examined the density profiles of the chain inside the pore. The density profiles would generally have two distinct features: a smiling face signifies that there is an accumulation of polymer beads near the surfaces, and a crying face signifies that there is a depletion of polymer beads near the surfaces. At the critical condition point, whether in a slit or in the square channel, the density profiles exhibit the smiling faces. Before reaching the critical condition point, the density profiles can be smiling face or crying face depending on the chain length and pore width. Currently it is not clear to us when the density profiles switch from the crying face to the smiling face. But apparently the point at which the density profiles switches between the two features is not unique and probably is not a good indicator for the critical condition. More investigations into this issue are planned in the future.

The next question is then which case is more relevant to the experimental studies? Is the channel more relevant or the slit pore? We note that the pore size used in liquid chromatography experiments is typically around $1.0R_g-2R_g$ of the average polymer size being analyzed. The range of D examined in our simulation study covers this range. In the case of channel, the largest width $D = 60$ is about $4R_g$ of the longest chain examined; it is therefore at the large end of pore size used in experiments. If the channel pore is more relevant to the experimental studies, then the effect we see in the channel should be observable in experimental studies. A test of these effects can be made if one determines the critical condition for the same polymer sample with the same solvent but in a column with different pore sizes. Berek et al.[27] have investigated the effect of pore size on the critical condition point. Their results are in qualitative agreement with the phenomenon observed in the square channel. In a column with smaller pore size, the critical condition identified in experiments had a solvent composition with a larger percent of the component that promotes adsorption of polymers to the pore surfaces. This means there is a stronger attraction between polymer units and the surface, which, translated in the simulation, is a more negative ϵ_w between the polymer bead and the surface site. The quantitative confirmation of the pore size dependence of the critical condition may be difficult in experiments because as the column changes from smaller pores to larger pores, the pore surface unfortunately changes unavoidably. It is then not all clear whether the change in the critical condition point is due to the physical change of the pore size or due to the change in the surface property of the pore. Experimental studies suggested that columns with smaller pores were not suitable for LCCC. The critical condition could not be located easily in the latter case, and the polymer recovery can be very poor near the critical condition.

Finally, we would like to further emphasize that the critical condition point does not correspond to the point at which $K = 1$. Several computational studies have defined the critical point as the point at which $K = 1$.[20,28,29] The point at which $K = 1$ may be termed as the "compensation point" where the exclusion and adsorption compensate with each other. But this compensation would require different polymer/surface interaction for different chain length in a given pore width, as can be seen from Figure 1. The same is also seen in the case of a slit channel.[19] When a self-avoiding walk chain is confined into a pore, there is a strong exclusion due to the restriction of the polymer conformation by the pore walls and the excluded-volume interaction within the confined chain. The narrower the pore is or the longer the chain is, the stronger the excluded-volume interaction within the confined chain. Consequently, it needs a stronger enthalpic interaction to overcome the exclusion by the walls and the excluded-volume interaction within the confined chain. This leads to a strong dependence of the compensation point on the chain length and pore width. Clearly this compensation point is not the critical condition used in experiments and probably has little relevance to the critical condition used in experiments. Our studies in the channel pore and in the slit pore both suggest that at the critical condition, the partition coefficient $K > 1$, the chains are in the adsorbed states. Experimental results also suggest this; i.e., the elution volume of the polymers is larger than the elution volume of the solvent.[5]

IV. Concluding Remarks

Our current study shows that the critical condition utilized in the experiment may not correspond to the critical adsorption point of a polymer above solid surfaces if the pore is channel-like. In a narrow channel pore, the partition coefficient can vary dramatically with the chain length when the polymer/surface interaction is at the critical adsorption point. Chains with sizes larger than the pore sizes are strongly excluded from the channel pore at the critical adsorption point. This phenomenon has actually been pointed out in experiments by Berek and was named as "enthalpy-assisted size exclusion chromatography".[30]

Since in experiments the critical condition is often determined as the point at which the retention volume of a polymer may become independent of the molecular weight, we propose to use the plot of standard deviation in ln K vs the surface interaction as a mean to locate the critical condition point. This critical condition point can be found as the minimum in the plot of $\sigma(\ln K)$ vs ϵ_w. In a channel pore, the critical condition point thus found, ϵ_w^{cc}, is found to increase (becomes more attractive) when the channel width D decreases. Only in the channel with large width D, ϵ_w^{cc} approaches the critical adsorption point. However, the shift in the critical condition is not observed in the case of a slit pore. In the latter case, the plot of $\sigma(\ln K)$ vs ϵ_w shows a minimum at the critical adsorption point regardless of the slit width D. The observed shift in the critical condition in a channel is large enough and should be observable if the pore is channel-like in real chromatography columns. Earlier experimental results are in agreement with the phenomenon observed in the square channel.[27]

Many experimental studies reported cases where a complete independence of the retention volume on the polymer molecular weight could not be found.[5,12] Our studies show that such findings may not be due to the unknown complications in experiments, but due to the nature of the excluded-volume interaction in a real polymer chain. Whether in a channel pore or in a slit pore, the partition coefficient will have some dependence on the molecular weight at the critical condition. The variation in the partition coefficient with the molecular weight gets smaller when the pore is larger. When there is a distribution of the pore size, further complications can occur. Polymers with high molecular weights may be excluded from the small pores while polymers with low molecular weights may be already adsorbed in the large pore. It will be more difficult to reach the "critical condition" desired in experiments under such circumstances. Our suggestion to the experimentalists based on our studies is to use large pores with more uniform size distribution whenever possible. Again experimental results already seem to suggest this principle.[27] LCCC could not be performed successfully in columns with smaller pores.

On the other hand, there are definitely other complications that could exist in real experiments that can lead to more complicated elution behavior. For example, Berek et al.[31] have observed "S" turn type of elution behavior in the plot of molecular weight vs elution volume. Our simulation results have only so far showed the existence of the "U" turn, but not the "S" turn. Within the current simulation model where polymers interact uniformly with the pore surface, the "S" turn will not exist. However, Berek et al.[31] have suggested a possible mechanism that could account for the observed "S" turn. The surfaces of the pore have two randomly distributed sites. The two sites have different interaction energies with polymer beads. They suggested that when the polymer chain gets longer, it could interact with the "minority" surface sites that have stronger attraction toward the polymer beads. A short polymer chain however cannot bridge over these minority sites, and hence it feels less enthalpic attraction. Simulations that will investigate the proposed mechanism on the elution behavior of polymer chains are under way.

Our results also point out the inadequacy to use the Gaussian chain model to study the critical condition in liquid chromatography of polymers.[14−16] The excluded-volume interaction ignored in the Gaussian chain model is very important to the exact location of the critical condition and to the partitioning rule of the chain at the critical condition. More Monte Carlo simulations with the excluded-volume chain are needed to examine the partitioning of block, star, and ring polymers near the critical condition. One may argue that in real experiments polymer chains are often in a Θ solvent or even a bad solvent where the excluded-volume interaction is less significant, and hence the use of the Gaussian chain may be justified. This argument is in fact inappropriate. A Gaussian chain is not equivalent to a polymer chain in a Θ solvent. In a Θ solvent, the second virial coefficient is zero, but higher order terms of interactions are still there and they cannot be ignored. We will present in the future that similar type of shift in the critical condition point in the square channel is also observed in the Θ solvent as well.

Currently we have only examined the elution behavior of a single polymer chain between the bulk and the pore. Our studies would be relevant to experiments where the concentration of polymer solutions employed are very dilute, much lower than the overlap concentration. The interaction between chains can then be ignored. If the initial concentration of polymer solutions employed is very dilute, then the polymer concentration in the pore will also be dilute as long as K is not orders of magnitude greater than unity. The consideration of interactions between polymer chains would be important, and we plan to examine the partitioning of chains at finite concentrations in the future.

These results also call for the development of a better theory, especially the scaling theory that can account for the observed phenomena. A good theory should be able to explain why the compensation point (defined as the point $K = 1$) is different for different chain length; why there is a minimum in the plot of $\sigma(\ln K)$ vs ϵ_w and what is the expected scaling dependence on ϵ_w near the critical condition point; why the critical condition point should shift in the one-dimensional channel-like pore whereas the critical condition point do not shift in two-dimensional slit pore.

The striking difference of the critical condition point in a slit from that in a channel also implies some interesting applications. One may use the shift in the critical condition as a mean to detect whether the pore is a one-dimensional channel-like or a two-dimensional slit-like pore. If the pore is known to be a one-dimensional channel-like pore, perhaps this can also be used to determine the average pore size. We also envision that some of the critical behavior, such as phase separation, or polymer coil-to-globular transition, may exhibit different behavior in different pore geometry. For example, the condition for the polymer coil collapse in a pore might be very different from that in the bulk and may be strongly dependent on the pore geometry.

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