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Theory and Principles of Interaction Chromatography

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Abstract: This chapter discuss theories that can help in understanding the separation of macromolecules in interaction chromatography. Beginning with an overview of the general framework of theories that can explain the separation mechanism in liquid chromatography, the author then focuses on computational studies that examine several applications of interaction chromatography to analyze block copolymers and ring polymers. The results are presented to illustrate the principles behind interaction chromatography, especially the liquid chromatography at the critical condition (LCCC).

Introduction

The terminology Interaction Chromatography (IC) used here refers collectively to a suite of polymer liquid chromatography methods operating in modes where polymer samples experience enthalpic adsorption interactions with the porous substrate in addition to entropic exclusion interactions. This is in contrast to Size Exclusion Chromatography (SEC) where polymer chains are presumed to only experience entropic exclusion from the porous substrate. IC includes Liquid Chromatography at the Critical Condition (LCCC)¹⁻⁵, thermal-

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gradient interaction chromatography (TGIC)^{6,7}, and gradient liquid adsorption chromatography.⁸⁻¹⁰ The development and applications of IC in the analysis of polymer samples containing heterogenous species have been discussed by several reviews.^{7,11-16} Here we will discuss theories and principles behind the IC separation in a historical context.

The starting point to understand the separation in polymer liquid chromatography is the relationship between the retention volume of polymer samples V_R with the partition coefficient K of polymer chains between the mobile phase and stationary phase, $V_R = V_0 + KV_p$, where V_0 is the volume of the mobile phase and V_p is the volume of the stationary phase (i.e., the porous regions). This relationship was proposed by Casassa¹⁷ under the quasichemical equilibrium assumption in the context of discussing Size Exclusion Chromatography also known as Gel Permeation Chromatography (GPC). In the case of Size Exclusion Chromatography, V_0 represents the volume of the “mobile phase” outside the porous beads of the packing materials and V_p represents the volume of the pores inside the porous beads. The partition of polymers between the two phases, characterized by partition coefficient K , determines the retention volumes of the polymers, with the implication that polymer solutes move through the column with the mobile phase outside the porous beads but are retained within the porous regions. V_0 could be determined as the exclusion limit using large solutes (polymers with high molecular weight). Solvent elution volume is related to $V_0 + V_p$, also referred as void volume since one might assume solvent molecules can penetrate the pores with partition coefficient $K=1$. This same relationship however could also be extended to the Interaction Chromatography (IC), although the exact values for V_0 and V_p might vary at different chromatography conditions.

Theory for SEC

With the above relationship established, one may pursue calculation of partition coefficients K for polymers between stationary phases and mobile phases to gain an insight about retention behavior of polymers in chromatography. An important consideration for the stationary phase is the nanoscale pore confinement exerted on polymer chains while the mobile phase is considered as an unrestricted dilute polymer solution. Casassa was the first to use the Gaussian chain model for polymer chains and computed the partition coefficient K for such chains partitioning into a slit pore and a cylindrical pore. The Gaussian chain model is a mathematical treatment of polymer chain configurations, where the end-to-end vector for a polymer chain \mathbf{r} is assumed to follow a Gaussian function. The distribution function $P_N(\mathbf{r})$ for a polymer chain with N -link that has end-to-end vector \mathbf{r} satisfy the following differential equation:

$$\nabla^2 P_N(\mathbf{r}) - \frac{6}{b^2} \frac{\partial P_N}{\partial N} = 0 \quad (1)$$

For a polymer chain in unconfined bulk solution, the solution to the above differential equation is a Gaussian function, $P_N(\mathbf{r}) = (2\sqrt{\pi}R)^{-3} \exp\left[-\left(\frac{\mathbf{r}}{2R}\right)^2\right]$, where $R = (Nb^2/6)^{1/2}$. The distribution function can also be written as a product of three Gaussian distribution functions for the three components, x , y and z respectively. For a chain inside a slit pore with width D , the solution needs to satisfy the boundary condition that $P_N(\mathbf{r}) = 0$ at the surface. Solutions to the above differential equation have been studied in mathematics for heat conduction problems. Therefore, one can draw on this knowledge to understand how the partition coefficient K varies with polymer molecular weight and the pore size. Important knowledge gained from these considerations is that K depends on the R/D , where R is the radius of gyration of a linear polymer chain, which is a characteristic measure of the size of polymer chains. Hence the theory supports the notion that polymer chains are separated according to size in SEC.

Theory for Interaction Chromatography (IC)

The principle of Interaction Chromatography is closely related to how a polymer chain might be adsorbed on a solid substrate. Polymer adsorption on solid substrates was an old topic in polymer science and was investigated by many approaches¹⁸. It has long been recognized that when a long flexible polymer chain is brought near a surface, there is an associated loss of entropy. This loss of entropy therefore restricts the polymer chain approaching the wall. The same mechanism restricts the polymer chain entering the pore in SEC. If the polymer repeating unit has an enthalpic gain when touching the solid wall, then this enthalpic gain can compensate for the entropy loss and leads to adsorption. One characteristic associated with this transition is how the density profiles of the polymer chain near the surface varies with the distance away from the surface. When there is no enthalpic adsorption, the density profile is depleted near the wall. On the other hand, when there is enthalpic adsorption, there is an excess polymer density built-up near the surface. Let's define ϵ_w to denote the interaction strength of the polymer repeating unit with the wall. Then $\epsilon_w = 0$ corresponds to the condition of SEC. However, the transition from forming a depletion layer near the wall to forming an excess density layer near the wall occurs at a critical interaction strength, $|\epsilon_w(CC)|$ (see Figure 1 for an illustrative drawing). One may intuitively expect this critical interaction strength should depend on chain length N , as shorter chains experience less conformational entropy loss than longer chains. However, $|\epsilon_w(CC)|$ quickly reach another critical value, commonly denoted as the Critical Adsorption Point (CAP) as chain length N increases. The CAP is normally defined as the adsorption transition point at the infinite chain length limit.

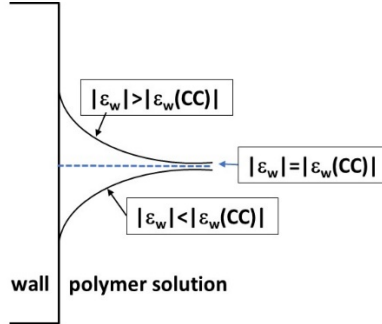


Figure 1: Illustrative drawing to show polymer density profiles near a wall at three different interaction conditions.

The earliest theoretical work that aims to elucidate Interaction Chromatography is by a Russian group, mainly by Skvortsov and Gorbunov.^{19,20} They have used the same Gaussian chain model as Casassa, but incorporated different boundary conditions. Instead of having $P_N(\mathbf{r}) = 0$ near the surface for SEC, the boundary condition changes to

$$\frac{1}{P_N} \frac{\partial P_N}{\partial z} \Big|_s = -c \quad (2)$$

where the parameter c could be positive, negative or zero. It was recognized that CAP discussed above corresponds to the condition $c=0$. At the CAP, the density profile near the wall will be flat, neither depleted nor enhanced. Solutions for $P_N(\mathbf{r})$ at different values of c are available, but the frequently used solution is an approximate solution valid at wide pore limit,

$$K = 1 + \frac{2R}{D} \left[\frac{(\exp((cR)^2)[1 - \operatorname{erf}(-cR)] - 1)}{cR} - \frac{2}{\sqrt{\pi}} \right] \quad (3)$$

where the $\operatorname{erf}(x)$ is the error function defined as $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-t^2) dt$. The above solution predicts that at the CAP, $K=1$ regardless of the pore size D and chain length N . In the adsorption regime, however, $K>1$ and increases nearly exponentially with the chain length. In the SEC regime, $K<1$ and K decreases with chain length N . The theoretical framework provided by Skvortsov and Gorbunov has been very useful to predict and understand the Interaction Chromatography. These two investigators have worked with different experimentalists and have published many insightful joint theoretical and experimental articles^{4,21-23}

Another slightly different theoretical framework that essentially produced the same results uses a lattice model of random walks to represent polymer chains.

This was done by Guttman et al²⁴ using a matrix generation method. For the lattice based chain model, the value of CAP is known and is given by a simple expression, $\varepsilon_w(\text{CAP}) = \ln(Z - \lambda_1/Z)$ where Z is the lattice coordination number and λ_1 is the number of steps forbidden due to the presence of the wall and, here, the value of ε_w is reduced by the thermal energy $k_B T$. For a Random Walk (RW) chain on simple cubic lattice with a solid wall, $\varepsilon_w(\text{CAP}) = -0.182$. Both the continuum Gaussian chain model and lattice based random walk models give similar results. They both affirm that at the CAP, $K=1$ and is independent of chain length and pore size.

Computer Simulations of Interaction Chromatography

Computer simulations of polymers partitioning into pores can provide direct and insightful results, circumventing cumbersome mathematical equations that are often difficult to understand. The earliest computer simulation that examined Interaction Chromatography is by Cifra and Bleha.²⁵ These two investigators used a straightforward Monte Carlo simulation approach, a lattice based simulation in a box that contained two connected regions, one region representing a confined slit pore having two interactive surfaces and the other region having periodic boundary conditions hence mimicking an unconfined bulk solution (twinbox method). Regular Monte Carlo moves governed by the Metropolis rule are used to equilibrate polymer chains between the two boxes. These authors used Self-Avoiding Walks (SAW) to represent the polymer chains, since SAW are more frequently used in computer simulations. Monte Carlo simulations provided equilibrium density profiles inside and outside the pores and the partition coefficient K is thus obtained from the average polymer densities determined. This Monte Carlo approach was first used by Wang and Teraoka²⁶ for the study of partitioning of non-dilute polymer solutions into pores. Cifra and Bleha introduced a segment/surface interaction ε_w in their simulations, and, by varying this segment/surface interaction ε_w , they investigated the transition from SEC to LAC. Perhaps because the earlier theoretical works predicted that $K=1$ is the condition for LCCC, these two authors tried to locate the transition point defined by $K=1$ condition. They found that for a fixed chain length $N=100$ at several pore widths D , the transition point at $K=1$ coincided at the same segment/surface interaction ε_w value. This crossing point was then identified as the Critical Point. However, they further showed that, at this transition point $\varepsilon_w(\text{CC})$, K for other chain lengths does not exactly equal one.

After hearing the interesting talk presented by Cifra about LCCC, Wang got intrigued about this transition. She and her students decided to consider this LCCC chromatography further using computer simulation. Since liquid chromatography operates at dilute polymer solution, the Monte Carlo simulation method used

earlier for the study polymer partitioning into pores for non-dilute polymer solution is not a convenient approach. Hence, Wang implemented a biased chain insertion method that allowed for the determination of the excess chemical potential of a single polymer chain in the pore and in the bulk solution. Using this approach, she and her students were able to obtain the partition coefficient K at the dilute solution limit (K_0 would be a better symbol to use) for different chain lengths and slit widths at different surface/segment interaction. Wang et al²⁷ investigated the transition from SEC to LAC by using both the Random Walk (RW) model and the SAW model. The use of RW model simplifies the discussion significantly since the numerical value of CAP for RW is known precisely for RW on simple cubic lattice. Wang et al found that indeed if one uses RW model for polymer chain, K_0 is nearly independent of chain length at the CAP and is very close to one. With the SAW model, however, K_0 has a non-linear dependence on chain length. One phenomenon revealed by their simulation studies with SAW is that the transition point defined by $K=1$ does not occur at the same segment/surface interaction for different chain lengths. Shorter chains crossover from $K<1$ to $K>1$ at smaller segment/surface interaction $|\epsilon_w|$ than longer chains. Nevertheless, one can still try to identify the “co-elution” point, equivalent to the experimental location of LCCC condition, as the point where K has the least dependence on chain length for a given range of chain length. Wang et al found that this co-elution point coincides to the Critical Adsorption Points defined in the infinite chain length limit.²⁸ Hence, their simulation studies using SAW model chains affirm earlier theoretical discussion that LCCC chromatography condition occurs at the CAP of a polymer chain. The only small caveat to be noted here is that K does not equal exactly one at the LCCC. Hence, one should not determine the theoretical critical point relevant to LCCC chromatography by looking at the point defined by $K=1$. Instead, one should try to determine the critical point following the method suggested by Wang et al,²⁹ the point at which K has the least dependence on chain length.

Does the CAP point shift with pore size?

After establishing the link between LCCC condition and CAP, one might ask a few questions regarding the nature of CAP. One question is whether the CAP for a given polymer/surface substrate would depend on pore size? This question was discussed by several theoretical studies outside the chromatography communities.³⁰⁻³³ Wang et al investigated this problem via computer simulations for RW model and SAW model. Their earlier study in 2004 reported a shift of CAP for the SAW chains toward stronger segment/surface interaction as pore size decreases if a pore was modeled as square channel, but no shift was observed if pore was modeled as a slit pore.²⁹ However, that study overlooked a small effect: polymer segments near the edge of a square channel interacts with two surface

sites rather than one surface site. The observed shift in CAP as the pore size of a square channel decreases is not entirely due to the geometrical effect. Later they re-examined this problem and took care of the edge effect.³⁰ They showed that for RW chain model, the CAP does not shift as the pore size of a square channel decreases after the edge effect is properly taken care of, but for SAW chain model, the CAP shifts toward stronger segment/surface interaction as the size of square channel pore decreases.

Experimental measurements of the potential shift in CAP could be performed by determining the LCCC condition for a given polymer system with chromatography columns packed with similar porous materials but with different pore sizes. Adbulahad and Ryu³⁴ performed such experiments using polystyrene standards and C18-bonded silica columns. The eluent used was fixed, a mixture of methylene chloride (MC) and acetonitrile (ACN), (MC/CAN=57/43, v/v%). The C18-bonded silica beads used have different average pore sizes (diameter =50Å, 100 Å, 120 Å and 300 Å). They determined LCCC conditions for polystyrene standards by varying the column temperature. The temperature at LCCC condition, T_{LCCC} was seen to decrease as pore size decreases, indicating a shift toward stronger segment/wall interaction. This trend of change agrees with the predictions by Wang group. However, experimental data on the dependence of T_{LCCC} on pore size could be subject to other unwanted factors, for example, the chemistry of the pore surfaces may not be exactly the same between C18-bonded silica beads with different average pore sizes. In fact, a closer examination of reported T_{LCCC} for polystyrene standards with the same fixed eluent in C18-bonded columns with different pore sizes sometimes exhibited a trend not meeting the expected change.²²

How does “chromatographically invisible blocks” impact the elution of visible blocks?

One interesting application of LCCC method is to mask the contribution of one block, making it chromatographically invisible, and thereby enabling the analysis of molecular weight of other blocks in block copolymers. Here “the invisible block” refer to the block that is at the LCCC condition established by its parent homopolymer. For example, if one wants to analyze the molecular weight distributions of polystyrene-*block*-polybutadiene (PS-*b*-PB) in terms of their respective blocks, the idea is that one elutes this block copolymer at the LCCC condition of polystyrene. Then the PS block is said to be the “invisible block” and the PB is the visible block. Earlier theoretical discussions suggested that partition coefficients of block copolymers should be controlled only by the visible A blocks for AB diblock, BAB triblock copolymers, star- A_mB_n with m -arms of A, n -arms of B or branched AB copolymers as long as the visible A blocks are not interposed

by the invisible B blocks. Wang et al³⁵⁻³⁷ examined this hypothesis carefully via computer simulations in collaboration with the experimental group led by Chang. It was found that if the visible A block is eluted in SEC mode, then the invisible B block will increase the retention of AB copolymers. The longer the invisible B block length, the larger the increase of retention. On the other hand, if the A block is eluted in the LAC mode, then the invisible B blocks will instead reduce the retention time.³⁸ Figure 2 presents an example for A-graft-B copolymer where the backbone A block is set as the visible block, and grafted B blocks are the invisible blocks. As the number of “grafted” B branches increases, the influence of B blocks on A-g-B retention increases, but they exert opposite effects on the elution when A is in SEC mode versus when A is in LAC mode. These effects are observed in actual experiments. These results should also warn the experimentalists that there might be inherent errors introduced when analyzing the molecular weight of individual blocks using LCCC method. Alternative ways to estimate molecular weight of individual blocks should be employed to verify the results.

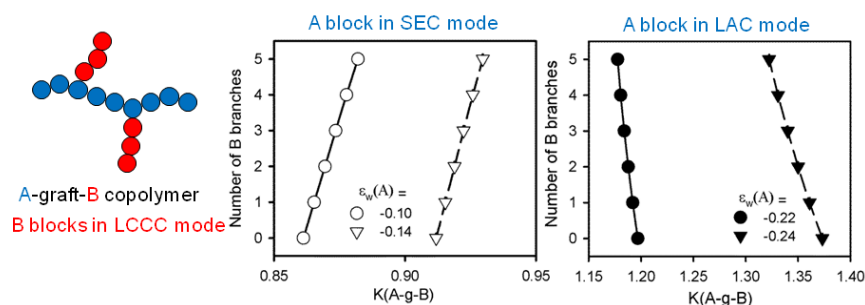


Figure 2: Impact of invisible “B” branches on the elution of A-g-B copolymer where the backbone A can be either eluted in (a) SEC mode or (b) in LAC mode. Simulation data were obtained using RW model on simple cubic lattice. Figure is reprinted from Ref³⁸, with permission from Elsevier, Copyright(2015).

How does the CAP for ring polymers compare with the CAP for linear polymers?

Ring polymers constitute another distinct class of polymers with special architecture. If one compares a polymer chain with the same number of repeating units, but one in linear chain form and the other in ring form, the number of allowed conformations of ring polymer is less than the linear chain because of the connection of the two ends. One may imagine that when ring polymer is brought near the wall, the associated loss of conformational entropy will be less than the linear chain. Hence the transition crossing over from $K < 1$ to $K > 1$ would occur at

smaller $|\varepsilon_w(\text{CC})|$ for a ring than for a linear chain. What this also means is that at a given chromatography condition rings are retained longer than linear chains since $K_{\text{ring}} > K_{\text{linear}}$. In fact, Chang's group in collaboration with Gorbunov has shown that rings are eluted after the linear polymers peak and is in the LAC mode if the linear polymers are eluted in LCCC mode.²²

If one has a set of ring polymers with different molecular weights, one could determine the coelution point of these ring polymers and denote that as the CAP for the ring polymers. How would the temperature at the coelution point for ring polymers, $T_{\text{LCCC}}(\text{ring})$ compares with temperature at the coelution point for the linear polymers, $T_{\text{LCCC}}(\text{linear})$? This comparison can be accurately done experimentally since one could search for the T_{LCCC} for ring polymer samples and linear polymer samples on the same chromatography column and the same eluent. The only caveat that might cause complexity is the end groups in the linear chain precursor might interact differently from the rest of monomer units along the chain. Assuming there is no such complexity, how would $T_{\text{LCCC}}(\text{ring})$ compare with $T_{\text{LCCC}}(\text{linear})$? Recently, Wang's group in collaboration with Chang's group investigated this problem both computationally and experimentally³⁹. In order to get accurate partition coefficient K for ring polymer, Wang group resorted back to the use of the twinbox simulation method, but implemented the Histogram Reweighting method, a relatively new Monte Carlo technique that allows for best use of statistical information obtained at different runs. They showed computationally that the co-elution point for ring polymers occurred at $|\varepsilon_w(\text{CAP}, \text{ring})|$ lower than co-elution point for linear polymers, $|\varepsilon_w(\text{CAP}, \text{linear})|$. Since in computational studies, ε_w is reduced by thermal energy. This implies at $T_{\text{LCC}}(\text{ring})$ should be higher than $T_{\text{LCCC}}(\text{linear})$. This is indeed observed in experiments. When the chromatography condition is set at $T_{\text{LCC}}(\text{ring})$, linear chain is eluted before ring and is in SEC mode. When the chromatography condition is set at $T_{\text{LCC}}(\text{linear})$, then ring polymers are eluted after the linear chains and are in LAC mode. The results are summarized in Figure 3.

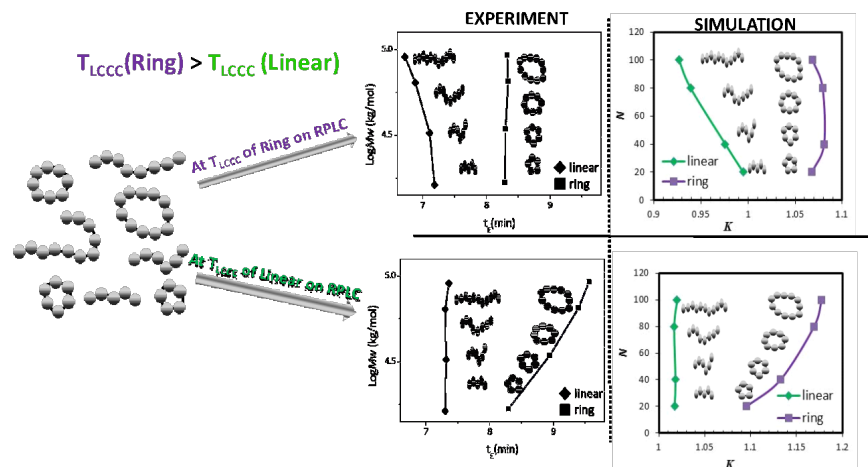


Figure 3: Comparison of retention of ring polystyrene with linear polystyrene samples in liquid chromatography column packed with C18 bonded silica surface. Figure is adapted with permission from ref³⁹ Copyright 2016 American Chemical Society.

Conclusion

A proper appreciation and understanding of Interaction Chromatography (IC) requires some fundamental knowledge on polymer adsorption. We have shown how knowledge gained long ago from the study of polymer adsorption on solid substrates helped the development of IC. The unique co-elution mode in LCCC is linked with the Critical Adsorption Point (CAP) known to exist in the discussion of polymer adsorption. Computer simulations that allow for flexibility to vary chain model, from RW model that does not account for excluded volume interaction to SAW model that accounts for excluded volume interaction, have been used by the author and her group to address multiple problems encountered in actual experiments. The simulations reveal interesting phenomena existed in LCCC experiments and help elucidate the true mechanism behind the observed phenomena.

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