Hindered Diffusion of Linear Polyelectrolytes

by

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Submitted to the Department of Chemical Engineering
in January 7, 1991 in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy in Chemical Engineering

Abstract

The diffusion of linear polyelectrolytes through porous media was studied theoretically and experimentally. We developed a model for predicting the equilibrium partitioning of polymers between a pore space and an adjoining bulk solution. The partition coefficient, defined as the equilibrium pore-to-bulk solution concentration ratio, quantifies this phenomenon. The partitioning model was combined with existing hydrodynamic results for porous membranes to predict the ratio D/D_∞ , where D is the effective transmembrane diffusion coefficient and D_∞ is the bulk solution diffusion coefficient. Experiments were conducted to measure D/D_∞ as well as to characterize all the size and charge parameters required as inputs to the model, allowing comparison of predicted and measured results.

For the partitioning model, the polymer chain was represented as a freely-joined chain consisting of N segments of fixed length. For $N >> 1$, a "diffusion equation" can be used to describe the statistics of the chain configurations, based on the analogy between the configuration of a freely-jointed polymer chain and the path traced by a Brownian particle undergoing a random walk. The diffusion equation approach developed by Casassa [32] was extended here to include the effects of long-range polymer-pore interactions. This method provides an efficient means for computing partition coefficients when long-range polymer-pore potentials are present, but when excluded volume effects are neglected. Results were obtained for square-well potentials, electrostatic double-layer potentials, and van der Waals potentials. Our results indicate that electrostatic repulsions and attractions can significantly affect partitioning. As seen most clearly with the square-well potentials, the important factor governing partitioning is how far-ranging the interaction is from the pore walls. The diffusion equation was also used to predict critical points for adsorption of polymer to surfaces for attractive square-well and electrostatic potentials. This analysis predicts that a transition from free to weakly adsorbed polymer occurs when the partition coefficient is approximately unity.

We have measured hindered and bulk-solution diffusion coefficients for anionic polymers in Nuclepore track-etch polycarbonate membranes, which carry a negative charge. Most experiments employed polystyrene sulfonate (PSS) as the diffusing polyanion. Various combinations of polymer and pore size were examined, and ionic strength was varied from 0.005 to 3.1 M by adjusting the KCl concentrations. The size and charge parameters of both the PSS and the membrane pores were measured in a series of independent experiments, allowing comparison between measured values of D/D_∞ and predicted values obtained by combining our partitioning model with existing hydrodynamic models. The model correctly predicts a dramatic reduction of polymer transport--due to enhanced electrostatic repulsion—as ionic strength decreases. In addition the model indicates that, in our experiments, partitioning was the

dominant factor governing the rate of diffusion. The model predictions were quantitatively accurate at low ionic strengths, when values of D/D_∞ were relatively small, but the theory tended to underestimate D/D_∞ when $D/D_\infty > \approx 0.6$. The underprediction of D/D_∞ at high ionic strengths can to some extent be explained by the relatively short PSS chains used in our experiments. However the underprediction of D/D_∞ for PSS in a Θ solvent (3.1 M KCl) suggests that the discrepancy may reflect limitations of the existing hydrodynamic models for motion of flexible polymers in pores.

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