

Effects of Macromolecule Concentration and Charge on Membrane Rejection Coefficients

by

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Abstract

A theoretical and experimental investigation has been conducted to study the untrafiltration of macromolecules through semipermeable membranes. A hydrodynamic model for the convection of rigid spherical solutes through cylindrical pores has been developed to examine the effects of solute concentration and charge on solute rejection by membrane pores. An experimental program to test the theoretical predictions has been conducted by measuring membrane rejection coefficients for a variety of macromolecule solutes using track-etch membranes with a uniform and well-defined pore geometry.

The theoretical model employs a statistical thermodynamic analysis to express the single particle distribution function in the pore by an expansion in powers of the bulk solution concentration. Expressions for the rejection coefficient as a function of bulk concentration are obtained by integrating these pore concentration profiles over the pore cross section. The contributions of both steric and long-range interactions (electrostatic double-layer and van der Waals dispersion forces) have been considered in evaluating the solute-solute and solute-pore pair potentials that determine the distribution of solute within the pore. Calculations have been performed for a wide range of charge conditions and the results are presented in terms of the membrane rejection coefficient at infinite dilution and a correction factor which accounts for the first order effects of concentration. For pores and solutes of like charge, the rejection coefficient is predicted to decrease with increasing feed concentration or ionic strength.

Experimentally membrane rejection coefficients were measured for dilute (volume fraction, $f = 0.001 - 0.002$) and concentrated ($f = 0.08$) macromolecule solutions using Nuclepore membranes with pore radii of 15 to 31 nm. The pore number densities of the membranes were obtained from scanning electron micrographs and combined with hydraulic permeability measurements to determine the pore radii. The three test solutes employed were bovine serum albumin (globular protein), ficoll (rigid, crosslinked polysaccharide), and dextran (flexible, nearly linear polysaccharide). The rejection coefficients, which were similar for the three solutes, increased with increases in the solute-to-pore size ratio and decreased with increases in bulk concentration. A few experiments were also performed with Millipore PTHK polymer matrix type membranes and the solute rejection exhibited a decrease with concentration quantitatively similar to that obtained using the Nuclepore membranes.

The theoretical predictions provide a good qualitative representation of the observed increase in rejection coefficient with solute-to-pore size ratio, but quantitatively

they significantly underestimate the solute rejection measured for both dilute and concentrated macromolecule solutions. The agreement between the theoretical predictions and experimental results is improved when the rejection coefficient measured with a concentrated solution is plotted as a function of the corresponding value obtained with a dilute solution. It was concluded that the model provided an adequate representation of the solute-solute interactions but predicts rejection coefficients that are too low because it underestimates the strength of the solute-pore interactions.

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