

# **Electrostatic Effects on the Restricted Diffusion of Macromolecules**

by

**Frank Glenroy Smith, III**

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## **Abstract**

A theoretical and experimental investigation has been conducted on the effect of electrostatic forces in the transport of charged colloidal particles within a porous medium that also supports an electric charge. A rigorous theoretical solution for the double-layer interaction potential between a spherical particle and a cylindrical pore has been obtained. This result for the electrostatic effect has been combined with existing hydrodynamic models of hindered transport to completely describe the process. An experimental program to test the theoretical predictions has been conducted by measuring the restricted diffusion of synthetic polyelectrolytes through Nuclepore track-etch membranes.

The theoretical model considers the solute particle as either a hard sphere with a uniform surface charge density or as a solvent-ermeated porous sphere having a uniform volumetric charge distribution. The solute is assumed to be in a dilute suspension in an electrolyte solution and translating through a straight cylindrical pore having a large aspect ratio. The physical situation of greatest interest is that in which the solute radius, and Debye length are of comparable dimensions. A Gouy-Chapman diffuse double-layer model has been employed and an exact solution to the Debye-Huckel linearized form of the Poisson-Boltzmann equation obtained for this geometry. This solution for the electrical potential has been used to obtain analytical expressions for the potential energy of interaction for the sphere at an arbitrary radial position. When combined with the hydrodynamic equations, predictions for solute partition coefficients and restricted diffusion coefficients may be computed with minimal numerical effort. Significant electrostatic effects are predicted to occur at moderate charge densities and electrolyte concentrations.

Experimentally the diffusion of solute particles approximately 1.8 to 4.5 nm in radius was measured through membranes having pore radii of 15 to 23 nm in the presence of from 0.005 to 0.10 M potassium chloride electrolyte solutions. The macromolecular solutes employed were dextran sulfate, a slightly branched glucose polymer crosslinked with epichlorohydrin. Dextran sulfate was found to behave as a free draining hydrodynamic particle while ficoll sulfate acted as a rigid porous structure that was essentially not free draining to solvent. The solutes were fractionated into narrow size distribution samples using gel column chromatography and tritium labeled to allow sensitive concentration determinations. The macroion Stokes-Einstein radii were

measured in free diffusion experiments and the solute charges determined using electrophoresis. Experiments to measure the membrane characteristic pore parameters of number density, length, radius and surface charge density were also conducted. This was accomplished by determining the membrane hydraulic permeability and by measuring glucose diffusion and streaming potentials across each membrane used. A key feature of the experimental program was the ability to determine the system parameters required for the theoretical calculations and for the experimental data analysis independently of the restricted diffusion measurement.

The experimental results showed that electrostatic effects quantitatively similar to the theoretical predictions are found. The pore and solute charges were of the same sign and, therefore, the electrostatic repulsive force increased the hindrance to solute diffusion. At 0.005 M electrolyte ionic strength, electrostatic effects reduced diffusion through the membranes by as much as an order of magnitude over high ionic strength values.

Thesis Supervisor: William M. Deen  
Title: Associate Professor of Chemical Engineering