Electrical Potential Distribution in Nanopores

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ABSTRACT

Using the principles of electrostatics combined with the Debye-Huckel theory of electrolytes we present an exact formalism for the computation of the electrical potential distribution within a nanopore carrying charged pendant groups.

2 INTRODUCTION

During recent years considerable interest, both from the points of view of fundamental and applied research, in the subject of fuel cells has emerged. In a variety of these devices the anode and cathode are separated by a polymer membrane, which conducts the ionic current (as protons) while the usable electronic current passes through the external circuit[1]. The efficiency of the cell operation, clearly, must be a function of the ionic conductivity of the membrane and thus of the morphology of the latter. A considerable body of structural information about these membranes is now available and it is known that the transport of protons occurs through a network of hydrated channels or pores supported by a hydrophobic matrix or medium that provides the requisite mechanical strength and chemical and thermal stability of the material.

The system of pores may be modeled as a network of channels each of which, due to their size, are referred to as nanopores. The structures of these hydrated nanopores are quite complex and vary from one polymeric material to another, however, for the present study the most relevant feature is the presence of negatively charged anionic groups attached to the pore walls. These groups are either distributed along the interior of the pore walls or may be present at the termini of short chains protruding into the pore interior. Since in the majority of cases the ionic species being conducted are hydronium ions it is evident that these negatively charged groups, which are most often $-SO_3^-$ groups, will play a critical role in determining the proton diffusion [1]. In this paper we present the requisite formalism for the computation of the electrical potential distribution within a nanopore.

3 BASIC EQUATIONS

Each nanopore for, simplicity, is assumed to be cylindrical in shape with radius R and length L in which the anionic sites are attached to the pore wall and constituting a lattice of negatively charged rings. Groenbech-Jensen and coworkers [4] developed an algorithm for the summation of Coulombic interactions in partially periodic systems, of infinite length, which posses some features in common with our problem. A brief description of this work is essential for reasons to be made evident shortly. The basic expression for the Coulombic force between the hydronium ions and the anionic groups is given by:

$$\vec{F} = \sum_{n=-\infty}^{\infty} \frac{qke}{4\pi\varepsilon} \frac{\vec{r}_n}{\left|\vec{r}_n\right|^3}$$

Where q is the charge of a single hydronium ion, k is the number of anions per ring, ε is the permittivity, and $\mathbf{r}_n$ is the distance between the hydronium and anion. Employing: (1) the Euler transformation, (2) the Poisson-Jacobi identity on each component of $\vec{F}$ and (3) using the standard methods of classical mechanics to relate the force with a potential energy we obtain: for the latter:

$$V_G = \frac{qke}{L_z} \sum_{n=1}^{\infty} \cos\left(2\pi n \frac{z}{L_z}\right) K_0\left(2\pi n \frac{(R-p-\rho)}{L_z}\right) - \frac{2qke}{L_z} \ln\left(R-p-\rho\right)$$

The variables appearing in this equation are as follows:

L_z = distance between anions
z = axial displacement from pore end
R = radial size of pore
p = anion pore penetration length
ρ = radial coordinate of hydronium ion

Here, K_0 is the modified Bessel function of order 0.

This calculation suffers from two serious drawbacks: firstly it envisages the charges to be linear arrays of point charges rather than as rings and secondly the assumption of infinite length results in a neglect of "end-effects"; which will be manifested, as a gradual decrease in the magnitude of the potential when a test charge approaches the pore-end.

Despite these inadequacies, Paddison, Paul and Zawodzinski [1] employed the n = 1 term:

$$V_1 = \frac{q f_n e}{L_z} \left| K_0 \left(2\pi \frac{(R - p - \rho)}{L_z} \right) \cos\left(2\pi \frac{z}{L_z} \right) \right|$$

from the above expression to calculate the diffusion coefficients of hydronium ions. They were able to produce excellent agreement with experimental measurements. This emphasizes the importance of V_G and in particular the approximation V_1 as a bench mark potential.

Given the success of V_1 in reproducing experimental results, we now present a derivation that is free of the afore-mentioned drawbacks but displays quantitative agreement with V_1.

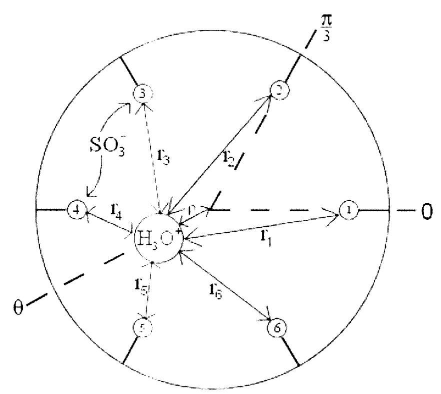

Figure 1: Axial view of the cylindrical pore.

Starting with the simple expression for Coulombic interactions within the finite-cylindrical pore we obtain the potential:

$$V_H = -\frac{e^2}{4\pi\varepsilon} \sum_{N=0}^{M-1} \sum_{j=0}^{k} \frac{1}{((x_j - \rho\cos(\theta))^2 + (y_j - \rho\sin(\theta))^2 + (NL_z - z)^2)^{\frac{1}{2}}}$$

Where the denominator is the distance between a point within the pore and one of the anionic groups on the pore wall. θ is the angular separation between the anion groups arranged on a single ring centered around the pore axis. 'M' is the number of rings and 'k' is the number of ions per ring. A plot of this potential as a function of the distance along the pore axis is as follows:

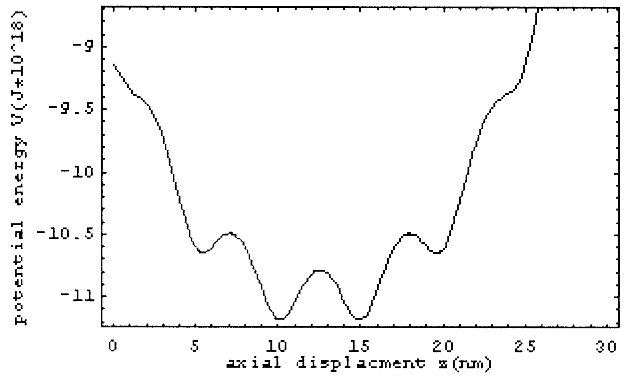

Figure2: Axial displacement vs potential energy of the hydronium ion with radial co-ordinate of 3.5 angstroms.

The overall curvature of this plot is a consequence of the "end effects" alluded to above. However, a comparison with V_1 shows a serious discrepancy in magnitude.

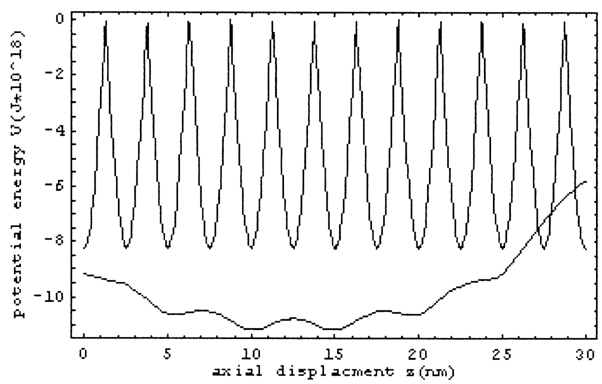

Figure 3: Axial displacement vs potential energy of the hydronium ion with radial co-ordinate of 3.5 angstroms. The regular, sinusoidal plot is V_1, the lower, plot is the potential derived with the finite, cylindrically symmetric, pore model.

The difference between the two plots becomes magnified at larger distances from the pore axis.

Therefore we are motivated to ask why a model, which is based on sound foundations, yields results that are incompatible with an expression that gave surprisingly good values for the diffusion coefficient? In view of the fact that V_H shows a consistently larger magnitude than V_1 the most likely explanation is to consider the possibility of shielding of the anionic sites by the hydronium ions.

The mechanism whereby shielding occurs in electrolyte solution is well known [3]. The basic alteration consists of introducing a Debye-Huckel screening constant in the Coulombic potential:

$$V = \frac{-1}{4\pi\varepsilon}\frac{q}{r}e^{-\kappa r}$$

Here κ is the screening constant and is the inverse of the thickness of the ionic atmosphere surrounding a given anionic site. Since the screening is caused by the hydronium ions the value of κ will depend on the hydronium ion density and charge. The expression for κ is well known:

$$\kappa^2 = \frac{z^2 e^2 n}{4\pi\varepsilon kT}$$

Where T is the temperature, k is Boltzmann constant, n is the number density of the hydronium ions, and z is the valence of the hydronium ion. The value of n can be estimated by adjusting κ until agreement with the potential V_1 is achieved. A plot comparing V_1 with the screened potential in a pore of finite length reveals dramatically better agreement, particularly at the radial coordinate of 2 Angstroms from the pore axis.

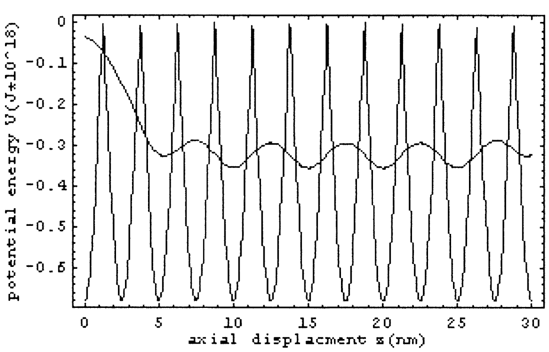

Figure 4: Axial displacement vs potential energy of the hydronium ion with radial co-ordinate of 2.0 angstroms

4 CONCLUSIONS

In most calculations that have thus far been carried out, where the central role of the charged pendant groups in proton transport has been recognized, the many-body effects of the protons themselves have been neglected. In this paper we have shown that even with a very simple Debye-Huckel model of the electrolyte the screening effect plays a very crucial.

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