

ON THE INTRODUCTION OF THE PORE WALL CHARGE IN THE SPACE-CHARGE MODEL FOR MICROPOROUS MEMBRANES

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Summary

We show that an extension of the space-charge model for electrolyte transport in charged capillary pores, which includes the dependence of the adsorbed pore wall charge on bulk concentration, has practical and theoretical interest, and can be easily accomplished. It is argued that an explicit dependence of the adsorbed charge on concentration may help to clarify the physical description.

Introduction

The space-charge (SC) model [1] for electrolyte transport in charged capillary tubes describes a number of interesting physical situations that arise when a charged porous medium separates two salt solutions. The quantitative accuracy of the model has recently been tested by Westermann-Clark et al. for aqueous [1] and nonaqueous [2] electrolyte solutions, and by Tejerina and co-workers [3,4].

The theoretical foundations of the SC model are based on the Gouy-Chapman approach for the double layer at the pore surface, the Nernst-Planck equation for the ion fluxes, and the Navier-Stokes equation for describing the solution flow through the charged capillary tubes. A key parameter of the model is the immobile, uniform charge density at the pore wall (σ). Transport parameters like the pore conductivity, the diffusion and streaming potentials, the membrane selectivity and the solute permeability of the pore critically depend on this charge density.

One of the most usual simplifications contained in the transport theory through charged tubes is to assume the charge density σ to be constant. The experimental results have shown that this wall charge is not constant, but

depends instead on the bulk electrolyte concentration [1–4]. Some recent studies with alkali chloride solutions suggest that Cl^- adsorbs to the pore wall [1,3]. Thus, even when a uniform electrolyte concentration is considered, comparison of theory and experiment requires taking into account a set of theoretical curves of parameter σ if different concentrations are to be used. (This is the case, e.g., in measuring the pore conductivity as a function of the electrolyte concentration [1].)

This note is intended to show that: (i) an extension of the SC model to include explicitly the case of concentration dependent, adsorbed pore wall charge can be easily accomplished, and (ii) considering the charge density σ to be a free parameter not only tends to obscure the possible contribution of adsorption processes to the wall charge values but also may lead to some non-observed asymptotic behaviours when studying the pore conductivity as a function of electrolyte concentration*. Our treatment is based on two simplified forms of the Poisson–Boltzmann equation.

Linearized Poisson–Boltzmann equation

The main assumptions included in the SC model have been considered in detail by Westermann-Clark and Anderson [1]. A solution to the linearized Poisson–Boltzmann equation is well-known (the basis of this solution can be found in ref. [6]) and can be written in terms of the modified Bessel function of order zero, I_0 , as:

$$\Psi(r/\lambda, x) = A I_0(r/\lambda) \quad (1)$$

where Ψ is the local electric potential, r and x are the radial and axial coordinates, respectively, λ is the Debye length defined as:

$$\lambda(x) = \left(\epsilon RT / F^2 \sum_i z_i^2 \bar{c}_i(x) \right)^{1/2} \quad (2)$$

and A is a parameter (not depending on the radial coordinate) to be determined. In eqn. (2), ϵ stands for the dielectric constant, F is the Faraday constant, R is the gas constant, T is the temperature, while z_i and \bar{c}_i denote the charge number and the axial molar concentration of the i th ion, respectively.

The parameter A entering in eqn. (1) is determined by imposing that the total charge in the pore has to be equal to the pore wall charge. This condition can be written in the form:

*Pore conductivity should reach a plateau for low bulk solution concentration if the pore wall charge is taken to be concentration independent. See Refs. [1] and [5] for details.

$$\int_0^a \rho(r, x) 2\pi r dr = -\epsilon \int_0^a \Delta\Psi 2\pi r dr = -2\pi a\sigma \quad (3)$$

where a is the pore radius, and ρ is the local volumic charge density. If we assume the radial fluxes to be zero, and linearize the resulting Boltzmann distribution for the radial concentration $c_i(r, x)$, eqns. (1) and (3) lead to:

$$A = \frac{\sigma\lambda}{\epsilon I_1(a/\lambda)} \quad (4)$$

where I_1 is the modified Bessel function of first order. From eqns. (1) and (4), the well-known final solution [6] is:

$$\Psi(r/\lambda, x) = \frac{\sigma\lambda}{\epsilon} \frac{I_0(r/\lambda)}{I_1(a/\lambda)} \quad (5)$$

The solution procedure clearly shows that an extension of the theoretical treatment to cover the case of non-constant, adsorbed σ can be easily obtained if the charge density σ in eqn. (5) depends on bulk concentration.

The question now is to introduce a functional dependence for $\sigma(c)$ in eqn. (5), where c is the bulk concentration. This poses a formidable problem, because other mechanisms in addition to coion adsorption can affect the pore wall charge [1,2]. Our treatment will be confined to those cases where σ depends only on the bulk electrolyte concentration. This seems to be a reasonable first approximation for aqueous alkali chloride solutions in track-etched mica membranes [1] and in microporous polycarbonate membranes [3,7]. For these cases an approximate dependence is given by:

$$\sigma(c) = bc^n \quad (6)$$

where b and n are empirical parameters to be determined in each case. For Nuclepore polycarbonate filters, electrokinetic measurements [7,8] show that $n \approx 1/3$, and b depends on the electrolyte salt and the membrane considered. Such a cube root dependence of σ on the concentration in very dilute solutions has been theoretically predicted, as quoted in ref. [8]. Note that if the membrane matrix is not intrinsically ionizable, it seems natural that its surface charge in electrolyte solutions may be due to some adsorption phenomena.

From eqns. (5) and (6), electrokinetic parameters like the pore conductivity or the streaming potential can be derived [1-4]. Since the electrokinetic parameters involve integration over the radial coordinate, and in some cases over the axial concentration \bar{c}_i , eqn. (6) incorporates no additional difficulty to the integration procedure provided that a bulk concentration be specified in these cases. Parameters b and n can be determined in each case by fitting calculations from the SC model to experimental data, as suggested by Westermann-Clark and Anderson for their free parameter σ [1].

The introduction of the Debye–Hückel approximation to linearize the Poisson–Boltzmann equation [4] clearly limits the applicability of eqn. (5) as we will see later, but we would like to emphasize that eqn. (6) can be incorporated to more complete numerical solutions of the full, non-linearized model [1,3].

Pore conductivity

This note is intended to discuss the items (i) and (ii) stated in the Introduction. Both questions will be analysed from the pore conductivity predicted by the SC model. Pore conductivity is an electrokinetic parameter that can be readily calculated since it depends only on the phenomenological coefficient L_{11} (see ref. [1] for details). Introducing eqn. (5) into eqn. (A.1) of ref. [1] and expanding the exponentials, a rather long but direct calculation gives for the pore conductivity, κ , the following expression:

$$\kappa = \frac{\epsilon(D_+ + D_-)}{2a^2} \left(\frac{a}{\lambda}\right)^2 \left\{ 1 - \frac{D_+ - D_-}{D_+ + D_-} \frac{2Fa\sigma}{\epsilon RT} \left(\frac{\lambda}{a}\right)^2 \right\} + \frac{\sigma^2}{\eta} \left\{ 1 + f\left(\frac{a}{\lambda}\right) \right\} \quad (7)$$

$$f\left(\frac{a}{\lambda}\right) = \frac{I_0(a/\lambda)}{I_1(a/\lambda)} \left[\frac{2\lambda}{a} - \frac{I_0(a/\lambda)}{I_1(a/\lambda)} \right]$$

where a binary 1:1 electrolyte has been considered and η is the solvent viscosity. Equation (7) differs from eqn. (21) of ref. [4] in that an additional term in σ^2 has been retained. (If this term is disregarded and we approximately take, as usual, the ratio of ionic diffusion coefficients to be that of an infinitely dilute aqueous solution, then eqn. (7) would simplify to the equation corresponding to a free electrolyte solution for the KCl case. Note also that the contribution due to the pore surface conductivity has been neglected in eqn. (7).)

In this section we refer to the bulk solution value of the Debye length as λ , while in the previous section λ was a function of x . Note that for pore conductivity measurements the two bulk solutions have the same concentration and therefore there is no dependence on x . Besides this, the axial concentration is equal to the bulk solution concentration for the linearized Poisson–Boltzmann case.

From eqn. (6), the dependence of σ on (a/λ) can be included in eqn. (7) by taking $\sigma = b' (a/\lambda)^{2n}$, where $b' = b(\epsilon RT/F^2 a^2)^n$. If we compare these theoretical values for κ with those measured experimentally in ref. [1], we will find that agreement between theory and experiment is only possible for $(a/\lambda) \gg 1$. Thus, the model only would work for values close to the bulk phase conductivities. Of course, this result could be anticipated since linearizing the Poisson–Boltzmann equation is a valid procedure only if:

$$\left| \frac{F\Psi_{\max}}{RT} \right| = \left| \frac{F}{RT} \frac{\sigma\lambda}{\epsilon} \frac{I_0(a/\lambda)}{I_1(a/\lambda)} \right| \ll 1 \quad (8)$$

Condition (8) is only fulfilled if $(a/\lambda) \gg 1$, since $\sigma \sim -10^{-2}$ C/m² in ref. [1]. (It can be proved that eqn. (7) would be valid for $(a/\lambda) \sim 1$ provided that $|\sigma| \ll 10^{-3}$ C/m²). The numerical solution employed in ref. [1] proves then to be necessary and our treatment would not be applicable when $(a/\lambda) \sim 1$.

In order to analyse the behaviour of κ for these values of a/λ , we have solved the full, non-linearized Poisson–Boltzmann equation under conditions of total coion exclusion (the limit in which only those ions of charge opposite to that of the pore wall would fill in the pore). In this case it is well-known that an analytical solution can be found. This solution is in our case:

$$\Psi = (2RT/F) \ln (1 - F^2 \bar{c} r^2 / 8\epsilon RT)$$

which leads to the conductivity:

$$\kappa = \bar{c} \delta \left\{ \frac{F^2 D}{RT} + \frac{2\epsilon RT}{\eta} \left[1 + \frac{\ln \delta}{1 - \delta} \right] \right\}$$

$$\delta \equiv 1 - \frac{\sigma Fa}{4\epsilon RT} \quad (9)$$

The electrolyte concentration in the cylindrical pore axis, \bar{c} , is related to σ through the expression:

$$\bar{c} = -\frac{2\sigma}{aF} \left(1 - \frac{Fa\sigma}{4\epsilon RT} \right)^{-1} \quad (10)$$

which can be readily obtained from eqn. (3).

Figures 1–3 show a comparison between the experimental pore conductivity values obtained in ref. [1] and those provided by eqns. (7) and (9). It can easily be noticed that each one agrees quite well with values from ref. [1] in their respective ranges of applicability.

Note that Figs. 3 and 4 in ref. [1] (pore conductivity in aqueous alkali chlorides vs. a/λ) give an asymptotic behaviour for the conductivity when the quotient (a/λ) takes values close to unity. It can be thought [1] that the theoretical curves asymptotically approach a constant value as $(a/\lambda) \rightarrow 0$ (where total coion exclusion is expected to hold). But this is only true if we assume that the pore wall charge is maintained constant even when the bulk solution concentration tends to zero. However, this predicted asymptotic behaviour is not followed by the experimental values which take instead decreasing values over the concentration interval flanking the quotient $(a/\lambda) = 1$. This is just the effect accounted for in eqns. (6), (9) and (10), since the limit $(a/\lambda) \rightarrow 0$ implies that $\sigma \rightarrow 0$, and then a continuous decreasing of κ with (a/λ) .

Conclusions

We concluded that considering an explicit dependence of σ on concentration leads to a theoretical behaviour perhaps clearer than taking σ as a free param-

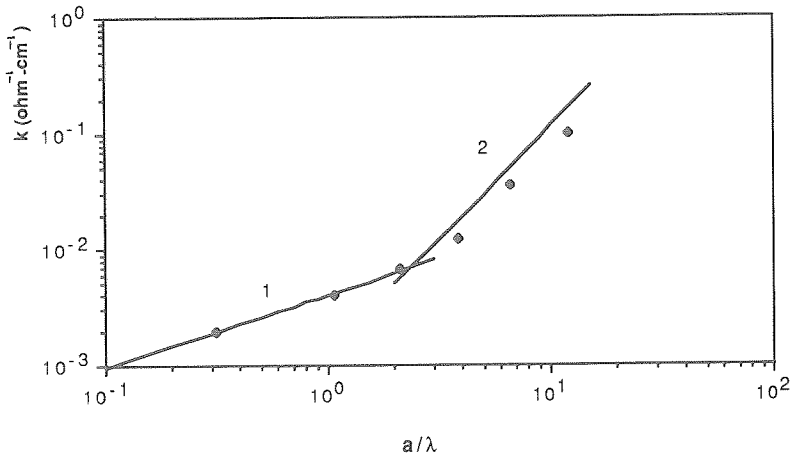


Fig. 1. Pore conductivity vs. (a/λ) for the KCl 34Å case, see ref. [1]. The expression $\sigma = -8.47 \times 10^{-7} (a/\lambda)^{0.594}$ has been used. Curve 1 corresponds to the case of total coion exclusion and curve 2 to the case of the linearized Poisson-Boltzmann equation.

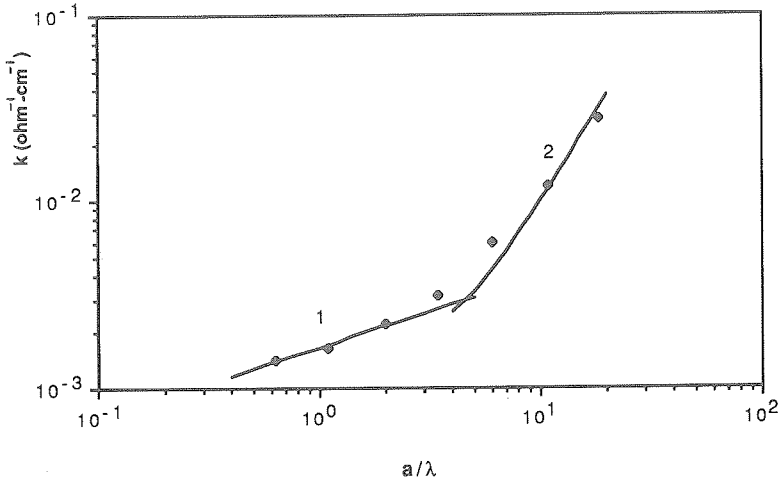


Fig. 2. Pore conductivity vs. (a/λ) for the NaCl 103Å case. The expression $\sigma = -1.31 \times 10^{-6} (a/\lambda)^{0.348}$ has been used. Curves 1 and 2 corresponds to the cases mentioned in Fig. 1.

eter. Note that the (non-observed) predicted behaviour for $(a/\lambda) \sim 1$ in ref. [1] arises from considering $\sigma = \text{constant}$ as we move from $(a/\lambda) \gtrsim 1$ to $(a/\lambda) \lesssim 1$, which is not in agreement with the observed adsorption phenomena. This is clearly stated in Fig. 5 of ref. [1] (surface charge densities determined by fitting calculations from the SC model to the experimental pore conductivities) and shows the need of taking a set of theoretical curves of parameter σ

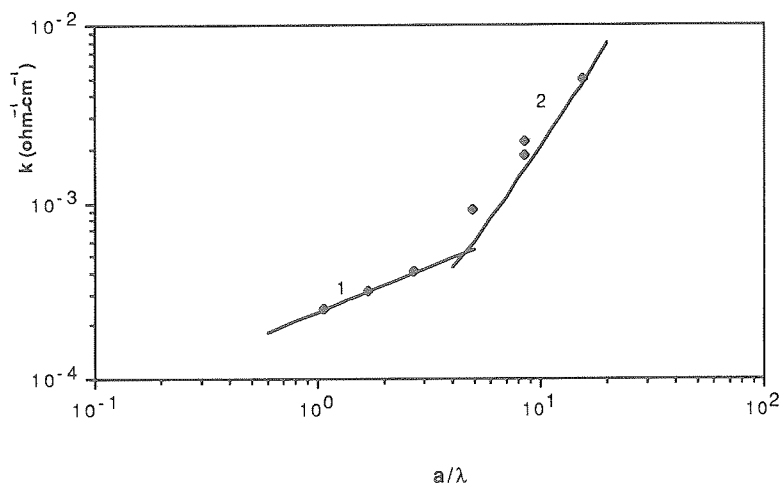


Fig. 3. Pore conductivity vs. (a/λ) for the KCl 265Å case. The expression $\sigma = -3.60 \times 10^{-7} (a/\lambda)^{0.475}$ has been used. Curves 1 and 2 corresponds to the cases mentioned in Fig. 1.

to compare theory and experiment, as done by Westermann-Clark and Anderson.

Thus, it can be anticipated that introduction of eqn. (6) into the numerical solution employed in ref. [1] would lead to a unique theoretical curve (containing the free parameters b and n) that would not show any asymptotic limit for $(a/\lambda) \sim 1$.

Although we have considered two non-exact treatments based on simplified forms of the Poisson-Boltzmann equation, Figs. 1-3 show that both treatments have practical interest. (Levine et al. [9] observed that the transition between the solutions of these two simplified forms is relatively smooth.) Likewise, the incorporation of eqn. (6) to the more complete, exact numerical treatments by Westermann-Clark and Anderson [1], and Tejerina and co-workers [3] seems to be feasible and the dependence of the diffusion potential on σ [1,3] may be studied from a viewpoint similar to that considered here for the pore conductivity.

It seems necessary to point out that eqn. (6) involves two free parameters (b, n) rather than one (σ). Likewise, eqn. (6) assumes some mechanism of adsorption to be the main origin of the pore wall charge, what can be only approximately valid [1,2]. However, parameters b and n have already proved to be useful for describing σ in previous experimental studies [7,8]. In fact, ref. [8] contains a simplified SC model with $\sigma = bc^{1/3}$. It might be argued that the fitting of these parameters could account indirectly for some side effects not included explicitly in the model*. Despite this we think that an explicit depen-

*Activity coefficients are usually assumed to be unity at any concentration in the SC model. A recent paper by Huerta and Olivares [10] is devoted to the calculation of the mean activity coefficient of an electrolyte solution inside a charged cylindrical micropore.

dence of the charge density σ on concentration may help to clarify the physical description in those cases where this dependence can be introduced.

Acknowledgements

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