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Ion size effects on the streaming potential of narrow charged pores

Javier Cervera, José A. Manzanares* and Salvador Mafé

Departament de Termodinàmica, Universitat de València, E-46100 Burjassot, Spain. E-mail: manzanar@uv.es

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The effects of ion size on the streaming potential of fixed charge membranes with narrow pores are studied theoretically as a function of the ratio between the ionic and the pore radii, and the ratio between the external concentration and the membrane fixed charge concentration. To this end, the radial distributions of the ionic concentrations, space charge density, pressure and electric potential are obtained for finite size and point ions using a generalised Poisson–Boltzmann equation. It is found that the streaming potential increases significantly with increasing ion size. The results are presented in terms of experimentally controlled parameters in order to stimulate targeted experimental work with well defined ionic species and membranes.

Introduction

Ionic transport processes occurring in artificial and biological membranes are usually studied on the basis of a physical model that simulates the fixed charge membrane by an array of parallel charged cylindrical pores.[1–5] The diffuse double layer theory can give a suitable description of the ion distribution in the pore cross-section only when the ionic concentrations are low enough. At high pore surface charge density and ionic concentrations, however, ion size effects need to be included in order to avoid unrealistic ion accumulation near the charged surface.[3–5] These effects are crucial in many problems of physical chemistry, *e.g.* the ion distribution in the vicinity of a planar charged surface immersed in an electrolyte solution,[6–8] the transport of ionic drugs across the aqueous paracellular pathway of cell monolayers where the effective pore radius is similar to that of the drug,[9] and the modelling of ionic transport in membranes.[10–12]

We have studied the effects of the ion size on the streaming potential of narrow charged cylindrical pores. The streaming potential is the ratio between the generated electric potential difference and the applied pressure difference under zero current flow conditions.[5,12–14] It is studied here as a function of two relevant experimental parameters: the ratio between the ionic radius and the pore radius, and the ratio between the external electrolyte concentration and the membrane fixed charge concentration. We have employed a generalised Poisson–Boltzmann (PB) equation that incorporates the ion size by means of the Bikerman equation.[8] Although molecular dynamics simulations[15] might be more appropriate than the Poisson–Boltzmann continuum approach for the length scales involved, extensions of this approach have often proved useful.[4–8,12–14]

Theoretical model

The membrane is modelled as an array of parallel cylindrical pores.[1–5] The fixed charges, responsible for the membrane permselectivity, are uniformly distributed on the pore walls with a surface density σ. The solution filling the pore has a net charge which exactly compensates for σ, so that

$$X \equiv \sum_i z_i \langle c_i \rangle = -\frac{2\sigma}{Fa} \qquad (1)$$

where z_i and $\langle c_i \rangle$ are the charge number and average molar concentration over the pore section of species i, F is the Faraday constant, and a is the pore radius, considered to be much smaller than its length. Fig. 1 shows a pore with $a_i/a = 0.1$, where a_i is the (hydrated) ion radius. When the membrane separates two identical aqueous solutions of a 1 : 1 binary electrolyte at concentration c^b and different pressure, the pore solution is pushed towards the region of lower pressure. Owing to its electrical charge density FX, the solution flow under the pressure difference Δp gives rise to a charge separation and, eventually, to the formation of a steady state electric potential difference ΔV. The streaming potential is the ratio $v = \Delta V/\Delta p$ when the electric current density is zero.

In the presence of convective flow, the molar flux density j_i of an ionic species in the membrane-fixed reference frame is given by the sum of two terms, the flux density in the barycentric reference frame ${}_u j_i$ and the convective flux density $c_i u$, where u is the solution velocity parallel to the pore axis.[16] The barycentric reference frame is defined by the condition $\sum_i {}_u j_i M_i + {}_u j_s M_s = 0$, where the sum extends over the (solute) ionic species, ${}_u j_s$ is the flux density of the solvent in this reference frame, and M_i, M_s are the molar masses of species i and the solvent, respectively. Due to the existence of this relationship between ionic and solvent flux densities in the barycentric reference frame, the flux density of species i, ${}_u j_i$, is not proportional to $\partial\tilde{\mu}_i/\partial x$, but rather to the axial gradient of $\tilde{\mu}_i/M_i - \mu_s/M_s$, where μ_s is the chemical potential of the solvent. The flux density of species i in the membrane-fixed reference frame constitutes the generalised Nernst–Planck equation[17]

$$j_i = uc_i - z_i D_i c_i \frac{F}{RT}\frac{\partial\phi}{\partial x} - \frac{D_i c_i}{RT}\left[v_i - \frac{M_i}{M_s} v_s\right]\frac{\partial p}{\partial x} \qquad (2)$$

where v_s and v_i are the partial molar volumes of the solvent and species i, D_i is the diffusion coefficient of species i, ϕ is the electric potential, R is the gas constant and T is the temperature. For the sake of simplicity, the two ionic species are

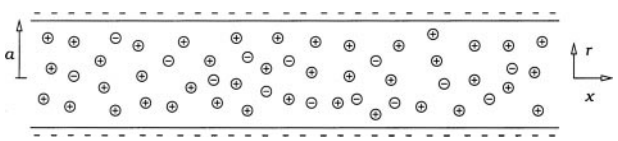

Fig. 1 Schematic view of a membrane pore with $\sigma < 0$ and $a_i/a = 0.1$.

considered to have the same partial molar volume v. In eqn. (2), the concentration c_i does not depend on the axial coordinate x, but it depends on the radial coordinate r due to the pore wall charge. Similarly, j_i, u, $\partial p/\partial x$ and $\partial\phi/\partial x$ are functions of r only (note that axial concentration gradients are absent here).

The Poisson equation

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial\phi}{\partial r}\right)+\frac{\partial^2\phi}{\partial x^2}=-\frac{\rho_e}{\varepsilon} \tag{3}$$

allows us to decompose ϕ as

$$\phi(r, x)=\frac{\Delta V}{\Delta x}x+\psi(r) \tag{4}$$

where the axial gradient $\Delta V/\Delta x=\partial\phi/\partial x$ is constant because the local space charge density $\rho_e\equiv F\sum_i z_i c_i$ does not depend on x and the electric permittivity of the solution, ε, is assumed to be constant. ψ is the radial distribution of the electric potential.

Since the pore wall is impermeable to both solvent and ionic species, their flux densities in the radial direction vanish, and no convective motion takes place along this direction. The continuity equations imply that the axial solution velocity u and the axial flux densities j_i and j_s must be a function of the radial position coordinate r only. The absence of radial convection requires the balance of mechanical and electrical forces[16]

$$0=\frac{\partial p}{\partial r}+\rho_e\frac{d\psi}{dr}. \tag{5}$$

Note that since $\rho_e\,d\psi/dr<0$, p increases with r. In addition, the absence of radial ionic flux densities requires that the radial gradients of $\tilde{\mu}_i/M_i-\mu_s/M_s$ vanish. This implies that the gradient of the electrochemical potential of each species divided by its molecular weight is constant

$$\frac{1}{M_i}\frac{\partial\tilde{\mu}_i}{\partial r}=\frac{1}{M_s}\frac{\partial\mu_s}{\partial r}\equiv\lambda. \tag{6}$$

If we multiply the constant λ by the density of the solution $\rho=\sum_i M_i c_i+M_s c_s$, we obtain

$$\lambda\rho=\sum_i c_i\frac{\partial\tilde{\mu}_i}{\partial r}+c_s\frac{\partial\mu_s}{\partial r} \tag{7}$$

which, together with the Gibbs–Duhem equation[16]

$$\frac{\partial p}{\partial r}+\rho_e\frac{d\psi}{dr}=c_s\frac{\partial\mu_s}{\partial r}+\sum_i c_i\frac{\partial\tilde{\mu}_i}{\partial r} \tag{8}$$

allows us to conclude that $\lambda=0$, so that μ_s and $\tilde{\mu}_i$ are constant along the radial direction (note that in these equations all coefficients of the gradients are positive). In particular, the condition $\partial\tilde{\mu}_i/\partial r=0$ implies that

$$c_i\frac{\partial\tilde{\mu}_i}{\partial r}=RT\frac{dc_i}{dr}+z_i c_i F\frac{d\psi}{dr}+vc_i\frac{\partial p}{\partial r}=0. \tag{9}$$

If we sum eqn. (9) for all ionic species and use eqn. (5) we obtain

$$RT\sum_i\frac{dc_i}{dr}=\left(1-v\sum_i c_i\right)\frac{\partial p}{\partial r} \tag{10}$$

that can be rewritten as

$$\frac{RT}{v}\frac{d}{dr}\left[\ln\left(1-v\sum_i c_i\right)\right]=\frac{\partial p}{\partial r}. \tag{11}$$

Since $\partial p/\partial r$ and $\partial p/\partial x$ are functions of r, the pressure varies linearly with x ($\partial p/\partial x\equiv\Delta p/\Delta x$ is a constant) and eqn. (11) can be integrated to give

$$p(x, r)=p(x, 0)-\frac{RT}{v}\ln\frac{1-v\sum_i c_i(r)}{1-v\sum_i c_i(0)} \tag{12}$$

which constitutes the generalisation of the Van't Hoff equation, $p-RT\sum_i c_i=$ constant. Note that $v_s c_s=1-v\sum_i c_i$, and since μ_s is constant along the radial direction, the increase of p with r is compensated by a decrease in c_s with r. Substituting eqn. (11) into eqn. (9), we obtain the relation between the ionic concentrations and the electric potential

$$\frac{c_i(r)}{c_i(0)}=\frac{1-v\sum_i c_i(r)}{1-v\sum_i c_i(0)}\exp\left\{-\frac{z_i F}{RT}[\psi(r)-\psi(0)]\right\}. \tag{13}$$

Eqn. (13) is known as the Bikerman equation, and represents the generalisation of the Boltzmann equation, $c_i=$ constant $\times\exp(-z_i F\psi/RT)$.

The radial distribution of u is determined by the axial component of the Navier–Stokes equation

$$\eta\frac{1}{r}\frac{d}{dr}\left(r\frac{du}{dr}\right)=\frac{\Delta p}{\Delta x}+\rho_e\frac{\Delta V}{\Delta x} \tag{14}$$

where η is the dynamic viscosity of the solution. Using eqn. (3) to eliminate the electric potential gradient for the space charge density ρ_e, we obtain

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d}{dr}\right)\left(\eta u+\varepsilon\frac{\Delta V}{\Delta x}\psi\right)=\frac{\Delta p}{\Delta x}. \tag{15}$$

Integrating eqn. (15) twice and applying the non-slip condition $u(r=a)=0$, the velocity of the centre of mass of the solution is

$$u(r)=-\frac{\Delta p}{\Delta x}\frac{a^2-r^2}{4\eta}+\frac{\Delta V}{\Delta x}\frac{\varepsilon}{\eta}[\psi(a)-\psi(r)]. \tag{16}$$

The two terms in the rhs of eqn. (16) have opposite signs and, therefore, the electric potential drop reduces the convective velocity u.

Substituting eqn. (16) into eqn. (2) the flux of species i can be obtained

$$\begin{aligned}J_i&=\int_0^a 2\pi r j_i(r)dr\\&=-\frac{\Delta V}{\Delta x}\int_0^a\left\{\frac{z_i F}{RT}D_i c_i+\frac{\varepsilon}{\eta}[\psi(r)-\psi(a)]c_i\right\}r\,dr\\&\quad-\frac{\Delta p}{\Delta x}\int_0^a\left[\frac{(a^2-r^2)}{4\eta}c_i+\frac{D_i}{RT}\left(v-\frac{M_i}{M_s}v_s\right)c_i\right]r\,dr.\end{aligned} \tag{17}$$

Applying the condition that the electric current $I=\sum_i z_i F J_i=0$, the streaming potential $v=\Delta V/\Delta p\,|_{I=0}$ is

$$v=-\frac{\sum_i\int_0^a\left[\frac{z_i F}{4\eta}(a^2-r^2)c_i+\frac{z_i F D_i}{RT}\left(v-\frac{M_i}{M_s}v_s\right)c_i\right]r\,dr}{\sum_i\int_0^a\left\{\frac{z_i^2F^2}{RT}D_i c_i+\frac{\varepsilon}{\eta}z_i F[\psi(r)-\psi(a)]c_i\right\}r\,dr}. \tag{18}$$

To calculate v, the potential $\psi(r)$ is needed. This potential results from the numerical integration (by the shooting method) of eqn. (3) subject to the boundary conditions

$$\left.\frac{d\psi}{dr}\right|_{r=0}=0 \tag{19}$$

due to the symmetry of the system and

$$\left.\frac{d\psi}{dr}\right|_{r=a^*} = \frac{\sigma}{\varepsilon}\frac{a}{a-a_i} \tag{20}$$

that can be derived from the Gauss law.[18] In eqn. (20), the ions have been modelled as hard spheres with a central charge. The corrected pore radius $a^* = a - a_i$ takes into account the closest approach distance of the ions to the pore walls. The use of eqn. (13) requires the ionic molar concentrations and electric potential at the pore centre. To relate these values to those of the external solutions, an equilibrium condition is assumed.[12] Equating the ionic electrochemical potentials in the external solutions and the pore centre, assuming a balance between forces, and following the procedure that leads to eqn. (12) and (13), we obtain

$$c_i(0) = \frac{1 - v\sum_i c_i(0)}{1 - 2vc^b}\, c^b \exp\left\{-\frac{z_i F}{RT}\left[\psi(0) - \psi^b\right]\right\}. \tag{21}$$

Finally, the ion size effects are introduced in the diffusion coefficients by means of the Renkin relation[9]

$$\frac{D_i}{D_i^0} = \left(1 - \frac{a_i}{a}\right)^2\left[1 - 2.104\left(\frac{a_i}{a}\right) + 2.09\left(\frac{a_i}{a}\right)^3 - 0.95\left(\frac{a_i}{a}\right)^5\right] \tag{22}$$

where

$$D_i^0 = \frac{kT}{6\pi\eta a_i} \tag{23}$$

is the diffusion coefficient in free solvent (Stokes–Einstein equation) and k is the Boltzmann constant. Eqn. (22) is valid only for $a_i/a < 0.4$.

Results and discussion

In the following calculations, we have assumed $T = 300$ K, $\eta = 1$ mPa s and $\varepsilon = 80\varepsilon_0$ where ε_0 is the vacuum permittivity. The ratio $M_i v_s/M_s v$ is fixed to 1. The results are presented in terms of the ratios a_i/a (characterising the size effect) and c^b/X (characterising the external concentration effect). The pore radius is $a = 15$ Å and σ is fixed by the condition $a/L_D = 2.5$, where $L_D \equiv (\varepsilon RT/F^2X)^{1/2}$ is the Debye length. The Debye length is comparable to the pore radius, but the ratio a/L_D is still high enough for the mean-field approximation characteristic of the continuum theories to be valid.[11] (Recent Brownian dynamics simulations have found agreement between the PB theory and simulations when a is greater than $2L_D$.[11]) The above values give $L_D = 6$ Å, $\sigma \approx -3.8$ μC cm^{-2} (one elementary charge per 500 Å^2) and $X \approx 0.53$ M, a typical concentration for fixed charge membranes.[12] The ratio $a_i/a = 0.2$ implies a solvated radius $a_i = 3$ Å. Since the electrolyte solution has been modelled as a gas of hard spheres, the free volume accessible to the ions is reduced by the volume the ions occupy. With this reduction of free volume, it can be shown from statistical mechanics[8] that the value used for the ionic radius is equivalent to a partial molar volume of $v = 545$ cm^3 mol^{-1}.

To understand the size effects, consider first the case of point ions, whose magnitudes are marked with a superscript 0 henceforth. In a charged membrane, the sum of ionic concentrations $\sum_i c_i^0$ is larger than in the external solution, $2c^b$, as follows from eqn. (21) by taking $v = 0$ and noting that $e^x + e^{-x} \geqslant 2$. Eqn. (19) and (20) impose that the electric potential ψ^0 and its gradient $d\psi^0/dr$ increase in absolute value with increasing r and, therefore, $\sum_i c_i^0$ must also increase with

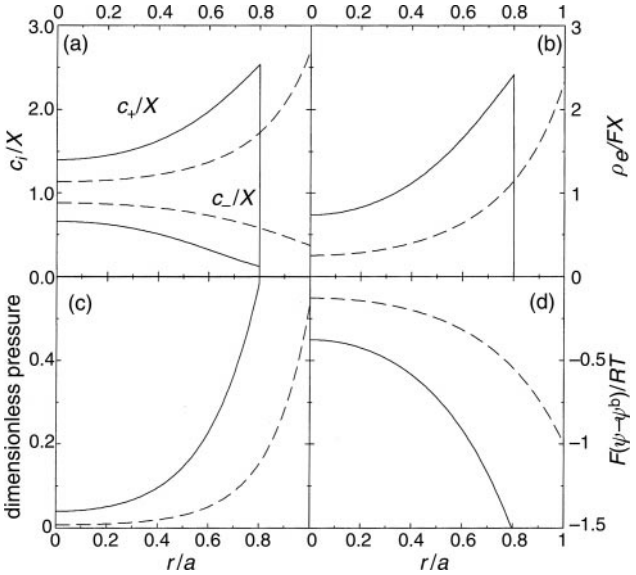

Fig. 2 Radial distributions of the normalised ionic concentrations, space charge density, pressure and electric potential for finite size (continuous line) and point (dashed line) ions for $a_i/a = 0.2$ and $c^b/X = 1.0$. The dimensionless pressure is taken as $[p(0, r) - p^b(0)]/\gamma$, where $\gamma = 2RTc^b$ for point ions, $\gamma = RT/v$ for finite size ions, and $p^b(0)$ is the lower external solution pressure. Note that for finite size ions, $a^* = a - a_i = 0.8a$ is the upper limit of the radial coordinate.

r. In turn, the increase of $|d\psi^0/dr|$ with r implies, by the Poisson equation, that $|\rho_e^0|$ increases with r, and the increase of $\sum_i c_i^0$ with r implies, by the Van't Hoff equation, that p^0 increases with r. All these trends are clearly shown in Fig. 2.

Now, for finite size ions, the size effects are given by the pressure–volume term (mechanical work) in the electrochemical potential of the species in solution (including the solvent). The tendency for the species to move towards the region of lower electrochemical potential implies then a tendency to move towards lower pressure regions. Thus, a first effect is to avoid entering the membrane pores, since the pressure there is larger than in the external solution. This tendency is manifested in a decrease in both the average coion and counterion pore concentrations, their difference being fixed by the electroneutrality condition of eqn. (1). In addition, the counterion concentration decreases near the pore wall with respect to the point ions, since the pressure increases with r (see Fig. 2), and increases at the pore axis to maintain electroneutrality. The increase in the space charge density $\rho_e(0)$ at the pore axis with respect to the point ions case, and the fact that the gradient $d\psi/dr$ is fixed at $r = a^*$ by eqn. (20), implies by the Poisson equation that ion size effects increase the magnitude of the electric potential gradient $|d\psi/dr|$ with respect to $|d\psi^0/dr|$, and hence the potential drop over the pore radius. Moreover, eqn. (12) shows that the pressure at any position within the pore is higher for finite size ions than for point ions, in agreement with the behaviour of real gases. These are the trends shown by the curves of Fig. 2.

Consider next the streaming potential v. This arises from the pore solution displacement induced by the pressure gradient, and implies a charge separation. The average charge density in the pore solution is fixed as $\langle\rho_e\rangle = -2\sigma/a$ by eqn. (1), independently of the ion size. Thus, a naive conclusion would be that v could not be affected by the finite ion size. However, the solution velocity is not uniform over the pore cross-section, and it is the space charge density $\rho_e(0)$ at the pore axis (where the solution velocity reaches its maximum) that dictates the behaviour of v. Since the ion size effects increase the value of $\rho_e(0)$ (see Fig. 2), $|v|$ is expected to increase with a_i/a, as shown in Fig. 3. Note also that v originates from and is a measure of the space charge in the pore

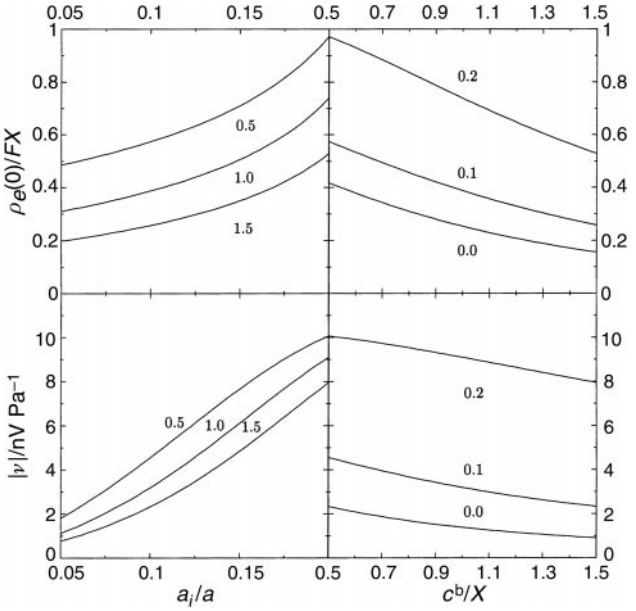

Fig. 3 Space charge at the pore centre and streaming potential as a function of a_i/a for the values of $c^b/X = 0.5$, 1.0 and 1.5 (left figures) and as a function of c^b/X for the values of $a_i/a = 0.0$, 1.0 and 0.2 (right figures).

solution. Experiments show that increasing the ratio c^b/X reduces the effect of the membrane fixed charge and the values of $|v|$,[2,12] in agreement with the results of Fig. 3, where $\rho_e(0)$ and $|v|$ are plotted as a function of a_i/a for the values of $c^b/X = 0.5$, 1.0 and 1.5 (left figures) and as a function of c^b/X for the values of $a_i/a = 0.0$, 0.1 and 0.2 (right figures).

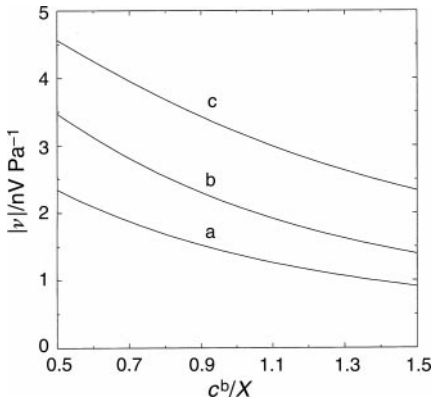

Fig. 4 Streaming potential calculated with the space charge distribution of: (a) point ions with D_i^0 in eqn. (23), (b) point ions with D_i in eqn. (22) and (c) finite size ions with D_i in eqn. (22).

The size effects have been introduced by modifying both the space charge distribution (see eqn. (3) and (13)) and the diffusion coefficients (see eqn. (22)). To clearly show the importance of the first modification, Fig. 4 shows the streaming potential calculated with the space charge distribution of point ions (using D_i^0 in eqn. (23), curve a; and D_i in eqn. (22), curve b) and with that of finite size ions (curve c). Usually, it is only the size effect given by eqn. (22) that is considered when studying the transport through narrow pores.[9] However, Fig. 4 shows that the size effect on the space charge distribution accounts for roughly half the total effect of the ionic size on v, and thus cannot be neglected.

Acknowledgements

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