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The Development of Pressure Across Membranes in

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Donnan Systems

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Supplementary Information File 1

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Numerical Analysis of Poisson Electric Equation for a Particular

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Donnan System

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The Poisson electric equation was solved numerically for the bulk water-filled pores

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within the membrane. The system is homogenous with respect to the y and z coordinates,

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and so the Poisson equation takes the form:

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$$d^2\phi/dx^2 = -\rho/(80\epsilon)$$

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where ϕ is the electric potential, ρ is the charge density, ϵ is the permittivity of free space

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and 80 is the dielectric constant of water.

17 We present the numerical analysis for a particular Donnan system that comprises the
18 following solutions:

19 On the left-hand side, i.e., at $x < 0$,

20 $C_{-\infty}$ (a monovalent counterion, e.g., C^+) = 0.9 mM

21 $C_{-\infty}$ (a monovalent coion, e.g., A^-) = 0.9 mM.

22 On the right-hand side, i.e. at $x > 0$,

23 C_{∞} (a monovalent counterion, e.g. C^+) = 8.1 mM

24 C_{∞} (a monovalent coion, e.g. A^-) = 0.1 mM

25 P_{∞} (charged polymer of valence $z_p = -8$) = 1.0 mM.

26 The system is in equilibrium as evidenced by the equality of the products of the permeant
27 cation and anion on the two sides of the membrane. As required, both solutions are
28 electroneutral far from the membrane.

29 Equilibrium is maintained by a potential difference between the two sides of the
30 membrane: if we set the reference potential $\phi(-\infty)$ to zero, the value of $\phi(\infty)$ is -58.7 mV
31 at 37°C. Since we assume that most of the equilibrium potential drop occurs across the
32 pores within the membrane, the numerical solution of the Poisson equation is intended to
33 describe the potential course within the pore from $x = -\infty$ to $x = 0$. As the potential becomes
34 more negative towards $x = 0$, the concentration of the ions in that layer changes according
35 to the Nernst equation:

36
$$C_i(\phi) = C_i(0) \exp(-z_i F \phi / RT) \quad [2].$$

37 The procedure for the numerical solution shown here proceeded at sequential layers of
38 water of thickness $\delta x = 1 \text{ \AA}$, after showing that further narrowing of δx does not affect the
39 results of the analysis. We start at a layer remote from the membrane that is temporarily

40 set at $x=0$. At this layer, ϕ and $d\phi/dx$ are set to zero, whereas $d^2\phi/dx^2$ is set at a very small
41 value. Generally, we applied the value of 10^{-5} mV/Å² to this initial layer. (Further
42 reduction of the initial value of $d^2\phi/dx^2$ did not affect the course of the potential near the
43 membrane; it just had the effect of moving the starting point farther away from the
44 membrane). Then we move closer to the membrane by repetitive 1 Å layer steps. The n 'th
45 layer is, therefore, at a distance of n Å from the starting point. Using Excel, we determine
46 for each layer of water the following parameters:

47 $\phi(n)$; This is determined as follows:

$$48 \quad \phi(n) = [d^2\phi/dx^2(n-1) + 2 * \phi(n-1) - \phi(n-2)] \quad [3],$$

49 where $d^2\phi/dx^2$ is given in units of mV/Å²

50 $[C^+](n)$ and $[A^-](n)$ are determined by the Nernst equation for 37⁰C and are given in

51 10^{-3} M/L, which is equivalent to M/m³.

52 $\rho(n)$ is equal to $\{[C^+](n) - [A^-](n)\}$ in units of 96.5 C/L = 96500 C/m³

$$53 \quad d^2\phi/dx^2 (n) = k\rho(n).$$

54 The proportionality constant k is the value of $d^2\phi/dx^2$ in mV/(Å)² when the ρ is 96500

55 C/m³.

56 Calculation of k is shown below.

57 The procedure is stopped at n_{final} where $\phi(n_{\text{final}}) = \phi^{\text{eq}}$ (or when absolute value of

58 $\phi(n_{\text{final}+1}) >$ the absolute value of ϕ^{eq}).

59 At this point it is possible to depict any of the calculated parameters as a function of their
60 distance from the membrane, m , where the n 'th layer is at a distance m ($m=n-n_{\text{final}}$) Å
61 from $x=0$, i.e., from the junction of pores and the solution on side 2. The curves for ϕ , ρ in
62 Supplementary Figure S1 are taken from such an analysis for the particular Donnan cell
63 described above. The curve for the pressure P in this Figure is based either on the
64 numerical analysis or on the combined numerical analysis of ϕ as a function of x and the
65 analytical results expressing the value of P as a function of ϕ (see text equation 5). In
66 comparing the two methods we found that the maximal difference between the P values
67 at a particular x were less than 2%.

68 The value of k was determined as follows:

69
$$d^2\phi/dx^2 = -\rho/(80\epsilon)$$

70 For $\rho = 96500 \text{ C/m}^3$ $d^2\phi/dx^2 = -96500/(80\epsilon)$

71 $\epsilon = 1/(36\pi * 10^9)$ in units of F/m; hence,

72 $d^2\phi/dx^2 = -96500/(80\epsilon) = 96500 * 36\pi * 10^9/80$ in units of V/m².

73 To convert it to units of mV/Å² we have to multiply it by 10⁻¹⁷ since 10³ mV = Volt, and

74 $10^{20} \text{ Å}^2 = \text{m}^2$.

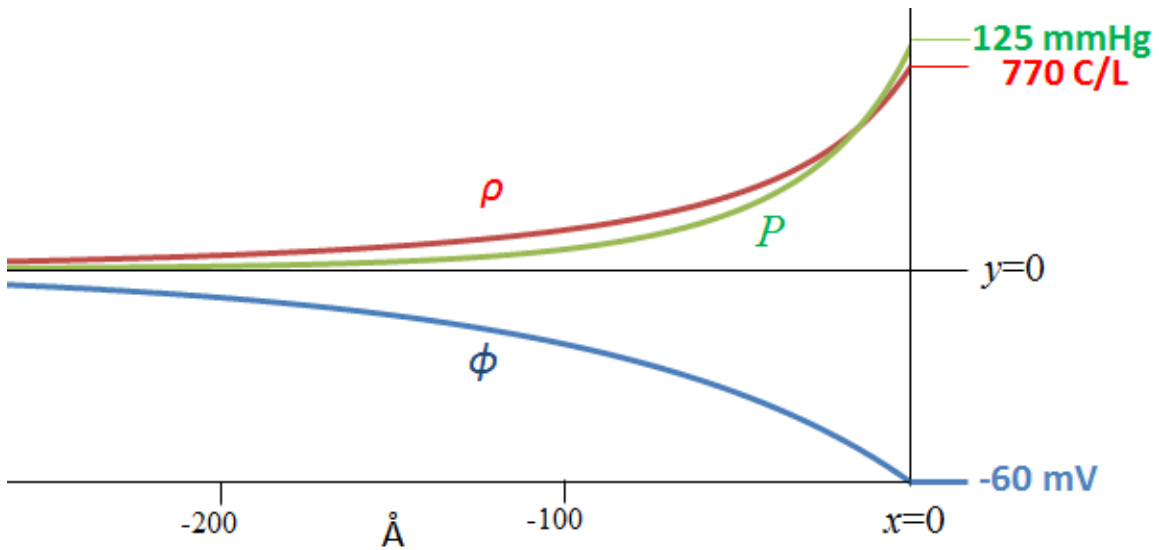
75 Therefore, $k = 0.001364$ in units of mV/Å²/mEq/L

76 The data of the numerical solution of the Donnan system described in Figure S1 is

77 presented in the Supplementary Excel file.

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81 Supplementary Figure S1: The course of ϕ , ρ and P as a function of distance from
82 the junction between the pores and the solution on side 2 (which is set at $x=0$) for the
83 particular Donnan system described above. It is assumed that the system behaves ideally,
84 i.e., activity coefficients of the solutes are close to unity. The value of P as a function of x
85 was obtained by two ways: 1), by the numerical solution of the cumulative force acting
86 on the charges in the pore and 2), from the analytical solution of $P(\phi)$ as expressed by
87 equation 5 in the text and the numerical resolution of $\phi(x)$ as shown here; the difference
88 between the two is below the resolution of the plot for all values of $x < 0$.

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93 Supplementary Information File 2

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95 The Contribution of the Action of the Electric Forces within Pores to the
96 Appearance of Pressure across Membranes in Donnan Systems

97 We begin by using the well-known expression for the Nernst potential, limiting ourselves
98 to dilute solutions (where activity coefficients are close to unity), and consider the side
99 containing only permeant ions (side 1 in text Figure 1):

100
$$C_i(\phi) = C_i(0) \exp(-z_i F \phi / RT),$$

101

102 where C_i is the concentration of permeant ion i (mol/m³), z_i is the valence, F is the
103 Faraday constant (C/mol), R is the universal gas constant (J/K/mol), T is the absolute
104 temperature (K), and ϕ is the potential (V); ϕ is set to 0 far from the membrane in the
105 *negative* direction.

106 The charge density ρ (C/m³) is

107
$$\rho = \sum_i C_i(0) z_i F \exp(-z_i F \phi / RT),$$

108 so that the force δf (J/m or N) acting on a thin layer of solution of area A (m²) and
109 thickness δx (m) is

110
$$\delta f = -\rho (A \delta x) (\delta \phi / \delta \mathbf{x})$$

111
$$= -\sum_i C_i(0) z_i F \exp(-z_i F \phi / RT) (A \delta x) (\delta \phi / \delta \mathbf{x}).$$

112 The pressure difference δP (N/m^2) across the layer is thus

113 $\delta P = \delta f / A$

114 $= -\sum_i C_i(0) z_i F \exp(-z_i F \phi / RT) \delta \phi,$

115 P being a function of x only through the dependence on ϕ , and

116 $\delta P(\phi) / \delta \phi = -\sum_i C_i(0) z_i F \exp(-z_i F \phi / RT).$

117 If now $\delta \rightarrow 0$, we can integrate $P(\phi)$ over ϕ to get

118 $P(\phi) = RT \sum_i C_i(0) \exp(-z_i F \phi / RT) + \text{constant}.$

119 The change in $P(\phi)$ when ϕ goes from 0 to its equilibrium value ϕ^{eq} , is thus simply

120 $\Delta P = P(\phi^{eq}) - P(0) = RT [\sum C_i(\phi^{eq}) - \sum C_i(0)].$

121 Note that 1 mol/m^3 , the units of C_i , is equivalent to $1000 \text{ mmol}/1000 \text{ L}$ or 1 mM .

122

123 The fact that ΔP is dependent on ϕ but independent of x , although ϕ is dependent on x ,

124 implies that the conclusion that ΔP accounts precisely for the difference between the

125 osmotic values of the two solutions in a Donnan system is true even if there are minor

126 discrepancies in the numerical values used for the various constants.

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