THE DONNAN EQUILIBRIUM

A Theoretical Study of the Effects of Interionic Forces

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ABSTRACT We investigate the conditions under which nonideality in solution influences the Donnan equilibrium. Of the various parameters that characterize this equilibrium, the osmotic pressure established across the Donnan membrane is found to be particularly sensitive to intermolecular interactions between the diffusible and nondiffusible ionic species. Under physiologically appropriate conditions, we find that it is almost never valid to use Debye-Hückel theory to calculate ionic activities: it is important to take proper account of ion size. When the diffusible species is a 1-1 electrolyte, this can be done using the mean spherical approximation (MSA) for a mixture of ions of different diameters. For 2-2, or higher-valent, electrolytes one should also include the effects of the second ionic virial coefficient, which the MSA omits.

INTRODUCTION

Consider a two-phase ionic system, in which one charged component is physically restricted to one phase, but ions of any other species can move freely between the two phases. Such a situation can arise when two electrolyte solutions are separated by a semi-permeable membrane, which allows small ions to pass through its pores, but blocks the passage of larger ions. It can also result from the inherently immobile nature of one charged component, such as the fixed protein filaments of a muscle lattice equilibrated in a salt solution. In either case, an uneven distribution of the diffusible ions over the two phases will develop, as their concentrations adjust to make their electrochemical potentials the same in each phase. In turn, this establishes an osmotic pressure difference and an electric potential difference between the phases. This type of ionic equilibrium is termed a Donnan equilibrium (Overbeek, 1956).

Experimental studies of the Donnan equilibrium in physiological systems can yield much valuable information, such as the charge density carried by filaments of muscle lattice (see for example Aldoroty et al., 1985). Values thus obtained are usually derived assuming the electrolyte solutions behave ideally. In this paper we report results that suggest that this may not always be a good approximation at typical physiological ionic strengths (~0.1 M). Our calculations also reveal the inadequacy of attempting to correct for nonideality by using Debye-Hückel theory. In the Donnan equilibrium the nondiffusible species may be a protein molecule with a diameter of 100 Å or more, and in calculating ionic activity coefficients it is clearly important to take proper account of ionic size effects.[1]

We have attempted to do this using the mean spherical approximation (MSA). The MSA for a neutral mixture of charged hard spheres of unequal diameters—i.e. the unrestricted primitive model of electrolyte solutions—has been solved analytically by Blum (1975) and Blum and Høye (1977). Triolo et al. (1977) have shown that it yields very good results for ionic activity and osmotic coefficients in 1-1 aqueous electrolyte solutions at concentrations up to 2 M. Romero-Rochín et al. (1984) have previously applied this theory to the Donnan equilibrium problem. Unfortunately, their calculations contain several errors, and they badly overestimate the effects of nonideality.

To extend the validity of our calculations beyond the 1-1 regime we include the effect of the second ionic virial coefficient (Friedman, 1962). This is a contribution to the ionic free energy that must be taken into account for 2-2 and higher-valent electrolytes at moderate ionic strengths, but is omitted by the MSA. It has been evaluated for the restricted primitive model (i.e., a symmetrically charged system of hard spheres of equal diameter) by Stell and Larsen (1979). In an appendix to this paper we calculate it for the more general unrestricted case.

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[1] Hill (1956, 1958) has previously treated these effects in an approximate fashion using a modified Debye-Hückel theory. However, his analysis neglects potentially significant contributions to the ionic activity. Our treatment includes these terms.

THEORY

We treat the simplest possible case, where the equilibrium is established between two ionic solutions of equal volume separated by a structureless membrane. One solution contains ions of two species, designated 1 and 2, which can pass freely across the membrane. The other solution also contains charged proteins, designated p. These can move freely about on their own side of the membrane, but cannot cross it. The ionic valences are z_1, z_2, and z_p. In the initial nonequilibrium state of the system, the molecular number densities in the first solution are ρ_{10}, ρ_{20}, and in the second solution they are ρ^*_{10}, ρ^*_{20}, and ρ_p. After equilibration these densities change to ρ_1 and ρ_2, and ρ^*_1, ρ^*_2, and ρ_p, respectively.

At equilibrium the electrochemical potential of the diffusible species will be the same on both sides of the membrane. That is

$$\mu_\alpha = \mu^*_\alpha, \quad \alpha = 1, 2, \tag{1}$$

where

$$\begin{aligned} \mu_\alpha &= \mu^0_\alpha (T) + kT \log a_\alpha + z_\alpha e\psi\,, \\ \mu^*_\alpha &= \mu^0_\alpha (T) + kT \log a^*_\alpha + z_\alpha e\psi^*\,. \end{aligned} \tag{2}$$

In Eq. 2 T is the absolute temperature, and k is Boltzmann's constant. e is the electronic charge, and ψ is the electric potential. $\mu^0_\alpha(T) = kT \log [h^3/(2\pi m_\alpha kT)^{3/2}]$, where h is Planck's constant, and m_α is the mass of a molecule of species α. $a_\alpha = \gamma_\alpha \rho_\alpha$ is the ionic activity (γ_α is the activity coefficient). Solving Eqs. 1 and 2, we obtain the Nernst-Planck equation relating the activities in the two phases

$$a_\alpha/\alpha^*_\alpha = \exp (z_\alpha e\Psi/kT), \quad \alpha = 1, 2, \tag{3}$$

where $\Psi = \psi^* - \psi$ is the electric potential difference across the membrane (the Donnan potential).

Eliminating Ψ from Eq. 3 we find

$$z_1^{-1} \log (\rho_1\gamma_1/\rho^*_1\gamma^*_1) = z_2^{-1} \log (\rho_2\gamma_2/\rho^*_2\gamma^*_2). \tag{4}$$

Electroneutrality on either side of the membrane demands that

$$\rho_1 z_1 + \rho_2 z_2 = 0 \tag{5}$$

and

$$\rho^*_1 z_1 + \rho^*_2 z_2 + \rho_p z_p = 0, \tag{6}$$

while a fourth relation among the ionic densities follows from the conservation law

$$\rho_2 + \rho^*_2 = \rho_{20} + \rho^*_{20}. \tag{7}$$

Provided we have some suitable prescription for calculating the activity coefficients (which are themselves functions of concentration), we can solve Eqs. 4–7 to determine the equilibrium ionic concentrations. Although an exact analytic solution is clearly out of the question, solution by a numerical, iterative procedure is quite straightforward. Once we have these concentrations we can compute any desired thermodynamic property of the Donnan system using standard methods. The Donnan potential comes directly from Eq. 3.

Activity Coefficients

We have performed the calculations at various levels of approximation, using activity coefficients from several different theories.

At the most basic level—complete neglect of all intermolecular interactions in solution—one has simply $\gamma_\alpha = 1$ ($\alpha = 1, 2, p$). This is the "ideal" case.

Debye-Hückel theory views the ions as point charges, and allows for the electrostatic interaction between these charges. The activity coefficients are given by

$$\log \gamma^{\mathrm{DH}}_\alpha = -z^2_\alpha \frac{\kappa\lambda}{8\pi}. \tag{8}$$

Here $\lambda = e^2/\epsilon\epsilon_0 kT$, where ϵ is the dielectric constant of the solvent and ϵ_0 is the permittivity of free space, and $\kappa = (\lambda\mu_2)^{1/2}$, where $\mu_2 = \Sigma_\alpha \rho_\alpha z^2_\alpha$ is the ionic strength. κ is called the "inverse Debye length." As is well known, Debye-Hückel theory fails badly at moderate ionic concentrations (Friedman, 1962). One of the chief reasons for this failure lies in the neglect of excluded volume effects. In reality ions are not point charges; a better model views them as charged hard spheres of diameter σ_α. In Debye-Hückel theory one expects to find ions of opposite charge separated by distances of order κ^{-1}; the theory therefore breaks down unless $\kappa^{-1} \gg \sigma_\alpha$, i.e. $\kappa\sigma_\alpha \ll 1$. This condition is satisfied only at very low concentrations. In our case the problem is made more acute by the very large size of the protein molecules ($\sigma_p \sim 100$ Å).

The mean spherical approximation (MSA) attempts to remedy this defect. The MSA is an integral equation theory based on the Ornstein-Zernike equation relating the total ($h_{\alpha\beta}$) and direct ($c_{\alpha\beta}$) correlation functions

$$h_{\alpha\beta} (r) = c_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \int c_{\alpha\gamma}(r')h_{\gamma\beta}(|\mathbf{r} - \mathbf{r}'|)\, \mathrm{d}\mathbf{r}' \tag{9}$$

(readers unfamiliar with this notation should consult Stell [1964]). For the unrestricted primitive model of electrolyte solutions the MSA supplies the following closures for Eq. 9:

$$h_{\alpha\beta}(r) = -1, \quad r < \sigma_{\alpha\beta}, \tag{10}$$

and

$$c_{\alpha\beta}(r) = -\beta u_{\alpha\beta}(r), \quad r > \sigma_{\alpha\beta}. \tag{11}$$

In these equations $\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_\alpha + \sigma_\beta)$, and $\beta = 1/kT$. $u_{\alpha\beta}(r) = z_\alpha z_\beta e^2/4\pi\epsilon\epsilon_0 r$ is the electrostatic potential energy of interaction of two ions. Eq. 10 is exact, but Eq. 11 is only approximately true. One expects the MSA to work best for uni-univalent electrolytes ($z_\alpha = 1$).

Blum (1975) and Blum and Høye (1977) have solved the MSA for this model. They show that the ionic activity coefficient can be written as a product of two terms, viz.

$$\gamma_\alpha^{\text{MSA}} = \gamma_\alpha^{\text{HS}}\,\gamma_\alpha^{\text{COUL}}. \tag{12}$$

$\gamma_\alpha^{\text{HS}}$ originates in the short-range repulsive forces between the ions; it is the activity coefficient for a mixture of (uncharged) hard spheres calculated in the Percus-Yevick approximation (Lebowitz and Rowlinson, 1964).[2] $\gamma_\alpha^{\text{COUL}}$ arises from the coulombic forces between the ions, and is given (to an excellent approximation) by

$$\log \gamma_\alpha^{\text{COUL}} = -z_\alpha^2 \frac{\lambda}{4\pi} \frac{\Gamma}{1 + \Gamma\sigma_\alpha}. \tag{13}$$

Here the parameter Γ is found by solving the implicit equation

$$2\Gamma = \left[\lambda \sum_\alpha \rho_\alpha \left(\frac{z_\alpha}{1 + \Gamma\sigma_\alpha}\right)^2\right]^{1/2}. \tag{14}$$

In the MSA 2Γ plays a role analogous to that of κ in Debye-Hückel theory.

It is worth noting that $\gamma_\alpha^{\text{HS}} > 1$, while $\gamma_\alpha^{\text{COUL}} < 1$. Hence we may have either $\gamma_\alpha^{\text{MSA}} > 1$ or $\gamma_\alpha^{\text{MSA}} < 1$, with the outcome depending on the relative values of the ionic charge (z_α) and size (σ_α). For the small, diffusible ions in the Donnan system it is invariably true that $\gamma_\alpha^{\text{MSA}} < 1$. Both possibilities have been observed for the protein, however.

In the limit of extreme dilution, MSA activity coefficients reduce to those calculated from Debye-Hückel theory. At moderate concentrations, however, there is generally an appreciable difference.

As noted previously, the MSA omits certain terms which may be significant for multi-valent electrolytes. One way to correct for this has been discussed by Stell and Larsen (1979). Under the conditions of the Donnan equilibrium, the most important correction is the second ionic virial coefficient, B_2. In an appendix we calculate the associated activity coefficient, $\gamma_\alpha^{B_2}$. The corrected activity coefficient is then calculated from

$$\gamma_\alpha^{\text{MSA}+B_2} = \gamma_\alpha^{\text{MSA}}\,\gamma_\alpha^{B_2}. \tag{15}$$

Osmotic Pressure

The Donnan equilibrium establishes an osmotic pressure difference across the membrane separating the two solutions. This is given by

$$\pi = p^* - p, \tag{16}$$

where p and p^* are the pressures on the two sides. If we assume ideal behavior, then

$$\beta p^{\text{ID}} = \sum_\alpha \rho_\alpha, \tag{17}$$

whereas the Debye-Hückel result is

$$\beta p^{\text{DH}} = \beta p^{\text{ID}} - \kappa^3/24\pi. \tag{18}$$

For the MSA we have

$$p^{\text{MSA}} = p^{\text{HS}} + p^{\text{COUL}}, \tag{19}$$

where p^{HS} is the Percus-Yevick hard sphere pressure (Lebowitz and Rowlinson, 1964), and

$$\beta p^{\text{COUL}} = -\Gamma^3/\,3\pi \tag{20}$$

(Blum and Høye, 1977). Finally, including the effect of the second ionic virial coefficient raises the pressure to

$$p^{\text{MSA}+B_2} = p^{\text{MSA}} + p^{B_2}, \tag{21}$$

where

$$\beta p^{B_2} = B_2 + \sum_\alpha \rho_\alpha \log \gamma_\alpha^{B_2}. \tag{22}$$

RESULTS

Our calculations are for aqueous solutions at 25°C, and assume a dielectric constant of 78.5. We have taken $\rho_{20} = \rho_{20}^* = 0.1$ M and $\rho_p = 0.001$ M. Diffusible ion diameters are $\sigma_1 = \sigma_2 = 4$ Å. For the protein we have used either $\sigma_p = 40$ Å or $\sigma_p = 80$ Å. These proteins would have molecular weights of about 25,000 and 200,000, respectively; the corresponding protein mass fractions would be about 2.5% and 20%. Diffusible ion valences are either $z_1 = -z_2 = 1$ or $z_1 = -z_2 = 2$. For the smaller protein we chose $-z_p = 5, 10,$ or 20, and for the larger protein $-z_p = 20, 40, 80,$ or 160—implying charges of about 1–10 e per 10,000 mol wt. Such values might be encountered under typical physiological conditions. For each set of parameters we computed the equilibrium ionic concentration ρ_1, osmotic pressure π and Donnan potential Ψ, using each of the theories discussed in the previous section. Our results appear in Tables I through IV.

We can summarize these results as follows:

(*a*) Debye-Hückel theory typically gets Ψ wrong by a

TABLE I

EQUILIBRIUM IONIC CONCENTRATION ρ_1(M), OSMOTIC PRESSURE π (atm) AND DONNAN POTENTIAL Ψ (mV): SMALL PROTEIN, 1-1 ELECTROLYTE

		ID	DH	MSA	MSA+B₂
	ρ_1	0.101	0.100	0.103	0.103
$z_p = -5$	π	0.0260	0.0177	0.0281	0.0280
	$-\Psi$	0.634	0.626	0.643	0.651
	ρ_1	0.102	0.097	0.104	0.104
$z_p = -10$	π	0.0304	−0.0867	0.0318	0.0310
	$-\Psi$	1.25	1.19	1.27	1.28
	ρ_1	0.105	0.088	0.105	0.105
$z_p = -20$	π	0.0478	−1.33	0.0315	0.0278
	$-\Psi$	2.45	2.12	2.45	2.46

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[2] Eq. 2.7 of this reference contains an error. For '+ log (1 − ξ)' read '− log (1 − ε)'.

TABLE II
LARGE PROTEIN, 1-1 ELECTROLYTE

		ID	DH	MSA	MSA+B_2
	ρ_1	0.105	0.088	0.116	0.116
$z_p = -20$	π	0.0478	−1.33	0.0795	0.0758
	$-\Psi$	2.45	2.12	2.74	2.75
	ρ_1	0.109	0.066	0.119	0.119
$z_p = -40$	π	0.113	−13.1	0.158	0.152
	$-\Psi$	4.68	3.35	5.17	5.17
	ρ_1	0.117	0.029	0.124	0.124
$z_p = -80$	π	0.351	−111	0.282	0.276
	$-\Psi$	8.65	4.93	9.26	9.26
	ρ_1	0.129	0.004	0.132	0.132
$z_p = -160$	π	1.14	−891	0.289	0.285
	$-\Psi$	15.1	7.7	15.5	15.5

TABLE IV
LARGE PROTEIN, 2-2 ELECTROLYTE

		ID	DH	MSA	MSA+B_2
	ρ_1	0.102	0.003	0.122	0.120
$z_p = -20$	π	0.0304	−9.56	−0.0298	0.0290
	$-\Psi$	0.627	0.318	0.779	0.828
	ρ_1	0.105	0.001	0.122	0.121
$z_p = -40$	π	0.0478	−29.8	0.0381	−0.0697
	$-\Psi$	1.22	0.61	1.47	1.47
	ρ_1	0.109	0.000	0.119	0.118
$z_p = -80$	π	0.113	−147	0.168	0.010
	$-\Psi$	2.34	1.17	2.58	2.55
	ρ_1	0.117	0.000	0.110	0.109
$z_p = -160$	π	0.351	−964	0.055	−0.111
	$-\Psi$	4.32	2.16	4.08	4.05

factor of 2, and its estimates of ρ_1 and π bear no resemblance to reality.

(*b*) For the smaller protein, the MSA offers very little improvement over ideal solution theory. For the larger protein, however, it yields values for ρ_1 and Ψ moderately different, and a value for π substantially different, from the ideal results.

(*c*) When the diffusible electrolyte is 1-1, adding B_2 has very little effect. For the 2-2 case ρ_1 and Ψ remain largely unaffected, but there is a large effect on π.

If the density of diffusible ions is reduced to $\rho_{20} = \rho_{20}^* = 0.01$ M, we find essentially the same results. Increasing the density to 1 M, we find a much larger effect of the MSA on π in the 2-2 case. Here the corrections are significant even for the smaller protein. On the other hand, the effects of adding B_2 are greatly reduced.

CONCLUSIONS

Our results suggest that conventional treatments of the Donnan equilibrium, which neglect interionic interactions and assume ideal behavior, may not always be adequate under typical physiological conditions. One should properly allow for the effects of both long-range electrostatic and short-range repulsive forces, using a statistical-mechanical theory such as the mean spherical approximation, perhaps augmented by the second virial coefficient. Otherwise, one runs the risk that characteristic properties of the system (e.g. the charge by the proteins), which are inferred from experimental data, may be in error.

TABLE III
SMALL PROTEIN, 2-2 ELECTROLYTE

		ID	DH	MSA	MSA+B_2
	ρ_1	0.101	0.006	0.103	0.103
$z_p = -5$	π	0.0248	−4.15	0.0254	0.0435
	$-\Psi$	0.160	0.082	0.164	0.193
	ρ_1	0.101	0.005	0.103	0.103
$z_p = -10$	π	0.0260	−5.22	0.0276	0.0610
	$-\Psi$	0.317	0.163	0.324	0.370
	ρ_1	0.102	0.003	0.103	0.101
$z_p = -20$	π	0.0304	−9.56	0.0315	0.0338
	$-\Psi$	0.627	0.318	0.629	0.673

It is not clear whether similar conclusions would apply were the proteins fixed, as in muscle, rather than freely mobile in solution. We are currently attempting to extend our work to cover this case also.

APPENDIX

Calculation of the Second Ionic Virial Coefficient

This calculation extends earlier work by Stell and Larsen (1979) on the restricted primitive model. We consider the more general unrestricted case.

The MSA prediction for the free energy, A^{MSA}, differs slightly from the true value, A. The leading correction is a quantity termed the second ionic virial coefficient, and denoted B_2. Thus

$$-\beta(A - A^{\text{MSA}})/V = B_2 + \cdots, \tag{23}$$

where V is the volume. As shown by Stell (1976),

$$B_2 = 2\pi \sum_{\alpha\beta} \rho_\alpha \rho_\beta \int_0^\infty \left\{ g_{\alpha\beta}^{\text{HS}}(r) \{\exp[q_{\alpha\beta}(r)] - 1 - q_{\alpha\beta}(r)\} - \frac{1}{2} q_{\alpha\beta}(r)^2 \right\} r^2 \, \mathrm{d}r. \tag{24}$$

In this equation $g_{\alpha\beta}^{\text{HS}}$ is the radial distribution function for a hard-sphere reference system. We will approximate $g_{\alpha\beta}^{\text{HS}}$ by its low-density limit, viz.

$$\begin{aligned} g_{\alpha\beta}^{\text{HS}}(r) &= 0, \quad r < \sigma_{\alpha\beta}, \\ &= 1, \quad r > \sigma_{\alpha\beta}. \end{aligned} \tag{25}$$

$q_{\alpha\beta}$ is termed a "chain function," and is basically a renormalized pair potential. For $r < \sigma_{\alpha\beta}$, $q_{\alpha\beta}(r) = 0$. For $r > \sigma_{\alpha\beta}$, to a good approximation

$q_{\alpha\beta}(r) = -\beta\phi_{\alpha\beta}^{\mathrm{DH}}(r)$, where $\phi_{\alpha\beta}^{\mathrm{DH}}$ is the Debye-Hückel potential of mean force

$$\phi_{\alpha\beta}^{\mathrm{DH}}(r) = \frac{z_\alpha z_\beta e^2}{4\pi\epsilon\epsilon_0 r}\exp(-\kappa r). \tag{26}$$

In Eq. 24 we expand exp $(q_{\alpha\beta})$ in powers, and integrate term-by-term. We thus obtain

$$B_2 = 2\pi\sum_{\alpha\beta}\rho_\alpha\rho_\beta\sigma_{\alpha\beta}^3\sum_{n=3}^{\infty}\frac{(-\beta_{\alpha\beta}^*)^n}{n!}E_{n-2}(nx_{\alpha\beta}), \tag{27}$$

where

$$E_n(z) = \int_1^\infty \frac{e^{-zr}}{r^n}\,\mathrm{d}r \tag{28}$$

is the *n*th order exponential integral, as defined by Gautschi and Cahill (1965). We have introduced the two dimensionless parameters $x_{\alpha\beta} = \kappa\sigma_{\alpha\beta}$ and $\beta_{\alpha\beta}^* = \beta z_\alpha z_\beta e^2/4\pi\epsilon\epsilon_0\sigma_{\alpha\beta}$.

The activity coefficient associated with Eq. 27 is then given by

$$\begin{aligned}\log\gamma_\alpha^{B_2} &= -\left(\frac{\partial B_2}{\partial\rho_\alpha}\right)_{\rho_\beta,\beta}\\ &= -4\pi\sum_\beta\rho_\beta\sigma_{\alpha\beta}^3\sum_{n=3}^{\infty}\frac{(-\beta_{\alpha\beta}^*)^n}{n!}E_{n-2}(nx_{\alpha\beta})\\ &\quad+\frac{\pi}{\mu_2}z_\alpha^2\sum_{\beta\gamma}\rho_\beta\rho_\gamma\sigma_{\beta\gamma}^3\sum_{n=3}^{\infty}\cdot\frac{(-\beta_{\beta\gamma}^*)^n}{n!}nx_{\beta\gamma}E_{n-3}(nx_{\beta\gamma}).\end{aligned} \tag{29}$$

While this expression may appear rather formidable, it is easily evaluated numerically.

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