Distribution of ions between different dielectric media: direct simulation of the Donnan equilibrium in the grand canonical ensemble

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Abstract

A modification of the original Grand Canonical Monte Carlo (GCMC) method to handle Donnan equilibrium is proposed that provides an equilibrium between two implicit-solvent bath electrolytes with different dielectric constants. A solvation energy penalty (described by the Born theory) and an electrical potential difference (Donnan potential) exist between the two baths, the 'system' under investigation and the 'reservoir'. These terms are deducted from the chemical potential of the 'reservoir', and the resulting chemical potential is used in the 'system'. The simulation performed with this chemical potential in the acceptance probabilities of the ion insertion/deletions is called Donnan GCMC and provides a thermodynamic state in the 'system' that is in equilibrium with the electrolyte in the 'reservoir'. The simulation provides the distribution of ions between the two baths (concentrations in both media) from a single run instead of a numerical procedure that requires several GCMC runs. Using individual ion insertion/deletions, the Donnan potential can be determined.

1. Introduction

Partitioning of ions between different environments is a fundamental phenomenon in physics and chemistry, and it also drives technological applications and biological processes. Examples are plentiful, from energy storage (e.g., supercapacitors [1]), nanotechnology (energy conversion [2]), water purification [3], and biology (calcium microdomains in a cell [4], interiors of and cavities in macromolecules [5–7], ion channels [8, 9]). At the heart of this partitioning is the question of how many ions are adsorbed from a bulk electrolyte into environments that are different from the bulk.

One way to create such a situation is to separate two bath electrolytes with a semipermeable membrane that generally does not let the bigger charged species through, thus creating a electrical imbalance between the two media. The cell membrane is the most common example [10]. The charged species that cannot pass the membrane can be many things, from polyelectrolytes to macromolecules. Gels and coacarvates can also prevent the polymer from escaping to the reservoir. [11]

Barr and Panagiotopoulos [12] proposed a Grand Canonical Monte Carlo (GCMC) simulation method that provides the thermodynamic equilibrium for such a system. They implemented individual ion insertion/deletion steps that made it possible to compute the electrical potential difference (Donnan potential) between the two baths. A variant of the method combined with the Grand-Reaction method simulates ionization equilibria at constant pH [13].

In this work we focus on another way of producing ion partitioning between two different media, namely, when they have different dielectric constants. Since the dielectric constant describes the ability of the medium to screen the charge of the ion q_i (or, vice versa, the ability of the ion to polarize the medium), dielectrics can differ from a number of reasons. (1) The solvent can be different in the two fluids. (2) Even the same solvent changes its ability to screen if an electric field is applied (dielectric saturation). This electric field can be produced by charges at functional groups on surfaces, by electrode charges, or by the ions themselves; the dielectric constant is smaller in a concentrated electrolyte than in a dilute one. [14] (3) Confinement can also constrain the behavior of a liquid, and thus, the dielectric constant.

When ions move between the two dielectric media, they necessarily pass a dielectric interface between the two baths. When the two baths are parts of the same simulation cell, the interface is also part of the cell. Ions passing through the

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dielectric boundary pose a numerical challenge whose solution is possible but complicated and requires considerable computational time. [15]

In this work, we propose a Monte Carlo (MC) simulation procedure for implicit-solvent (primitive) models of electrolytes to directly simulate the distribution of ions between two bulk (homogeneous) electrolytes with dielectric constants $\epsilon^{\rm sys}$ and $\epsilon^{\rm res}$ (Fig. 1) without including the dielectric boundary. The notations "sys" and "res" refer to the system that we simulate and the reservoir that is virtual and defined by its chemical potentials, respectively. Our long-term goal is a method for cases when one or both of the systems are inhomogeneous (a pore or a slit, for example). However, as a first step, here we focus on partitioning between two bulk fluids.

The method is based on the GCMC algorithm and can be regarded as an extension of that of Barr and Panagiotopoulos [12] for the case of different dielectric constants. In the original GCMC formalism, an open system with volume V, temperature T, and chemical potentials of ionic species i, μ_i, is in equilibrium with a virtual reservoir described by these variables [16]. However, most importantly for us, a reservoir whose dielectric constant is the same as that of the system. Here, we abandon this assumption and ask the question: what happens when the dielectric constants differ between the simulated system and the bath with which it is in equilibrium.

In an earlier paper, we developed a method for passing an ion through a sharp dielectric boundary while diffusing from the bath into the interior of an ion channel, for example. [15] The difference between that work and our proposed method is that in the previous work the bath that equilibrates the system is part of the simulation cell, whereas in the proposed work it is not (i.e., it is a virtual bath). This requires technical changes to the GCMC method even when the target system is another bulk. These changes are the focus of this work. What additional technical steps are needed for inhomogeneous target systems is an open question.

The system of two bulks that we consider is similar to a classic Donnan system [17], wherein two baths are separated by a semipermeable membrane and, in order to equilibrate, an electrostatic potential difference is generated (the Donnan potential). In the sense that the dehydration energies of the ions moving from a high-dielectric medium to a low-dielectric medium replicate the effects of a semipermeable membrane, our system of interest is a classic Donnan system. However, the dielectric constant also defines the interaction potential between ions in the primitive model of electrolytes. In that sense, the two-dielectric media system is a generalization of the classic Donnan case. Given these similarities, we call our method Donnan GCMC (D-GCMC).

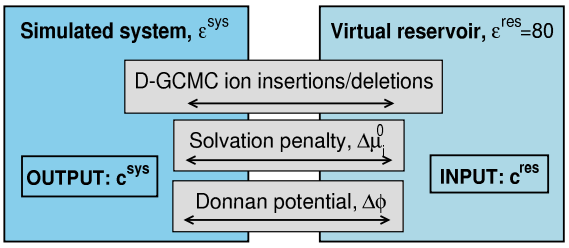

Figure 1: Schematic drawing of the coexisting systems. Left hand side: system (sys), right hand side: reservoir (res).

2. Model and method

2.1. Donnan equilibrium

Let us denote the various properties in the system and the reservoir with "sys" and "res" in superscripts, respectively. The electrochemical potentials for ionic species i are defined as

$$\mu_i^{\rm sys} = \mu_i^{0,{\rm sys}} + kT\ln c_i^{\rm sys} + \mu_i^{\rm ex,sys} + q_i\phi^{\rm sys} \qquad (1)$$

for the system and

$$\mu_i^{\rm res} = \mu_i^{0,{\rm res}} + kT\ln c_i^{\rm res} + \mu_i^{\rm ex,res} + q_i\phi^{\rm res} \qquad (2)$$

for the reservoir, where q_i is the ionic charge, $\mu_i^{\rm ex,sys}$ and $\mu_i^{\rm ex,res}$ are the excess chemical potentials originating from the interactions between the ions (it is zero in infinite dilution), $\phi^{\rm sys}$ and $\phi^{\rm res}$ are the mean electrical potentials in the respective baths, while $\mu_i^{0,{\rm sys}}$ and $\mu_i^{0,{\rm res}}$ are self (or reference) terms that contain T-dependent terms and, most importantly, the solvation terms that describe the interaction of the ion with the surrounding dielectric medium (solvent) undisturbed by other ions.

For equilibrium, we equate the electrochemical potentials in the two baths (setting $\mu_i^{\rm sys} = \mu_i^{\rm res}$). These equalities and the condition of charge neutrality define Donnan equilibrium:

$$\mu_+^{\rm c,sys} + \Delta\mu_+^0 + q_+\Delta\phi = \mu_+^{\rm c,res}, \qquad (3)$$

$$\mu_-^{\rm c,sys} + \Delta\mu_-^0 + q_-\Delta\phi = \mu_-^{\rm c,res}, \qquad (4)$$

$$\sum_i q_i c_i^{\rm sys} = 0, \qquad (5)$$

where $\Delta\phi = \phi^{\rm sys} - \phi^{\rm res}$ is the Donnan potential and $\Delta\mu_i^0 = \mu_i^{0,{\rm sys}} - \mu_i^{0,{\rm res}}$ is the difference of the solvation free energy between the two baths. The quantities

$$\mu_i^{\rm c,sys} = kT\ln c_i^{\rm sys} + \mu_i^{\rm ex,sys} \qquad (6)$$

and

$$\mu_i^{\mathrm{c,res}} = kT \ln c_i^{\mathrm{res}} + \mu_i^{\mathrm{ex,res}} \tag{7}$$

are the configurational chemical potentials.

The system contains three equations and three unknowns, c_+^{sys}, c_-^{sys}, and $\Delta\phi$. Each ionic species added to the electrolyte adds an equation and one unknown to the system.

2.2. Grand Canonical Monte Carlo

The configurational chemical potential is the one we generally use in the acceptance criterion of the insertion/deletion steps in GCMC simulations as

$$p_{i,\chi} = \frac{N_i! V^{\chi}}{(N_i+\chi)!} \exp\left(-\frac{\Delta U - \chi \mu_i^{\mathrm{c}}}{kT}\right). \tag{8}$$

Here, N_i is the number of ions of species i before insertion/deletion, ΔU is the energy change resulting from particle interactions in the system after insertion/deletion, $\chi = 1$ for insertion, and $\chi = -1$ for deletion.

Note that in the original formalism of GCMC simulations of electrolytes, neutral groups of ions (e.g., cation-anion pairs for 1:1 systems) were inserted/deleted to maintain charge neutrality. [18]

Eq. 8, however, allows insertion/deletion of individual ionic species. This simulation technique was previously shown to be suitable to leading to charge neutrality on average, while allowing charge fluctuations, as soon as "appropriate" chemical potentials, are used. [19] A key step is to find the "appropriate" excess chemical potentials in the reservoir $\{\mu_i^{\mathrm{ex,res}}\}$ that produce a charge neutral system with prescribed concentrations $\{c_i^{\mathrm{res}}\}$, namely, $\sum_i q_i c_i^{\mathrm{res}} = 0$. We use the Adaptive GCMC (A-GCMC) method [19] for this purpose. This is an iterative method based on individual ion insertions/deletions. Once c_i^{res} and $\mu_i^{\mathrm{ex,res}}$ are available, Eqs. 7 and 2 provide the configurational and electrochemical potentials. Note that Barr and Panagiotopoulos [12] also used individual ion insertions/deletions.

We use the minimum image convention with periodic boundary conditions in our simulations. We consider interactions between ions that are inside a central cubic simulation cell. Interactions outside the central simulation cell (long-range corrections) are ignored. This ensures that charge imbalances in the central simulation cell are not magnified by the periodic images. The effect of the, otherwise natural, charge fluctuations can be decreased by increasing the system size, approaching the thermodynamic limit. The effect of ignoring periodic images can also be decreased that way. We checked system-size dependence to ensure that the simulation box is large enough (see Fig. 1 of Ref. [19]). In our experience, this approach proved to be approriate in the implicit-solvent framework, because the Coulomb interactions are reduced by ϵ.

Eqs. 3-5 can also be solved with other statistical mechanical methods such as the Mean Spherical Approximation (MSA) theory [20] or any of its modifications [21–23]. In this work, we check our results against those given by the Extended Mean Spherical Approximation (MSAX) theory. [22]

2.3. Donnan Grand Canonical Monte Carlo

The basic idea of the proposed method is to use the configurational chemical potential of the ϵ^{sys} system, $\mu_i^{\mathrm{c,sys}}$, in the Boltzmann-factor of Eq. 8, as expressed from Eqs. 3-4, namely,

$$\exp\left(-\frac{\Delta U - \chi\left[\mu_i^{\mathrm{c,res}} - \Delta\mu_i^0 - q_i\Delta\phi\right]}{kT}\right). \tag{9}$$

The procedure then is that

1. Specify the concentrations of the reservoir: $\{c_i^{\mathrm{res}}\}$
2. Compute the excess and configurational chemical potentials with A-GCMC: $\{\mu_i^{\mathrm{c,res}}\}$
3. Use those chemical potentials in the acceptance criterion of D-GCMC (Eq. 9) and subtract the solvation penalty ($\Delta\mu_i^0$) and the interaction with the Donnan potential ($q_i\Delta\phi$). The simulation provides the concentrations in the simulated system: $\{c_i^{\mathrm{sys}}\}$
4. The Donnan potential used as an input does not necessarily provide a charge neutral system. Therefore, an outer loop is needed to find the $\Delta\phi$ value that provides $\sum_i q_i c_i^{\mathrm{sys}} = 0$.

The proposed procedure could also be used with the traditional GCMC method inserting neutral groups of ions if we are not explicitly interested in computing the Donnan potential $\Delta\phi$, but only the concentrations $\{c_i^{\mathrm{sys}}\}$. In that case we would equilibrate the salt and equate the mean electrochemical potentials,

$$\mu_{\pm} = \frac{\nu_+\mu_+ + \nu_-\mu_-}{\nu_+ + \nu_-}, \tag{10}$$

instead of the individual ones (ν_i is the stoichiometric coefficient), so the condition of equilibrium is just

$$\mu_{\pm}^{\mathrm{c,sys}} + \Delta\mu_{\pm}^0 = \mu_{\pm}^{\mathrm{c,res}} \tag{11}$$

instead of Eqs. 3-5. The acceptance criterion would contain $\sum_i \nu_i q_i \Delta\phi$, which is zero, so the Donnan potential would not appear in the simulations.

Solving the full system (Eqs. 3-5), however, requires simulations for the individual ionic species,

and simulations where the total charge of the system is not necessarily zero, but an output of the simulation. That is required to find the correct Donnan potential that produces charge neutrality.

2.4. The solvation term

The solvation term for the reservoir can be estimated from Born's theory [24] as

$$\mu_i^{0,\mathrm{res}} = \frac{q_i^2}{8\pi\epsilon_0 R_i}\left(\frac{1}{\epsilon^{\mathrm{res}}} - 1\right). \tag{12}$$

A similar equation applies for $\mu_i^{0,\mathrm{sys}}$ with ϵ^{sys} in it. This can be obtained from the electrostatic energy change of the insertion of a spherical bubble of radius R_i with a charge q_i in its center in the continuum characterized by a dielectric constant. The solvation penalty of moving the ion from the ϵ^{res} medium to the ϵ^{sys} medium is

$$\Delta\mu_i^0 = \frac{q_i^2}{8\pi\epsilon_0 R_i}\left(\frac{1}{\epsilon^{\mathrm{sys}}} - \frac{1}{\epsilon^{\mathrm{res}}}\right). \tag{13}$$

If we take this equation as one that describes the ϵ^{sys} dependence of $\Delta\mu_i^0$ (i.e., the inverse relation), we can reformulate it by using the solvation free energy at ϵ^{res} instead of the radius, R_i, to get

$$\Delta\mu_i^0 = \mu_i^{0,\mathrm{res}}\,\frac{\epsilon^{\mathrm{sys}} - \epsilon^{\mathrm{res}}}{\epsilon^{\mathrm{sys}}\left(\epsilon^{\mathrm{res}} - 1\right)}. \tag{14}$$

This expression was proposed in the work of Nonner et al. [25] describing the distribution of ions between two dielectric media. Because it contains only experimental parameters (solvation free energy at infinite dilution, $\mu_i^{0,\mathrm{res}}$, and dielectric constants ϵ^{sys} and ϵ^{res}), it was used in the II+IW theory that splits the chemical potential into terms corresponding to ion-ion (II) and ion-water (IW) interactions. [26–28] This theory was able to reproduce the non-monotonic concentration dependence of ionic activity coefficients without using any adjustable parameters [26–28].

2.5. Electrolyte model

The ions of the electrolyte are modeled as hard spheres with point charges in their centers, the "primitive" model (PM) of electrolytes. The spheres cannot overlap with each other. The interaction between ions in the system is

$$u(r) = \begin{cases} \infty & \text{for} \quad r < R_i + R_j \\ \dfrac{1}{4\pi\epsilon_0\epsilon^{\mathrm{sys}}}\dfrac{q_i q_j}{r} & \text{for} \quad r \geq R_i + R_j \end{cases}, \tag{15}$$

where R_i and R_j are the ionic radii of species i and j, ϵ_0 is the permittivity of vacuum, and r is the distance between the centers of the ions.

Note that the ionic radius, R_i, used in the interaction potential does not have to be the same as that used in the Born equation (Eq. 12). We can use a different one in Eq. 12 (called Born radius). Doing that and binding the value of the Born radius to the solvation energy, $\mu_i^{0,\mathrm{res}}$), we obtain Eq. 14.

3. Results and discussion

We show results for various electrolytes in order to illustrate the workings of the proposed method. In most cases, the radii of the two ionic species are the same, $R_+ = R_- = 1.5$ Å (Restricted Primitive Model, RPM), but we also consider size-asymmetric ions. The anions are always monovalent in our simulations, so the salt concentration is $c^{\mathrm{res}} = c_+^{\mathrm{res}}$. The dielectric constant in the reservoir is $\epsilon^{\mathrm{res}} = 80$. The temperature is $T = 298.15$ K.

The top panel of Fig. 2 shows various terms of the electrochemical potential (in kT unit) on the ϵ^{sys}-side as functions of ϵ^{sys} for a 1:1 RPM electrolyte. The input concentration at $\epsilon^{\mathrm{res}} = 80$ is $c^{\mathrm{res}} = 0.1$ M. The horizontal black line shows the configurational chemical potential in the reservoir, the one to which all the other terms, $\ln c_i^{\mathrm{sys}}$, $\mu_i^{\mathrm{ex,sys}}$, and $\Delta\mu_i^0$, add up. The Donnan term, $q_i\Delta\phi$, is zero for the symmetric system ($q_+ = |q_-| = 1$, $R_+ = R_-$).

The $\ln c_i^{\mathrm{sys}}$ term corresponds to the concentration curve shown in the bottom panel (red lines with open squares). The excess term is quite small due to the small concentration ($c^{\mathrm{res}} = 0.1$ M). For small concentrations, it exhibits a minimum as a function of ϵ^{sys} due to the competition of two effects (see the inset of the top panel). As ϵ^{sys} decreases, concentration, c^{sys}, decreases (bottom panel), which makes $\mu_i^{\mathrm{ex,sys}}$ less negative. The Coulomb interactions, however, get stronger as ϵ^{sys} decreases, which makes $\mu_i^{\mathrm{ex,sys}}$ more negative.

The solvation term, $\Delta\mu_i^0$, becomes increasingly positive as ϵ^{sys} decreases because the ions are moved into a less efficiently screening environment ($\epsilon^{\mathrm{res}} \to \epsilon^{\mathrm{sys}}$).

The bottom panel shows the $c^{\mathrm{sys}}/c^{\mathrm{res}}$ (also called Nernst distribution coefficient) vs. ϵ^{sys} relationship. They are very similar for small concentrations, while deviations occur for $c^{\mathrm{res}} = 1$ M, due to increasing non-ideality.

In Fig. 2, every state point was obtained from a single D-GCMC simulation. To illustrate the advantages of the D-GCMC technique, we show how the results are obtained from the traditional GCMC (or, A-GCMC) simulations in Fig. 3 for $\epsilon^{\mathrm{sys}} = 60$. In that case, a system of equations for the electrochemical potentials of every species

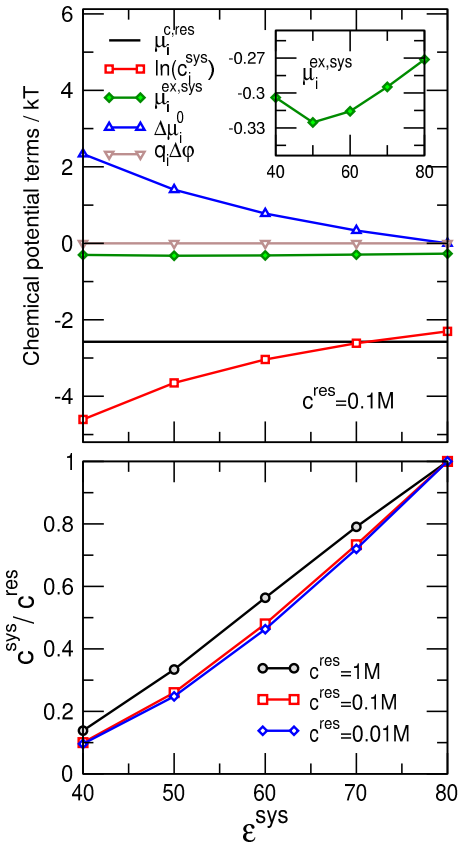

Figure 2: Top panel: the electrochemical potential terms that appear in Eqs. 3-4 for a 1:1 RPM at $c^{res} = 0.1$ M. Here, and in latter figures, the chemical potentials are measured in kT, while the concentration in M. The configurational chemical potential refers for the reservoir side, while all the other terms for the system side. The curves are the same for cation and anion. Bottom panel: the ϵ^{sys}-side concentrations normalized by the reservoir concentrations as functions of ϵ^{sys} for different values of c^{res}.

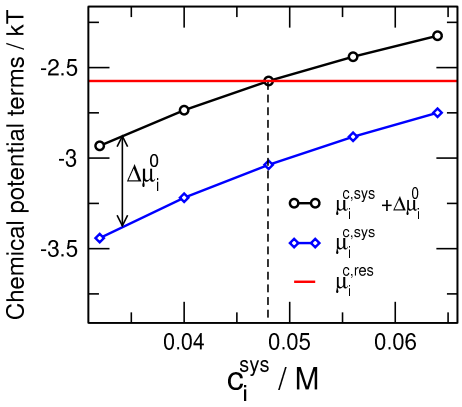

Figure 3: Illustration of the Donnan equilibrium for the 1:1 RPM system with $c^{res} = 0.1$ M and $\epsilon^{sys} = 60$. The red curve is the configurational chemical potential in the reservoir (Eqs. 3-4). The points of the blue curve, $\mu_i^{c,sys}$, have been obtained with separate A-GCMC simulations that provide the $\{c_i^{sys}\}$ vs. $\{\mu_i^{ex,sys}\}$ relationship. The black curve is the sum of $\mu_i^{c,sys}$ and the solvation penalty, $\Delta\mu_i^0$. This sum must be equal to $\mu_i^{c,res}$. The result obtained this way agrees with the result obtained with the D-GCMC method (Fig. 2).

(Eqs. 3-4) need to be solved with the constraints that (1) the correct relationship between $\{c_i^{sys}\}$ and $\{\mu_i^{ex,sys}\}$ holds, and (2) charge neutrality is satisfied (Eq. 5). The variables for which we solve are $\{c_i^{sys}\}$ and the Donnan potential, $\Delta\phi$.

This is relatively easy for the 1:1 RPM shown here because the Donnan potential is zero. It becomes increasingly difficult, however, as the electrolyte becomes asymmetric and/or the system increasingly complex (e.g., electrolyte mixtures). Even in the case of Fig. 3, every state point requires a separate GCMC (or A-GCMC) simulation.

This is not a burden using a theory (MSAX, for example), but in the case of computer simulations, it is a significant overhead. With the application of the D-GCMC technique, all the calculations behind the numerical solution of the Donnan equilibrium such as in Fig. 3 can be replaced by a single D-GCMC run.

The Donnan potential, $\Delta\phi$, is non-zero if the electrolyte is asymmetric, i.e., if the ions are different in size or charge. This is illustrated in Fig. 4 by plotting $\Delta\phi$ as a function of the size ratio R_+/R_- (Fig. 4A) and the charge ratio $q_+/|q_-|$ (Fig. 4B). The concentrations, c^{sys}, are shown in the insets.

If $R_+ > R_-$, the solvation penalty is smaller for the cation. The system, therefore, becomes positive without a Donnan potential. A positive $\Delta\phi$ is needed to recover charge neutrality. The concentration c^{sys} is smaller for smaller R_+/R_- ratios, because the solvation penalties are larger for smaller cations.

If $q_+ > |q_-|$, the solvation penalty is larger for the cation. The system, therefore, becomes negative without a Donnan potential. A negative $\Delta\phi$ is needed to recover charge neutrality. The concentration c^{sys} is smaller for larger $q_+/|q_-|$ ratios, because the solvation penalties are larger for cations with larger charges.

In these calculations, the dielectric constants were fixed at $\epsilon^{sys} = 60$ or 40. Fig. 5 shows the ϵ^{sys}-dependence for a 2:1 electrolyte by plotting the various terms of the electrochemical potential (similar to the top panel of Fig. 2). The conclusions are similar to those discussed at the 1:1 system (Fig. 2) except that the Donnan term (brown lines with triangles) is nonzero here. The other difference is that different curves refer to the cations and the anions (top and bottom panels).

Fig. 4 also shows the MSAX data ($\times$ symbols). The agreement with the D-GCMC results is reassuring both for D-GCMC (it is a new method) and

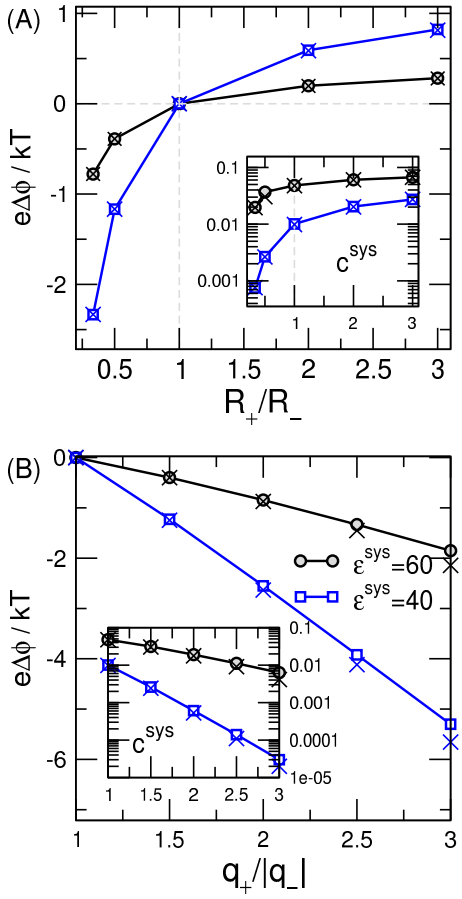

Figure 4: The Donnan potential, $\Delta\phi$, as a function of (A) the size ratio R_+/R_- and (B) the charge ratio $q_+/|q_-|$ for two values of $\epsilon^{\rm sys}$ (60 and 40). The anion properties were fixed at $R_- = 1.5$ Å and $q_- = -e$, while the cation properties were changed. The reservoir concentration is $c^{\rm res} = 0.1$ M. The insets show the system-concentrations, $c^{\rm sys}$. The × symbols denote MSAX data. [22]

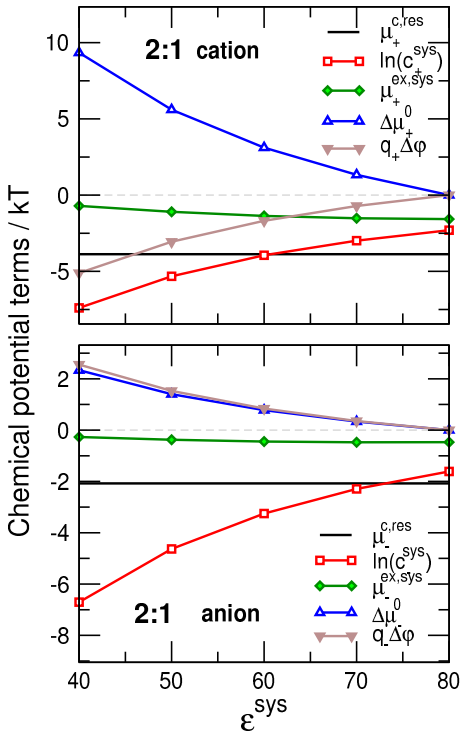

Figure 5: The electrochemical potential terms that appear in Eqs. 3-4 for a 2:1 RPM at $c^{\rm res} = 0.1$ M. The configurational chemical potential refers for the reservoir side, while all the other terms for the system side. Top and bottom panels refer to cation and anion, respectively.

for MSAX (it is an approximate theory). Small deviations occur only for large $q_+/|q_-|$ ratios.

In the D-GCMC simulation, the Donnan potential is an input parameter. To obtain the Donnan potential that produces charge neutrality, an outer loop is needed. Here, the $\sum_i q_i c_i^{\rm sys}$ vs. $\Delta\phi$ relationship is linear, so the appropriate Donnan potential was easy to find after a few iterations over blocks of the simulation on the basis of a linear regression.

Asymmetries can also be introduced by ions with different solvation free energies. To illustrate this case, we show results (Table 1) for a NaCl model using Pauling radii, experimental dielectric constant [29] for the $\epsilon^{\rm res}$ medium, and experimental hydration free energies (Eq. 14) as in the II+IW model. [26–28] Data for the corresponding RPM model are also shown.

The solvation penalties for the NaCl are smaller than those calculated from Eq. 13 using the Pauling radii in the Born equation. Also, they are different for Na^+ and Cl^-. The Donnan potential, therefore, is nonzero in this case. Interestingly, the concentration in the $\epsilon^{\rm sys} = 60$ medium is less affected.

Finally, we show some results for the classical case when charge imbalance is caused by ions that cannot leave the system (let us denote them with X), so they are absent in the reservoir. This case was simulated by Barr and Panagiotopoulos [12] for charged colloids, by Landsgesell et al. [13] for weak polyelectrolytes, and by us [9, 30, 31] for calcium channels, just to mention a few. Our simulations were performed by equilibrating the selectivity filter of the ion channel with the baths in the same single simulation cell. The charged groups (COO^-) of the amino acid side chains created the charge imbalance between channel and bath. The Donnan equilibrium was solved by Nonner et al. [8, 25] for this situation using MSA.

Here, we mimic this situation by placing an ionic species X in the system in a given concentration $c_{\rm X}^{\rm sys}$ (its charge is $q_{\rm X} = e$, while its radius is $R_{\rm X} = 1.5$ Å). Insertions/deletions are not performed for these ions, only displacements. The ions that can traffic between the reservoir and the system are those of the 1:1 RPM electrolyte con-

Table 1: Results for ionic partitioning between the $\epsilon^{\rm sys}$ and $\epsilon^{\rm res}$ baths for the 1:1 RPM electrolyte (Fig. 2) and a NaCl model with Pauling radii. The bulk dielectric constant for NaCl is $\epsilon^{\rm res} = 76.82$ for concentration $c^{\rm sys} = 0.1$ M. It is an experimental value from the measurements of Buchner et al. [29]. The system dielectric constant is $\epsilon^{\rm res} = 60$ for both cases. The solvation terms, $\Delta\mu_i^0$, have been calculated from Eq. 13 for the RPM model, and from Eq. 14 for NaCl using hydration free energies $\mu_+^{0,\rm res} = -424$ kJ/mol and $\mu_-^{0,\rm res} = -304$ kJ/mol. Outputs of the simulations are shown in boldface.

	RPM	NaCl
R_+/Å	1.5	0.95
R_-/Å	1.5	1.81
$\epsilon^{\rm sys}$	60	60
$\epsilon^{\rm res}$	80	76.82
$c^{\rm sys}$/M	**0.048**	**0.0498**
$c^{\rm res}$/M	0.1	0.1
$e\Delta\phi/kT$	**0**	**−0.0892**
$\Delta\mu_+^0/kT$	0.7785	0.6313
$\Delta\mu_-^0/kT$	0.7785	0.4525

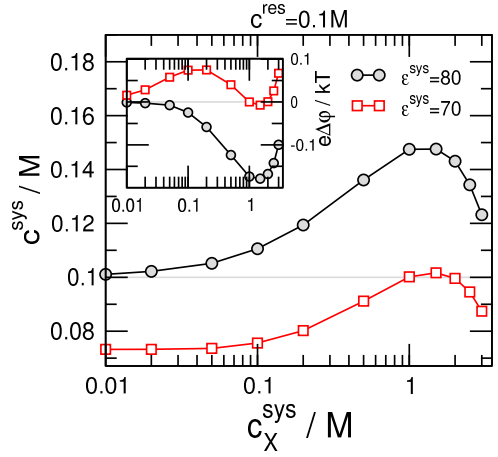

Figure 6: The concentrations $c^{\rm sys}$ of the 1:1 RPM electrolyte (see Fig. 2) in a system where monovalent positive ions (denoted by X) are present at concentration $c_{\rm X}^{\rm sys}$. The X ions are absent in the reservoir. The $c^{\rm sys}$ data are shown as functions of $c_{\rm X}^{\rm sys}$ for two different values of $\epsilon^{\rm sys}$ (70 and 80). The inset shows the Donnan potential. The concentration of the RPM electrolyte in the reservoir is $c^{\rm res} = 0.1$ M.

sidered at Fig. 2.

Figure 6 shows the concentration of the RPM ions, $c^{\rm sys}$, as a function of $c_{\rm X}^{\rm sys}$ for $\epsilon^{\rm sys} = 80$ and 70. In the case of $\epsilon^{\rm sys} = 80$, the black curve starts from $c^{\rm sys} = c^{\rm res} = 0.1$ M and increases as the X ions are added to the system. A turnover can be observed above 1 M where hard-sphere exclusion effects inhibit the adsorption of the RPM ions into the system.

For $\epsilon^{\rm sys} = 70$, a similar trend is observed, but with smaller $c^{\rm sys}$ concentrations due to the solvation penalty. Therefore, a competition takes place between the attractive electrostatic effect of the X ions, the repulsive effect of solvation, and the repulsive effect of hard-sphere exclusion. The inset shows that the Donnan potential exhibits similar behavior.

4. Closing remarks

In this study, we suggested a simple extension of the GCMC algorithm with which we can equilibrate a bulk electrolyte of dielectric constant $\epsilon^{\rm sys}$ with a virtual reservoir of dielectric constant $\epsilon^{\rm res}$ by including the solvation penalty and the interaction with the Donnan potential in the acceptance probability of the ion insertion/deletion attempts.

Ions are partitioned between the two media, so the basic question that we pose is how ions are distributed between the two dielectric media. This question can be reduced to the relation between the concentrations in the two systems, so this is practically Nernst's distribution law applied for ionic systems.

Our simulation method avoids the problem arising when the two bath electrolytes are present in a single simulation cell, so the computational problem of an ion crossing the boundary between them does not occur. Also, the concentration in one bath associated to the concentration in the other bath is obtained via a single D-GCMC simulation instead of performing several GCMC simulations to solve the Donnan equilibrium.

The method is a promising start for extensions where one of the coexisting systems is a pore, a slit, or any confined inhomogeneous system that are relevant for technological applications.

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