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Structure of primitive electrolytes in semi-permeable shells

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ABSTRACT

We have theoretically studied the competing adsorption of the two- and three-component electrolytes with different sizes and ionic valences near a semi-permeable shell. The present theory provides interesting insights about the steric charge separation occurring at the shell, which cannot be explained by the linearized and nonlinear Poisson-Boltzmann theories. The smaller and divalent ions interact more strongly with the shell than the larger and monovalent ions because the smaller ions can approach more closely to the shell surface and the divalent ions interact more strongly with the charged shell than the monovalent ions. The large steric charge separation occurs at a highly asymmetric electrolyte and a high bulk concentration. The competition between the cations and anions gives rise to the charge reversal and charge inversion even for an uncharged shell. A positively charged surface enhances the charge surface amplification because the shell is impermeable for the anion, whereas a negatively charged surface enhances the charge reversal. The excess osmotic pressure, which is based on a nonlinear Poisson-Boltzmann theory, depends only on the permeated ion density at the shell, and increases with increasing the shell size and surface charge density.

1. Introduction

The distribution of ions near charged surfaces has been a subject with a long history of theoretical studies. One of the important physicochemical question for electrolytes near a charged surface is an understanding of how electrolytes affect the interfacial structure and how they are distributed close to the interfaces [1–3]. Donnan equilibria, which arise in the presence of semi-permeable membranes, are of considerable importance in many areas of science and technology. A great deal of research has recently been devoted to understand the Donnan equilibria in charged systems with the planar- and spherical-type semi-permeable membranes. The aggregation and sedimentation stability of polyions in the semi-permeable membranes filled with polyelectrolytes are strongly influenced by ionic Donnan equilibrium between inside and outside membranes, being impermeable to the large polyions, but allowing the small counterions. Typical examples of such membrane are vesicles and liposomes with ionic channels various types of polyelectrolyte microcapsules [4].

The ionic density distributions near a semi-permeable microcapsule have been studied by experiments [5–7] and theories [8–13]. For example, Vinogradova et al. [10,11] have applied the linearized Poisson-Boltzmann (PB) theory to study the electro-osmotic equilibrium acting on a semi-permeable shell in polyion solution [14]. They have calculated the concentration profiles for the polyions and counterions, and excess osmotic pressure of polyion solution excluded on the shell. Tang and Denton [13] have theoretically studied the ionic density deviations in a semi-permeable ionic microcapsule by implementing the mean-field approach in a cell model. However, their studies are limited to the linearized and nonlinear PB theories. The neglect of the ion-ion correlation in the nonlinear PB theory is generally valid for a weakly-correlated monovalent ion, but questionable for more strongly correlated multivalent ions. Furthermore, the finite size and multivalence of the electrolyte solution will affect the redistribution of ionic densities i.e., steric charge separation, and the ionic density deviation inside the membrane because the smaller and multivalent ions interact more strongly with the membrane than large and monovalent ions. The quantitative understanding of electrostatic interactions involving a semi-permeable membrane is still challenging. A reliable theory for explaining the ionic density distribution inside and outside the shell is needed. It is known that the density functional theory (DFT), based both on the fundamental-measure theory (FMT) for the hard sphere [15–17] and on the mean-spherical approximation (MSA) [18–20] for the electrostatic residual contribution, provides rational explanation for the structure of electrolytes over a wide range of the electrolyte concentrations and surface charge densities. We will apply the DFT for studying the electrostatic interaction between size-asymmetric ions in a semi-permeable shell. This work

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perhaps might be considered as additional evidence to highlight the relevance of the ionic size asymmetry, excluded volume effects, and ion correlations in a spherical geometry.

In this paper, we use the DFT, based on the FMT for the hard spheres and MSA for a coupling of Coulombic and hard-sphere interactions, to evaluate the ionic density distributions, cumulated charge distributions, and correlation interactions between ions inside and outside the shells. We compare our results with those obtained from the computer simulations, as well as with the prediction of nonlinear PB theory. We study the competing adsorption properties of the two- and three-component electrolytes with different sizes and ionic valences. We calculate the excess electro-osmotic pressure (excess osmotic pressure) on the shell within the nonlinear PB theory. Finally, we discuss the charge inversion, charge reversal, and charge amplification of electrolyte solutions near a semi-permeable shell.

2. Theory

The semi-permeable membrane is modeled as a spherical shell of radius R immersed in the electrolyte solution. The shell has a uniform surface charge density $Q = eZ/4\pi R^2$, where Z is the valence and e the electronic charge. We consider a three-component primitive electrolyte. The ions are taken to be the charged hard spheres of diameter σ_i with a centered point charge ez_i. Two types of ions with the diameter σ_i (here, $i = 1$ and 2) can permeate freely through the shell, whereas the shell excludes the third ion with the diameter σ_3. In this case, the interaction between two ions is given by the Coulomb force. The solvent is represented by a continuous dielectric medium. For simplicity, we have assumed that the membrane dielectric constant is equal to that of the solvent, such that the image forces need not be considered.

For two types of ions which allows the permeation through the shell, the ion density distribution $\rho_i(\vec{r})$ is given by

$$\ln\left[\frac{\rho_i(\vec{r})}{\rho_i}\right] = -\beta e z_i \psi(\vec{r}) + c^{(1)}_{hs,i}\left(\vec{r};\{\rho_i(\vec{r})\}\right) - c^{(1)}_{hs,i}(\{\rho_i\}) + c^{(1)}_{el,i}\left(\vec{r};\{\rho_i(\vec{r})\}\right) - c^{(1)}_{el,i}(\{\rho_i\}), i = 1,2 \quad (1)$$

where ρ_i is the bulk density of ionic species i which can permeate through the shell, $\psi(\vec{r})$ the mean electrostatic potential (MEP) due to the combination of the Coulombic correlation with the external potential, and $\beta = 1/k_BT$ the inverse temperature. For the third ion which excludes inside the shell, it becomes

$$\ln\left[\frac{\rho_3(\vec{r})}{\rho_3}\right] = -\beta e z_3 \psi(\vec{r}) + c^{(1)}_{hs,3}(\vec{r};\{\rho_i(\vec{r})\}) - c^{(1)}_{hs,3}(\{\rho_i\}) + c^{(1)}_{el,3}(\vec{r};\{\rho_i(\vec{r})\}) - c^{(1)}_{el,3}(\{\rho_i\}) \quad r \geq R + \sigma_3/2 \quad (2)$$

where ρ_3 is the bulk density of ionic species 3.

In Eqs. (1) and (2), $c^{(1)}_{hs,i}(\vec{r};\{\rho_i(\vec{r})\})$ and $c^{(1)}_{el,i}(\vec{r};\{\rho_i(\vec{r})\})$ are the one-particle direct correlation functions (DCFs) for the hard-sphere and the electronic residual contribution, respectively. For the one-particle DCF for the hard spheres, $c^{(1)}_{hs,i}(\vec{r};\{\rho_i(\vec{r})\})$, we adopt the Fundamental-measure theory (FMT) of Rosenfeld [15], which is known to be a successful theory for the hard-sphere system

$$F_{hs}\left[\{\rho_i(\vec{r})\}\right] = \int d\vec{r}\,\Phi_{hs}\left[n_\alpha(\vec{r})\right] \quad (3)$$

where $\Phi_{hs}[n_\alpha(\vec{r})]$ is the excess free energy of a hard-sphere system per volume. The system-averaged fundamental geometric measure of the ions, $n_\alpha(\vec{r})$, is assumed as $n_\alpha(\vec{r}) = \sum_{i=1}^{3} \int d\vec{s}\rho_i(\vec{s})\omega^i_\alpha\left(|\vec{r}-\vec{s}|\right)$, where $\omega^i_\alpha(r)$ is the weight function depending on the geometrical properties of species i. The set of four scalar and two vector weighting functions are defined as $\omega^i_3(\vec{r}) = \theta(\sigma_i/2 - r)$, $\omega^i_2(\vec{r}) = \delta(\sigma_i/2 - r)$, $\omega^i_1(\vec{r}) = \omega^i_2(\vec{r})/2\pi\sigma_i$, $\omega^i_0(\vec{r}) = \omega^i_2(\vec{r})/\pi\sigma_i^2$, $\vec{\omega}^i_2(\vec{r}) = (\vec{r}/r)\delta(\sigma_i/2 - r)$, and $\vec{\omega}^i_1(\vec{r}) = \vec{\omega}^i_2(\vec{r})/2\pi\sigma_i$, where $\delta(r)$ is the delta function and $\theta(r)$ the Heaviside step function. Then, $c^{(1)}_{hs,i}(\vec{r};\{\rho_i(\vec{r})\}) - c^{(1)}_{hs,i}(\{\rho_i\})$ becomes

$$c^{(1)}_{hs,i}(\vec{r};\{\rho_i(\vec{r})\}) - c^{(1)}_{hs,i}(\{\rho_i\}) = -\int d\vec{s}\sum_\alpha \frac{\partial\Phi_{hs}[n_\alpha(\vec{s})]}{\partial n_\alpha(\vec{r})}\omega^i_\alpha\left(|\vec{r}-\vec{s}|\right) + \sum_\alpha \frac{\partial\Phi_{hs}(n_\alpha)}{\partial n_\alpha}\int d\vec{r}\omega^i_\alpha(r), \quad i = 1,2,3. \quad (4)$$

As the approximation for the electronic residual contribution, $c^{(1)}_{el,i}(\vec{r};\{\rho_i(\vec{r})\})$, we use the density functional Taylor expansion of $c^{(1)}_{el,i}(\vec{r};\{\rho_i(\vec{r})\})$ with respect to the bulk density ρ_i and only take the first-order term in the Taylor expansion. Then, $c^{(1)}_{el,i}(\vec{r};\{\rho_i(\vec{r})\})$ becomes

$$c^{(1)}_{el,i}(\vec{r};\{\rho_i(\vec{r})\}) - c^{(1)}_{el,i}(\{\rho_i\}) = \sum_{j=1}^{3}\int d\vec{s}\; c^{(2)}_{el,ij}(\vec{r}-\vec{s},\{\rho_i\})[\rho_j(\vec{s})-\rho_j], i = 1,2,3 \quad (5)$$

where $c^{(1)}_{el,i}(\{\rho_i\})$ is the electronic residual contribution in bulk phase and $c^{(2)}_{el,ij}(r,\{\rho_i\})$ is the two-particle DCF for the electronic residual contribution. An analytic expression for the charged hard-sphere mixture provided by the MSA solution [18–20], which yields in reasonable accuracy, has been used to calculate the two-particle DCF $c^{(2)}_{el,ij}(r,\{\rho_i\})$.

The mean electrostatic potential (MEP) $\psi(\vec{r})$ due to the combination of the Coulombic correlation with the external potential satisfies the Poisson equation

$$\nabla^2\psi(\vec{r}) = -\frac{4\pi}{\epsilon}\sum_{i=1}^{3} e z_i \rho_i(\vec{r}) - \frac{4\pi}{\epsilon}Q\delta(R - r) \quad (6)$$

where the boundary conditions for the electric field and potential at $r = R$ are given by

$$\psi(r = R^-) = \psi(r = R^+) \quad \text{and} \quad \left(\frac{d\psi(r)}{dr}\right)_{R^+} - \left(\frac{d\psi(r)}{dr}\right)_{R^-} = Q.$$

It should be noted that at the center of spherical shell $\left(\frac{d\psi}{dr}\right)_{r=0} = 0$. Then, the Poisson equation Eq. (6) can be written by

$$\psi(r) = \frac{4\pi}{\epsilon}\int_r^\infty dr' \sum_{i=1}^{3} e z_i \rho_i(r')\left(r' - \frac{r'^2}{r}\right), \quad r \geq R + \sigma_3/2 \quad (7)$$

$$\psi(r) = \psi(r = R + \sigma_3/2) - \frac{4\pi}{\epsilon}\left(\frac{1}{r} - \frac{1}{R + \sigma_3/2}\right)\int_{R+\sigma_3/2}^{\infty} dr' \sum_{i=1}^{3} e z_i \rho_i(r') r'^2 + \frac{4\pi}{\epsilon}\int_r^{R+\sigma_3/2} dr' \sum_{i=1}^{2} e z_i \rho_i(r')\left(r' - \frac{r'^2}{r}\right), \quad R \leq r \leq R + \sigma_3/2 \quad (8)$$

$$\psi(r) = \psi(r = R) - \frac{4\pi}{\epsilon}\left(\frac{1}{r} - \frac{1}{R}\right)\int_R^\infty dr' \sum_{i=1}^{3} e z_i \rho_i(r') r'^2 + \frac{4\pi}{\epsilon}\int_r^R dr' \sum_{i=1}^{2} e z_i \rho_i(r') r'^2 + \left(\frac{1}{r} - \frac{1}{R}\right)\frac{QR^2}{\epsilon} \quad 0 < r \leq R \quad (9)$$