



โครงการ
การเรียนการสอนเพื่อเสริมประสบการณ์

ชื่อโครงการ ผลของไฟฟ้าสถิตต่อสัมประสิทธิ์การแบ่งกันของอนุภาคคอลลอยด์รูปทรง
กลมเข้าสู่เมมเบรนซึ่งมีรูพรุน
Electrostatic effects on partition coefficient of spherical colloid into
porous membranes

ชื่อนิสิต นายพงษ์พิชญ์ พันธุ์ยุวรา เลขประจำตัว 5833432023

ภาควิชา ฟิสิกส์

ปีการศึกษา 2561

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของโครงการทางวิชาการที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)

เป็นแฟ้มข้อมูลของนิสิตเจ้าของโครงการทางวิชาการที่ส่งผ่านทางคณะที่สังกัด

The abstract and full text of senior projects in Chulalongkorn University Intellectual Repository(CUIR)
are the senior project authors' files submitted through the faculty.

Chulalongkorn University

Senior Project

2304499

Electrostatic Effects on Partition Coefficient of
Spherical Colloids into Porous Membranes

Author :

Pongpitch Panyura

Advisor :

Asst. Prof. Panadda Dechadilok

Project title Electrostatic effects on partition coefficient of spherical colloid into porous membranes

Author Mr. Pongpitch Panyura ID 5833432023

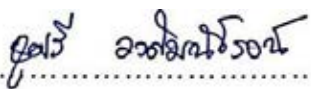
Project advisor Asst. Prof. Panadda Dechadilok (Ph.D.)

Department Physics

Academic year 2018

This report is submitted to the Department of Physics, Faculty of Science, Chulalongkorn University, in partial fulfillment of the requirements for the degree of Bachelor of Science

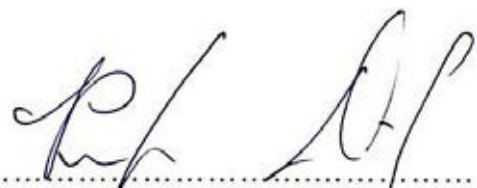
This report has been approved by the committee:


..... Chairman

(Assistant Professor Choosri Wongmanerod)


..... Committee

(Assistant Professor Patcha Chatraphorn, Ph.D.)


..... Advisor

(Assistant Professor Panadda Dechadilok, Ph.D.)

Project title	Electrostatic effects on partition coefficient of spherical colloid into porous membranes
Author	Mr. Pongpitch Panyura ID 5833432023
Project advisor	Asst. Prof. Panadda Dechadilok (Ph.D.)
Department	Physics
Academic year	2018

Abstract

Electrostatic effects on partitioning of spherical colloids into a porous membrane consisting of long straight cylindrical pores filled with an electrolytic solution are investigated through a mathematical model. The colloids and the pore surface potential are assumed to be constant, and are such that the Debye-Huckel approximation can be applied. Assuming that the solution is diluted, the effects of colloid-colloid interactions is negligible. The cations and anions are viewed as point charges, and the electric potential is obtained as a solution of a linearized Poisson-Boltzmann equation. The colloid equilibrium partition coefficient, the ratio between the intrapore colloid concentration and that in the external bulk solution, is dependent on the difference between the electrostatic free energy of the system of a colloid confined in a cylindrical pore and the addition of the electrostatic free energy of a system of an isolated colloid in an unbounded fluid and that of an empty cylindrical pore. Effects of colloid size, colloid surface potential and Debye length on the colloid equilibrium partition coefficient are investigated.

Acknowledgement

The thankful of this project is consist of many parts. First, I would like to very thank to my advisor (Asst. Prof. Dr.Panadda Dechadilok) who always teach and support me for many thinks I do not understand. Next, I would like to express my sincere gratitude for both committees, Asst. Prof. Choosri Wongmanerod and Asst. Prof. Dr.Patcha Chatraphorn for their intention and guidance for making the completion of this project possible. I am also grateful for the opportunity to create this project from Department of Physics, Faculty of Science, Chulalongkorn University. Finally, I would like to thank to the financial support from the Development and Promotion of Science and Technology Talents Scholarship, The Institute for the Promotion of Teaching Science and Technology, The Royal Thai Government.

Pongpitch Panyura

Contents

	Page
Abstract.....	ii
Acknowledgement.....	iii
Contents.....	iv
Table of Figures.....	1
Chapter 1.....	3
1.1) Motivation.....	3
1.2) Project objectives.....	6
1.3) Definitions of variables and parameters.....	6
Chapter 2.....	8
2.1) Linearized Poisson-Boltzmann equation.....	9
2.2) The particle-pore electrostatic potential energy of interaction.....	10
2.3) Calculation procedure.....	11
2.3.1) Calculation of E_s	11
2.3.2) Calculation of E_c	12
2.3.3) Calculation of E_{sc}	13
Chapter 3.....	15
3.1) Electrostatic potential energy of interaction.....	15
3.2) Calculation of the colloid equilibrium partition coefficient.....	20
Chapter 4.....	25
References.....	26

Table of Figures

	Page
Fig. 1. An image of fenestrated endothelial cell layer of the glomerular capillary wall obtained from electron microscopy [1].....	5
Fig. 2. An image of a cross-section of a track-etched membrane, a membrane with long straight cylindrical pores [2].....	5
Fig. 3. A schematic drawing of a longitudinal cross-section of a charged cylindrical pore containing a charged sphere. Diffuse layers of counter-ions form at the solid-electrolytic solution interface.....	8
Fig. 4. The electrostatic free energy of an isolated colloid (\hat{E}_s) is plotted as a function of κR . $\alpha = 0.2, 0.4$ and 0.6 with dimensionless surface potential = 1	16
Fig. 5. The electrostatic free energy of an empty pore (\hat{E}_c) is plotted as a function of κR with dimensionless surface potential = 1	16
Fig. 6. Dimensionless electrostatic free energy of a system consisting of a colloid inside the pore (\hat{E}_{sc}) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = \hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1	17
Fig. 7. Dimensionless electrostatic free energy of a system consisting of a colloid inside the pore (\hat{E}_{sc}) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1	18
Fig. 8. Dimensionless electrostatic free energy of a system consisting of a colloid inside the pore (\hat{E}_{sc}) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1	18
Fig. 9. Dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = \hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1	19
Fig. 10. Dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1	20

- Fig. 11. Dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 120
- Fig. 12. The partition coefficient of interaction (Φ) as a function of a relative sphere size (α) at $\kappa R = 0.5$ with.....21
- Fig. 13. The partition coefficient of a colloid inside pore where $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 1$ (Φ_{sc}) is plotted as a function of relative sphere size (α) with κR equal to 0.25, 0.5, 1 and steric interaction (uncharged)22
- Fig. 14. The partition coefficient of a colloid inside pore where $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$ (Φ_s) is plotted as a function of relative sphere size (α) with κR equal to 0.25, 0.5, 1 and steric interaction (uncharged)23
- Fig. 15. The partition coefficient of a colloid inside pore where $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$ (Φ_c) is plotted as a function of relative sphere size (α) with κR equal to 0.25, 0.5, 1 and steric interaction (uncharged)23

Chapter 1

Introduction

1.1) Motivation

Partitioning of colloidal particles into porous membranes is observed in biological transport processes such as solute filtration across the fenestrated endothelial cell layer (as shown in Fig. 1 [1]), and in separation processes with applications in industry and biotechnology including chromatography and sieving through track-etched membranes (as shown in Fig. 2 [2]). During these transport processes, it is often desired to relate experimentally measurable quantities, such as the solute concentration in the external bulk solution, and those within the membrane pores that cannot be measured directly. If thermodynamic equilibrium is assumed, the ratio between the averaged intrapore colloid concentration and the external bulk solute concentration is referred to as the equilibrium partition coefficient (Φ). For the simplest model system of a dilute solution containing rigid spherical colloids transported into a membrane with long straight cylindrical pores, Φ can be expressed as follows.

$$\Phi = \frac{\langle C_s(x=0) \rangle}{C_{s\infty}(x=0)} = \frac{\langle C_s(x=L) \rangle}{C_{s\infty}(x=L)} = \frac{\int_0^{2\pi} \int_0^{1-\alpha} e^{-\frac{E}{k_B T}} \beta d\beta d\phi}{\int_0^{2\pi} \int_0^1 \beta d\beta d\phi} \quad (1)$$

where C_s and $C_{s\infty}$ are the averaged intrapore colloid concentrations and the colloid concentrations in the bulk solution, respectively. The upstream end of the pore is denoted as $x=0$, whereas $x=L$ refers to the downstream end with L being the membrane thickness.

$\frac{E}{k_B T}$ is the ratio between the electrostatic potential energy of interaction between the colloid and the pore wall and the thermal energy (the product of Boltzmann's constant and the

temperature in Kelvin). The Boltzmann factor involving E is a measure of the probability of finding a solute center at a given radial position(β), whereas $\beta = 0$ appeared above in Eq. (1) is the sphere radius (normalized by the pore radius). Likewise, β is the particle radial position scaled with the pore radius. The limit of integration extends from $\beta = 0$ (at the pore centerline) to $\beta = 1 - \alpha$ due to the fact that the distance between the center of a rigid sphere and the pore surface cannot be less than the sphere radius. (In other words, if both the sphere and the pore wall are rigid, $E \rightarrow \infty$ for $\beta > 1 - \alpha$.) If the sphere and pore wall are uncharged and the colloid-pore wall interaction is a steric interaction, $E = 0$ for $\beta < 1 - \alpha$. Eq. (1) reduces to simply $\Phi = (1 - \alpha)^2$.

If, instead, the pore shape is that of a slit pore (consisting of parallel infinite plates), the equilibrium partition coefficient can be expressed as follows.

$$\Phi = \frac{\int_0^{1-\alpha} e^{-\frac{E}{k_B T}} d\beta}{\int_0^1 d\beta} \quad (2)$$

where, in this case, β is defined as the transverse colloid position scaled with the pore half-width. If the colloid and the slit pore are uncharged, and the only interaction between them is the steric interaction, $\Phi = 1 - \alpha$.

In the present work, a model of electrostatic double layer interactions between spherical colloids and cylindrical pores is developed in order to evaluate the contribution of surface charges to E through analytical calculation augmented with finite element solution. The Debye-Huckel approximation valid for systems with small electric potential ($\psi \ll \frac{k_B T}{e}$) was employed in the computation of E and, subsequently, the partition coefficient for colloids and pores with constant surface potential. The solvent is an electrolytic solution

viewed as a continuum medium with small ions viewed as point charges. The pores are assumed to be long enough such that the hydrodynamic end effects are negligible, and the colloidal solution is assumed to be diluted such that solute-solute interaction can be neglected. This project will start with the partition coefficient of charged colloids into cylindrical pores, and, then, the computation will be extended to include the case of partitioning of charged colloids into slit pores.

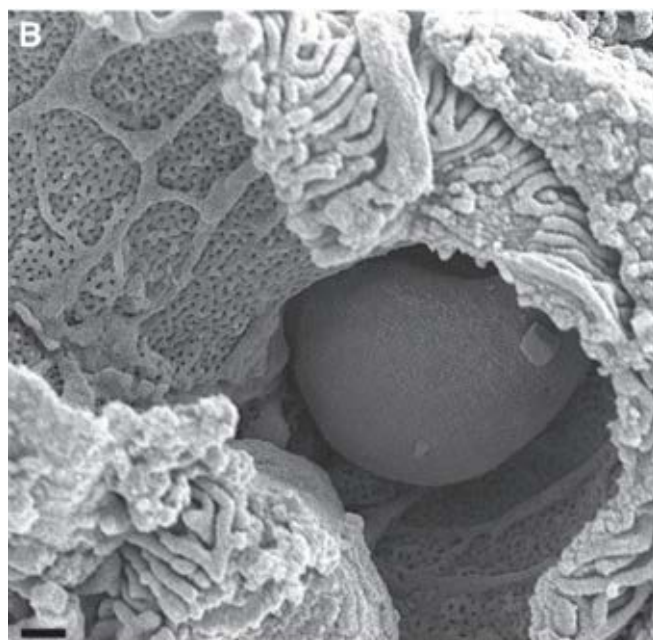


Fig. 1. An image of fenestrated endothelial cell layer of the glomerular capillary wall obtained from electron microscopy [1]

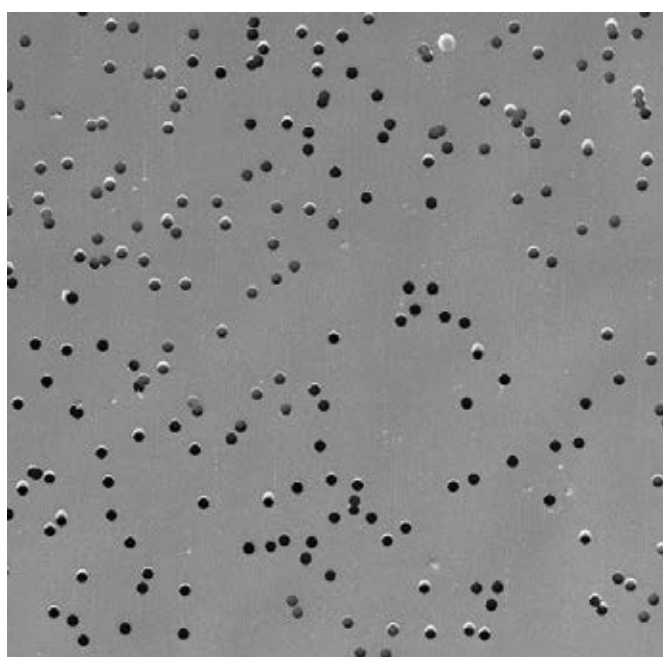


Fig. 2. An image of a cross-section of a track-etched membrane, a membrane with long straight cylindrical pores [2]

1.2) Project objectives

(1) Compute the electrostatic energy of interaction between charged rigid colloids and surfaces of pores with constant surface potential as a function of colloid intrapore radial position.

(2) Calculate the equilibrium partition coefficient of colloids as a function of relative particle size, particle and pore surface potential, and Debye length.

1.3) Definitions of variables and parameters

- α : Relative sphere size
- β : Radial position
- R : Pore radius
- Φ : Equilibrium partition coefficient
- κ : Inverse of the Debye length
- C_s : Averaged intrapore colloid concentrations
- $C_{s\infty}$: Colloid concentrations in the bulk solution
- ψ : Electric potential
- k_B : Boltzmann's constant
- T : Absolute temperature
- e : Elementary charge
- ϵ_0 : Vacuum permittivity
- ϵ_r : Relative permittivity of the electrolytic solution
- $C_{i\infty}$: Bulk concentration of electrolyte specie " i "
- z_i : Valence of electrolyte specie " i "

E_i : Electrostatic free energy of the system “ i ”

q_i : Surface charge density of the system “ i ”

A : Charged surface

\vec{N} : Ion flux

D_i : Diffusion coefficient of electrolyte specie “ i ”

Chapter 2

Model Development

The objective of the present project is to calculate the equilibrium partition coefficient of a spherical particle with constant surface potential (ψ_s) into a membrane with long straight cylindrical pores with constant surface potential (ψ_c). Depicted in Fig. 3 is a longitudinal cross-section of the cylindrical pore; the sphere radius is denoted as a , whereas the pore radius is R ; the dimensionless sphere radius α ; $\alpha = a/R$. The dimensionless particle radial location is denoted as β ; $\beta = r_s/R$. When a charged surface is submerged into an electrolytic solution, a diffuse layer of counter-ions (small ions with the charges opposite to that of the charged surface) is formed at the solid-liquid interface as shown in Fig. 3. This diffuse layer of counter-ions, often referred to as the electrical double layer, strongly influences the value of the potential energy of interaction (E), and hence, the value of the partition coefficient. In Sec. 2.1, the governing equation for the intrapore electric potential, the linearized Poisson-Boltzmann equation, is introduced, and, in Sec. 2.2, the calculation of E is discussed in details. The numerical procedure is presented in Sec. 2.3.

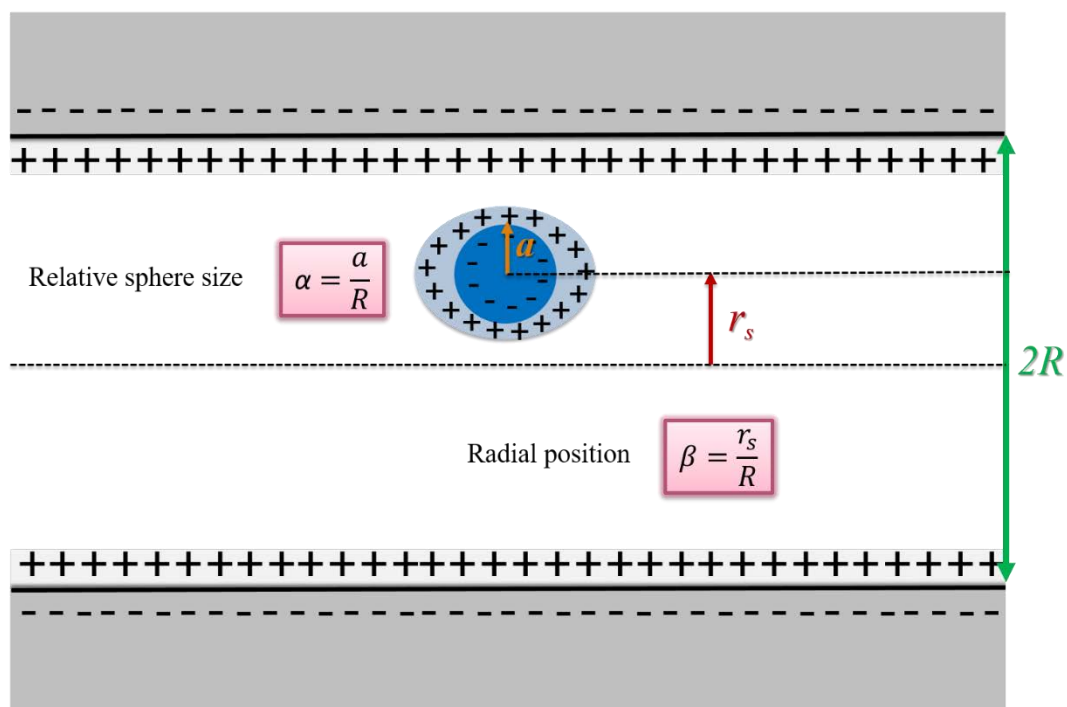


Fig. 3. A schematic drawing of a longitudinal cross-section of a charged cylindrical pore containing a charged sphere. Diffuse layers of counter-ions form at the solid-electrolytic solution interface

2.1) Linearized Poisson-Boltzmann equation

In absence of fluid motion, an ionic flux of a small ion i contained in an electrolytic solution (\vec{N}_i) can be expressed as follows.

$$\vec{N}_i = -D_i[\vec{\nabla}C_i + z_i C_i \left(\frac{e}{k_B T}\right) \vec{\nabla}\psi] \quad (3)$$

where C_i is the concentration of the ion “ i ”. D_i is its diffusivity, whereas z_i is its valence. ψ is the electric potential, and e is the elementary charge. Eq. (3) is often referred to as the Nernst-Planck equation; the first term on the right hand side is simply the diffusion term, whereas the second term is the contribution to the ionic flux due to electromigration. Under the assumption of vanishing fluxes at equilibrium, C_i follows the Boltzmann distribution as shown below.

$$C_i = C_{i\infty} e^{\frac{-z_i e \psi}{k_B T}} \quad (4)$$

$C_{i\infty}$ is bulk concentration of electrolyte specie “ i ” where $\psi = 0$. For a univalent-univalent binary electrolytic solution, substitutions of the ionic concentrations into the Poisson equation lead to the Poisson-Boltzmann equation written in a dimensionless form as shown below.

$$\hat{\nabla}^2 \hat{\psi} = (\kappa R)^2 \sinh(\hat{\psi}) \quad (5)$$

where $\hat{\psi} = \frac{\psi}{k_B T / e}$: the electric potential scaled with the thermal potential. R , the pore radius, is employed as the length scale, whereas κ is the inverse of the Debye length often viewed as the “thickness” of the electrical double layer. (The change of the electric potential vanishes outside the electrical double layer.) The expression for κ is as follows.

$$\kappa = \left(\frac{e^2}{\varepsilon_0 \varepsilon_r k_B T} \sum_{i=1}^2 C_{i\infty} \right)^{\frac{1}{2}} \quad (6)$$

where ε_0 is vacuum permittivity. ε_r is the relative permittivity of the electrolytic solution. It is worth noting that the Debye length decreases as a function of the ionic concentration. κR , therefore, is the ratio between the pore radius and the Debye length, and it strongly influences the electrostatic interaction between the colloids and the pore wall.

If $\hat{\psi} \ll 1$ (with the electric potential being much less than 25 mV at 300 K), $\sinh(\hat{\psi})$ can be approximated as $\hat{\psi}$ (an approximation referred to as the Debye-Huckel approximation), resulting in the Poisson-Boltzmann equation becoming linearized as shown (in the dimensionless form) below

$$\hat{\nabla}^2 \hat{\psi} = (\kappa R)^2 \hat{\psi} \quad (7)$$

The intrapore electric potential in a system of our interest can be obtained by solving Eq. (7) with the boundary conditions of constant surface potential at the colloid surface

$$(\hat{\psi} = \hat{\psi}_s = \frac{\psi_s}{k_B T / e}) \text{ and the pore surface } (\hat{\psi} = \hat{\psi}_c = \frac{\psi_c}{k_B T / e}).$$

In addition to the intrapore electric potential, the electric potential in a system of an isolated sphere (with the same particle surface potential) in an unbounded fluid obtained as a solution of Eq. (7) that satisfies the constant surface potential boundary condition at the sphere surface ($\hat{\psi} = \hat{\psi}_s$), and a condition of vanishing electric potential far from the sphere, and the electric potential in an empty cylindrical pore (with the same pore surface potential) obtained as a solution of Eq. (7) that satisfies the constant surface potential boundary condition at the pore wall ($\hat{\psi} = \hat{\psi}_c$) are also required as will be discussed below in Sec. 2.2. The method of obtaining the solution of the linearized Poisson-Boltzmann is presented in Sec. 2.3.

2.2) The particle-pore electrostatic potential energy of interaction

After $\hat{\psi}$ is obtained, the electrostatic free energy can be determined from the following expression proposed and proven by Verway and Overbeek [4].

$$E_j = - \int_A \int_0^{\psi} q_j dq dA \quad (8)$$

where q_j is the surface charge density. In this work, j can be s , c or sc . E_s is the electrostatic free energy of a system of an isolated spherical colloid with constant surface potential, whereas E_c is the electrostatic free energy of a system consisting of an empty cylindrical pore (or an empty slit channel) also with the constant surface potential. E_{sc} is the electrostatic free energy of the system of a colloid inside the pore. As indicated in Eq. (8),

the electrostatic potential energy of interaction is the integration of the energy per unit surface area required in bringing an uncharged surface to a surface charge density q_j over all charged surfaces (denoted above as A). If the Debye-Huckel approximation is employed, the system free energy is reduced to

$$E_j = -\frac{\psi_j}{2} \int_A q_j dA \quad (9)$$

The electrostatic potential energy of interaction, E , a measure of the probability of finding the colloid at the radial position inside the pore, can be found as the difference of the free energy of the colloid being within the pore, and the addition of the free energy of the system of an isolated colloid and that of an empty pore as follows.

$$E = E_{sc} - E_s - E_c \quad (10)$$

After E is determined, the partition coefficient, computed by using Eq. (1) if the pore is cylindrical, is presented as a function of relative particle radius, Debye length as well as the colloid and pore surface potential.

2.3) Calculation procedure

In this project, E_s and E_c are calculated from an analytical solution of the linearized Poisson-Boltzmann equation as presented below in Sec. 2.3.1 and 2.3.2. E_{sc} , on the other hand, is obtained from a finite element solution as will be discussed in Sec. 2.3.3. $E(\beta)$ in the Boltzmann factor is computed as indicated in Eq. (10).

2.3.1) Calculation of E_s

In order to determine E_s , the electric potential in the fluid surrounding the isolated sphere (with constant surface potential) with the dimensionless radius α ($\alpha = a/R$) must be first computed. The symmetry of the geometry of a system of an isolated sphere in an unbounded fluid allows us to solve Eq. (7) as an ordinary differential equation as shown below.

$$\frac{1}{\hat{r}^2} \frac{\partial}{\partial \hat{r}} \left(\hat{r}^2 \frac{\partial \hat{\psi}}{\partial \hat{r}} \right) = (\kappa R)^2 \hat{\psi} \quad (11a)$$

The solution of Eq. (11a) that satisfies the following boundary conditions must be obtained.

$$\hat{\psi}(\hat{r} = \alpha) = \hat{\psi}_s \quad (11b)$$

$$\hat{\psi}(\hat{r} \rightarrow \infty) = 0 \quad (11c)$$

where \hat{r} , a distance in a spherical coordinate, is normalized by the pore radius (R). Given the above boundary conditions, the linearized-Poisson Boltzmann equation becomes an ordinary differential equation and can be solved analytically. The dimensionless surface potential is found to be

$$\hat{\psi} = \frac{\hat{\psi}_s \alpha}{\hat{r}} e^{-\kappa R(\hat{r}-\alpha)} \quad (12)$$

As a result, the sphere surface charge density can be computed as follows.

$$\hat{q}_s = -\hat{n} \cdot \hat{\nabla} \hat{\psi} \Big|_{\hat{r}=\alpha} = \hat{\psi}_s \left(\kappa R + \frac{1}{\alpha} \right) \quad (13)$$

where \hat{n} is the normal vector perpendicular to the sphere surface. Substituting \hat{q}_s from Eq. (13) into Eq. (9), the dimensionless free energy of a system of an isolated sphere in an unbounded fluid is found to be

$$\hat{E}_s = -2\hat{\psi}_s \pi \alpha^2 \left(\kappa R + \frac{1}{\alpha} \right) \quad (14)$$

where \hat{E}_s is the dimensionless free energy of a system of an isolated sphere in an unbounded fluid and E_s is the dimensional free energy of a system of an isolated sphere in an unbounded fluid that can be calculated as follows

$$E_s = \varepsilon R \left(\frac{k_B T}{e} \right)^2 \hat{E}_s \quad (15)$$

2.3.2) Calculation of E_c

Next, the same procedure was repeated but with a system being that of an empty cylindrical pore. Once again, the symmetry of the geometry of the system of an empty cylindrical pore allows us to solve the linearized Poisson Boltzmann equation as an ordinary differential equation as follows

$$\frac{1}{\hat{\rho}} \frac{\partial}{\partial \hat{\rho}} \left(\hat{\rho} \frac{\partial \hat{\psi}}{\partial \hat{\rho}} \right) = (\kappa R)^2 \hat{\psi} \quad (16a)$$

where $\hat{\rho} = \rho/R$. The dimensionless electric potential in an empty pore of Eq. (16a) has to satisfy the following boundary conditions.

$$\hat{\psi}(\hat{\rho} = 1) = \hat{\psi}_c \quad (16b)$$

$$\frac{\partial \hat{\psi}}{\partial \hat{\rho}}(\hat{\rho} = 0) = 0 \quad (16c)$$

The first boundary condition, Eq. (16b) indicates that, the pore surface potential is constant, whereas the second boundary condition, Eq. (16c), is due to symmetry. By solving Eq. (7) with boundary condition stated in Eqs. (16b) and (16c), we found that the solution is in the form of the modified Bessel function of the first kind as follows.

$$\hat{\psi} = \frac{\hat{\psi}_c I_0(\kappa R \hat{\rho})}{I_0(\kappa R)} \quad (17)$$

As a result, the surface charge density of the cylindrical pore was found to be

$$\hat{q}_c = \hat{n} \cdot \hat{\nabla} \hat{\psi} \Big|_{\hat{\rho}=1} = \frac{\hat{\psi}_c \kappa R I_1(\kappa R \hat{\rho})}{I_0(\kappa R)} \quad (18)$$

Substituting \hat{q}_c from Eq. (18) into Eq. (9), the dimensionless free energy of isolated cylinder is

$$\hat{E}_c = \frac{-\hat{\psi}_c \pi R^2 l \kappa R I_1(\kappa R)}{I_0(\kappa R)} \quad (19)$$

where \hat{E}_c is the dimensionless free energy of isolated cylinder and E_c is the dimensional free energy of isolated cylinder that can be calculated as follows

$$E_c = \varepsilon R \left(\frac{k_B T}{e} \right)^2 \hat{E}_c \quad (20)$$

2.3.3) Calculation of E_{sc}

In order to determine E_{sc} , an intrapore electric potential in the electrolytic solution surrounding the spherical particle must be first computed from finding the solution of

linearized Poisson-Boltzmann equation, Eq. (7), that satisfies the following boundary conditions;

$$\hat{\psi}(\hat{r} = \alpha) = \hat{\psi}_s \quad (21)$$

$$\hat{\psi}(\hat{\rho} = 1) = \hat{\psi}_c \quad (22)$$

The boundary conditions in Eqs. (21) and (22) are due to the fact that the particle and pore surface potential are constant. In absence of the geometrical symmetry of the system consisting of the spherical particle confined within a cylindrical pore, Eq. (7), being the partial differential equation, is solved by using a finite element method (COMSOL Multiphysics 5.2a, Stockholm, Sweden). The employed meshes are Lagrange-quadratic meshes, and the solver is the default linear solver. E , is then, determined as the difference between the free energy of a system of a sphere confined in a cylindrical pore and the addition between the free energy of a system of an isolated sphere in an unbounded fluid and that of a system of an empty pore. To validate the accuracy of the obtained finite element solution, our calculated $E(\beta = 0)$ is compared to and found to agree with $E(\beta = 0)$ computed by the method of eigenfunction expansion by Smith and Deen [4] within 0.5 %. The partition coefficient is, then, calculated as indicated by an expression in Eq. (1) with the cross-sectional integration completed by using numerical integration (MATLAB, Netick, Massachusetts, USA). Calculated results are discussed in Chapter 3.

Chapter 3

Results and Discussion

Calculated results are presented below, beginning with the calculated electrostatic potential energy of interaction in Sec. 3.1. First, \hat{E}_s and \hat{E}_c , the dimensionless electrostatic free energy of a system of a sphere (with constant surface potential) in an unbounded electrolytic solution and that of an empty cylindrical pore (also with constant surface potential), are presented as a function of κR (the pore radius divided by the Debye length). \hat{E}_{sc} , the electrostatic free energy of a system of a confined sphere in a cylindrical pore (also made dimensionless as discussed in Chapter 2), are presented as a function of the sphere location on the cross-section of the pore. The dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) is then discussed as a function of the sphere location as well. Finally, the partition coefficient calculated as a function of the sphere size (relative to that of the pore) will be presented in Sec. 3.2.

3.1) Electrostatic potential energy of interaction

The dimensionless electrostatic free energy of a system of an isolated spherical colloid surrounded by an unbounded electrolytic solution (\hat{E}_s) from an analytical calculation is shown as a function of κR (the ratio between the pore radius and the Debye length) in Fig. 4. Results are presented for $\alpha = 0.2, 0.4$ and 0.6 . As shown below, \hat{E}_s decreases as a function of κR (or, in other words, increases as a function of Debye length).

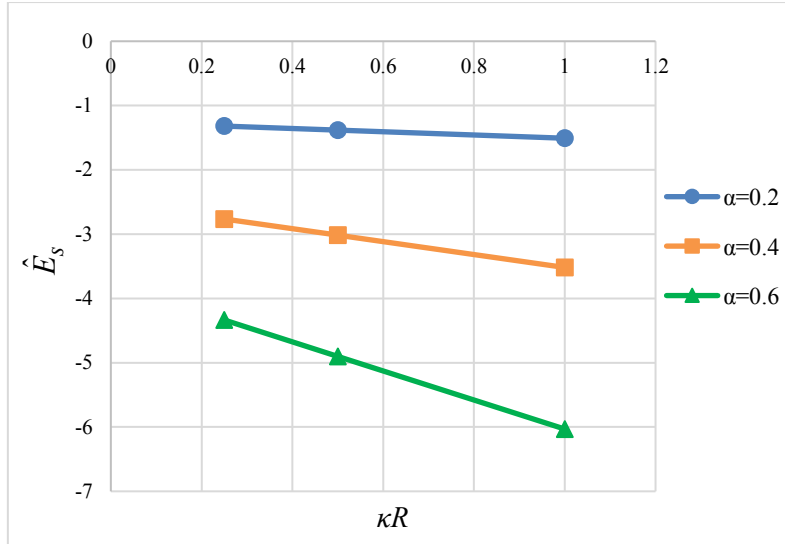


Fig. 4. The electrostatic free energy of an isolated colloid (\hat{E}_s) is plotted as a function of κR . $\alpha = 0.2, 0.4$ and 0.6 with dimensionless surface potential = 1

In Fig. 5, the (dimensionless) electrostatic free energy of a system of an empty cylindrical pore containing an electrolytic solution, \hat{E}_c , obtained from an analytical solution of Eq. (16a) is plotted as a function of κR . Similarly, to the trend observed for \hat{E}_s , \hat{E}_c also decreases as the Debye length decreases.

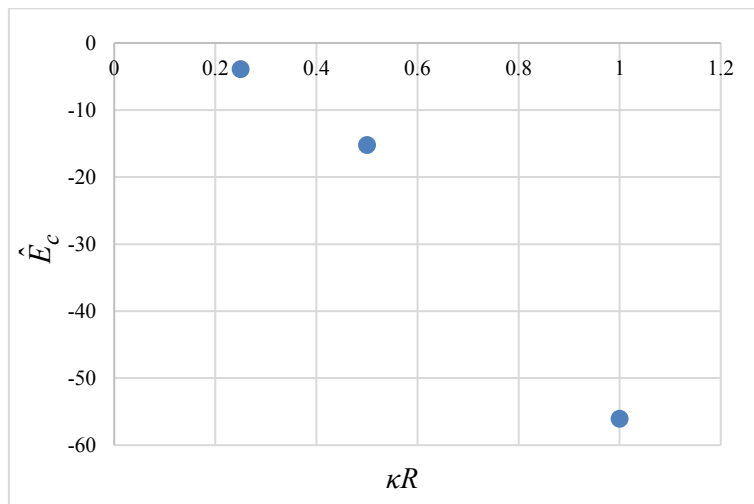


Fig. 5. The electrostatic free energy of an empty pore (\hat{E}_c) is plotted as a function of κR with dimensionless surface potential = 1

Next, the electrostatic free energy of a system consisting of a spherical colloid inside a cylindrical pore, \hat{E}_{sc} , is plotted as a function of the distance between the sphere center and the pore centerline scaled with the pore radius ($\beta = r_s/R$) in Figs. 6 – 8. $\alpha = 0.4$, resulting in

the sphere-pore steric interaction preventing β being larger than 0.6 (as the distance between the sphere center and the rigid pore wall cannot be smaller than the sphere radius). Results are presented for the cases where $\hat{\psi}_s = \hat{\psi}_c = 1$ (in Fig. 6), $\hat{\psi}_s = 1$ whereas $\hat{\psi}_c = 0$ (in Fig. 7), and $\hat{\psi}_s = 0$ whereas $\hat{\psi}_c = 1$ (in Fig. 8). As indicated in Fig. 6, if $\hat{\psi}_s = \hat{\psi}_c = 1$, \hat{E}_{sc} remains approximately constant for all presented values of β . If $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$ or $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$, however, \hat{E}_{sc} decreases as a function of β with $\beta = 0.6$ (the location where the sphere touches the pore surface) is a favorable radial position as shown in Figs. 7 and 8. As shown in all the figures, \hat{E}_{sc} decreases as a function of κR or increases as a function of Debye length.

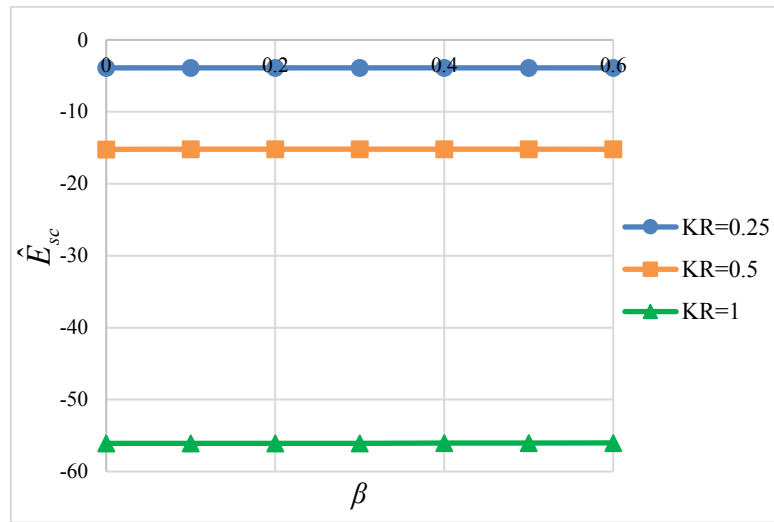


Fig. 6. Dimensionless electrostatic free energy of a system consisting of a colloid inside the pore (\hat{E}_{sc}) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = \hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1

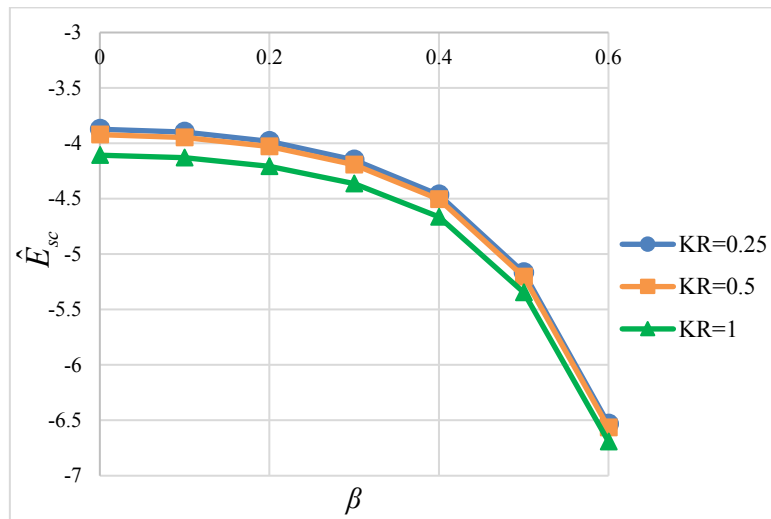


Fig. 7. Dimensionless electrostatic free energy of a system consisting of a colloid inside the pore (\hat{E}_{sc}) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1

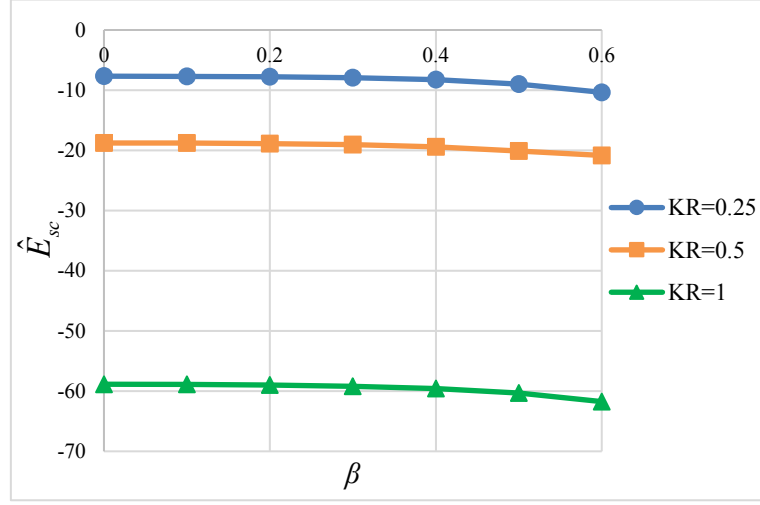


Fig. 8. Dimensionless electrostatic free energy of a system consisting of a colloid inside the pore (\hat{E}_{sc}) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1

As aforementioned, the probability of finding the spherical colloid at a certain radial position inside the pore depends on the electrostatic potential energy of interaction (\hat{E}) contained in the Boltzmann factor that can be found as the difference between the electrostatic free energy of a system of a cylindrical pore containing the confined sphere (\hat{E}_{sc}) and the addition of the electrostatic free energy of a system of an isolated sphere in an unbounded fluid (\hat{E}_s) and that of the empty pore (\hat{E}_c). In Fig. 9, \hat{E} is presented as a function of the distance between the pore centerline and the sphere radial position scaled with the pore radius ($\beta = r_s/R$) for κR equal to 0.25, 0.5 and 1. $\alpha = 0.4$. $\hat{\psi}_s = \hat{\psi}_c = 1$. Although not apparent in Fig. 9, the most favorable radial position for a spherical colloid is at $\beta = 0$ (the pore centerline) where $\hat{E}(\beta)$ is found to be lowest. As shown in the figure, the variation of $\hat{E}(\beta)$ as a function of β is very small, implying that the probability of finding the sphere at all value of β is almost equal. This is to be expected since the particle and pore surface potential are equal. The increase in κR (or a decrease in the Debye length if R is kept constant) elevates the value of \hat{E} which is positive implying that the particle and pore surface are of the same charge, resulting in the intrapore location being less energetically

favorable than the location in the external bulk fluid. This indicates that the probability of finding the sphere confined in the pore decreases as the Debye length decreases.

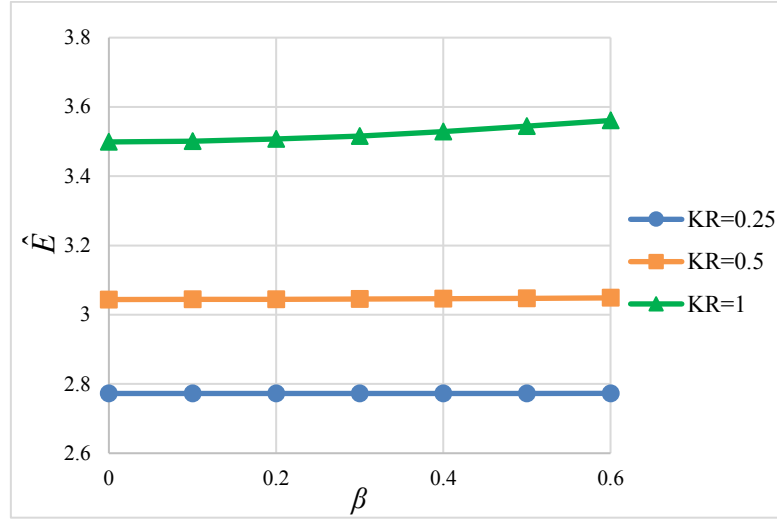


Fig. 9. Dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = \hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1

As shown below, \hat{E} is presented as a function of the distance between the pore centerline and the sphere radial position scaled with the pore radius ($\beta = r_s/R$) for $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$ (in Fig. 10) and $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$ (in Fig. 11), respectively. In both figures, $\kappa R = 0.25, 0.5$ and 1. \hat{E} is found to be negative, indicating that the sphere being in the pore is more energetically favorable than it being outside the pore. The most energetically favorable location on the pore cross-section is at $\beta = 0.6$ (the location where the sphere touches the pore wall). The fact that \hat{E} is negative implies that the particle and pore surface charges are of opposite signs, resulting in an particle-pore electrostatic attraction. If either the particle or pore surface potential is zero, the partition coefficient (the ratio between the intrapore colloid concentration and that outside the pore) results from the competition between the electrostatic interaction (that enhances the partitioning of the colloids into the pore) and the steric interaction (preventing the sphere entering the pore) as discussed further in Sec. 3.2.

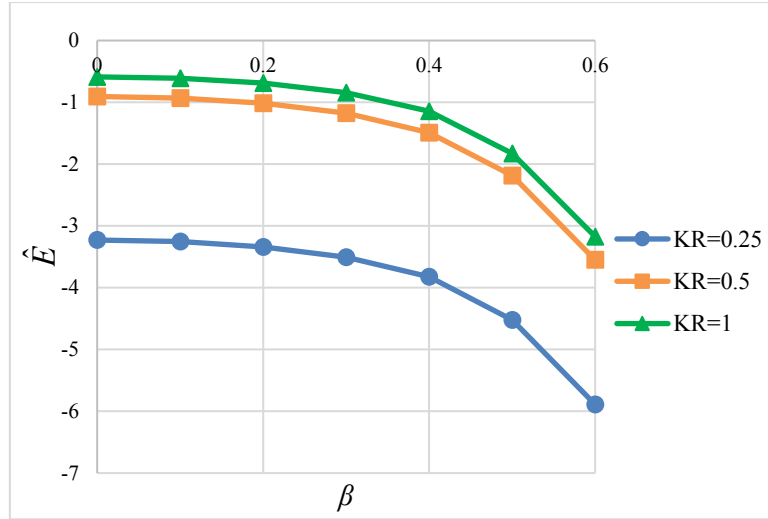


Fig. 10. Dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1

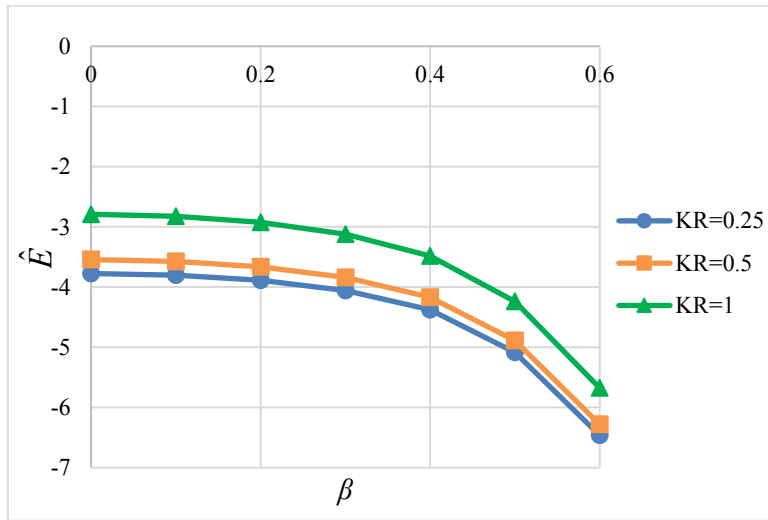


Fig. 11. Dimensionless electrostatic potential energy of interaction ($\hat{E} = \hat{E}_{sc} - \hat{E}_s - \hat{E}_c$) as a function of scaled sphere radial position ($\beta = r_s/R$). $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$. The relative sphere size (α) = 0.4. $\kappa R = 0.25, 0.5$ and 1

3.2) Calculation of the colloid equilibrium partition coefficient

The electrostatic energy of interaction as shown in Figs. 9 – 11 are, then, substituted into Eq. (1) in order to compute the partition coefficient (Φ) of a spherical colloid (with a constant surface potential) in a cylindrical pore (with a constant pore surface potential). In Fig. 12, Φ is presented as a function of the relative colloid size ($\alpha = a/R$). Similar to an uncharged system where the only colloid-pore interaction is the steric interaction, Φ declines

as a function of α . As shown below, for a system with $\hat{\psi}_s = \hat{\psi}_c$, an increase in the particle and pore surface potential amplifies the decrease in the partition coefficient, as expected, since, as shown in Fig. 9, E is positive indicating that the colloid-pore interaction is that of an electrostatic repulsion between surfaces of like charge. The increase in the surface potential corresponds to the increase in the surface charge density, resulting in the decrease in the amount of colloid being partitioned into the membrane.

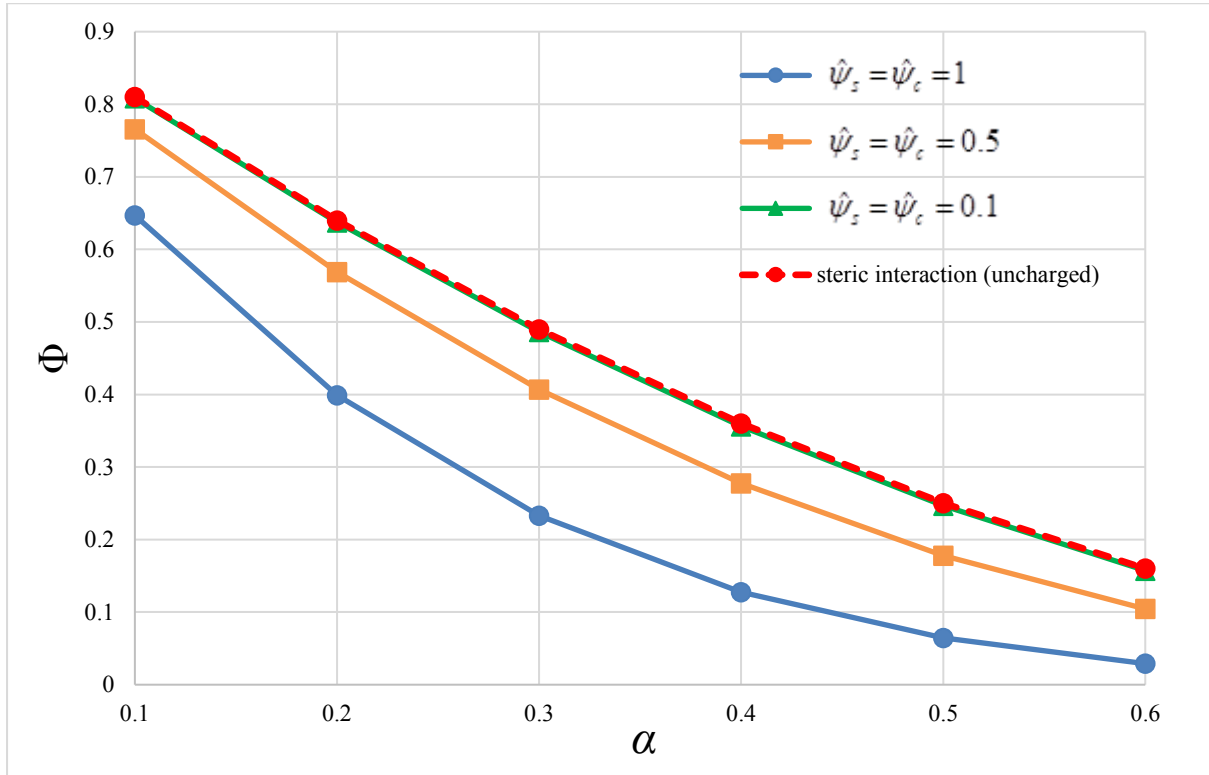


Fig. 12. The partition coefficient of interaction (Φ) as a function of a relative sphere size (α) at $\kappa R = 0.5$ with

$$\hat{\psi}_s = \hat{\psi}_c = 1, \hat{\psi}_s = \hat{\psi}_c = 0.5, \hat{\psi}_s = \hat{\psi}_c = 0.1 \text{ and steric interaction (uncharged)}$$

Effects of Debye length on the equilibrium partition coefficient is presented in Figs. 13 – 15. For a sphere confined in a pore (with sphere and pore charge densities being constant), it has been demonstrated that the decrease in Debye length leads to an increase in Φ [3]. For a sphere with constant surface potential confined in a cylindrical pore with constant surface potential, however, an increase in Debye length (a decrease in κR) causes a decrease in the partition coefficient. Another difference from the partition coefficient of a sphere and a pore with constant surface charge densities is the fact that, for a system of a sphere and a pore with constant surface potential, it is possible for the partition coefficient to be larger than that of an uncharged sphere in an uncharged pore (where the only sphere-pore interaction is the steric interaction) as shown in Figs. 14 and 15.

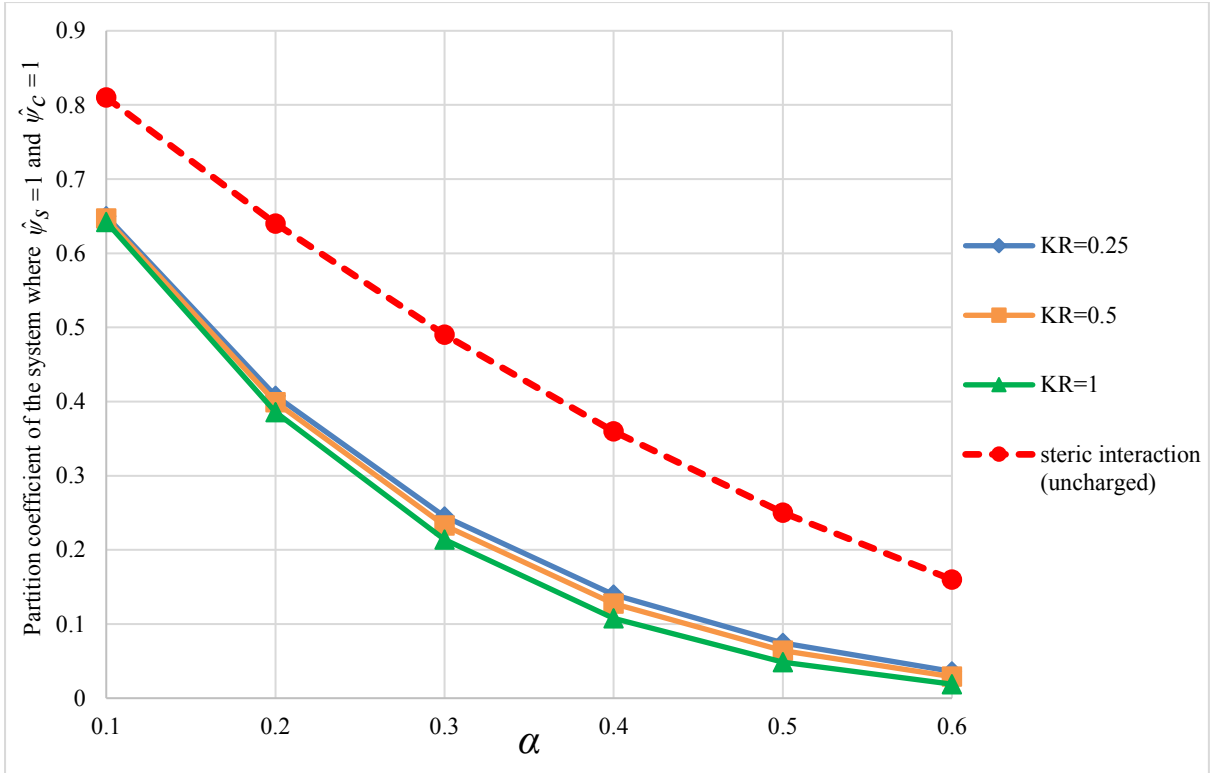


Fig. 13. The partition coefficient of a colloid inside pore where $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 1$ (Φ) is plotted as a function of relative sphere size (α) with κR equal to 0.25, 0.5, 1 and steric interaction (uncharged)

As shown in Fig. 13, if $\hat{\psi}_s = \hat{\psi}_c = 1$, Φ is smaller than 1, and much smaller than the partition coefficient of an uncharged system where the particle-pore interaction is purely a steric interaction. As demonstrated earlier in Fig. 9, E of a system where $\hat{\psi}_s = \hat{\psi}_c = 1$ is found to be positive, implying that the pore and particle surfaces are of like charge. The repulsive electrostatic interaction between the particle and the pore results in the decline in the probability of finding the particle inside the pore, and, thus, a reduction of the equilibrium partition coefficient. Φ declines as a function of α .

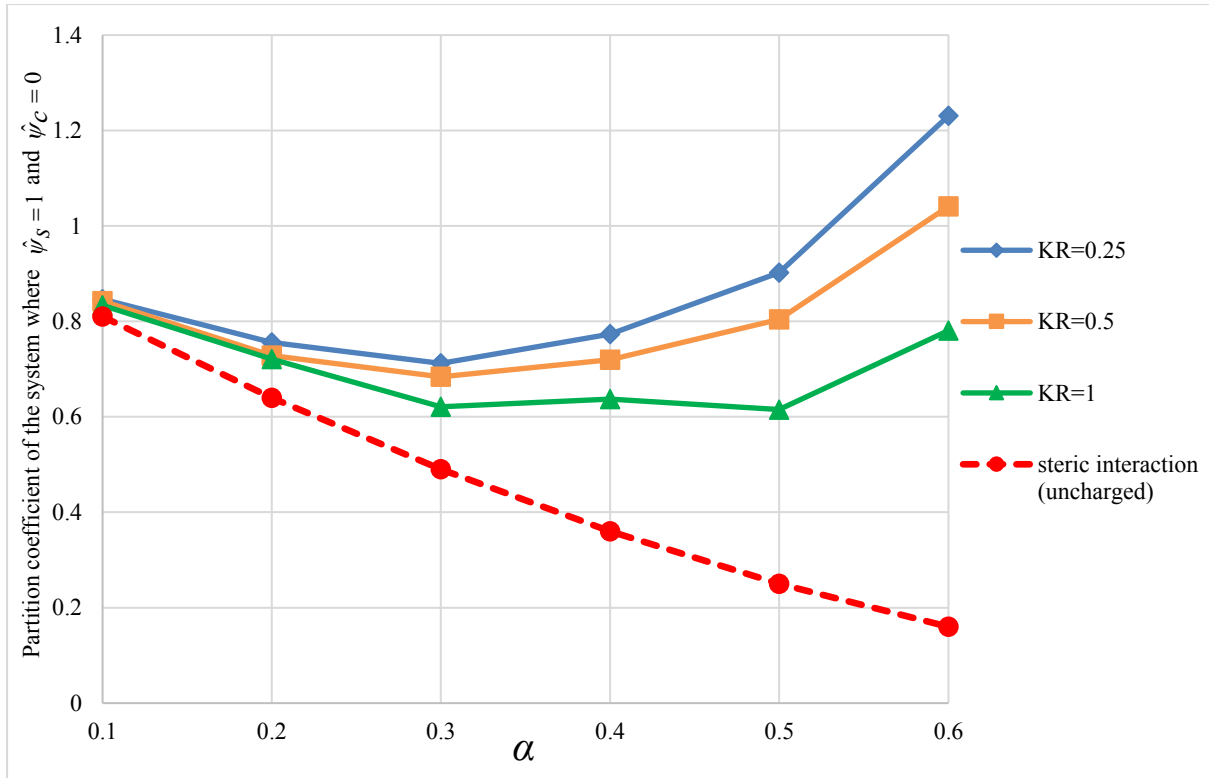


Fig. 14. The partition coefficient of a colloid inside pore where $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$ (Φ) is plotted as a function of relative sphere size (α) with κR equal to 0.25, 0.5, 1 and steric interaction (uncharged)

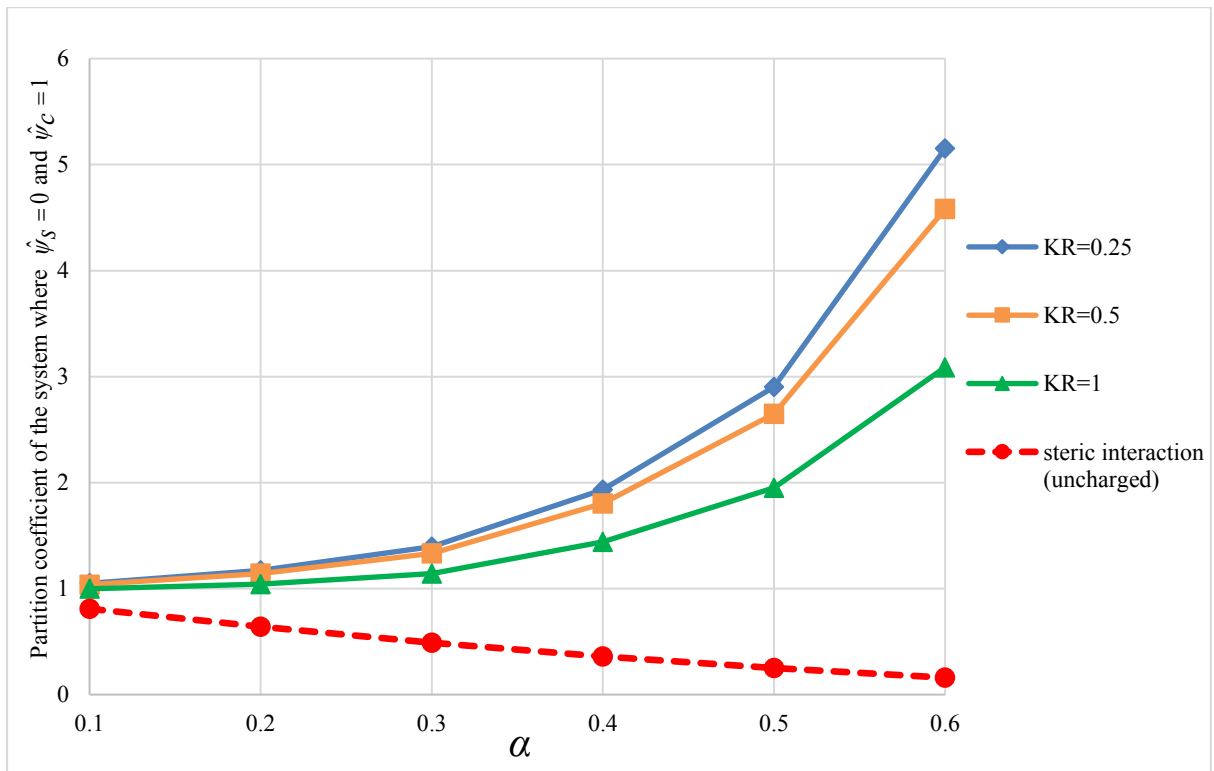


Fig. 15. The partition coefficient of a colloid inside pore where $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$ (Φ) is plotted as a function of relative sphere size (α) with κR equal to 0.25, 0.5, 1 and steric interaction (uncharged)

In contrast to results presented in Fig. 13, when either $\hat{\psi}_s$ or $\hat{\psi}_c$ is 0, Φ is found to increase as a function of α . In addition, its value is larger than the partition coefficient of an uncharged system. This is to be expected since, as shown earlier in Figs 10 and 11, E is found to be negative, implying that the particle-pore electrostatic interaction is an attractive electrostatic interaction. For certain values of α and κR , $\Phi > 1$, indicating that the particle concentration inside the pore is higher than that outside the pore. As aforementioned, if either $\hat{\psi}_s$ or $\hat{\psi}_c$ is 0, the value of the partition coefficient is a result from a competition between the steric interaction preventing the pore wall-sphere center distance being less than the sphere radius (and, thus, reducing the location on the pore cross-section where the sphere center can be found) and the attractive electrostatic interaction causing these locations on the pore cross-section (where a sphere center can be found) to be energetically more favorable than that outside the pore. If $\hat{\psi}_s = 1$ and $\hat{\psi}_c = 0$, the steric interaction dominates when the value of α , causing Φ to be smaller than 1. As α becomes larger, the attractive electrostatic interaction becomes more prominent, causing Φ to be larger than 1. For the case where $\hat{\psi}_s = 0$ and $\hat{\psi}_c = 1$, $\Phi > 1$ for the entire range of α presented, indicating that the attractive electrostatic interaction dominates, resulting in the intrapore particle concentration being larger than that in the external bulk solution.

Chapter 4

Conclusion

The present calculation of the partition coefficient of spherical colloids into porous membranes by employing Debye-Huckel approximation in finding the solution of the Poisson-Boltzmann equation confirms that the presence of the electrical double layer causes an alteration in the amount of colloids that is partitioned into the pores. The decrease in the Debye length is found to reduce the partition coefficient. If either the colloid or the pore is of zero surface potential, the colloid partition coefficient increases as a function of its size. It is possible for the partition coefficient of the colloid to be larger than that of an uncharged colloid in an uncharged pore. In fact, for certain values of Debye length and relative colloid size, the intrapore colloid concentration can be larger than that of the external bulk solution as the effect of the electrostatic attraction outweighs that of the steric interaction. If both the colloid and the pore are of non-zero constant surface potential, however, the partition coefficient is found to be smaller than that of the uncharged system as the pore and colloid surfaces are of like charge; the partition coefficient decreases as a function of colloid size. Directions for future work include an investigation of the electrokinetic effect on the partitioning of colloids into pores under the condition of charge regulation where the boundary condition is the Robin boundary condition.

References

- [1] Haraldsson, B., Nyström, J., & Deen, W. M. (2008). Properties of the Glomerular Barrier and Mechanisms of Proteinuria. *Physiological Reviews*, 88(2), 451-487.
doi:10.1152/physrev.00055.2006
- [2] Track Etched Alternative. Retrieved from <http://www.precisionmembranes.com/track-etched-alternative>
- [3] Smith, F. G., & Deen, W. M. (1983). Electrostatic effects on the partitioning of spherical colloids between dilute bulk solution and cylindrical pores. *Journal of Colloid and Interface Science*, 91(2), 571-590. doi:10.1016/0021-9797(83)90371-5
- [4] Smith, F. G., & Deen, W. M. (1980). Electrostatic double-layer interactions for spherical colloids in cylindrical pores. *Journal of Colloid and Interface Science*, 78(2), 444-465.
doi:10.1016/0021-9797(80)90584-6
- [5] Verwey, E. J. (1999). *Theory of the stability of lyophobic colloids*. Mineola, NY: Dover Publications, c 1999, 22-25, 66-68
- [6] Dechadilok, P., Intum, C., Manaratha, S., & Sathanon, U. (2016). Effect of Relaxation on Drag Forces and Diffusivities of Particles Confined in Rectangular Channels. *Journal of Fluids Engineering*, 138(12), 121105, 1-3, 15. doi:10.1115/1.4033914
- [7] Pujar, N. S., & Zydney, A. L. (1997). Charge Regulation and Electrostatic Interactions for a Spherical Particle in a Cylindrical Pore. *Journal of Colloid and Interface Science*, 192(2), 338-349. doi:10.1006/jcis.1997.5017
- [8] Sharp, K. A., & Honig, B. (1990). Calculating total electrostatic energies with the nonlinear Poisson-Boltzmann equation. *The Journal of Physical Chemistry*, 94(19), 7684-7692. doi:10.1021/j100382a068