Korean J. Chem. Eng., **18**(6), 816-823 (2001)

Molecular Simulation Study on the Colloidal Suspension Within Dilute Fibrous Media: The Effect of Particle Concentration on Partitioning

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(*Received 2 April 2001 • accepted 24 July 2001*)

Abstract−We investigated the molecular simulations based on the Gibbs ensemble Monte Carlo method, which was previously applied to the colloidal suspensions confined with a narrow pore. The long-range electrostatic interactions between the particle and the adjacent fiber and between pairs of particles are evaluated by adopting the earlier methods. For uncharged cases, the partition coefficient with non-dilute particle concentration decreases with increases in the ratio of particle radius to fiber radius. For charged systems with constant surface charges of both the particle and the fiber, the electrostatic interactions result in a different behavior according to the variations of particle concentration. Note that the particle concentration is associated with the effects of steric exclusion as well as particle-particle interaction. By developing an effective adjusting trial, the particle concentration in the bulk region has been kept as a constant during the simulation. The predicted density profiles of colloids around a fiber indicate that, whether the particles are uncharged or charged, the particle-particle interaction plays a significant role.

Key words: Gibbs Ensemble Monte Carlo, Electrostatic Interaction, Equilibrium Partitioning, Fibrous Media, Radial Density Profile

INTRODUCTION

Colloidal suspensions confined with solid walls are a frequently encountered situation, although most studies have focused on colloids in unbounded spaces [Larson, 1999]. Among the confined systems, the fibrous media have relevance to many processes such as gel chromatography, gel electrophoresis, fibrous membranes, controlled drug delivery, and many kinds of therapeutic or physiological devices [Johnson et al., 1995; Tong and Anderson, 1996]. One of the basic properties of colloidal suspension within fibrous media is the concentration distribution between the fiber matrices and the bulk. This static property is characterized by the partition coefficient [Buck et al., 2001], which is necessary to the estimation of dynamic properties.

Over 40 years ago, the earliest study provided a theoretical result of the equilibrium partitioning of a spherical particle in a randomly oriented array of straight, cylindrical fibers [Ogston, 1958]. Statistically considering only steric interactions with infinitely dilute system, the partition coefficient K defined by the ratio of the average particle concentration in the fibrous media to that in the bulk was given by

$$K = \exp\left[-\phi_f\left(1+\frac{r_p}{r_f}\right)^2\right]. \quad (1)$$

Here, ϕ_f is the fiber volume fraction, and r_p and r_f are the radii of the spherical particle and the cylindrical fiber, respectively. It will be discussed later that the steric effect of particles themselves appeared to play an important role on the partitioning.

The partition coefficients for the concentrated uncharged particles were obtained by employing both density functional theory and grand canonical Monte Carlo simulations [Fanti and Glandt, 1990a, b]. Applying a superposition approximation to the density profile of particles around a single fiber, the partition coefficient at low to moderate fiber volume fractions is given by

$$K = \exp[l\int_0^\infty 2\pi t(g_{sf}^o(t)-1)dt]. \quad (2)$$

Here, l is the length of fiber per unit volume, t denotes a radial distance from a fiber axis to a sphere center, and g_{sf}^o is the solute-fiber pair correlation function. Under dilute conditions, Eq. (2) becomes identical to Eq. (1) for uncharged systems. As mentioned in their paper, however, this method provides the upper limit of the partition coefficient of the system instead of the exact value. Moreover, the superposition approximation could be invalid in the system having randomly overlapped fibers and even involving long-range electrostatic interactions between pairs of particles and between the particle and the fiber.

Recently, the partitioning behavior including the effect of electrostatic interactions between a particle and a gel fiber was studied [Johnson and Deen, 1996]. They modified Ogston's model by introducing the Boltzmann probability distribution of energy states. The partition coefficient for an infinitely dilute system was provided as

$$K = \int_0^\infty\left[\exp\left(-\frac{E(h)}{kT}\right)\right]\left\{2\phi_f(1+\lambda+h)\exp[-\phi_f(1+\lambda+h)^2]\right\}dh \quad (3)$$

where λ is the ratio of particle to fiber radius, r_p/r_f, h dimensionless surface-to-surface distance between a particle and a fiber divided by the fiber radius, E the electrostatic interaction energy, and kT the Boltzmann thermal energy.

Very recently, the effect of solute concentration on the equilib-

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rium partitioning of colloidal solutes was examined with bovine serum albumin (BSA) and α-lactalbumin in agarose hydrogels [Buck et al., 2001]. Their theoretical results for the partition coefficient based on the integration equation method showed disagreement with their experimental results for the second virial coefficient. It is obvious, therefore, that a more rigorous approach is necessary to verify the experimental results for the wide range of experimental conditions where the electrostatic interactions are included.

In what appears to be the relevant study to date, a Gibbs ensemble Monte Carlo (GEMC) simulation was performed for the partitioning of spherical colloids within the confined spaces of slit-like pores [Chun and Phillips, 1997] as well as cylindrical pores [Chun et al., 2000]. The advantage of the GEMC method is that it predicts explicitly the partitioning for the cases of charged solutes even at non-dilute concentrations. Nonetheless, little insight has been provided into the justification of this method. A random array of fibers is disordered and indeed complicated. However, when the fiber concentration is dilute, the effect of fiber-fiber interactions is negligible. As a result, we can favorably apply a GEMC scheme to the dilute fibrous media considering the density profiles of particles around a single fiber as well as those within the bulk region. The purpose of the present molecular simulation study is to investigate the effects of particle concentration, the ratio of particle to fiber radius, and electrostatic interaction. Simulated results of the partition coefficient are presented with density profiles, and we discuss the encountered behavior.

ELECTROSTATIC PARTITIONING IN INFINITELY DILUTE SYSTEMS: A WELL-ESTABLISHED PROBLEM

For infinitely dilute charged systems, it is straightforward to calculate the partition coefficients by using Eq. (3). We consider the electrostatic repulsion alone as a long-range interaction. Another long-range interaction of van der Waals attraction is not considered, since it cannot act operatively in the suspensions of bio or polymer colloids with the condition of solution ionic strength applied in the present study. The electrostatic interaction energy between the particle and the fiber was determined by using the previously reported method [Johnson and Deen, 1996]. Based on a finite element method to solve the linearized Poisson-Boltzmann equation, the energy in terms of a quadratic function of the surface charge densities of the fiber and the spherical particle (i.e., σ_f and σ_p, in respect) can be determined. One finds that

$$E_{fp}(h) \equiv \frac{\sigma_f}{2}\int_{S_f}(\Psi-\Psi_{f,\infty})dS_f + \frac{\sigma_p}{2}\int_{S_p}(\Psi-\Psi_{p,\infty})dS_p$$
$$= \varepsilon r_p (kT/e)^2 [A_1\sigma_p\sigma_f + A_2\sigma_p^2 + A_3\sigma_f^2] \quad (4)$$

where ψ is the dimensionless electrostatic potential, ε the dielectric constant, e the elementary charge, and both S_f and S_p the surface areas scaled by r_p^2. The coefficients A_1, A_2, and A_3 in Eq. (4) are a function of particle-to-fiber distance, particle radius, and λ, whose correct values are provided in the literature [Johnson and Deen, 1996, 1997]. The respective dimensionless surface charge densities are given by

$$\sigma_f = \Psi_{f,\infty}\kappa r_p \frac{K_1(\kappa r_f)}{K_0(\kappa r_f)} \quad \text{(for fiber)}, \quad (5a)$$

$$\sigma_p = \Psi_{p,\infty}(1+\kappa r_p) \quad \text{(for particle)} \quad (5b)$$

where K_0 and K_1 are modified Bessel functions of the second kind, and $\psi_{f,\infty}$ and $\psi_{p,\infty}$ denote the isolated surface potentials normalized by kT/e. The surface potentials of both the particle and the fiber given as 25.69 mV (i.e., kT/e) are low enough to apply the linearized Poisson-Boltzmann equation. Solution ionic strengths of 1, 3, 10, 30, and 100 mM 1-1 type electrolyte correspond to the dimensionless inverse Debye lengths (i.e., κr_p) of 1.037, 1.795, 3.278, 5.678, and 10.37, respectively.

The interaction energy between pairs of spherical particles was calculated by using a singularity method [Phillips, 1995], and more detailed descriptions can be found therein. An accurate solution at separation distance h can be obtained by integrating the electrostatic force acting on the sphere with surface S in a relevant (y) direction as follows:

$$E_{pp}(h) \equiv \int_{-\infty}^{h} F_y dy = \int_{-\infty}^{h} [e_y \cdot \int_S T_{ij} n_j dS] dy. \quad (6)$$

Here, T_{ij} is the Maxwell stress tensor, e_y a unit vector in y-direction, and n_j a unit normal vector. Once the electrostatic potential is obtained, then the Maxwell stress tensor can be determined from the electric field vector (i.e., $-\nabla\psi$) as well as the osmotic pressure. The previous study suggested that the pairwise additive principle would be legitimate for the multi-particle interactions in the case of proper Debye lengths such as $\kappa r_p \geq 1.0$. Accordingly, our simulations for

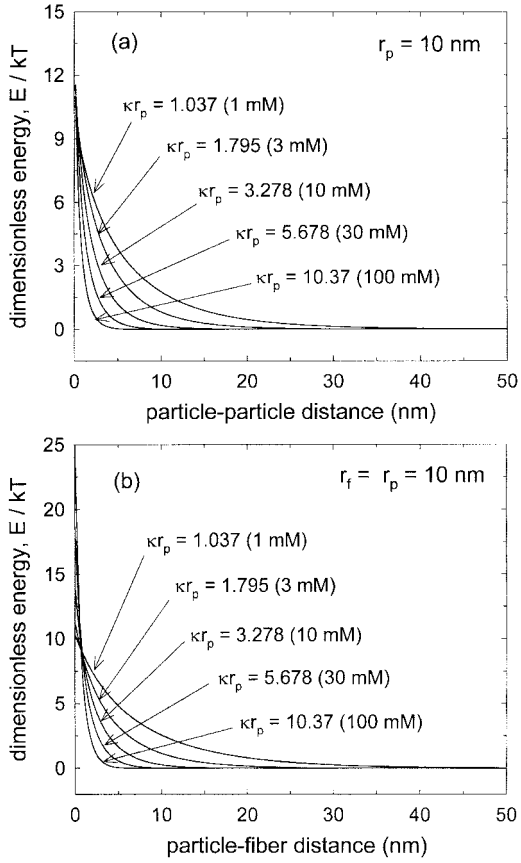

Fig. 1. Electrostatic energy profiles as a function of surface-to-surface distance of (a) particle-particle and (b) particle-fiber interactions for different inverse Debye lengths.

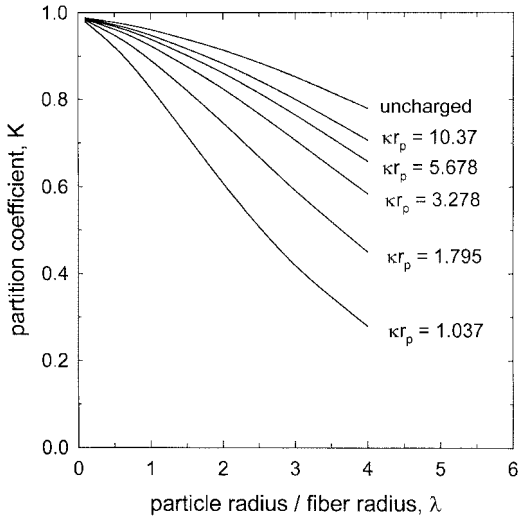

Fig. 2. Partition coefficients of uncharged and charged systems at infinite dilution as a function of λ.

charged systems are designed to satisfy this condition.

Fig. 1 shows the electrostatic energy profiles both between pairs of particles and between the particle and the fiber calculated by using the above methods. As expected, the interaction energies decrease with increasing of the ionic concentration due to an ionic screening effect by the electrolytes surrounding the particles and the fiber. Fig. 2 presents the partition coefficients for charged systems with infinite dilution by using Eq. (3), where 5×10^4 data points up to the maximum distance between the particle and the fiber were applied so as to obtain a converged partition coefficient. As expected, the partition coefficients for charged as well as uncharged systems in dilute limit decrease with increasing of λ due to the enhanced steric exclusion. In addition to the effect of steric exclusion, the electrostatic interactions between the particle and the fiber in the charged case cause the partition coefficients to fall below the uncharged case. As the inverse Debye length κ (or ionic concentration) is decreased, the partition coefficients are decreased.

MOLECULAR SIMULATIONS FOR NON-DILUTE SYSTEMS

1. The Statistical Probability and GEMC Scheme in the Fiber-Bulk System

The basic principle of GEMC can be readily found in the literature [Sadus, 1999]. The GEMC simulation consists of three kinds of processes of particle displacement: (NVT), particle exchange (μVT), and volume exchange (NPT). In origin, the GEMC technique was previously developed in the problems of phase equilibria [Panagiotopoulos, 1987a; Panagiotopoulos et al., 1988] and adsorption phenomena [Panagiotopoulos, 1987b]. As described above, recent studies showed that the GEMC simulation can be successfully applied to the partitioning problem with the well-defined geometries of confined pores [Chun and Phillips, 1997; Chun et al., 2000]. Note that the GEMC method allows one to simulate the coexisting subsystems consisting of a confined space and a bulk space, where the exchanges of the volume between the two regions do not need to be included.

In a similar way, both the NVT and the μVT processes are performed in the computational cycle of the present study. The probability criteria for the acceptance of the new configurations in the processes are as follows:

NVT (canonical ensemble, Metropolis) process:

$$p_{NVT}=\min[1,\exp(-\Delta E/kT)], \tag{7}$$

μVT (grand canonical ensemble) process:

$$p_{\mu VT}=\min\left[1,\frac{N^d V^r}{(N^r+1)V^d}\exp\left\{-\left(\frac{\Delta E^d+\Delta E^r}{kT}\right)\right\}\right]. \tag{8}$$

In Eqs. (7) and (8), ΔE ($=E_{new}-E_{old}$) indicates the changes in interaction energy caused by random moves, and the superscripts d and r indicate the subsystems donating a particle and receiving a particle, respectively. If the probability is unity, the trial will be always accepted. When the probabilities evaluated from Eqs. (7) and (8) are less than unity, a comparison with a random number is needed. The respective moves are accepted if the probabilities are larger than the random number generated between 0 and 1.

In order to treat the fiber-bulk system, two simulation cells representing both the bulk and the fiber regions are constructed as shown in Fig. 3. The periodic unit cell of the bulk region is a cube with Cartesian coordinates, where both the number of particles and the particle concentration determine the dimension of unit cell. The periodic unit cell of the fiber region is square-shaped in x and y-coordinates, in which a cylindrical fiber is vertically located at the center. For the unit cell of the fiber region, the length from the center to the periodic wall is determined by

$$W_f=\frac{r_f}{2}\sqrt{\frac{\pi}{\phi_f}}. \tag{9}$$

Here the height of the unit cell determined by the particle concentration is equal to the fiber length. Since the periodic boundary conditions are imposed for all directions, the fibrous media can be fairly

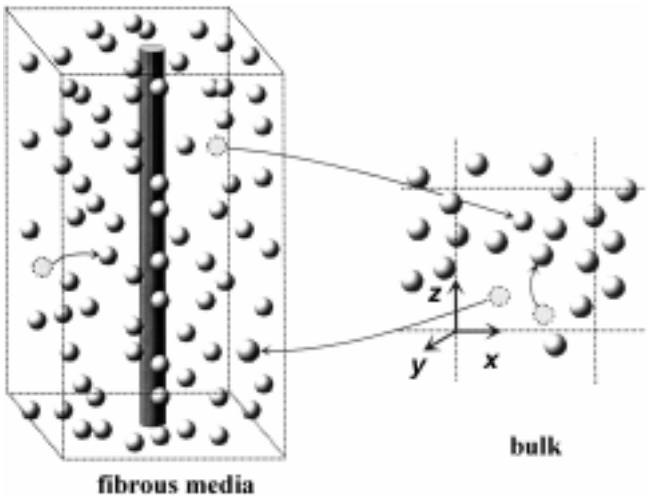

Fig. 3. GEMC scheme for the simulation of colloidal suspension within fibrous media: periodic boundary conditions are represented by dotted lines. Each cycle consists of random particle displacements in each region (NVT) and particle interchange between the two regions (μVT).

regarded as a regular array of cylindrical straight fibers. The real system has a random network of fibers and even the overlap between fibers to some extent. Unlike the diffusion phenomena, however, the orientation of fibers does not have a significant effect on the equilibrium partitioning in the case of lower fiber volume fraction. In this case, both the orientation effect and the degree of overlap between fibers become negligible. It is evident that the fiber volume fraction taken to 1 vol % in this study is sufficiently low to explain this condition [Fanti and Glandt, 1990a].

The interaction energy at arbitrary separation distances is instantaneously determined by interpolating with Newton-Gregory forward polynomials of degree nine [Chun and Phillips, 1997]. The number of tabulated points for the interpolation was 40. Total energies of both regions after particle displacements and interchanges are evaluated by using a pairwise additive principle. Fiber radii are taken to be of 5, 10, 20, 30, and 40 nm with setting the particle radius of 10 nm, and five particle concentrations are adopted as 1, 5, 10, 20, and 30 vol %.

2. Adjusting the Particle Concentration in the Bulk

Due to the successive particle exchanges between the bulk and the fiber region during the GEMC simulation, a constant particle concentration is hardly maintained in the bulk region unless the particle concentration in the bulk is high enough. For this reason, an adjusting trial is required in order to maintain the particle concentration in the bulk what we want. Basically, the problem could be accomplished by the random addition (or removal) of particles when the particles in the bulk are removed (or added). The computation time should be increased, however, because an additional relaxation process might be needed subsequently in the bulk. Therefore, a more effective algorithm is applied in the present study. When a particle needs to be removed from the bulk, the particle supplemented at a previous configuration is selected. When a particle needs to be added to the bulk, the empty site is selected as a reserved site. With this algorithm, a configurational disturbance occurring from the adjustment in the simulation is minimized as much as possible. In addition, the probability criteria provided in Eqs. (7) and (8) do not need to change since the chemical potential in the bulk is always constant during the simulation.

SIMULATION RESULTS AND DISCUSSION

1. Concentration Partitioning of Non-Dilute Charged Colloids

Over 400 particles were initially arranged in face-centered cubic lattices in the simulation unit cells. Because the initial configuration of particles in the cells results in unrelaxed configurational stresses in the systems, we randomly displaced the particles in the fiber as well as the bulk regions with 100 cycles. After the initial relaxation process, 6.4×10^4 cycles were performed to allow the systems to reach an equilibrium state. Subsequently, 1.6×10^4 cycles were performed to get the average partition coefficient. With visualization software POV-Ray™ Version 3.1 (cf., http://www.povray.org), Fig. 4 illustrates the changes of particle configurations in the bulk and the fiber regions, respectively. As demonstrated in Fig. 5, total 8.0×10^4 cycles were sufficient to get a statistically reliable partition coefficient, regardless of uncharged or charged cases.

Fig. 6 presents the variations of the partition coefficient with λ for different particle concentrations C_p in the charged system. Note

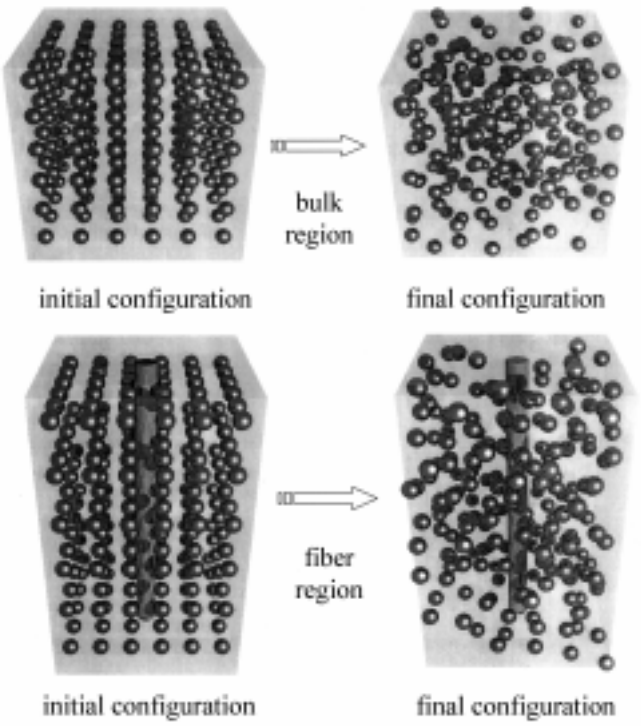

Fig. 4. Snapshots of particles in both the bulk and the fiber regions by performing of GEMC simulation for charged system with λ=1.0, ϕ_f=0.01, and particle concentration of 10 vol%.

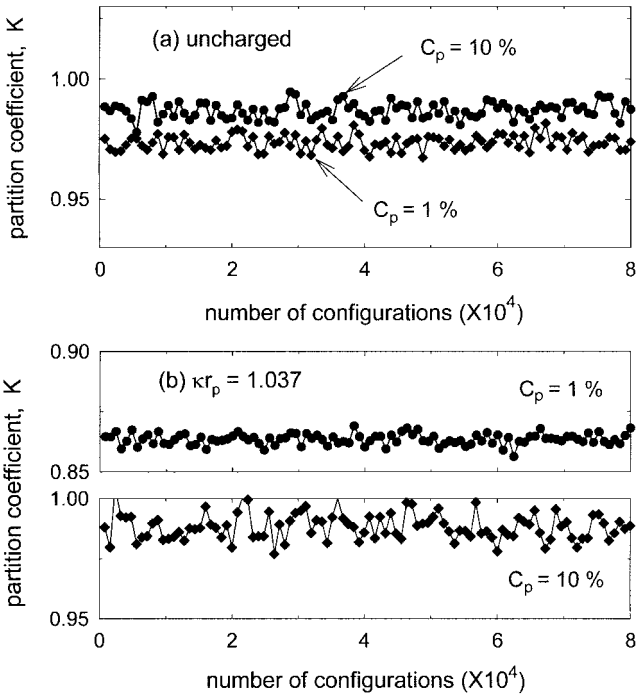

Fig. 5. Fluctuations of the partition coefficients as the GEMC simulation proceeds for λ=1.0: (a) uncharged case, particle concentrations of 1 and 10 vol%, and (b) charged case with κr_p=1.037, particle concentrations of 1 and 10 vol%.

that the cases for C_p of 20 and 30% at λ of 0.5 and C_p of 30% at λ of 3 and 4 are excluded in the simulation because their cells in the

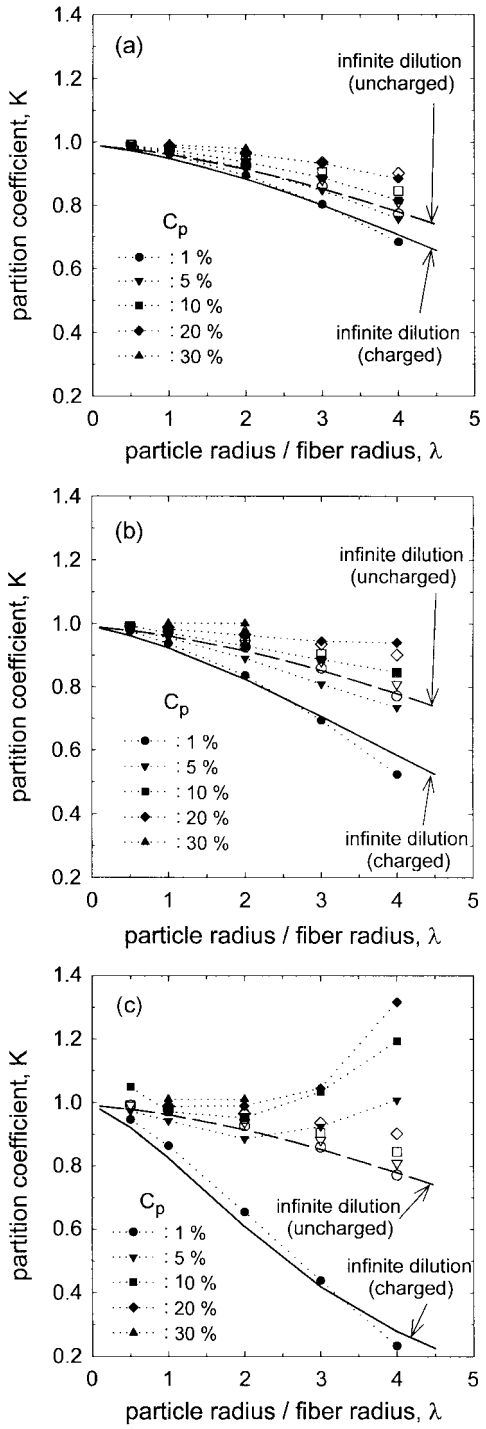

Fig. 6. GEMC results of the partition coefficients at various particle concentrations as a function of λ for charged systems with (a) κr_p=10.37, (b) κr_p=3.278, and (c) κr_p=1.037: Each of the open symbols corresponds to the uncharged case matching with the same shaped symbols.

fiber have abnormal dimensions due to an extremely small size of the width or the height. The partition coefficient is increased with the increase of particle concentration, which can be readily understood by considering the effect of particle-particle interaction. The increase of the particle-particle interaction thrusts the particles more favorably into the fiber region.

Considering the plot for C_p of 1%, one can recognize that over a certain value of λ the infinite dilution partition coefficient increases somewhat larger than is seen in the case of C_p of 1%. This phenomenon leads us to suppose that particle concentration relates to another effect on the partitioning. As both the particle concentration and λ increase, the effect of steric exclusion between particles would become greater. It should be noted that there exist two opposite effects associated with the particle concentration. One is an increasing effect on the partition coefficient due to the relatively strong particle-particle interaction in the bulk compared with the fiber region. The other is a decreasing effect on the partition coefficient due to the steric exclusion caused by the particle itself.

At the weak electrostatic repulsive interaction (i.e., large κr_p) given in Fig. 6(a), the partition coefficients in uncharged cases appear to be larger than in charged cases over the entire range of particle concentration. However, at the moderate electrostatic interaction given in Fig. 6(b), the partition coefficients in charged cases are shown to be larger than in uncharged cases for the C_p above 10%. At the low particle concentration, the electrostatic repulsion between the particle and the fiber may be comparable to that between particles since the particles are possibly far away from each other. As the particle concentration increases, however, particles tend to move into the fiber region due to the relatively strong interaction between particles in the bulk rather than in the fiber region. Further, this tendency becomes more pronounced with increasing of λ. In Fig. 6(c) matching the case of strong electrostatic interaction, the plots of the partition coefficients with λ display a parabolic shape, except for the C_p of 1%. These can be explained by the strong electrostatic effect on partitioning dominating over the effect of steric exclusion. The partitioning behavior can be also changed by the variations of both the fiber surface potential and particle surface potential. The increase of fiber surface potential $\psi_{f,\infty}$ obviously results in the decrease of partitioning. For the condition of higher particle concentration, it is possibly expected that the partitioning is increased with the increase of particle surface potential $\psi_{p,\infty}$.

Fig. 7 reveals the effects of particle concentration with various electrostatic interactions for different λ. The effects of particle concentration combined with electrostatic interactions appear to be enhanced with the increase of λ. It is also recognized that, at low particle concentration, the partition coefficients in charged cases are lower than in uncharged cases and decrease with the increase of the electrostatic interaction. This is due to the fact that the particles in the fiber region experience more electrostatic stresses by the existence of fiber rather than in the bulk region. As the particle concentration increases, however, this situation is changed. It is worth noting that the partition coefficients in charged cases are larger than in uncharged cases above a certain particle concentration referred to as "threshold concentration." This concentration depending on the electrostatic interaction decreases with increasing of λ. In Fig. 7(c), we find that the partition coefficients in the dilute limit are larger than in C_p of 1%. As mentioned above, the effect of particle-particle interaction would not be important at low particle concentration compared with the effect of steric exclusion resulting from both the particles and the fiber. Moreover, the steric exclusion would be more pronounced with the increases of electrostatic interaction as well as λ.

2. Radial Density Profile

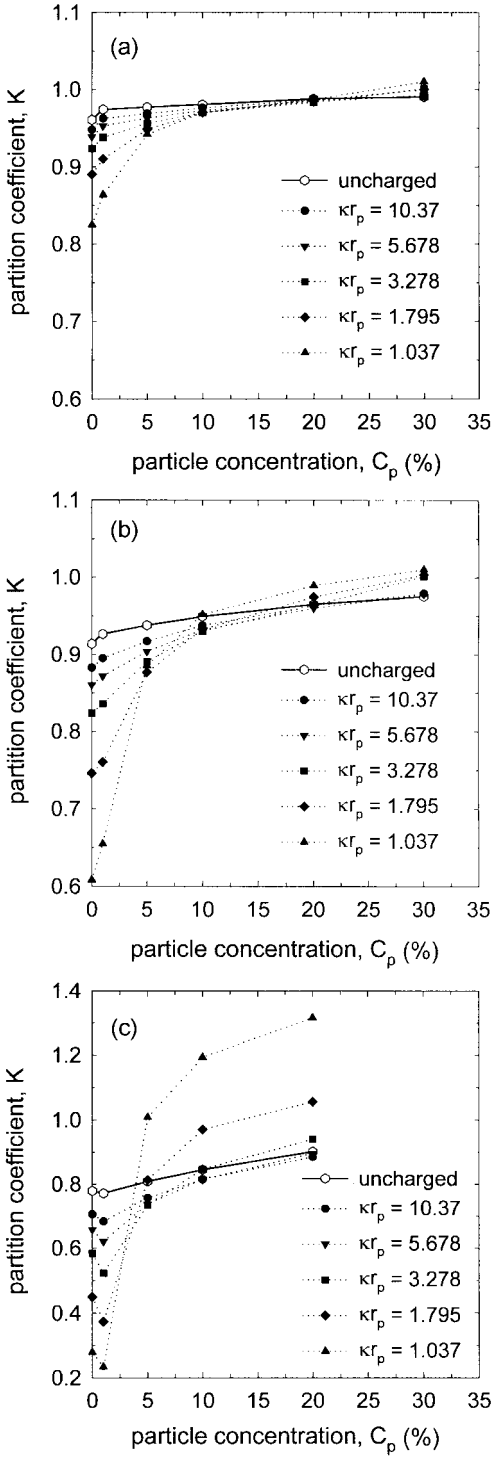

Fig. 7. Effect of particle concentration on partition coefficient at various inverse Debye lengths for (a) λ=1.0, (b) λ=2.0, and (c) λ=4.0.

From the overall results of Fig. 7, it can be summarized that the partition coefficient with the electrostatic interaction seems to be intensively dependent on the particle concentration. The increase of partition coefficient with the particle concentration indicates that the particles tend to approach to the fiber so as to avoid the stress caused by the particle-particle interactions whether the system is charged or not. Since both the particle and the fiber are charged with the same values of surface potential of like-charge in the present study, it is expected that at low particle concentration the particles locate more far away from the fiber with the increase of electrostatic repulsion. In contrast, the particles entirely approach to the fiber due to a stronger particle-particle interaction with the increase

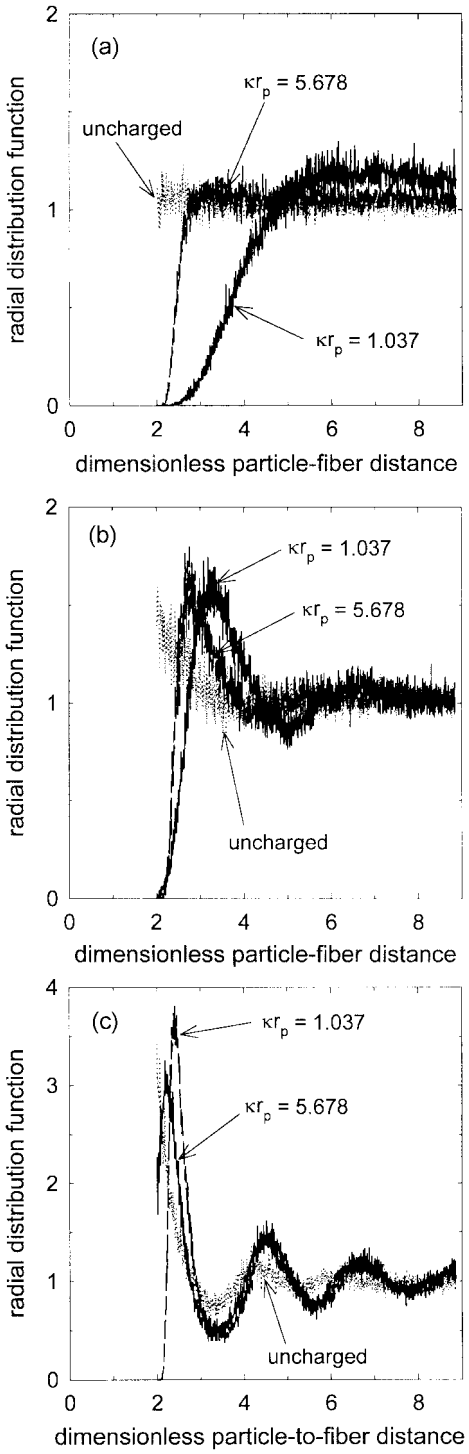

Fig. 8. Comparison of radial density profiles of particles around a fiber with different electrostatic interactions for λ=1.0 and several particle concentrations C_p of (a) 1 vol%, (b) 10 vol%, and (c) 30 vol%.

of particle concentration.

This trend is obvious for the case of stronger electrostatic repulsion, as demonstrated in Fig. 8. The density profile of particles in the fiber region can be considered in terms of the radial distribution function around a fiber. Stochastic features of the radial distribution function have been explored in the previous result of the grand canonical ensemble Monte Carlo simulations for a confined space [Suh and Park, 1994]. The probability density is zero when the distance is less than the addition of fiber radius and particle radius, and far from the fiber the density profile is almost uniform. As shown in Fig. 8(a), it is evident that, for the strong electrostatic interaction with low particle concentration, the density profile close to the fiber exhibits a depleted density. As the particle concentration increases provided in Figs. 8(b) and (c), the particles tend to shift to the vicinity of the fiber. The peak of the density profile is highly increased in the case of stronger electrostatic interaction, which suggests that the degree of fluctuation in the density profile depends sensitively on the stress what the system experiences.

CONCLUSIONS

Traditional approaches such as virial expansion and density functional methods are unable to rigorously examine the partitioning and microstructural behavior of charged colloids within fibrous media with non-dilute particle concentration. In this study, a molecular simulation to treat the disordered geometry of dilute fibrous media has been successfully performed by employing a combined stochastic process of both the canonical and the grand canonical ensembles.

We found that there are two opposite effects on the equilibrium partitioning: one is the steric exclusion by the particles themselves decreasing the partition coefficient, and the other is the particle-particle interaction increasing the partition coefficient. Besides the steric effect caused by the fiber, the steric effect resulting from the particles appears to be increasingly important with the increases of particle concentration as well as particle size. The effect of particle-particle interaction seems to be considerably enhanced depending on the electrostatic repulsive interaction. Contrary to the case of lower particle concentration, the partition coefficients in the higher particle concentration were increased with the increase of electrostatic interaction. Radial density profiles within fibrous media allow us to understand the electrostatic effects on the microstructural property of particles in terms of the particle concentration.

ACKNOWLEDGEMENT

M.-S. C. thanks Professor Ron J. Phillips at the Dept. of Chem. Eng. and Materials Sci. of Univ. of California, Davis, for suggesting the development of a periodic simulation cell in the fibrous media and valuable discussions on the fiber-solute interaction. This work was funded in part by the KIST (2E16220).

NOMENCLATURE

A_1, A_2, A_3 : coefficients used in Eq. (4) [-]
E : electrostatic interaction energy [J]
e : elementary charge [Coul]
e_y : unit vector in y-direction [-]
F : electrostatic force [N]
g^o_{sf} : solute-fiber pair correlation function [-]
h : dimensionless surface-to-surface distance [-]
K : partition coefficient [-]
K_0, K_1 : modified Bessel functions of the second kind [-]
k : Boltzmann constant [J/K]
l : length of fiber per unit volume [1/nm^2]
N : number of particles [-]
n_j : unit normal vector [-]
p : probability [-]
r_f : radius of fiber [nm]
r_p : radius of particle [nm]
S : surface [nm^2]
T : absolute temperature [K]
T_{ij} : Maxwell stress tensor [N/nm^2]
t : radial distance from a fiber axis to a sphere center [nm]
V : volume [nm^3]
W_f : length from center to periodic wall in the fiber cell [nm]
y : coordinate [-]

Greek Letters

ε : dielectric constant [Coul^2/J·nm]
ϕ_f : fiber volume fraction [-]
κ : inverse Debye length [nm^{-1}]
λ : ratio of particle to fiber radius [-]
σ : dimensionless surface charge density [-]
ψ : dimensionless electrostatic potential [-]
ψ_∞ : dimensionless isolated surface potential [-]

Subscripts

p : particle [-]
f : fiber [-]

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