



Theoretical study of inclusion complex formation of cyclodextrin and single polymer chain



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ABSTRACT

We study the inclusion complex formation of cyclodextrins and a single polymer chain by a grand canonical Monte Carlo simulation and by a statistical-mechanical theory. The filling ratio of the polymer chain by threaded cyclodextrins is calculated and shows good agreement with reported experimental results. The adsorption isotherm of the filling ratio is also derived by the statistical-mechanical theory. We confirm the significance of hydrogen bonds between cyclodextrins for the inclusion complex formation. When hydrogen bonds can be formed between cyclodextrins, the filling ratio drastically increases at a certain concentration of the cyclodextrins, and inclusion complexes are formed. However, inclusion complexes are rarely formed without hydrogen bonds. We also find the expansion of size of the polymer chain with the development of one-dimensional aggregates constructed by threaded cyclodextrins along the polymer chain.

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1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharide consisting of several glucose units linked by α -1,4-glycoside bonds and called as α -CD, β -CD, γ -CD and others according to the number of glucose units. The CDs can include various molecules into those hydrophobic inner cavities. Because of this inclusion mechanism, the CD materials have been researched and developed in a wide field such as drug delivery, molecular recognition, and molecular machine [1,2]. Since the inclusion complexes (ICs) referred to as polyrotaxanes (PRs) consisting of polymers by end-capping with bulky groups and CDs were found by Harada et al. [3–5], various PRs with CDs and CD derivatives have been extensively studied as components of new functional materials because of their unique structures and properties [6–8].

The typical PRs composed of α -CDs and end capped poly(ethylene glycol)s (PEGs) are used as precursors of slide-ring gels [9]. The slide-ring gels made by crosslinking between the threaded CDs of PRs can rearrange the positions of crosslinks along polymer chains; therefore, these gels have attracted great attention as a novel type of functional gels [10–17]. The slide-ring gels are able to release stress produced

by extrinsic stimulus with the relaxation of network structures [10,11,13,16] and show distinguishing mechanical properties such as softness and high extensibility [12,14,17]. The significance of the cross-linking ratio of CDs and the filling ratio of PRs in the properties of slide-ring gels has been reported [10,11,15,17]. Therefore, understanding of formation mechanisms of ICs, which are precursors of PRs, is fundamentally important to control the properties of slide-ring gels.

Due to precipitable crystallization and aggregation of PRs, direct analysis of ICs formation mechanisms is difficult. However, researches of IC formation mechanisms recently reported with preventing precipitation by grafting polymer chains onto a solid substrate or latex particles [18–20]. These reports revealed the important role of the aggregation of CDs in addition to the hydrophobic interaction between polymer chains and the inner cavities of CDs [20], the existence of a lower limit CD concentration for IC formation [19], the discrepancy between the filling ratio of ICs and the Langmuir adsorption isotherm [19], and the elongation of polymer chains with IC formation [18,19].

A lot of theoretical studies of the IC have been reported [21–34]. Most of them concerned ICs composed of CDs and guest molecules with low molecular weight and were based on an all-atom model, i.e., there was a few researches of PR. Simulation results based on the all-atom model of PR showed the orientation of CDs, the arrangement of CDs, the free energy of ICs, the conformation of a polymer chain, and others [21,22,29,30], but did not pay attention

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to the formation process of ICs. The formation of ICs involves polymer chains and many CDs; therefore, we need analyze the problem by a statistical-mechanical coarse-grained model rather than a detailed molecular structure model. Urakami et al. investigated the formation process of pseudopolyrotaxane (PPR) by a coarse-grained molecular dynamics simulation with hydrophobic interactions between the inner cavities of CDs and polymer chains, and reported the orientation of PPRs, the arrangement of CDs, and the dynamics of threaded CDs [28]. Pinson et al. derived the force-elongation curve of a PR and revealed the enhancement of stiffness at low force [33]. Sevick et al. calculated the entropy loss by threading a circular ring or a circular cylinder or a tube onto a long rod and showed the IC formation is a very rare event [34]. However, in existing theoretical reports, the effects of hydrogen bonds between CDs or CD concentration on IC formation have been rarely studied.

In this paper, we aim to understand the molecular mechanisms of IC formation process and the relation between the filling ratio and the CD concentration. We calculate the IC formation process of α -CDs and a PEG by a grand canonical Monte Carlo (GCMC) simulation and a statistical-mechanical theory, and derive the adsorption isotherm of the filling ratio.

2. Grand canonical Monte Carlo (GCMC) simulation

2.1. Simulation model

We first present the results of GCMC simulation. In the GCMC simulation, we employ an off-lattice bead-spring model for both the polymer chain and the CDs. The model polymer chain consists of 100 beads and the model CD consists of 16 beads, which compose 2 connected ring structures consisting of 8 beads shown in Fig. 1. The bead diameter is defined as σ and used as the unit of length in the simulation. In this model, the CD has the geometric structure with the height 2σ , the outer diameter $\sim 3.6\sigma$, the cavity diameter $\sim 1.6\sigma$, and the volume of cavity $\sim 4.1\sigma^3$. If we assume $\sigma = 0.39$ nm, the geometric structure of this model CD becomes nearly equal to the one of α -CD. This CD can also include two polymer beads; therefore, the stoichiometric ratio of this model IC is similar to the one of the PR consisting of α -CDs and PEGs [6]. In this study, to calculate the molecular mechanisms of the IC formation involving many CDs, we use the coarse-grained mesoscopic model and mainly focus on the two attractive interactions: the hydrogen bond interaction between the CDs and the interaction between the polymer chain and the hydrophobic inner cavities of CDs. We then assume the effective

attractive interactions mediated by solvents act between the specific beads for simplicity, *i.e.*, we employ implicit solvent molecules in our simulation. Solvent molecules play an important role in the IC formation at the atomistic level. For example, in an aqueous solution, the inner cavities of CDs are occupied by water molecules, and are substituted by guest molecules with the IC formation [1]. If we introduce explicit solvent molecules, we can calculate the atomistic mechanisms of the IC formation.

We use the conventional finitely extensible nonlinear elastic (FENE) potential [35] for the elastic energy potential between all neighboring beads:

$$\beta U_b(l_i) = -\frac{\beta k_b}{2}(l_{\max} - l_0)^2 \ln \left[1 - \left(\frac{l_i - l_0}{l_{\max} - l_0} \right)^2 \right]. \quad (1)$$

Here, $\beta \equiv 1/k_B T$ is the reciprocal of temperature; k_B is Boltzmann's constant; T is the temperature; k_b is the spring constant; and l_i , l_0 , l_{\max} are the instantaneous length of bond i , the equilibrium bond length, and the maximum bond length, respectively. We fixed $\beta k_b = 50$, $l_0 = \sigma$, and $l_{\max} = 1.2\sigma$ to avoid chain crossing in the simulation. To maintain the structure of the CD, we introduce cosine harmonic potentials for angle bending potentials of bond angles of the CDs:

$$\beta U_\theta(\theta_i) = \frac{\beta k_\theta}{2}(\cos\theta_i - \cos\theta_0)^2, \quad (2)$$

$$\beta U_\varphi(\varphi_i) = \frac{\beta k_\varphi}{2}(\cos\varphi_i - \cos\varphi_0)^2. \quad (3)$$

Here, θ_i and φ_i are the instantaneous bond angles within the ring structure, *e.g.*, $\theta_i = \angle ABC$ in Fig. 1b, and that to one ring structure of a bond connecting the two ring structures, *e.g.*, $\varphi_i = \angle A'AB$ in Fig. 1b, respectively; k_θ and k_φ are the spring constants; and θ_0 and φ_0 are the equilibrium bond angles. We fixed $\beta k_\theta = \beta k_\varphi = 50$, $\theta_0 = 135^\circ$, and $\varphi_0 = 90^\circ$ in the simulation.

The hydrogen bond interaction between beads belonging to different CDs is assumed to be given by the square-well potential with a narrow interaction range:

$$\beta U_h(r_{ij}) = \begin{cases} \infty & : (r_{ij} \leq \sigma) \\ -\beta \epsilon_h & : (\sigma < r_{ij} \leq r_h) \\ 0 & : (r_h < r_{ij}) \end{cases}. \quad (4)$$

Here, r_{ij} is the distance between the bead i and bead j ; r_h is the maximum distance of the hydrogen bond interaction; and ϵ_h is the strength of the hydrogen bond interaction. In the crystal state of the IC, α -CDs form head-to-head or tail-to-tail sequences with the height 1.64 nm $\approx 4.2\sigma$ [20,36]. To form the dimer with the height $\sim 4.2\sigma$, we set the maximum distance of hydrogen bond interaction as $r_h = 1.2\sigma$. To introduce the other characteristics of hydrogen bonds such as saturability and directivity, we impose the following two restrictions in addition to eq (4): One bead can interact with one bead at a maximum by hydrogen bonding interaction, and a bead can form hydrogen bond on the surface $z \geq \sigma/\sqrt{2}$ where we define the z -axis with the origin at the bead center and with the direction along the bond connecting 2 ring structures, *e.g.*, the direction from A to O in Fig. 1c. The non-bonding interaction for a pair of other beads is assumed to be given by the ordinary hard-sphere potential. The interaction between the polymer chain and the hydrophobic fields of inner cavity of the CD is assumed to be given by the energy change $-\beta \epsilon_p$ of when the distance between the center of a polymer bead and the center of mass of a CD molecule becomes less than or equal to σ .

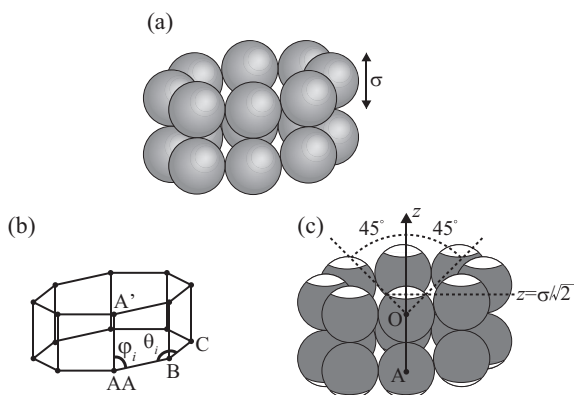


Fig. 1. (a) Schematic illustration of the bead-spring CD model. (b) Backbone structure of the model CD. (c) Active and inactive areas of the bead surfaces. White and gray surfaces indicate active and inactive areas for hydrogen bonding, respectively.

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