



Molecular dynamics simulation of cyclodextrin aggregation and extraction of Anthracene from non-aqueous liquid phase



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HIGHLIGHTS

- β CD aggregation in NAPL increased by 30% when temperature raised from 298 to 328 K.
- β CD aggregation in water changed little when temperature raised from 298 to 328 K.
- Formation of ANT- β CD complex in NAPL was a thermodynamic-limited process.
- Direct formation of ANT- β CD complex at water-oil interface was kinetic-controlled.
- ANT clusters were entrapped in the porous structure of β CD aggregates in water.

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ABSTRACT

Cyclodextrin (CD) extraction is widely used for the remediation of polycyclic aromatic hydrocarbons (PAH) pollution, but it remains unclear about the influence of CD aggregation on the PAH transport from non-aqueous liquid phase to water. The atomistic adsorption and complexation of PAHs (32 anthracenes) by CD aggregates (48 β -cyclodextrins) were studied by molecular dynamics simulations at hundreds of nanoseconds time scale. Results indicated that high temperature promoted the β CD aggregation in bulk oil, which was not found in bulk water. Nevertheless, the fractions of anthracenes entrapped inside the β CDs cavity in both scenarios were significantly increased when temperature increased from 298 to 328 K. Free energy calculation for the sub-steps of CD extraction demonstrated that the anthracenes could be extracted when the β CDs arrived at the water-oil interface or after the β CDs entered the bulk oil. The former was kinetic-controlled while the latter was thermodynamic-limited process. Results also highlighted the formation of porous structures by CD aggregates in water, which was able to sequester PAH clusters with the size obviously larger than the cavity diameter of individual CD. This provided an opportunity for the extraction of recalcitrant PAHs with molecular size larger than anthracenes by cyclodextrins.

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1. Introduction

There are over three million contaminated sites with different types of pollutants [1]. The polycyclic aromatic hydrocarbons (PAH) are a large group of persistent organic pollutants with teratogenic, carcinogenic and mutagenic properties [2]. Solvent extraction has been intensively investigated for PAHs clean-up during the past decades [3,4]. Cyclodextrins (CDs) and their derivatives

naturally originating from cellulose microbial degradation are non-toxic and biodegradable alternatives to organic solvents for PAH recovery from contaminated soils [5]. Moreover, there are scientific interests in the application of cyclodextrin extraction for the assessment of PAH bioavailability, because a linear relationship was observed between CD-extractability and PAHs biodegradability [6]. These applications benefit from the structure of cyclodextrins with hydrophobic interior cavity and hydrophilic exterior shell, which provides them with a remarkable capacity to form inclusion complexes with organic molecules especially aromatics. In addition to the considerable experiments on cyclodextrin extraction, modeling and simulation works have also been carried out to gain insights into the mechanisms of CD-guest inclusions. For example, Morillo

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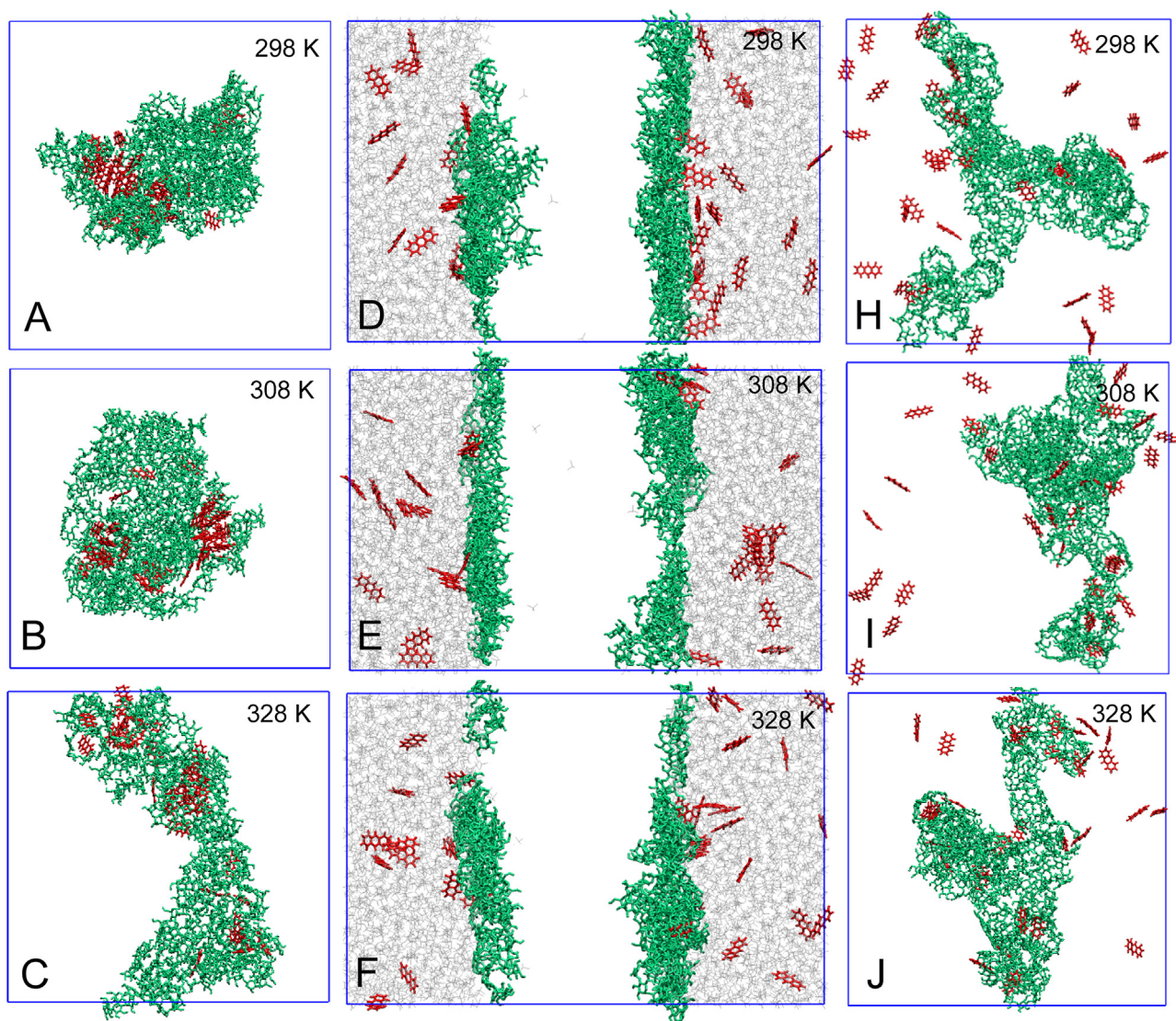


Fig. 1. Snapshots of the final configurations of β CD (green) and ANT (red) in bulk water (A–C), at water–oil interface (D–F) and in bulk oil (H–J). To highlight the structure of β CD and ANT, water molecules are not shown in A–F and oil molecules (grey) are not shown in H–J. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

et al. [7] attempted to correlate the PAH solubility with the stability of PAH-CD complex by computing the complex energy. Ren et al. [8] aimed to clarify the inclusion dynamics between phenanthrene and β -cyclodextrins (β CD) in aqueous medium and bacterial membranes by calculating the potential mean forces. These studies demonstrated the capability of molecular dynamics (MD) simulations for a direct study on the cyclodextrins-pollutants interactions at the molecular level especially in the area that are difficult, expensive or unfeasible for instrumental analysis. However, previous simulations mainly focused on the complexation of a guest molecule in a CD monomer or dimer without considering the CDs aggregation at high concentrations. The tendency to aggregate was an impact factor for the CDs complexation behavior [9], but there are knowledge gaps between our understanding of the CDs aggregation and the observed variances on the extraction efficiency at different concentrations.

In spite of many efforts on characterizing the CDs aggregation in bulk aqueous solutions, investigations devoted to CDs at interfaces are scarce. The first study on the adsorption and aggregation of CDs at the water–air interface by MD simulation was reported by Mixcoha et al. [10]. Most recently, Elk and Benjamin [11] high-

lighted the role of the structure of a β CD molecule adsorbed at the water–bromobutane interface for the reverse phase transfer process. Although it is known that the presence of CDs can promote the partitioning of PAHs from the non-aqueous phase liquid (NAPL) to the aqueous solutions, it remains unclear about the mass transport limitation processes that dominate the overall dynamics of CDs extraction. It demands future works to clarify the role of CDs aggregation for the PAH inclusion in the bulk NAPL and at the NAPL–water interface, which is essential for understanding the mass transfer processes limiting contaminants availability to microorganisms [12,13].

Additionally, temperature is an important factor influencing solvent extraction efficiency. However, early studies demonstrated insignificant changes in the PAH extraction by CDs against temperature [14]. It implied that there should be several counterbalancing processes sensible to temperature that were critical for the overall performance of CD extraction. For example, a high temperature was expected to enhance PAH solubility that was beneficial for extraction [15]. It was also possible to influence the stability of CD-PAH complex and CD-CD aggregates. It remains unclear how

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