



# Grand canonical Monte Carlo simulation study of cyclohexane, oxane, 1,4-dioxane, and 1,3,5-trioxane confined in carbon slit pore

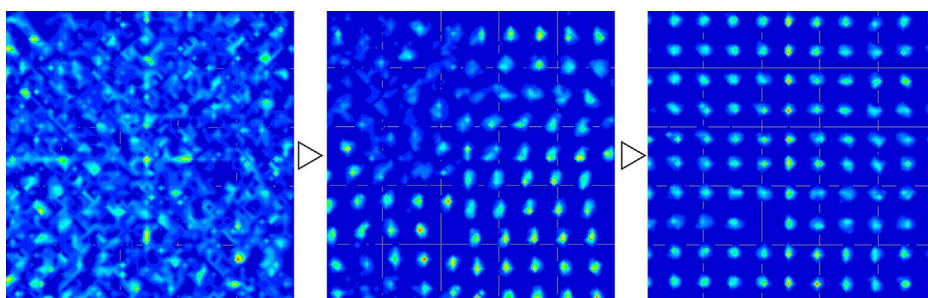


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## GRAPHICAL ABSTRACT

1,4-Dioxane confined in a carbon slit pore with a width of 0.8 nm changes from a liquid-like state to a solid-like state during adsorption.



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## ABSTRACT

A grand canonical Monte Carlo (GCMC) simulation has been conducted to investigate the adsorption of cyclohexane, oxane, 1,4-dioxane, and 1,3,5-trioxane into a carbon slit pores with widths of 0.8, 1.0, and 1.2 nm at 298 K. Particular emphasis has been paid to the effect of molecular size and shape on the intermolecular structure of the adsorbate confined in the carbon slit pore. Simulations showed that cyclohexane and oxane form a disordered single layer structure at saturation, while 1,4-dioxane and 1,3,5-trioxane form a bilayer structure in the 0.8 nm wide pore. Among the four adsorbates, 1,4-dioxane forms the most regular packing structure in the 0.8 nm wide pore at saturation; most 1,4-dioxane molecules are parallel to the pore surface and form a square lattice packing structure, which may be associated with the square molecular shape. In addition, 1,4-dioxane molecules are oriented so that the O–O axes in the molecule are alternately arrayed vertically and horizontally to avoid Coulomb repulsion between intermolecular oxygen atoms with negative charges. In addition, this packing structure is formed via two transitions (a gas to a liquid-like state and a liquid-like state to a solid-like state), as determined from analysis of the isothermal compressibility and 2D occupancy maps. These transitions are manifested as a step and a sub-step in the adsorption isotherm. On the other hand, triangular 1,3,5-trioxane forms a hexagonal lattice packing structure in the 0.8 nm wide pore at saturation; however, no definite sub-step appeared in the adsorption isotherm. The pore size dependence of the packing structures of these molecules is also discussed.

## 1. Introduction

Confinement of a liquid in a nanopore is known to alter the behavior

of the liquid. When fluid molecules are confined in a nanopore, they are spatially restricted by the pore walls and are held strongly by the solid surface that constitutes the pore wall through solid–fluid interaction. As

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a result, fluids confined in nanopores demonstrate behavior that is significantly different from that in the bulk phase. For example, melting temperature is dependent on the pore radius, the magnitude of fluid–fluid interaction, and the nature of the pore surface [1–5]. Such restriction in pores means that the intermolecular structure of the fluid molecules also differs from that in the bulk state. The intermolecular structures of simple molecules in carbon micropores have been extensively studied using various experimental techniques and molecular simulations [6–13]. The behavior of molecules with more complex chemical structures confined in nanopores is also of interest; however, the research on the intermolecular structures of such complex molecules is not sufficient. We have examined the intermolecular structure of lower alcohols, such as methanol, ethanol, propanol, and butanol confined in a carbon slit micropore using direct measurements of the differential heat of adsorption and molecular simulations [14]. The results indicated that hydrogen bonding in both fluid–fluid interaction and fluid–solid interaction plays an important role with respect to the intermolecular structure. Fukano et al. revealed that propylene carbonate molecules are oriented perpendicular to the pore wall in a 0.7 nm wide carbon slit micropore using X-ray diffraction and reverse Monte Carlo simulation [15]. Recently, Fomin et al. clarified that cyclohexane, a six-membered cyclic molecule, forms a layer structure with defective hexagonal packing in carbon nanopores and crystallizes at temperatures as high as 20 K above the melting temperature in the bulk state using a molecular dynamics (MD) simulation [16]. The reason for the hexagonal packing structure may be the symmetrical hexagonal shape of cyclohexane molecule and the lack of electrical charge. Investigation of the confinement effect on the intermolecular structure of molecules in relation to molecular symmetry or shape is of great importance in fundamental science and for many technological applications. In the present study, the intermolecular structure of 1,4-dioxane in a carbon slit pore is examined, and compared with the intermolecular structures of cyclohexane, oxane, and 1,3,5-trioxane. Oxane, 1,4-dioxane, and 1,3,5-trioxane have a structure in which one, two, and three CH<sub>2</sub> group (s) of cyclohexane are substituted with one, two, and three O atoms, respectively.

In the present study, the intermolecular structure of 1,4-dioxane confined in a carbon slit pore was investigated mainly from a scientific interest perspective; however, the results obtained will be important for technological applications. For example, 1,4-dioxane has been widely used as an industrial solvent and as a stabilizer for chlorinated solvents. However, 1,4-dioxane is a suspected carcinogen and is classified as a priority pollutant by the US Environmental Protection Agency [17]. 1,4-Dioxane is soluble in water, nonvolatile and recalcitrant to microbial degradation; therefore, it can migrate swiftly through aquifers and cause widespread contamination in both surface and groundwater [18], which is difficult to remove by biological or physicochemical treatment. For this reason, an effective capture and storage technique is required. The utilization of adsorption phenomenon by porous solids is considered to be a promising technique. The present study is related to the adsorption of 1,4-dioxane in the gas phase; therefore, this will not necessarily lead to a capture and storage technology for 1,4-dioxane from aqueous solution without further investigation. However, a precise understanding of the intermolecular structure of 1,4-dioxane confined in a pore is expected to contribute to the design of optimal porous solids in the future.

Molecular simulation is a suitable method to obtain insights into the intermolecular structures of molecules confined in micropores. Molecular simulation attempts to reproduce a real adsorption system with the assumption of fluid–fluid and fluid–solid interactions [19]. Therefore, molecular simulation can be used to calculate not only the adsorption isotherm but also the coordinates of molecules confined in pores. By making a snapshot from the coordinates of molecules and calculation of the radial distribution function, it is possible to directly analyze the intermolecular structure of the molecules confined in the pores. In addition, thermodynamic properties such as the isothermal

compressibility can be calculated to reveal the changes of the adsorbed state during adsorption [11,20–22]. Experimental research is also necessary; however, molecular simulation is useful as fundamental preliminary research. The adsorption of cyclohexane and three types of six-membered cyclic ether (oxane, 1,4-dioxane, and 1,3,5-trioxane) were investigated using molecular simulations. In particular, the intermolecular structure of 1,4-dioxane was analyzed in detail.

We present simulated adsorption isotherms and simulation snapshots of cyclohexane, oxane, 1,4-dioxane, and 1,3,5-trioxane in carbon slit pores. 2D occupancy maps and radial distribution functions are also calculated for a detailed analysis of the intermolecular structure. The importance of the molecular shape and size with respect to the intermolecular structure of molecules confined in carbon slit pores is discussed. The isothermal compressibility is also calculated to investigate the change of the adsorbed state during adsorption. In addition, the pore size effect on the intermolecular structures of 1,4-dioxane is discussed.

## 2. GCMC simulation method

The grand canonical Monte Carlo (GCMC) method [19] was used to simulate the adsorption of cyclohexane, oxane, 1,4-dioxane, and 1,3,5-trioxane into carbon slit pores. Simulation code was written in our laboratory. Considered trial moves were displacement (translation or rotation or torsion), insertion, and deletion of fluid molecules, which were randomly chosen with equal probability. The maximum translational distance was automatically adjusted to obtain an acceptance ratio of approximately 0.5. Rotations were obtained using the quaternion method. No limitation was imposed on the maximum rotation angle. The system was equilibrated for  $8.5 \times 10^8$  Monte Carlo steps, after which data were collected for another  $0.5 \times 10^8$  steps.

An ideal gas chemical potential  $\mu$ , was used for the present study. The ideal gas chemical potential was calculated by the following equation:

$$\mu = k_B T \ln \left( \frac{p\Lambda^3}{k_B T} \right), \quad (1)$$

where  $k_B$ ,  $T$ ,  $p$ , and  $\Lambda$  are the Boltzmann constant, the temperature, the pressure, and the thermal de Broglie wavelength, respectively. The simulation results, such as adsorption isotherms, will be presented on a logarithmic scale; therefore, the values of the chemical potential were chosen so that the plotted data points were equally spaced on a logarithmic scale.

### 2.1. Intermolecular and intramolecular potential

Cyclohexane, oxane, 1,4-dioxane, and 1,3,5-trioxane were represented by the transferable potentials for phase equilibria-United Atom (TraPPE-UA) model [23]. The interaction potential between fluid molecules  $i$  and  $j$  was described by the following equation:

$$u_{ij} = \sum_{a=1}^A \sum_{b=1}^B 4\epsilon_{ij}^{ab} \left[ \left( \frac{\sigma_{ij}^{ab}}{r_{ij}^{ab}} \right)^{12} - \left( \frac{\sigma_{ij}^{ab}}{r_{ij}^{ab}} \right)^6 \right] + \sum_{c=1}^C \sum_{d=1}^D \frac{q_i^c q_j^d}{4\pi\epsilon_0 r_{ij}^{cd}}, \quad (2)$$

where  $A$  and  $B$  are the number of Lennard–Jones (LJ) sites on molecules  $i$  and  $j$ , respectively, and  $C$  and  $D$  are the number of charges on molecules  $i$  and  $j$ , respectively.  $r_{ij}^{ab}$  is the distance between the LJ site  $a$  on molecule  $i$  and the LJ site  $b$  on molecule  $j$ , and  $r_{ij}^{cd}$  is the distance between the charge  $c$  on molecule  $i$  and the charge  $d$  on molecule  $j$ , having charges of  $q_i^c$  and  $q_j^d$ , respectively.  $\epsilon_0$  is the permittivity of a vacuum. The  $\epsilon_{ij}^{ab}$  and  $\sigma_{ij}^{ab}$  parameters are the cross well depth of the interaction potential and the cross collision diameter of two sites, respectively, which are calculated according to the Lorentz–Berthelot mixing rule, as follows:

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