

*Environmental Chemistry*SORPTION KINETICS OF TOLUENE IN HUMIC ACID:  
A COMPUTATIONAL APPROACH

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**Abstract**—Molecular dynamics, a computational technique aiming to describe the time-dependent movement of molecules, has been applied to study the sorption kinetics of volatile organic contaminants in soil organic matter. The molecular dynamics simulation results obtain reasonably accurate estimates of diffusion rates and activation energy of the penetration of a volatile organic compound molecule into a model humic substance. The sorption rate of toluene to humic acid decreases with the density of the humic acid matrix and increases with temperature. All the present results indicate that the sorption of toluene into humic acid is mainly diffusion controlled. Finally, the present studies have shown that molecular dynamics of volatile organic compounds in humic substances yields meaningful results, which help in the understanding of diffusion at the molecular level and which facilitate the problem-solving capability for removing the contaminants from the soils.

**Keywords**—Molecular dynamics simulations    Volatile organic compounds    Humic acid    Diffusion

## INTRODUCTION

Sorption of organic molecules in humic substances is a subject of primary importance in the environmental sciences, because the sorption process contributes significantly to pollutant fate modeling and remediation of contaminated sites. Sorption kinetics of volatile organic compounds (VOCs) with different types of environmental sorbents has been studied [1–9]. These previous studies focused on measuring the rates of sorption in complex organomineral aggregates or humic substances at large length scales. Whereas experimental measurements of sorption rate constants can provide necessary information for soil remediation, it would be highly beneficial if we could predict the sorption rate constants by computer simulations. If this is possible, then not only can some hazardous experiments be reduced but some information about the sorption mechanisms also can be obtained [10].

Computer simulation provides a new way of studying the sorption process of VOCs in the environment. A number of researchers have applied the molecular modeling techniques to study environmental phenomena, such as the sorption mechanisms of organic contaminants adsorbed onto clays and minerals [11–15], the interactions of natural organic matter and organic contaminants [16] and inorganic contaminants [17], and the persistence of toxaphene components in mammals [18]. Increased computing power of affordable computer systems has made it possible to simulate more complicated systems using molecular dynamics. Molecular dynamics simulation, which is based on the description of molecular motion by classical mechanics, allows calculation of thermodynamic properties of the molecular system with respect to time. To our knowledge, the molecular modeling techniques rarely have been applied to study sorption kinetics and thermodynamic properties of VOCs in soil organic matter (SOM).

Therefore, in the present study, we first used the molecular dynamics simulation technique to verify our method by comparing the sorption kinetics and thermodynamic results by simulation with experimental data. Experimental diffusion coefficients and sorption enthalpies were measured using a microbalance under dry conditions in our laboratory [4]. Experimental diffusivities of three VOCs—toluene, hexane, and acetone—were quantified by the diffusion model in Aldrich humic acid (sodium form) disks. Activation energies of toluene for sorption and desorption into the humic acid disks also were determined at temperatures ranging from 25 to 45°C in the experiments. Next, we investigated the possible mechanism governing the sorption of toluene in humic acid matrix. Finally, we evaluated some of the thermodynamic properties of toluene in a humic acid.

## MATERIALS AND METHODS

*Structural model and simulation method*

The chemical structure of the building block of humic acid, Temple-Northeastern-Birmingham (TNB) humic acid monomer, was described previously [19] and used to build the multiple-element structural models of humic acid [20]. The average structural unit of humic acid, the proposed TNB structure, was obtained from chemical analysis by Davis et al. [19]. Both Davis et al. and Sein et al. [20] indicated that chemical studies suggest TNB humic acid building blocks link through amide bonds. The structural properties of the humic acid model were in agreement with the real experimental conditions [20]. The basic building block structure of humic acid was produced in the present study using the Cerius<sup>2</sup> Builder (Molecular Simulation, San Diego, CA, USA). A stable confirmation of the humic acid model, consisting of eight monomers, was built by gradually adding one monomer after another; at the same time, energy minimization calculations were executed. Finally, the target compound (i.e., the toluene molecule) was inserted into

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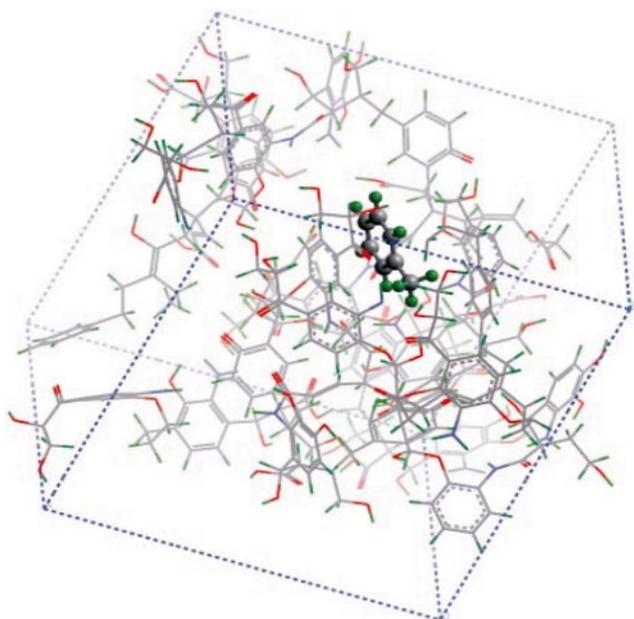


Fig. 1. The lowest-energy humic acid model containing a toluene molecule (the ball-and-stick form). Carbon atoms are gray, nitrogen atoms blue, oxygen atoms red, and hydrogen atoms green.

the open space formed among chains within the humic acid to establish our structural model, as shown in Figure 1. The unit-cell dimensions are  $19.95 \times 20.37 \times 20.87$  Å, and  $\alpha = 85.60^\circ$ ,  $\beta = 88.53^\circ$ , and  $\gamma = 93.87^\circ$ . Different density structures were obtained by performing energy minimization gradually after each dimension of the unit cell of the humic acid structure was reduced slightly.

The molecular dynamics technique involves calculating the time evolution at an atomic level for an ensemble of particles acting under specified interatomic forces by numerically solving the equation of motion in an iterative manner. The interatomic force parameters used for toluene and humic acid throughout all the molecular dynamics simulations were taken from the universal force field described by Rappe et al. [21] and distributed by Molecular Simulation Inc. (San Diego, CA, USA). Atomic charges were calculated using the  $Q_{eq}$  method [22]. A cutoff distance of 8.5 Å was used for the van der Waals interactions. The Ewald summation technique was employed for the calculation of the intermolecular coulombic potential. All the calculations were performed on SGI Origin 2000/3800 workstations at the National Center for High-Performance Computing in Hsingchu, Taiwan, Republic of China.

Our simulation procedure was as follows: First, simulations of the structural model of humic acid plus toluene were run using the Dynamic module of the Cerius2 molecular modeling suite with the NVT ensemble and the periodic boundary conditions. In the NVT ensemble, the number of molecules (N), volume (V), and temperature of the system (T) are kept constant. The Open Force Field module was used as the simulation engine. These simulations at 300, 350, and 400 K were equilibrated for 50 picoseconds (ps) and then run for 200 ps, when data were collected for mean-squared displacement of the migrations. The constant time step of 1 femtosecond (fs) is taken for all the simulations of the present study. The temperature was maintained by coupling the system to a temperature bath using the Nose-Hoover approach [23]. From the molecular dynamics trajectories of the system, we were able to calculate

the diffusion coefficient via the Einstein relationship, which is discussed below.

#### Dynamics

The diffusion coefficients are related to the time-dependent, mean-squared displacement and can be calculated according to statistical mechanical principles [24,25]. In short, the diffusion coefficient was extracted from the proportionality constant according to the Einstein form of diffusion

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle [r_i(0) - r_i(t)]^2 \rangle \quad (1)$$

where  $D$  is the diffusion coefficient and  $r_i(t)$  is the position vector of penetrant  $i$  at time  $t$ .

Considering a binary system consisting of the polymerized humic acid and the penetrant toluene molecule, the mean-squared displacement from the dynamics trajectory was equated to the average of the displacement in Equation 1 for the calculation of the diffusion coefficient. The temperature dependence of diffusion coefficient can be described by the Arrhenius equation [4,6,26]

$$\frac{d \ln D}{dt} = \frac{E}{RT^2} \quad (2)$$

where  $E$  is the activation energy of the diffusion process,  $R$  is the ideal gas constant, and  $T$  is the absolute temperature. The apparent diffusional activation energy can be estimated by plotting  $\ln D$  versus  $1/T$ .

## RESULTS AND DISCUSSION

### Sorption kinetics of VOCs in humic acid model

The humic acid model, which is based on the combination of the average structural unit of humic acid obtained from chemical analysis and modeling by Sein et al. [20], was proposed to study sorption kinetics of VOCs, with toluene as a model compound (Fig. 1). Sein et al. indicated a link between the amine and carboxylate of these molecules, which generates a stable helical structure. Our structural model of humic acid has a feature very similar to their helical humic acid structure. The toluene was inserted at three different positions to get the lowest energy conformation before the equilibration step in the simulation procedure.

Li et al. [10] used 10 to 20 ps to obtain the diffusion coefficients of chemicals in amorphous polymers. We examined the effect of the simulation time on the calculated values of diffusion coefficient. The calculated value of the diffusion coefficient approached a steady value as the simulation time became longer, and it reached a stable lowest value at approximately 200 ps (Fig. 2).

The averaged diffusivity of toluene in humic acid estimated from the collected trajectories in the molecular dynamics simulations using Equation 1 was  $2.92 \times 10^{-8}$  cm<sup>2</sup>/s at  $296 \pm 8.7$  K (mean  $\pm$  standard deviation). Compared to the experimental diffusivity of  $6.6 \times 10^{-9}$  cm<sup>2</sup>/s for sorption and  $1.2 \times 10^{-9}$  cm<sup>2</sup>/s for desorption at 298 K estimated by Chang et al. [4], the value in the present study was approximately one order of magnitude larger than the experimental results. Because of the slight inconsistency between our calculated and experimental diffusion coefficients, we compared the density used for the modeled humic acid and that measured for the humic acid used in the experiment. The modeled humic acid had a density of 1.08 g/cm<sup>3</sup>, and the experimental humic acid had a density of 1.23 g/cm<sup>3</sup> [4].

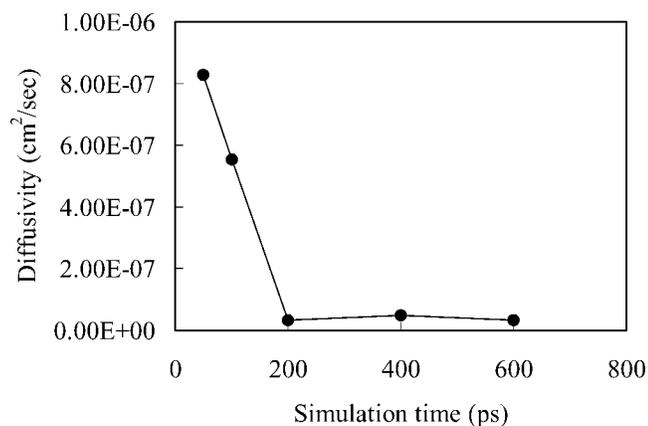


Fig. 2. Effect of simulation time on diffusivity of toluene in the humic acid model.

The calculated diffusion coefficient values are functions of the density of these humic acid models (Fig. 3). The toluene molecule has lower diffusion coefficients at higher densities of humic acid structures. The same trend is observed for several chemicals in two polymers [10]. Penetrants are expected to move faster in a looser network of the same humic acid polymer, because the void volume of the polymer matrix provides the diffusional pathway for the penetrants.

The averaged diffusivity of toluene in humic acid at a density of 1.20 g/cm<sup>3</sup> was  $8.43 \times 10^{-9}$  cm<sup>2</sup>/s at  $297 \pm 9.5$  K. A higher density of the polymer would result in a lower mobility of the penetrants and, thereby, a decreased diffusivity. Compared to the experimental diffusivity of toluene in humic acid under dry conditions at 298 K [4], the value in the present study was on the same order of magnitude as the experimental results.

Based on the results of molecular simulation in the present study and in comparison to experimental results reported in the literature [4–7], we propose that the VOC sorption rates measured in some previous sorption work [4–7] were controlled by diffusion of VOC molecules in the humic substance matrix. Also, the value of the diffusivity in humic substances was far less than that in air or in water and, instead, was more like that in synthetic polymers. Furthermore, the apparent diffusivities of toluene into soil humic substances (humic acid, fulvic acid, and humin) are on the order of approximately  $10^{-9}$  cm<sup>2</sup>/s [4–7]. Holmen and Gschwend [27] reported the thick-

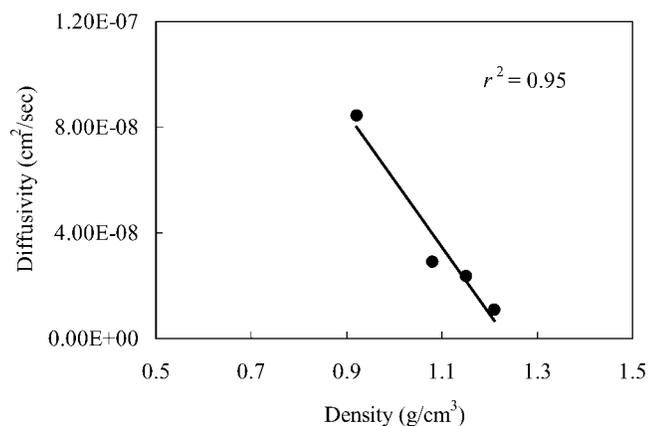


Fig. 3. Effect of the density of humic acid models on diffusion coefficients.

Table 1. Calculated diffusion coefficients of toluene in the humic acid model at three different temperatures

Temperature (K)	Diffusivities (cm <sup>2</sup> /s)
$297 \pm 9.5$	$8.43 \times 10^{-9} \pm 6.12 \times 10^{-9}$
$346 \pm 10$	$6.36 \times 10^{-8} \pm 9.22 \times 10^{-8}$
$394 \pm 11$	$3.82 \times 10^{-7} \pm 5.26 \times 10^{-7}$

ness of humic substances coating three sandy aquifers was approximately 10 to 100  $\mu$ m. Piatt and Brusseau [5] suggested that the organic coating thickness was approximately 20  $\mu$ m for two soils. According to these length scales in soils and the diffusivity, the time that toluene molecules need to penetrate a SOM matrix could be only a few minutes in the environment.

#### Thermodynamics

The average diffusivities of  $6.36 \times 10^{-8}$  cm<sup>2</sup>/s at approximately 350 K and  $3.82 \times 10^{-7}$  cm<sup>2</sup>/s at approximately 400 K are shown in Table 1 and Figure 4. The diffusivity of toluene increases with temperature, which is consistent with the experimental results of Chang et al. [4]. A higher temperature will increase the rate of diffusion because of an increase in energy that facilitates the displacement of polymer segments and helps the mobility of VOC molecules. These influences also can be observed in the results of the molecular dynamics simulation.

As shown in Figure 4 and estimated by Equation 2, an activation energy barrier of 7.8 kcal/mol is required when toluene molecules are squeezing through the macromolecular matrix. This value is slightly lower than the activation energies of toluene at 10.1 kcal/mol for sorption and at 15.7 kcal/mol for desorption into the humic acid at 15 to 45°C [4].

The reason for the observed difference between the activation energy in the simulation and the experimental study is that there would be reduced hindrance for vapor movement in a dehydrated humic acid network. The humic acid used in the previous experimental work by Chang et al. [4] was dried with nitrogen gas; nevertheless, some water molecules persisted in the humic acid matrix. However, the humic acid for the simulation did not contain any water molecules. Dehydrating the humic acid with water increases the partitioning capacity of the humic acid for nonpolar organic compounds, an indication

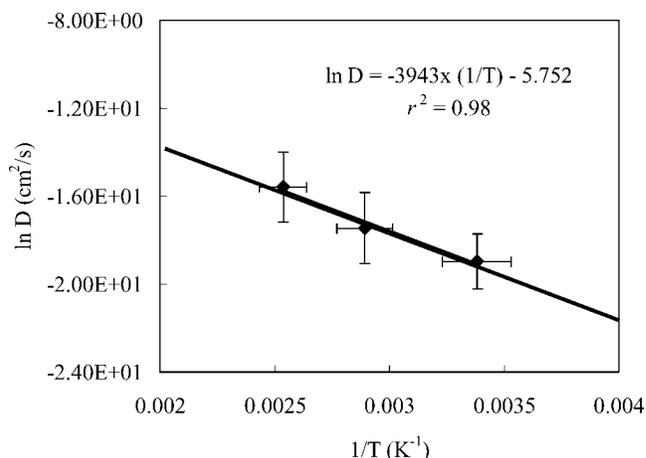


Fig. 4. The  $\ln D$  versus  $1/T$  (K) for toluene sorption in the humic acid model. Temperature ranges from 300 to 400 K. Error bars represent one standard deviation of triplicates in the simulations.

Table 2. Calculated diffusion coefficients of toluene in the water-humic acid model at three different temperatures

Temperature (K)	Diffusivities (cm <sup>2</sup> /s)
298 ± 8	4.22 × 10 <sup>-9</sup> ± 3.16 × 10 <sup>-9</sup>
345 ± 10	4.77 × 10 <sup>-8</sup> ± 2.66 × 10 <sup>-8</sup>
396 ± 10	2.00 × 10 <sup>-7</sup> ± 1.21 × 10 <sup>-7</sup>

that the overall polarity of the hydrated humic acid is decreased [28,29]. As a result of the humic acid dehydration, the humic acid molecular network might become less cross-linked. Schaumann and Leboeuf [30] also indicated that water-based cross-links in a SOM matrix decreased with decreasing water content. As a consequence, the diffusional activation energy of toluene within the molecular humic acid model that is used should be smaller than the value estimated from humic acid under typical environmental conditions.

#### Diffusion of VOCs in a water-humic acid model

Different numbers of water molecules were inserted into the humic acid model. Each of these water-humic acid models was re-equilibrated by energy minimization, and dynamic simulation procedures were performed. Increasing the number of water molecules up to five in the humic acid model, the order of magnitude of the diffusivity was kept at approximately 10<sup>-9</sup> cm<sup>2</sup>/s. After adding six water molecules in the model, the average diffusivity of replicates at 300 K, 1.02 × 10<sup>-14</sup> cm<sup>2</sup>/s, was far from the experimental data (10<sup>-9</sup> cm<sup>2</sup>/s). For the model with seven water molecules, the diffusivity was 2.65 × 10<sup>-16</sup> cm<sup>2</sup>/s. The diffusivity was far less than the experimental measurements after adding more than five water molecules. The water-humic acid model including five water molecules was selected to investigate the sorption kinetics of VOC molecules.

In Table 2, the averaged diffusivity of toluene in the water-humic acid model is 4.22 × 10<sup>-9</sup> cm<sup>2</sup>/s at 300 K. This value is close to the averaged experimental data that were estimated in our laboratory [4]. Because of the hydrogen-bond formation between polar functional groups and water molecules, the humic acid molecular network might become more cross-linked. Schaumann and Leboeuf [30] also found that water molecules may increase the degree of the cross-links in SOM matrix because of the formation of hydrogen bond-based cross-links between water molecules and SOM side chains. The averaged diffusivities at three different temperatures are shown in Table 2 and Figure 5. The activation energy of toluene into water-humic acid is approximately 9.3 kcal/mol. The energy barrier increases after adding water molecules. The hindrance of water molecules on the mobility of toluene molecule was observed in the computer dynamic simulations. The mobility of toluene molecule is hindered by water molecules and the cross-linked structure because of the hydrogen bonding of water molecules and polar functional groups of humic acid.

The diffusivities of organic chemicals in some polymers are 1.8 × 10<sup>-7</sup> cm<sup>2</sup>/s for toluene in butyl rubber at 30°C [31] and 5.2 × 10<sup>-7</sup> cm<sup>2</sup>/s and 1.7 × 10<sup>-7</sup> cm<sup>2</sup>/s for benzene and *o*-xylene, respectively, in natural rubber at 25°C [32]. The complicated cross-linked network of humic acid may cause the smaller diffusivities of VOCs than are found in these polymers.

Li et al. [10] and Wang [33] have done molecular dynamics simulation of organic molecular diffusion in amorphous polymers. The difference between the calculated and experimental

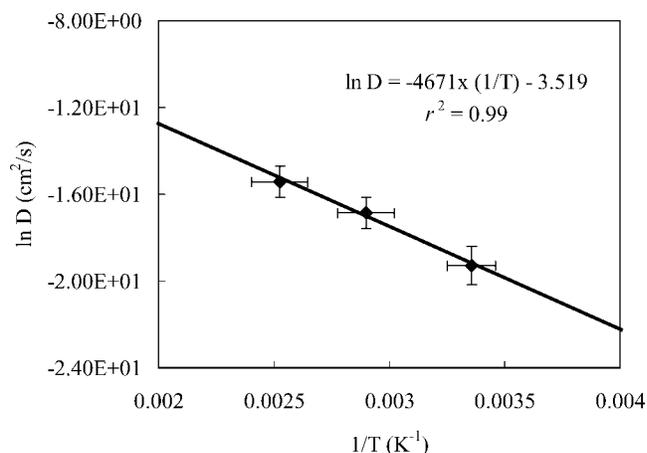


Fig. 5. The  $\ln D$  versus  $1/T$  (K) for toluene sorption in the water-humic acid model. Temperature ranges from 300 to 400 K. Error bars represent one standard deviation of triplicates in the simulations.

diffusion coefficients was as large as 24,000-fold [10]. The accuracy of calculations and the correlation with experimental values could be improved by using the different force field parameters, simulation time, and size of molecular models. Furthermore, the computer simulation should reflect exactly the experimental system and condition, so the density and water effect were considered for the humic acid model in the present study.

The similar trend between the molecular simulation and the macroscopic experimental results show that the molecular dynamics method can mimic molecular motion in actual humic acid systems.

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