

# ผลของความเข้มข้นเชิงพื้นผิวต่อโครงสร้างและพลวัตของ โมเลกุล 18-คราวน์-6 ที่รอยต่อระหว่างน้ำ - คาร์บอนเตตระคลอไรด์: ศึกษาด้วยวิธีจำลองพลวัตเชิงโมเลกุล

## The Effect of Surface Concentration on the Structure and Dynamics of the 18-Crown-6 Molecule at the Water Carbon Tetrachloride Interface: A Molecular Dynamics Simulation Study

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### บทนำ

การจำลองพลวัตเชิงโมเลกุลถูกนำมาใช้เพื่อศึกษาสมบัติเชิงโครงสร้างและสมบัติเชิงพลวัตของโมเลกุล 18-คราวน์-6 ที่รอยต่อของเหลวระหว่างน้ำ - คาร์บอนเตตระคลอไรด์ ได้ทำการจำลองระบบหลายค่าความเข้มข้นเชิงพื้นที่ซึ่งสอดคล้องกับโมเลกุล 18-คราวน์-6 จำนวน 5, 10, 15, 20, 25, และ 30 โมเลกุล ตามลำดับต่อพื้นที่ขนาด 4.4 x 4.4 ตารางนาโนเมตร ที่อุณหภูมิ 300 เคลวินและความดัน 1 บรรยากาศ ผลการจำลองแสดงให้เห็นว่าโมเลกุล 18-คราวน์-6 ส่วนใหญ่จะถูกดูดซับอยู่ที่รอยต่อสำหรับทุกความเข้มข้นเชิงพื้นที่ การเพิ่มขึ้นของความเข้มข้นเชิงพื้นผิวมีผลต่อโครงสร้างความเป็นชั้นของน้ำและมีผลต่อการกระจายความหนาแน่นของโมเลกุล 18-คราวน์-6 ที่บริเวณรอยต่อ สัมประสิทธิ์การแพร่ในระนาบรอยต่อของโมเลกุล 18-คราวน์-6 มีค่าลดลงตามการเพิ่มขึ้นของความเข้มข้นเชิงพื้นผิว

### Abstract

A molecular dynamic simulation has been used to study the effect of surface concentration on the structural and dynamical properties for the 18-crown-6 molecule at the water-carbon tetrachloride liquid interface. Several surface concentrations, corresponding with a number of 18-crown-6 molecules of 5, 10, 15, 20, 25, and 30 per an area of 4.4 x 4.4 nm<sup>2</sup>, have been simulated at a temperature of 300 K and pressure of 1 atm. The simulations show that most of the 18-crown-6 molecules were adsorbed at the interface for all surface concentrations. Increasing the surface concentration affects the layered structure of water and the density distribution of the 18-crown-6 molecules at the interface. The lateral diffusion coefficient of the 18-crown-6 molecules in the interface plane decreases as the surface concentration increases.

**คำสำคัญ:** 18-คราวน์-6, การจำลองพลวัตเชิงโมเลกุล, ความเข้มข้นเชิงพื้นผิว

**Keywords:** 18-crown-6, molecular dynamics simulation, surface concentration

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## Introduction

Crown ethers are macrocyclic polyethers which have a remarkable characteristic for the selectivity of ion binding depending on the size of cavity, donor atoms, and environment presence. Due to this special characteristic, they have been proposed as agents for an ion extraction process (Vayssi re and Wipff, 2003). It is well known that an extraction process occurs at the interface between two immiscible liquid solutions such as water and carbon tetrachloride ( $\text{CCl}_4$ ). In past decades experimental efforts have focused on investigating the thermodynamic properties and chemical processes at the liquid interfaces (Eisenthal, 1996; Schlossman, 2002). Although these investigations provided a macroscopic picture of the interfaces and were able to determine the important factors that affected interfacial chemical reactions, a detailed understanding of the liquid interfaces remains limited due to the complexity of the interfacial systems. An additional complication arises due to the fact that the interface region can occur on length scales anywhere from angstroms to nanometers. Therefore it is difficult to characterize such properties. Nevertheless, with the advent of new experimental techniques and more powerful computer resources, nowadays the interfacial problems have been resolved (Benjamin, 1996; Schlossman, 2005). Recently computer simulation techniques such as Monte Carlo (MC) and molecular dynamics (MD) methods have been widely used to examine equilibrium properties and the transfer of ion or solute across the liquid-liquid interface (Lauterbach, et al., 1998; Scatena and Richmond, 2001).

The 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane), one of crown ether family, has been widely studied by both experimental and

theoretical researchers (Bryan, et al., 1990; Glendening, et al., 1994; Fukuhara, et al., 1995; Glendening and Feller, 1996; More, et al., 1999; Kongsuk, et al., 2003) due to its simple structure but high selectivity for binding with various metal cations. These studies indicate that the 18-crown-6 has the D3d conformation in aqueous solution as shown in Figure 1(a). Thus, there is an abundance of information concerning such a molecule that presents in both gas and bulk liquid phases. However, few theoretical works have focused on structure and dynamics of the 18-crown-6 molecule at the two immiscible liquid interfaces. Wipff and co-workers (Troxler and Wipff, 1998; Vayssi re and Wipff, 2003) have performed the MD simulations of the 18-crown-6 and its complex with metal ions at the water-chloroform and the water-supercritical  $\text{CO}_2$  interfaces. Their studies show that the 18-crown-6 molecules were adsorbed at the interface and arranged their orientations when metal cations were present at the interface. In addition, this study indicated the role of counterions on the mechanism of the ion extraction process. Watanabe and co-workers (Watanabe, et al., 1990) indicated that the 18-crown-6 orientation could have a great effect on the metal-binding at the interface. Troxler and Wipff (Troxler and Wipff, 1998) showed that an increase of the salt and ligand concentrations strongly affects the interfacial behavior of crown ethers. So far there is no data on the uncomplexed 18-crown-6 and its complexes with metal cations at the water- $\text{CCl}_4$  interface. Therefore, in this study we have addressed the effect of surface concentration on the structural and dynamical properties of the 18-crown-6 molecule at the water- $\text{CCl}_4$  interface. The molecular dynamics technique has been employed for such a problem.

## Computational Details

### 1. Potential Model

The potential energy model describing atomic interactions of the system is composed of bond and non-bond interaction terms as in eq. 1 (Berendsen, 1995). The first three terms represent

$$U = \sum_{\text{bonds}} K_b (b - b_{eq})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} K_\phi [1 + \cos(n\phi + \gamma)] + \sum_i \sum_j \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \right\} \quad (1)$$

In eq. (1),  $b$  is the bond length;  $\theta$  is the valence angle;  $\phi$  is the dihedral or torsion angle and  $r_{ij}$  is the distance between atoms  $i$  and  $j$ . Parameters, the terms that represent the actual force field, include the bond force constant and equilibrium distance,  $K_b$  and  $b_{eq}$ , respectively, the valence angle force constant and equilibrium angle,  $K_\theta$  and  $\theta_{eq}$ , respectively and the dihedral force constant, multiplicity and phase angle,  $K_\phi$ ,  $n$ , and  $\gamma$ , respectively. Collectively, these represent the intramolecular parameters. Non-bonded parameters between atoms  $i$  and  $j$  include the partial atomic charges,  $q_i$  and  $q_j$ , the LJ well-depth,  $\epsilon_{ij}$ , and minimum interaction radius,  $\sigma_{ij}$ , used to treat the van der Waals (vdW) interactions. Typically,  $\epsilon_i$  and  $\sigma_i$  are obtained for individual atom types and then combined via the Lorentz-Berthelot combination rule to yield  $\epsilon_{ij}$  and  $\sigma_{ij}$ . The 18-crown-6 was treated as a flexible molecule with the united atom approximation for CH<sub>2</sub> groups, while the water and the CCl<sub>4</sub> were fixed as a rigid molecule. The CCl<sub>4</sub>-CCl<sub>4</sub> interaction was described by OPLS-AA force field (Jorgensen and Tirado-Rives, 1996) while the SPC (Berendsen, et al., 1981) model was employed for the water-

the bond interactions which consist of bond stretching, valence angle, and dihedral angle interactions, respectively. The last term is the non-bond interactions which contain repulsion, dispersion and Coulomb terms, respectively. Generally the repulsion and dispersion terms are combined in the Lennard-Jones (LJ) potential model.

water interactions. The Lennard-Jones parameters for the 18-crown-6 were taken from the Gromacs force field (Berendsen, 1995). All non-bonded parameters for describing interaction between atoms in the system are summarized in Table 1.

### 2. Simulation Method

In this work the molecular dynamics simulations of the 18-crown-6 at the water-CCl<sub>4</sub> interface have been performed in the NVT-ensemble at the temperature of 300 K. Several surface concentrations, corresponding with a number of 18-crown-6 molecules of 5, 10, 15, 20, 25, and 30 per an area of 4.4 x 4.4 nm<sup>2</sup>, have been simulated in a rectangular box having XxYxZ dimension lengths of 4.4x4.4x10.0 nm<sup>3</sup>. The z-axis was chosen to be perpendicular to the interface plane (xy-plane). The number of the 18-crown-6, the water and the CCl<sub>4</sub> molecules for all systems is given in Table 2. Initially, the bulk water and the bulk CCl<sub>4</sub> phase have been separately simulated for an equilibration at the desired temperature and density. After that, these two bulk solutions are joined together and then the 18-crown-6

molecules are inserted as a regular alignment at the water-CCl<sub>4</sub> interface as shown in Figure 1(b). It is important to note that the initial structure of 18-crown-6 is assumed to be the *D*<sub>3d</sub>-conformation (Figure 1(a)) as observed in pure water solution (Thompson, 1995). The SHAKE algorithm (Ryckaert, et al., 1977) was used to constrain the geometry of the water and the CCl<sub>4</sub> molecules. A periodic boundary condition was applied for all three directions. Long-range interactions were treated via the particle mesh Ewald method (PME) with a 9 Å cutoff. A time step of 1 fs was used for integrating the equations of motion. The simulation time of 2 ns was required to bring all systems to the equilibrium state, which was then followed by 1 ns for data collection. The data were save every 2 ps. All systems were performed using the Gromacs program (Berendsen, 1995).

## Results and Discussion

### 1. Density Distribution Profile

The interfacial behavior of 18-crown-6 and solvent molecules can be characterized in terms of density profile which represents a molecular density distribution as a function of *z* coordinate. The density profiles of solute and solvent molecules for all surface concentrations are presented in Figure 2. and Figure 3. In Figure 2, the density profiles of the 18-crown-6 molecule for all systems have a sharp peak at nearly the same position (*z* ~ 5 nm) which is the interface position, defined by the intersection of solvent density curves (Vayssie' re and Wipff, 2003). This means that all of the 18-crown-6 molecules are adsorbed at the interface. An increase of the surface concentrations affects not only the density peak of 18-crown-6 but also their migration into the bulk water phase. It is clearly seen from Figure 2. that a few of the 18-crown-6 molecules start to diffuse into the bulk water phase

for the higher surface concentrations (systems D-F). In addition, one can observe from the density plots that all 18-crown-6 molecules do not move to the bulk CCl<sub>4</sub> phase. This implies that the 18-crown-6 molecules prefer to interact with the water molecule. Comparing the ab initio calculation results (Kongsuk, et al., 2006) shows that the binding energy of the 18-crown-6 with water is greater than that with CCl<sub>4</sub>. Therefore, it could be anticipated that all 18-crown-6 molecules should move to the water phase. However, in fact most of the 18-crown-6 molecules are localized at the interface region. Why is this so? To best answer this question, we have adopted two reasons proposed by Troxler and Wipff (Troxler and Wipff, 1998). The first reason is that the 18-crown-6 molecule prefers to orient its molecular plane perpendicular to the interface plane which enhances the stability of this molecule. The second one is due to the solvent cavitation energy since the surface tension of the water (71.99 mN.m-1) is much higher than that of the CCl<sub>4</sub> (26.43 mN.m-1) (Lide, 2003). Consequently, the energy cost for creating a cavity in the water is much higher than in the CCl<sub>4</sub> which it is too large to be compensated by the changes in the solute-solvent interactions. The behavior of free 18-crown-6 molecules adsorbed at the interface is similar to the characteristic of surfactants observed at the water-CCl<sub>4</sub> interface (Schweighofer, et al., 1997) as well as at the water-supercritical CO<sub>2</sub> and the water-chloroform interfaces (Troxler and Wipff, 1998; Vayssie' re and Wipff, 2003).

In Figure 3. the density profiles of the water and the CCl<sub>4</sub> for all systems are displayed. It is clearly seen that the water density profiles for all systems stay at the experimental value in the bulk water phase and then fall off quickly to zero into the bulk CCl<sub>4</sub> phase. The same behavior also is observed for the CCl<sub>4</sub> density profiles. The CCl<sub>4</sub> and

the water bulk phases are well separated. This indicates that the two solvents are immiscible. The overlap of the density of the  $\text{CCl}_4$  and of the water at the interface region suggests that this interface is not flat at a molecular level due to thermal fluctuations. However, the water density profiles significantly change near the interface region for the higher concentrations (systems D-F) because the slope of the density curvature is decreasing.

## 2. Dynamics of 18-Crown-6

Displacement of the average center of mass of the 18-crown-6 molecules in the z-direction from the interface position ( $z = 5.0$  nm) as a function of time is calculated to follow their position as shown in Figure 4. It is clearly seen that the z-displacement of the 18-crown-6 molecules shows small oscillation near the interface position for the lower surface concentrations (systems A-C), but further away for the higher surface concentrations (systems D-F). The averaged displacement of the system D is much greater than for other systems. However, one can see from this plot that the 18-crown-6 molecules are still adsorbed at the interface for the lower surface concentrations but they are pushed into the water bulk phase for the higher concentrations. This also indicates that these molecules are not static at the interface, but in motion.

## 3. Lateral Diffusion of 18-Crown-6

It is interesting to study the dynamics of the 18-crown-6 in the plane of the interface (xy-plane) because most of 18-crown-6 molecules stay at the interface. To examine this property, the average mean-squared displacement in the xy-plane ( $\langle u_{xy}^2(t) \rangle$ ) of the center of mass of the 18-crown-6 molecules is evaluated and the two-dimensional diffusional coefficient ( $D_{xy}$ ) obtained from the slope of the mean-squared displacement using the well-known Einstein's relation

$$D_{xy} = \frac{\langle u_{xy}^2(t) \rangle}{2d} \quad (2)$$

where  $d$  is the dimensionality of the system (in this present case  $d = 2$ ). The calculated values of the diffusional coefficient for all systems are summarized in Table 2. Figure 5. shows the average mean-squared displacement plot. It is clearly seen that the 18-crown-6 molecules are not static, but quite mobile, especially for the lowest concentration (system A). One can also observe from this plot that the mobility of 18-crown-6 for all systems, except system E, trends to decrease as surface concentration increases. The appearance of the greatest diffusion coefficient for the lowest surface concentration (system A) corresponds to the highest mobility of the 18-crown-6 molecules in the interface plane.

## Conclusion

In this study the structural and dynamical properties of the 18-crown-6 molecules at the water- $\text{CCl}_4$  interface have been investigated using the molecular dynamics simulation techniques. Several surface concentrations of the 18-crown-6 molecules were modeled under the same simulation conditions. This study reveals that the most 18-crown-6 molecules were adsorbed at the interface for all surface concentrations. Even the interaction between the 18-crown-6 and the water is much greater than that between the 18-crown-6 and the  $\text{CCl}_4$ ; most 18-crown-6 molecules still remain at the interface. We can conclude from this that the 18-crown-6 molecule has high interfacial activity and this characteristic is necessary for the ion extraction process. An increase of surface concentration not only significantly affects the density distribution of the solute and the solvent molecules, but also the mobility of the solute molecule at the interface.

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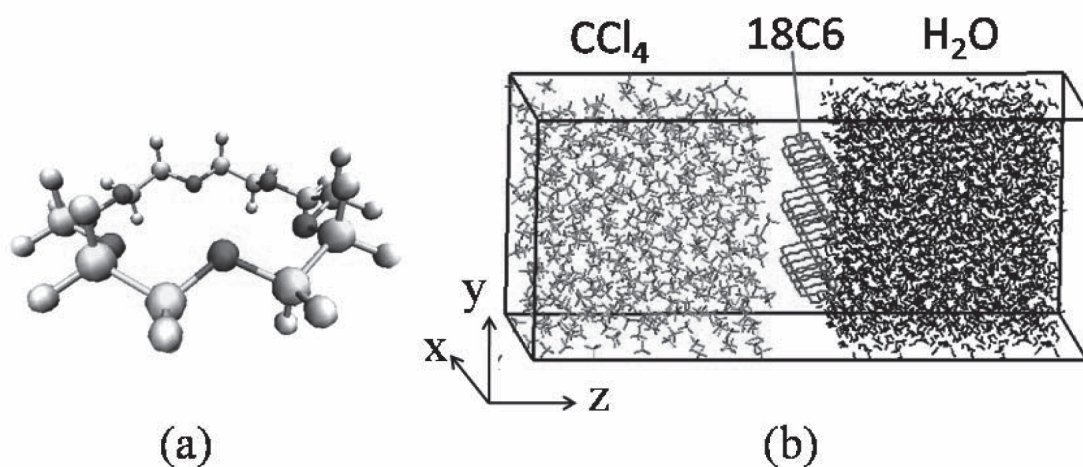
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**Table 1.** Atomic charge and Lennard-Jones parameters for 18-crown-6, water and  $\text{CCl}_4$  molecules

Molecules	Atom Type	Charge	$\epsilon$ , $\text{kJ.mol}^{-1}$	$\sigma$ , nm
18-Crown-6	O	-0.484	1.7244	0.2626
	$\text{CH}_2$	0.242	0.5857	0.3965
$\text{H}_2\text{O}$	O	-0.820	0.6500	0.3166
	H	0.410	0.0000	0.0000
$\text{CCl}_4$	C	0.248	0.2093	0.3800
	Cl	-0.062	1.1137	0.3470

**Table 2.** A number of 18-crown-6, water and  $\text{CCl}_4$  used in MD simulations and the calculated lateral diffusion coefficient for all surface concentrations

System	No. 18-crown-6	A ( $\text{nm}^{-2}$ )	No. Water	No. $\text{CCl}_4$	$D_{xy} \times 10^{-5}$ ( $\text{cm}^2.\text{s}^{-1}$ )
A	5	0.262	2550	512	$2.50 \pm 1.34$
B	10	0.524	2531	512	$1.48 \pm 0.67$
C	15	0.786	2520	512	$1.53 \pm 0.39$
D	20	1.048	2507	512	$1.43 \pm 0.12$
E	25	1.311	2497	512	$1.62 \pm 0.38$
F	30	1.573	2475	512	$1.32 \pm 0.56$



**Figure 1.** (a) The  $D_{3d}$  conformation of 18-crown-6 (18C6) molecule consisting of atoms of carbon (yellow), oxygen (red) and hydrogen (gray) and (b) schematic representation for simulation box in which the z-axis is chosen to be perpendicular to the interface. The 18C6 molecules (red) are placed at the interface between bulk  $\text{CCl}_4$  (green) and bulk water phases (black)



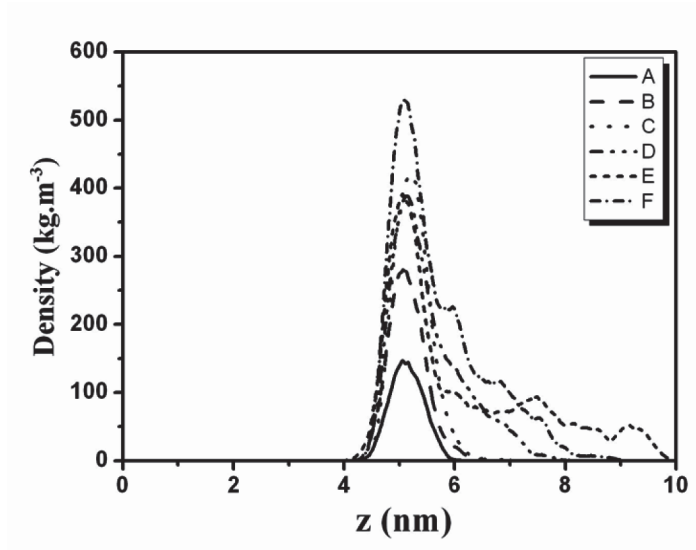


Figure 2. Molecular density distribution as a function of z coordinates for the 18-crown-6 molecules at the water-CCl<sub>4</sub> interface for all surface concentrations

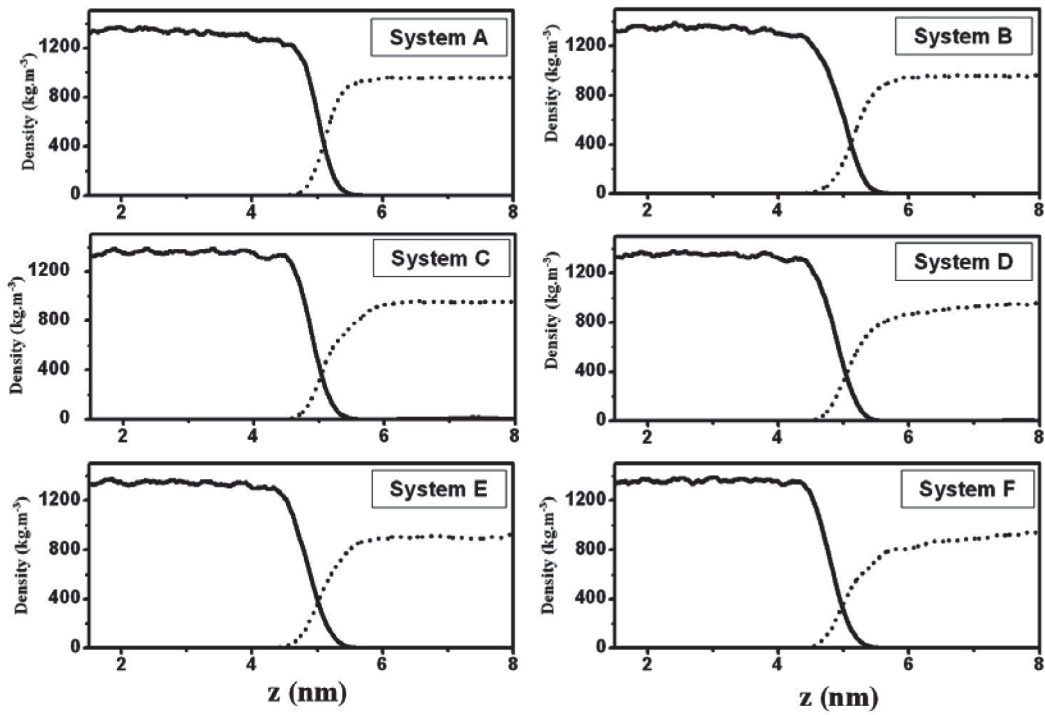


Figure 3. Molecular density distribution as a function of z coordinates for water (dashed line) and CCl<sub>4</sub> (solid line) molecules for all surface concentrations

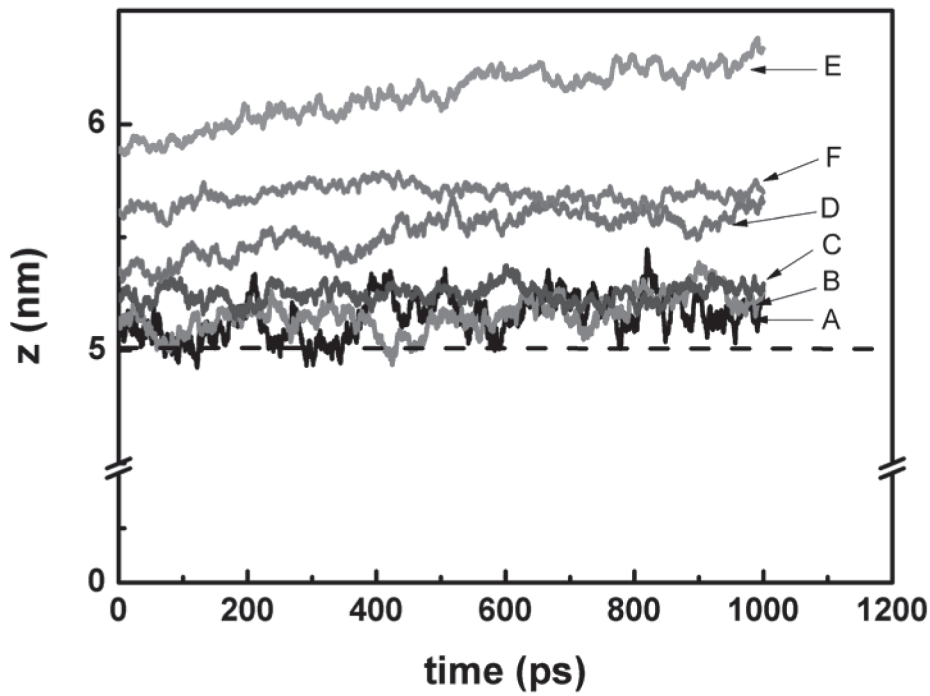


Figure 4. Displacement of the averaged center of mass of the 18-crown-6 molecule from the interface position in the z-direction as a function of simulation time for all surface concentrations.

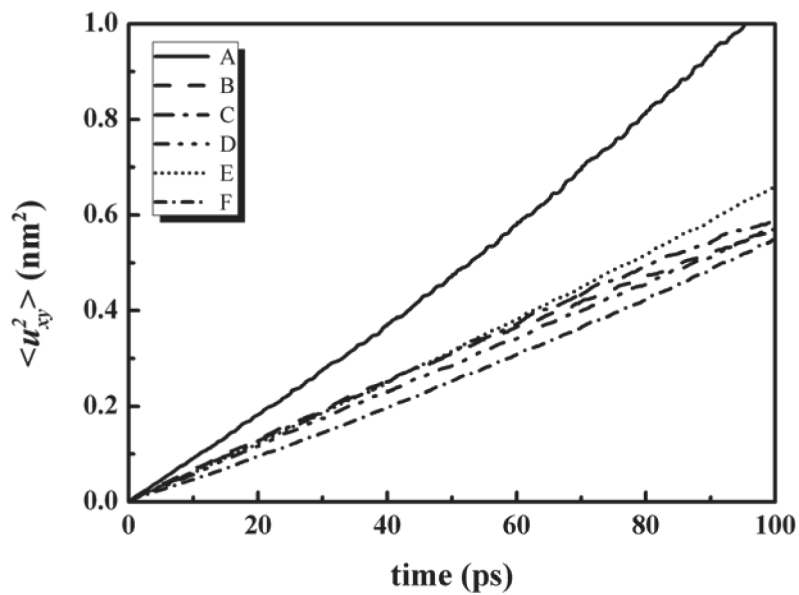


Figure 5. Time evolution of the mean-squared displacements (MSD) of the center of mass of the 18-crown-6 in the plane of the interface. The diffusion coefficient ( $D_{xy}$ ) value was estimated from a linear fit of the data for all surface concentrations