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Molecular understanding of dynamical properties of the vapor/ethanol-aqueous-solution interface

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The variation of dynamical properties of the vapor/ethanol-aqueous-solution interface with excess adsorption of ethanol is investigated by a molecular dynamics (MD) simulation. Five independent NVT ($T = 298.15$ K) constant MD runs were performed, where a slab of ethanol-aqueous-solution with ethanol mole fraction χ_e of 0.0052, 0.012, 0.024, 0.057 and 0.12, respectively, reached an equilibrium state of adsorption. The positional dependence of molecular self-diffusivity was evaluated by profiles of the self-diffusion coefficient of ethanol and water along the axis normal to the interface. The profile of the ethanol self-diffusion coefficient showed local extrema at the interface, the degree of which is weakened with increase of χ_e . Lateral self-diffusivity of an adsorbed ethanol molecule was also evaluated by the two-dimensional (2D) self-diffusion coefficient at the interface, which is a monotonically decreasing function of ethanol excess adsorption. Moreover, the desorption probability of an adsorbed ethanol molecule was estimated, which monotonically increases with ethanol excess adsorption. The molecular origin of the variation of these dynamical properties was explained by correlating them with the profile of the free energy change.

Keywords: Ethanol aqueous solution; Monolayer; Self-diffusion coefficient; Anisotropy; Desorption probability; Free energy profile

1. Introduction

Surfactant aqueous solutions play important roles in various fields such as surface chemistry [1] and atmospheric sciences [2], where a molecular understanding of the interfacial properties of a solution rather than the bulk properties of solution is essential in the development of an appropriate model of phenomena. An ethanol aqueous solution is one example of an aqueous solution containing a soluble surfactant. In the last two decades, the molecular structure of the vapor/ethanol-aqueous solution has been actively investigated by many kinds of experimental techniques. Li *et al.* provided the first insight onto the density profile and orientation of adsorbed alcohol at an interface using grazing incidence X-ray reflectivity (GIXR) [3]. They concluded that ethanol molecules at the interface are arranged with their hydrophobic tail projecting towards the vapor [3]. Information about the tilting angle of alcohol molecules was presented from studies using sum-frequency generation spectroscopy (SFG) [4,5]. Sung *et al.* [5] suggested that the tilting angle of ethanol molecules is unchanged with increased adsorption. Contrastively, the dynamical

properties of the vapor/ethanol-solution interface is rarely investigated, which may be attributable to an insufficiency of both the spatial and time resolving power of existing experimental techniques.

In that context, a molecular dynamics (MD) simulation [6] is the best suited tool to obtain structural and dynamical information of the vapor/solution interface at a molecular level. Recently, much interest has been invested on the vapor/ethanol-aqueous-solution interface [7–12]. Their calculations successfully reproduced the structural properties of the interface, including the thickness of the interface and the tilting angle of the adsorbed ethanol molecules [7–9], and also provided predictive information about the state of intermolecular hydrogen bond (HB) at the interface [8] and molecular clustering via HBs [10]. Dynamical properties of the interface was principally evaluated by means of a mass accommodation coefficient of vaporized ethanol molecules into the solution [8,11,12], the calculated value of which became almost unity. Additionally, our recent MD study provided novel insight into the two-dimensional (2D) phase behavior of an adsorbed monolayer of ethanol, showing it behaves as a 2D supercritical fluid at temperatures under 298.15 K [9].

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In this paper, following in sequence with our previous work [9,10], our main interest is on the dynamical properties of the vapor/ethanol-aqueous-solution interface. The positional dependence of self-diffusivity of each kind of molecule, was evaluated by the profile of the self-diffusion coefficient along the axis normal to the interface. Lateral self-diffusivity of adsorbed ethanol molecules on the interface was also evaluated by 2D self-diffusion coefficient, which became a monotonically decreasing function of ethanol excess adsorption. Furthermore, the desorption kinetics of adsorbed ethanol molecules was evaluated by a desorption probability. It is shown that adsorbed ethanol molecules easily desorb into the bulk solution when excess adsorption is increased. Finally, the molecular origin of the variation of these dynamical properties with excess adsorption was explained by correlating them with the profile of the free energy change.

2. Simulation method

OPLS-UA [13] is selected as the potential model of an ethanol molecule, and SPC/E [14] is selected as that of a water molecule. The initial configuration of the unit cell is described elsewhere [9], where a 10 nm thick slab of ethanol aqueous solution was placed at the center of a unit cell with $L_x = 4$ nm, $L_y = 4$ nm, $L_z = 24$ nm. Five independent 12 ns NVT ($T = 298.15$ K) constant MD runs were performed under a three-dimensional (3D) periodic boundary

condition, reaching an equilibrium state of adsorption where the ethanol aqueous solution slab had an ethanol mole fraction χ_e of 0.0052, 0.012, 0.024, 0.057 and 0.12, respectively. With this adsorption equilibrated configuration, an additional data gathering 5 ns MD run was performed. Newton's equation of motion is numerically solved by the leap-frog algorithm with $\Delta t = 2$ fs, while the intramolecular constraints are retained by the SHAKE algorithm [6]. The temperature is controlled by the Berendsen thermostat [15]. The Lennard-Jones interaction was cut off at 1.33 nm, and the Coulomb interaction is fully accounted for by the Ewald summation technique [6]. Usage of the MDGRAPE-2 board [16] enabled us to calculate the two-body interaction at reasonably high speed.

3. Results and discussion

3.1. Self-diffusion coefficient

To evaluate the positional dependence of the self-diffusivity of the molecule, depth-dependent self-diffusion coefficient, $D(z)$, is calculated by the following procedure; the unit cell was divided into an aggregate of small volumes ($L_x \times L_y \times \Delta z$, $\Delta z = 0.1$ nm), and the particle average of the mean square displacement (m.s.d.) of the molecular mass center $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$ is taken per each small volume, followed by the self-diffusion coefficient at the z -position being calculated through the Einstein relation [6]. Figure 1

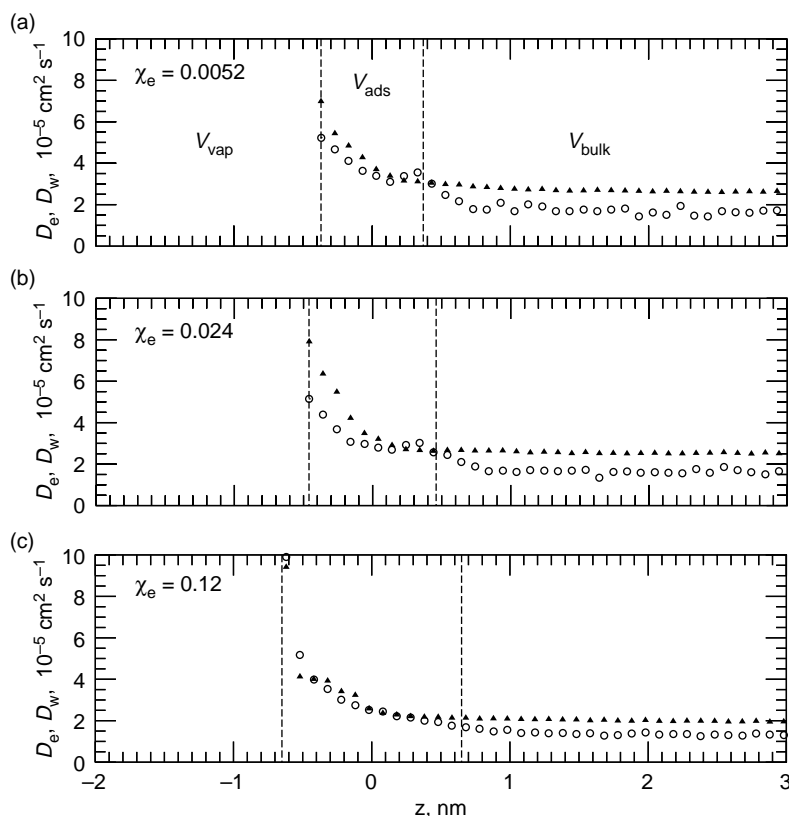


Figure 1. Profile of self-diffusion coefficient along the z -axis: ethanol (open circles) and water (closed triangles). The dashed lines are the boundaries between V_{vap} and V_{ads} , V_{ads} and V_{bulk} , respectively. The bulk values of the ethanol mole fraction χ_e are depicted in each figure.

shows the self-diffusion coefficient profile of ethanol and water, $D_e(z)$ and $D_w(z)$, where the origin of the z -axis is taken at the position of the peak maximum of ethanol excess adsorption. As is expected, $D_e(z)$ and $D_w(z)$ approach a constant value in the bulk solution region (V_{bulk}). At the interfacial region (V_{ads}), $D_w(z)$ monotonically increases toward the vapor side independent of χ_e . On the other hand, $D_e(z)$ is an increasing function toward the vapor region (V_{vap}) with a local maximum; the height of which becomes smaller with larger χ_e .

The origin of the appearance of a local maximum in $D_e(z)$ can be clarified by resolving the self-diffusion coefficient in each axial direction. The profile of the ethanol self-diffusion coefficient along the x -axis $D_{e,x}(z)$ is calculated by the same procedure in $D_e(z)$ where the particle average of the m.s.d. of the x -component of molecular mass center $\langle |x(t) - x(0)|^2 \rangle$ is taken per each small volume in place of $\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$. In the same way, $D_{e,y}(z)$ and $D_{e,z}(z)$ are calculated. Figure 2 shows the results of $D_{e,x}(z)$, $D_{e,y}(z)$ and $D_{e,z}(z)$. It is apparent that the diffusion along x - and y -axes is similar, but that along z -axis is different; i.e. $D_{e,z}(z)$ had a maximum at the boundary between V_{ads} and V_{bulk} , and showed a minimum at $z = 0$. An interesting point is that the well depth of $D_{e,z}(z)$ becomes shallower with increase of χ_e , resulting in a disappearance of the local maximum in $D_e(z)$.

The molecular origin of the maximization and minimization of $D_{e,z}(z)$ will be explained in Section 3.4.1.

As in previous works [7–9], the adsorbed ethanol molecules form a self assembled monolayer (SAM) at the interface. Thus, it is of fundamental interest to estimate the lateral self-diffusivity of adsorbed ethanol at the interface and its variation with excess adsorption. It is assumed that dynamics of the adsorbed molecule is isotropic in the x - and y -direction. The 2D self-diffusion coefficient of ethanol D_e^{2D} is calculated by the particle average of the m.s.d. of adsorbed ethanol molecule's mass center $\langle |\mathbf{r}^{2D}(t) - \mathbf{r}^{2D}(0)|^2 \rangle$ where \mathbf{r}^{2D} is a coordinate vector on the xy -plane. Figure 3 shows D_e^{2D} versus the area occupation probability density defined in Ref. [9],

$$\Theta = \pi \left(\frac{\sigma_{\text{eff.}}}{2} \right)^2 \rho^{\text{ads}}, \quad (1)$$

where $\sigma_{\text{eff.}}$ is the effective diameter of the adsorbed ethanol molecule projected on the interface (0.465 nm) and ρ^{ads} is the 2D number density of the adsorbed ethanol molecules. It is clear that D_e^{2D} is proportional to an inversed power law of Θ , which indicates that the lateral self-diffusivity of adsorbed ethanol molecules is continuously reduced with increase in ethanol excess adsorption. The absolute values of D_e^{2D} becomes on average 2.1 times larger than those in the bulk solution (see also figure 1).

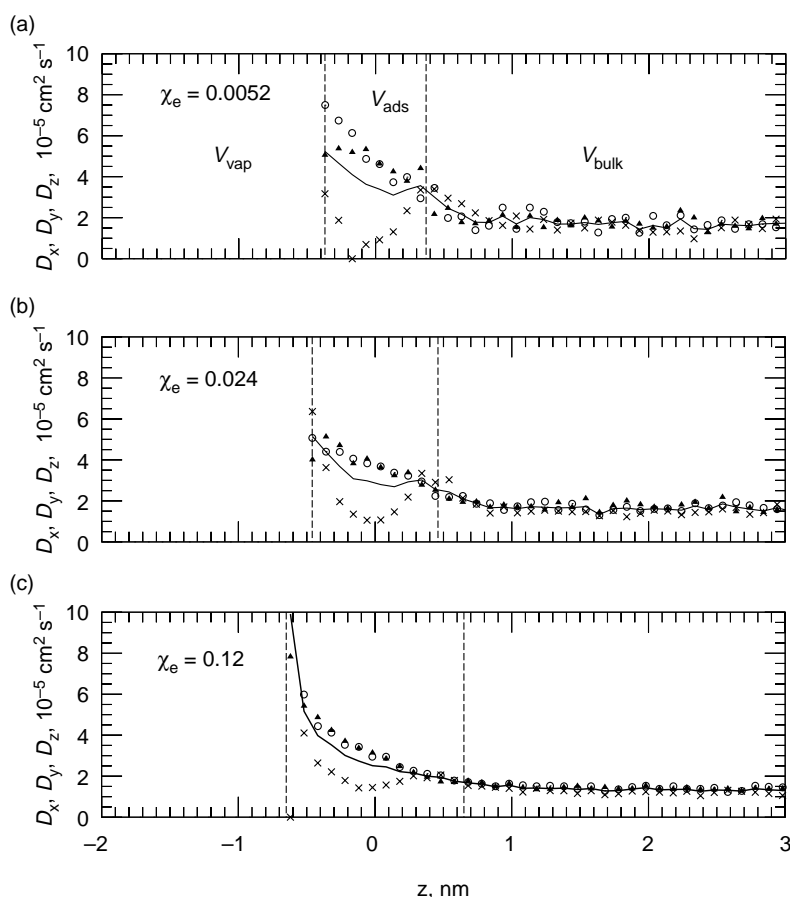


Figure 2. Profile of ethanol self-diffusion coefficient along each axial direction: the x (open circles), y (closed triangles) and z (cross marks) axis. The solid lines are $D_e(z)$. The dashed lines have the same meaning in figure 1.

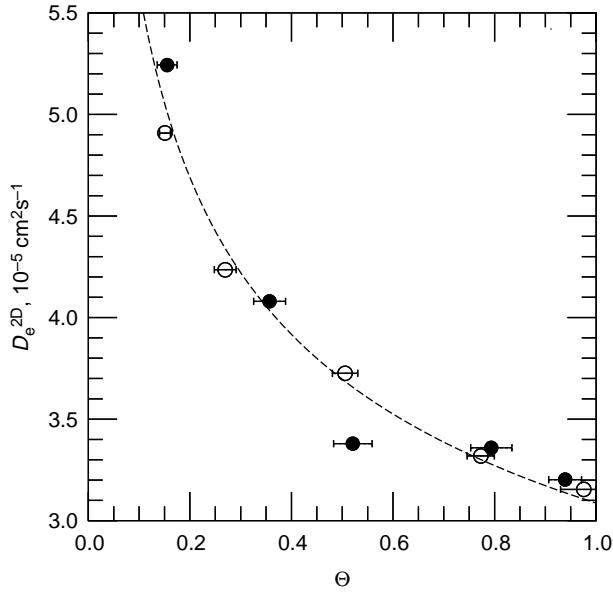


Figure 3. 2D self-diffusion coefficient of ethanol on the interface D_e^{2D} as a function of Θ . The simulation system has two vapor/liquid interfaces, corresponding to the open and closed circles. Dashed line is a fitting curve of $D_e^{2D} = a\Theta^{-\eta_e}$.

3.2. Desorption probability

The desorption probability of an adsorbed ethanol molecule from the interface to the bulk solution α_{des} is estimated by the autocorrelation function method [17,18]. By this method, a desorption mass flux \mathbf{J}_{des} and collision desorption mass flux $\mathbf{J}_{\text{des}}^{\text{col}}$ are estimated as the time derivatives of two types of autocorrelation functions $C_1(t_{\text{cor}})$, $C_2(t_{\text{cor}})$, and then α_{des} is given as \mathbf{J}_{des} divided by $\mathbf{J}_{\text{des}}^{\text{col}}$. In this case, $C_1(t_{\text{cor}})$ and $C_2(t_{\text{cor}})$ are defined as,

$$C_1(t_{\text{cor}}) \equiv \left\langle \sum_i \sigma_i(t_0) \sigma_i(t_0 + t_{\text{cor}}) \right\rangle_{t_0}, \quad (2)$$

$$C_2(t_{\text{cor}}) \equiv \left\langle \sum_i \sigma_i(t_0) \sigma_i(t_0 + \Delta t) \sigma_i(t_0 + 2\Delta t) \dots \sigma_i(t_0 + t_{\text{cor}}) \right\rangle_{t_0}, \quad (3)$$

where $\sigma_i(t)$ is a discrete function related to the position of ethanol mass center,

$$\sigma_i(t) = \begin{cases} 1 & \text{if } i \text{ th ethanol molecule is included in } V_{\text{ads}} \text{ at } t \\ 0 & \text{if } i \text{ th ethanol molecule is included in } V_{\text{bulk}} \text{ at } t \end{cases} \quad (4)$$

and $\langle \dots \rangle$ shows the ensemble average. The calculated $C_1(t_{\text{cor}})$ and $C_2(t_{\text{cor}})$ showed an exponential decay with the relaxation time of τ_1 and τ_2 , giving α_{des} as the fraction of τ_2 to τ_1 .

Figure 4 is a plot of α_{des} against Θ . It is apparent that α_{des} monotonically increases with Θ , becoming about 0.44 in a saturated monolayer ($\Theta = 1$). This result says that the

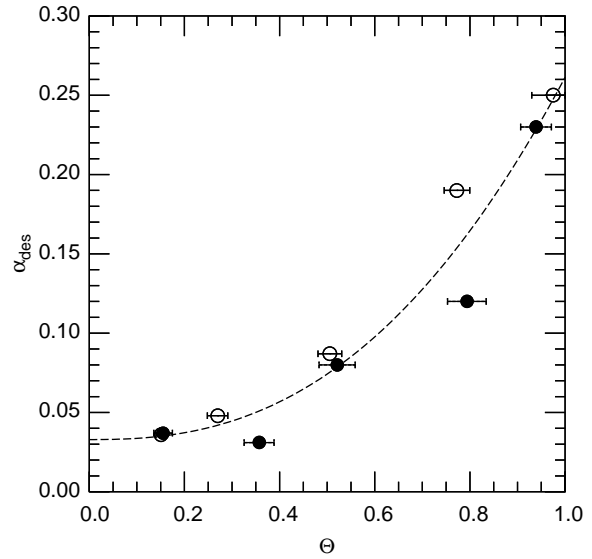


Figure 4. Desorption probability of adsorbed ethanol molecules into bulk solution α_{des} as a function of Θ . The difference in symbols reflects the difference in the interface observed. Dashed line is a fitting curve of $\alpha_{\text{des}} = b\Theta^{\nu_e} + \alpha_0$.

adsorbed ethanol molecules tend to desorb more easily when ethanol excess adsorption is increased. When considering that τ_1 decreases with Θ (not shown), it is also the case that the frequency of molecular desorption along the z -axis is promoted when excess adsorption is increased. Another feature of α_{des} 's variation is a non-zero convergence in $\Theta \rightarrow 0$ limit. This is in good agreement with previous MD results [11,12,8] in which the existence of an activation barrier for the desorption process of ethanol in a dilute limit ($\chi_e \rightarrow 0$) is reported. The least squares fitting of data points to $\alpha_{\text{des}}(\Theta) = b\Theta^{\nu_e} + \alpha_0$ gave $\nu_e = 2.47$ and $\alpha_0 = 0.0329$. The molecular origin of these features in α_{des} 's variation will be discussed in Section 3.4.2.

3.3. Profile of the Helmholtz free energy

To acquire a molecular understanding of the dynamical properties of the vapor/ethanol-aqueous-solution interface, it is essential to estimate the profile of the change of the Helmholtz free energy in the process of the unimolecular transfer of an ethanol molecule $\Delta A(z)$. By the thermodynamic integration (TI) method [19], $\Delta A(z)$ were estimated for all χ_e cases. Because ethanol is perfectly soluble in water, the mean force $\langle \mathbf{F}(z) \rangle$ is simply obtained as the particle and time average at the z -position. $\Delta A(z)$ was then given by numerically integrating $\langle \mathbf{F}(z) \rangle$ along the z -axis.

Figure 5 shows the results of $\Delta A(z)$ where the origin of $\Delta A(z)$ is taken at that of the bulk solution. It is clearly shown that $\Delta A(z)$ was minimized at the interface, as is expected by the fact that there is ethanol excess adsorption. When $\chi_e = 0.0052$, the well depth of $\Delta A(z)$ is 5.8 kJ/mol, which agrees well with that given in previous MD studies (5.9 kJ/mol [12]). The well depth of

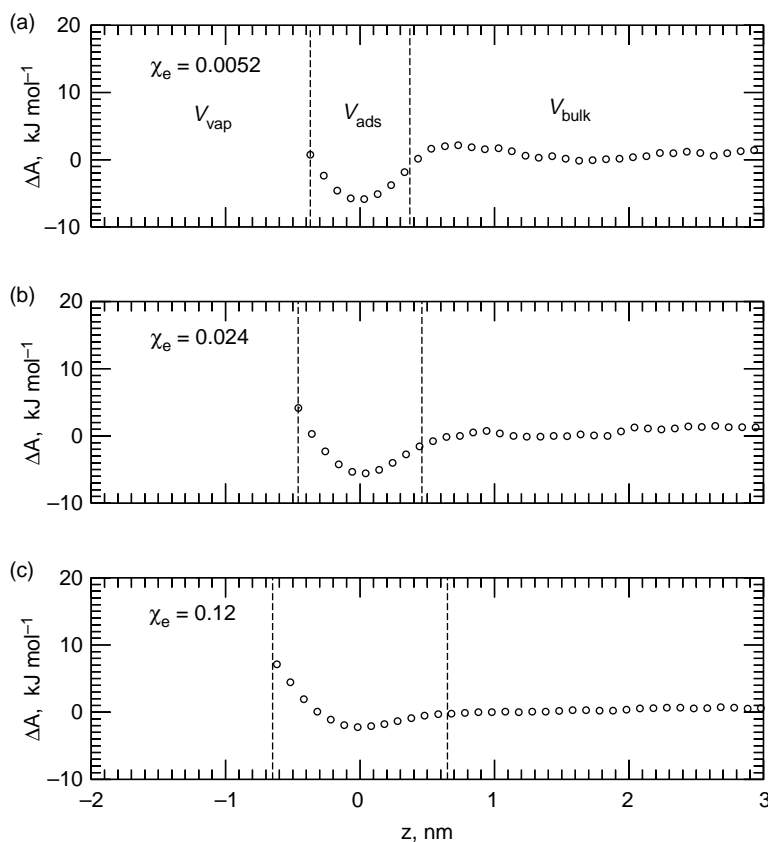


Figure 5. Profiles of the Helmholtz free energy change in the process of the unimolecular transfer of ethanol molecule. The bulk values of ethanol mole fraction χ_e are depicted in each figure. The dashed lines have the same meaning in figure 1.

$\Delta A(z)$ continuously decreases with increasing χ_e , resulting in the value of 2.2 kJ/mol when $\chi_e = 0.12$. Contrastively, in the cases of small χ_e , there exists a tiny barrier in the free energy of the process of adsorption from the bulk solution to the interface, and the barrier height immediately decreases with increase of χ_e . The fact that the fraction of the height of the free energy barrier in adsorption process to $k_B T$ is about 1.0 says that this activation free energy barrier can be easily overcome by the thermal translational motion of ethanol molecule itself, which corresponds to the conclusion produced by the MD results that the adsorption process of ethanol is not a kinetic-controlled but an diffusion-controlled process [11].

3.4. Explanation of molecular origin of dynamical properties of the vapor/ethanol-aqueous-solution interface

3.4.1. Self-diffusion coefficient. As is shown in Section 3.1, $D_e(z)$ and $D_w(z)$ became an increasing function of z toward the vapor region, while only $D_e(z)$ showed a local maximum at the boundary between the interface and bulk solution, which is mainly caused by the anisotropic behavior of $D_{e,z}(z)$. The maximum followed by the minimum in $D_e(z)$ at the interface gradually disappeared with increase of χ_e . Additionally, D_e^{2D} was about 2.1 times

larger than the value of the bulk solution, and monotonically decreased with Θ . The relative enlargement of the self-diffusion coefficient has already been discussed for the vapor/ethanol–liquid interface [20]. It is concluded that the faster lateral self-diffusion of ethanol at the interface results from the reduction of intermolecular interactions by decreasing the number density of neighboring molecules. We consider that the increase of $D_e(z)$ and $D_w(z)$ toward the vapor side is caused by the same mechanism.

A similar explanation can be made for the origin of the variation of D_e^{2D} with Θ . The ethanol molecules are adsorbed to the interface with their hydrophobic hydrocarbon tail projecting to the vapor side, and can therefore be regarded as a 2D fluid interacting via hydrophobic interaction [9]. At the interface with small Θ (i.e. small excess adsorption), the adsorbed ethanol molecules are permitted to move freely. The increase of Θ makes the collision between adsorbed ethanol molecules more frequent, resulting in the reduction of D_e^{2D} . The continuous reduction in the inverse power law of Θ implies that an occurrence of the percolation transition at $\Theta = 0.40$ [9] does not have a strong influence on the variation of D_e^{2D} .

On the other hand, the origin of the anisotropic behavior of $D_{e,z}(z)$ can be explained with the gradient of $\Delta A(z)$. We consider the case when an ethanol molecule is located at $z = 0$ where the free energy of the system is minimized (figure 5). Across this point the signs of $\nabla \Delta A(z)$ change,

forming field of the mean force where the ethanol molecule is constrained around $z = 0$. This is why $D_{e,z}$ shows relative decrease at $z = 0$. In contrast, we consider the case when an ethanol molecule is located at the boundary between V_{ads} and V_{bulk} . At this point an absolute value of $\nabla\Delta A(z)$ is maximized, forming field of the mean force where the ethanol molecule is forced to transfer toward V_{ads} . This is the reason that $D_{e,z}$ shows relative increase at the boundary. It should be noticed that the condition of an adsorption equilibrium (a steady amount of ethanol excess adsorption) causes the transfer of ethanol molecules from V_{ads} to V_{bulk} to the same extent as that by $\nabla\Delta A(z)$, which will also contribute to increase of $D_{e,z}$. With this scenario, the reduction of the well depth of $\Delta A(z)$ with increase of $\partial\epsilon\chi_e$ causes the disappearance of the local extrema in $D_{e,z}(z)$.

3.4.2. Desorption probability. As is shown in figure 5, there exists an activation free energy barrier ΔA_{des} in the process of desorption. If the desorption is assumed to be an unimolecular process, the probability that an ethanol molecule overcomes the activation barrier is given by $\exp(-\Delta A_{\text{des}}/k_B T)$ where k_B is the Boltzman constant. Figure 6 shows a plot of α_{des} against $\exp(-\Delta A_{\text{des}}/k_B T)$. It is apparent that α_{des} is positively correlated with $\exp(-\Delta A_{\text{des}}/k_B T)$, implying that the increase of χ_e originates from the decrease of an activation barrier in the desorption process. These quantities agree well when $\alpha_{\text{des}} \leq 0.10$, but deviations are observed in larger Θ regions. The origin of this deviation is hard to determine at this stage. It is suggested that the desorption mass flux may be slightly reduced under the existence of the adsorption mass flux with opposite direction.

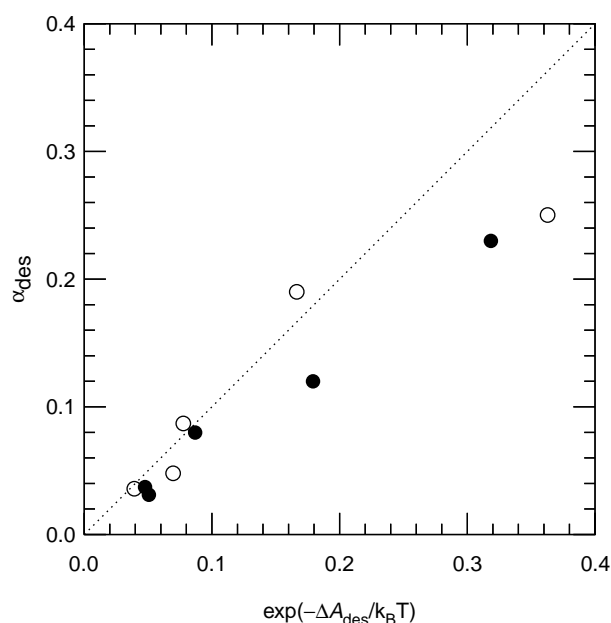


Figure 6. A plot of α_{des} against $\exp(-\Delta A_{\text{des}}/k_B T)$. The simulation system has two vapor/liquid interfaces, corresponding to the open and closed circles. The dotted line corresponds to $\alpha_{\text{des}} = \exp(-\Delta A_{\text{des}}/k_B T)$.

4. Conclusion

The variation of the dynamical properties of the vapor/ethanol-aqueous-solution interface with excess adsorption of ethanol is investigated by a MD simulation. Five independent NVT ($T = 298.15$ K) constant MD runs were performed, where a slab of the ethanol-aqueous-solution with ethanol mole fraction χ_e of 0.0052, 0.012, 0.024, 0.057 and 0.12, respectively, reached an equilibrium state of adsorption. The positional dependence of molecular self-diffusivity was evaluated by the profiles of the self-diffusion coefficient of ethanol and water along the axis normal to the interface. The profile of ethanol self-diffusion coefficient showed local extrema at the interface, the degree of which is weakened with increase of χ_e . The lateral self-diffusivity of an adsorbed ethanol molecule was also evaluated by the 2D self-diffusion coefficient at the interface, which is a monotonically decreasing function of ethanol excess adsorption. Moreover, a desorption probability of an adsorbed ethanol molecule was estimated, which monotonically increases with ethanol excess adsorption. The molecular origin of the variation of these interfacial properties with increase of χ_e was explained by correlating them with the profile of the free energy change.

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