Molecular dynamics study on the surface structure of alcohol-water mixture

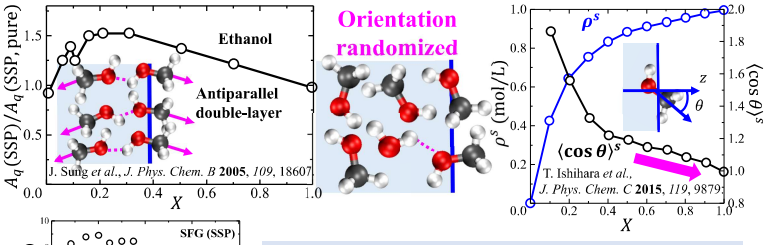
Mayu Hirose[1], Tatsuya Ishiyama[1]

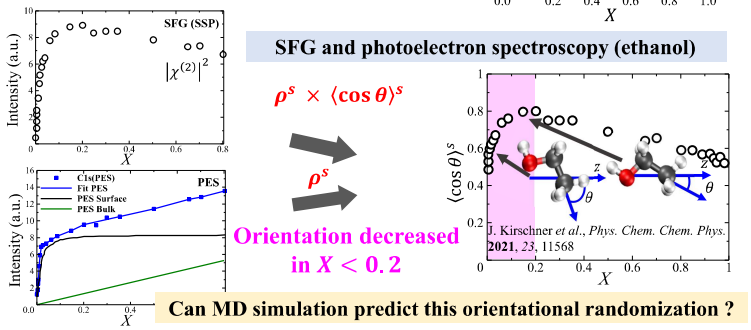
1 Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan

Introduction

Aqueous alcohol solutions are widely used in our daily lives, and considerable attention has been devoted to understanding the surface structure in detail.

Sum-frequency generation (SFG) vibrational spectroscopy (ethanol) | **Molecular dynamics (MD) simulation (methanol)**





SFG and photoelectron spectroscopy (ethanol)

Can MD simulation predict this orientational randomization ?

Objective

We reproduce the characteristics of orientation randomization in the low concentration region (X<0.2) of alcohols by MD and discuss its molecular mechanism.

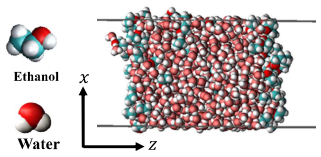
Methods

Force field
Ethanol: OPLS-AA[1]
Water: TIP4P2005[2]

Number of molecules
1000 molecules

Computational time
Equilibration 50ns
Production 50 ns

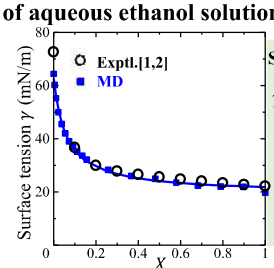
Box size
30 Å × 30 Å × 200 Å
NVT ensemble (T=298K)



[1] W. Jorgensen *et al., J. Am. Chem. Soc.,* **1996**, *118*, 11225
[2] J. L. F. Abascal, and C. Vega, *J. Chem. Phys.***2005**, *123*, 234505

Surface tension, activity, surface excess

We compared the calculated surface tension, activity, and surface excess of aqueous ethanol solution to the experimental ones.



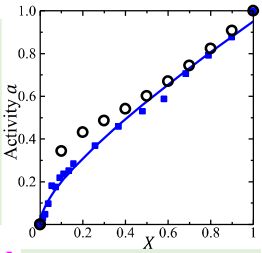
Surface tension[3]

$$\gamma = \frac{L_z}{2}\left\langle p_{zz} - \frac{1}{2}(p_{xx} + p_{yy})\right\rangle$$

p_{ii} : ii component of the pressure tensor

Fitting function

$$\gamma = A\exp\left(-\frac{x}{B}\right) + C$$



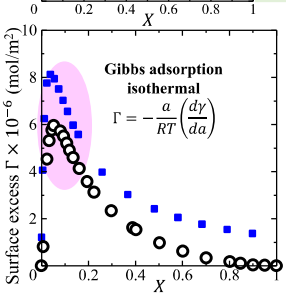
Activity [4]

$$a(X) = \rho(X)/\rho^*$$

$\rho(X)$:vapor phase density
ρ^*:vapor phase density of the pure ethanol

Fitting function

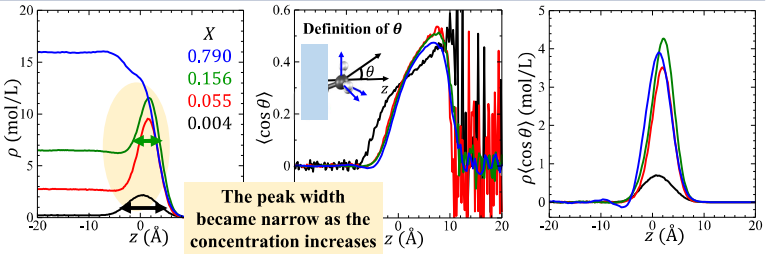
$$a(X) = A\tanh(BX) + CX$$



MD results could qualitatively or quantitatively reproduce the experimental results.

[1] R. Belda *et al., Physics and Chemistry of Liquids* **2005**, *43*, 1, 91
[2] A. Chodzinska *et al. J Solution Chem* **2012**, *41*, 2226
[3] D. Bhatt *et al., J. Phys. Chem. B* **2004**, *108*, 9077
[4] M. Bley, *et al., Molecular Physics* **2018**, *116*, 15-16, 2009

Number density and orientation of ethanol



The peak width became narrow as the concentration increases

Gaussian distribution function

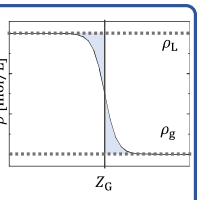
$$n_e(z) = n_e^0 \exp\left[\frac{-4\ln(z - z_e^0)^2}{\sigma_e^2}\right]$$

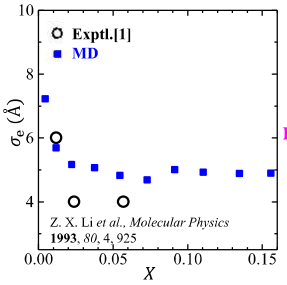
n_e^0: distribution height
σ_e: distribution width at a half-height
z_e^0: the position of a distribution peak

Gibbs deviding surface z_G

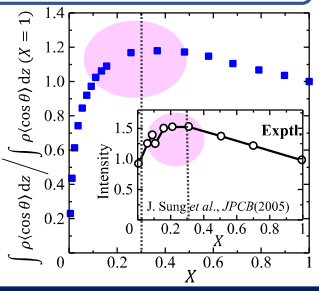
$$\Gamma = \int_{-\infty}^{Z_G} [\rho_\ell - \rho(Z)]\,dZ + \int_{Z_G}^{\infty} [\rho_g - \rho(Z)]\,dZ = 0$$

Γ: surface excess
ρ:density of water
ρ_l:concentration of liquid phase
ρ_g: concentration of gas phase



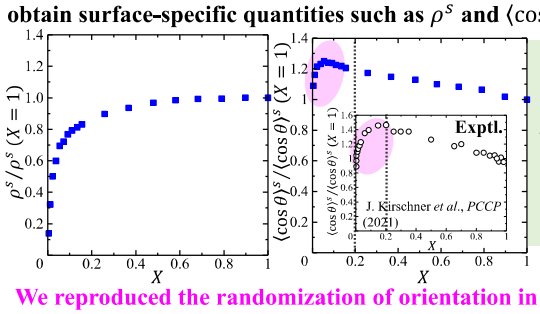


The present MD could reproduce the experimental observation.



The orientation of ethanol on the surface

The concentration and orientation of ethanol on the surface were analyzed for each concentration. $\rho\langle\cos\theta\rangle$ was used as the weight function $w(z)$ to obtain surface-specific quantities such as ρ^s and $\langle\cos\theta\rangle^s$.



$$\rho^s = \frac{\int w(z)\rho\,dz}{\int w(z)\,dz}$$

$$\langle\cos\theta\rangle^s = \frac{\int w(z)\langle\cos\theta\rangle\,dz}{\int w(z)\,dz}$$

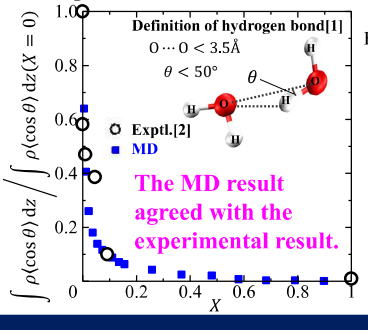
$$w(z) = \rho\langle\cos\theta\rangle$$

T. Ishihara *et al.*, *J. Phys. Chem. C* **2015**, *119*, 9879.

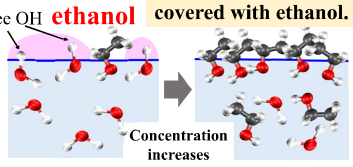
We reproduced the randomization of orientation in the low concentration.

H-bond structure of water on the surface

The hydrogen bonding structure of water on the surface of the aqueous solution is believed to be significantly disrupted by the presence of ethanol. Thus we calculated $\rho\langle\cos\theta\rangle$ of free OH of water on the surface with respect to the concentration.



Isolated ethanol | **The surface was covered with ethanol.**



Packing structure made $\langle\cos\theta\rangle^s$ increase.

[1] Fujie. T. *et al., J. Chem. Theory Comput.* **2018**, *14*, 357
[2] Xiaoqing. Y. *et al., J. Phys. Chem. B* **2021**, *125*, 37, 10639

Conclusion

- **We reproduced experimental results of surface tension, surface excess, distribution width, and SFG by MD simulation qualitatively or quantitatively.**
- **We reproduced the characteristic orientation of the ethanol, which decreases in low concentrations by MD simulation.**
- **In the low concentration region ($X < 0.2$), there was isolated ethanol on the surface and the surface was covered with ethanol with increasing concentration.**

⇒This indicated that the packing structure made the orientation increase in the low concentration region.