

SUMMARY OF Ph.D. DISSERTATION

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<p>Title</p> <p>Two-dimensional supercritical behavior of an ethanol monolayer at the vapor/ethanol-aqueous solution interface and molecular explanation of dynamical properties of the interface: A molecular dynamics study</p>		
<p>Abstract</p> <p>Alcohol aqueous solutions are widely used in technological fields. For more efficient applications, it is required to develop a molecular understanding about interfacial properties of solutions rather than bulk properties. Old experimental studies have provided molecular insights to structural properties of the vapor/alcohol-aqueous-solution interface. However, many issues still remain to be clarified.</p> <p>In this thesis, the author carried out a series of molecular dynamics (MD) simulations of vapor/ethanol-aqueous-solution interfaces, providing new insights to the following issues:</p> <ol style="list-style-type: none">(1) Two dimensional (2D) phase behavior of an ethanol monolayer at the interface(2) Clustering of ethanol molecules at the interface(3) Molecular interpretation of dynamical properties of the interface <p>The periodic unit cell dealt with in the present simulations contains a 10 nm thick ethanol solution layer with ethanol mole fraction of 0.010, 0.022, 0.045, 0.10 or 0.20. Five independent <i>NVT</i> ($T = 298.15$ K) constant MD calculations were carried out, until an equilibrium state of adsorption is established.</p> <p>In (1), it was revealed that an ethanol monolayer at the vapor/ethanol-aqueous-solution interface behaves as a 2D supercritical fluid under the temperature condition of 298.15 K. Cluster analyses on adsorbed ethanol molecules were carried out on the basis of the percolation theory. It was revealed that the ethanol monolayer exhibits a percolation transition, instead of a nucleation, with an increase in the surface excess of ethanol, which is particular to a supercritical fluid.</p> <p>In (2), it was revealed that clustering of ethanol molecules is enhanced at the interface. There exist plenty of ethanol oligomers in an ethanol monolayer, while most ethanol molecules exist as monomers in the bulk solution. The mean size, number density and size distribution of ethanol one-component clusters located at the interface or in the bulk solution were thoroughly investigated. The same analyses were made on ethanol/water binary clusters.</p> <p>In (3), the molecular origin of an anisotropy of an ethanol self-diffusion coefficient along the perpendicular to the interface was explained on the basis of special free energy profiles. The molecular origins of the monotonic decrease of a 2D self-diffusion coefficient of ethanol and monotonic increase of a desorption probability of adsorbed ethanol molecules with an increase of the surface excess of ethanol were also explained.</p>		