Division of Environmental Chemistry
- Solution and Interface Chemistry -

http://www.scl.kyoto-u.ac.jp/~yoeki/

Assoc Prof
MATUBAYASI, Nobuyuki
(Ph D)

Assist Prof
WAKAI, Chihiro
(D Sc)

Program-Specific Res
KARINO, Yasuhito
(D Sc)

PD
PURQON, Acep
(D Sc)

Researchers

KUBOTA, Yoshiyuki
FURUKAWA, Hirotoshi

Students

YASAKA, Yoshiro (D3)
KIMURA, Hiroshi (D1)
SHINTANI, Megumi (D1)
IYOKU, Hiroomi (M2)
MIYA, Shingo (M2)
ZENIYA, Yuki (M1)
SAKAI, Yoshiyuki (M1)

Visitors

Dr CHAU, Pak-Lee	Pasteur Institute, France, 8–13 April 2009
Prof ROSSKY, Peter J	University of Texas at Austin, 25–30 June 2009
Prof JUNGWIRTH, Pavel	Czech Academy of Science, Czech Republic, 8–14 July 2009
Dr FEDOROV, Maxim	Max Planck Institute, Germany, 11 November 2009

Scope of Research

The structure, dynamics, and reaction of solutions with nano-scale inhomogeneity and/or with fine tunability are investigated by computer simulation, and statistical-mechanical theory of solutions, NMR spectroscopy, and vibrational spectroscopy. Solvation is systematically elucidated for ionic liquids and supercritical fluids from both the static and dynamic viewpoints, and noncatalytic reactions of environmental importance are developed. The structural organization and fluctuation and the molecular binding are investigated for soft, self-organizing systems such as micelle, protein, and lipid membrane.

Research Activities (Year 2009)

Publications

Yasaka Y, Wakai C, Matubayasi N, Nakahara M: Water as an In-situ NMR Indicator for Impurity Acids in Ionic Liquids, *Anal. Chem*. **81**, 400-407 (2009).

Yoshida K, Matubayasi N, Nakahara M: Self-diffusion Coefficients for Water and Organic Solvents in Extremely Low-density Supercritical States, *J. Mol. Liq.* **147**, 96-101 (2009).

Presentations

Free-Energy of Solvation in the Energetic Perspective, Matubayasi N, International Symposium on Multi-Scale Dynamics of Protein Complex Formation and Function, Tokyo, Japan, 14–16 July 2009.

Solvation Free Energy of Globular Proteins: A Molecular Dynamics Study, Saito H, Mizukami T, Matubayasi N, Nishikawa K, Nagao K, International Conference on Computational Science 2009, Bali, Indonesia, 27–28 October 2009.

Grants

Matubayasi N, Free-Energy Analysis of Nanoscale, Molecular Aggregates with the Method of Energy Representation, Next-Generation Integrated Nanoscience Simulation Software Project, 1 April 2008–31 March 2013.

Matubayasi N, Informational Coarse-Graining Models of Biomolecules and their Interactions, Japan Science and Technology Agency, 1 October 2007–31 March 2012.

Matubayasi N, Free-Energy Analysis of ATP Hydrolysis, Grant-in-Aid for Scientific Research on Innovative Areas, 1 December 2008–31 March 2012.

Matubayasi N, MD and NMR Study of Molecular Binding into Lipid Membrane, Grant-in-Aid for Scientific Research (B), 1 April 2009–31 March 2013.

Free-Energy Analysis of the Configuration of Transmembrane Protein in Model Membrane

The configuration of a protein molecule in lipid-membrane environment plays important roles in the functions of bio-related membranes and the elaboration of drug-delivery systems. In the present work, we examine two contrast configurations of a transmembrane protein in a model membrane system. The purpose is to elucidate the factor to control the preferred configuration at atomic resolution. In the first configuration called the vertical configuration, the protein stays in the direction normal to the membrane surface, and in the second one called the horizontal configuration, it is buried in the membrane core, as shown in Figure 1. We investigate the effects of the different configurations in membrane by performing structural and free-energy analysis to reveal the roles of lipid and water.

The transmembrane protein employed in the present work is the transmembrane domain of glycophorin-A. It consists of the residues 73-95 of glycophorin-A, and holds the α-helical structure. The lipid molecule used is DMPC. The free-energy analysis was carried out using the method of energy representation.

The free-energy change of the protein binding into the membrane from vacuum is -133 kcal/mol for the vertical configuration and is -113 kcal/mol for the horizontal. The binding free energy is more favorable for the vertical configuration. The free-energy decomposition into the contributions from lipid and water shows that the lipid contribution is more favorable for the horizontal configuration. This is in agreement with the common notion of hydrophobicity. The water effect overturns the lipid one to stabilize the vertical configuration. Actually, the difference in the attractive interactions between the two configurations is by far larger for the protein-water interaction than for the protein-DMPC, and leads to the preference of the vertical configuration.

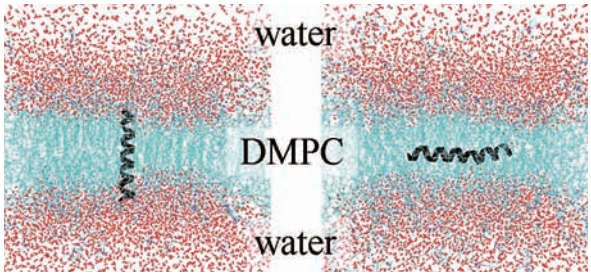

Figure 1. The vertical (left) and horizontal (right) configurations of the 23-residue protein in DMPC membrane system.

Slow Rotational Dynamics in Ionic Liquids

Ionic liquids are organic molten salts which are in the liquid state at ambient temperature. Ionic liquids are often in the deeply super-cooled liquid state at room temperature and show a glass transition at lower temperatures. They have very high viscosity compared with common organic solvents (~100-fold even above the melting point) as a reflection of the strong Coulombic interactions between the positive and negative charges. The dynamics in ionic liquids is bimodal in the sense that the short-time local dynamics and the long-range slow dynamics are both significant.

The MD simulation was performed on the 248 ion pairs of [bmim$^+$][Cl$^-$] (the ionic liquid, 1-butyl-3-methylimidazolium chloride) with 8 water or benzene molecules. The initial configuration (NaCl-type lattice) was equilibrated in the *NPT* ensemble and then the trajectory was generated in the *NVT* ensemble. Several system temperatures were investigated in the range of 323-1250 K to analyze the temperature effect on the slow component of the rotational dynamics of the solutes.

The second-order rotational correlation function $C_2(t)$ of the C-H bond of benzene in [bmim$^+$][Cl$^-$] is shown in Figure 2 at several temperatures. The functional form of $C_2(t)$ at 323 K is far from exponential and is well fitted by the stretched exponential (linear function in the log t vs log(-log $C_2(t)$) plot) in the sub-ns time region. This is a glassy characteristic. The stretched exponential behavior is persistent above ~500 K (the decomposition temperature of ionic liquids in the real system). The crossover from the Gaussian-type relaxation in the short time region to the stretched-exponential type in the long time region is observed at ~1 ps.

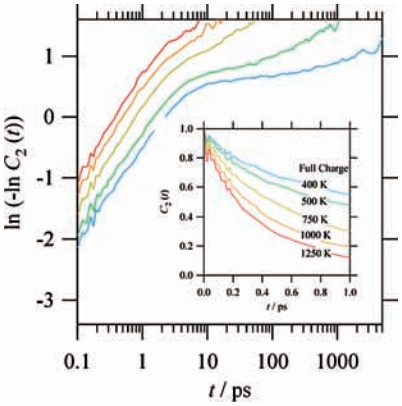

Figure 2. The second-order rotational correlation function of benzene in [bmim$^+$][Cl$^-$] on the logarithmic time scale. The temperatures are 1250, 1000, 750, 500, 400, and 323 K from top to bottom. The linear scale plot is shown in the inset.

Wakai C, NMR Study on Dynamics of Water Molecule, Organic Molecules, and Ions in Ionic Liquids, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2010.