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- Solution and Interface Chemistry -

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Visitor

VACHA, Robert Czech Academy of Science, Czech Republic, 9 November–20 December 2008

Scope of Research

The structure, dynamics, and reaction of solutions with fine tunability and/or with nano-scale inhomogeneity are investigated by NMR spectroscopy, computer simulation, and statistical-mechanical theory of solutions. Solvation is systematically elucidated for ionic liquids and supercritical fluids from both the static and dynamic viewpoints, and non-catalytic 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 2008)

Publications

Giordani C, Wakai C, Yoshida K, Okamura E, Matubayasi N, Nakahara M: Cholesterol Location and Orientation in Aqueous Suspension of Large Unilamellar Vesicles of Phospholipid Revealed by Intermolecular Nuclear Overhauser Effect, *J. Phys. Chem. B*, **112**, 2622-2628 (2008).

Matubayasi N, Shinoda W, Nakahara M: Free-energy Analysis of the Molecular Binding into Lipid Membrane with the Method of Energy Representation, *J. Chem. Phys.*, **128**, 195107 (13 pages) (2008).

Presentations

Free-Energy Analysis of Nano-Organized Systems in Solution, Matubayasi N, The 2nd International Symposium on “Molecular Theory for Real Systems”, Okazaki, Japan, 4–6 August 2008.

High-Temperature Multinuclear-Magnetic-Resonance Probe for the Analysis of Structure, Dynamics, and Chemical Reactions in Supercritical Water, Nakahara M, The 15th International Conference on the Properties of Water and Steam, Berlin, Germany, 7–11 September 2008.

Grants

Nakahara M, 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 Molecular Binding into Membrane in the Method of Energy Representation, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2008–31 March 2010.

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.

Award

Matubayasi N, Award for Distinguished Achievement and Nose Memorial Award, The Japan Society of Molecular Simulation, 18 November 2008.

Free-Energy Analysis of Molecular Binding into Lipid Membrane

The lipid membrane distinguishes one side of the solution from the other, and plays important roles in distribution and transport of a molecule. A key quantity to govern the membrane function is the free energy of molecular binding. We have established a new and fast scheme of free-energy calculation for the molecular binding in membrane by combining a new theory of solutions with molecular simulation. The new theory is called the method of energy representation, and expresses the free energy in solution in terms of the information of the intermolecular interaction energy. It accelerates the free-energy calculation by several tens time faster than the conventional methods, and nano-inhomogeneous solutions such as micelle and membrane is now well within the scope of all-atom calculation.

Figure 1 shows the free energy $\Delta\mu$ of binding of hydrophobic solute into DMPC (1,2-dimyristoyl-*sn*-glycero-3-phosphatidylcholine) bilayer. A hydrophobic solute is free-energetically stabilized within the membrane inside compared to bulk water. The stability is quite high even in the polar and hydrophilic headgroup region. This is due to the interaction with water present outside the membrane; the effect of excluded volume, which is the source of hydrophobicity, reduces drastically in the interfacial region, while the medium-range attraction by dispersion interaction persists. Corresponding experimental information, especially in the headgroup region, is now being obtained. It is also possible to calculate the membrane-water partition coefficient from Figure 1. This is a good step toward material design using soft, lipid membranes.

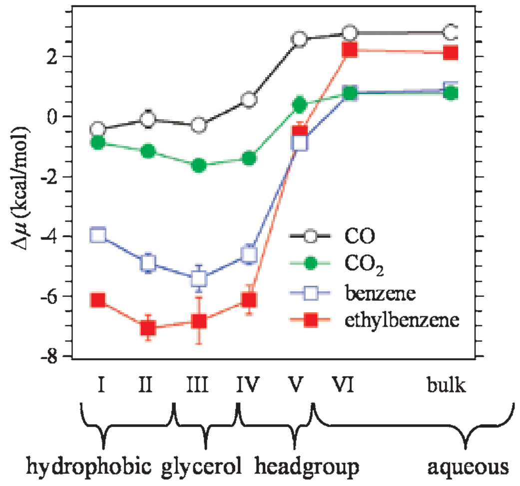

Figure 1. The free-energy change $\Delta\mu$ of inserting a hydrophobic solute into DMPC membrane. Six regions are introduced with an interval of 5 Å and are numbered I....VI from the membrane inside to outside.

Water as an In-Situ NMR Indicator for Impurity Acids in Ionic Liquids

Molten salts which have relatively low melting points are called ionic liquids (ILs). ILs are attracting much interest as environmentally-friendly, new and unique reaction medium. In investigating the solvent effect of ILs, it is important to establish an analytical method to certify the purity of ILs studied. Acids can be the most detrimental impurity to the reaction study due to its catalytic activity. Although titration and electrochemical methods are popular in aqueous systems, they are not sufficiently sensitive when applied to ILs.

In the present work, we have developed a sensitive in-situ NMR spectroscopic analysis method for the detection of impurity acids contained in ionic liquids (ILs). The chemical shift of water dissolved into the tested IL was used to measure the impurity level. Water was adopted as the impurity indicator, and its chemical shift changes with the concentration of the coexisting acid through proton exchange. Owing to the high resolution power of NMR, the detection limit is below the level of 10^{-3} mol kg^{-1}. A new method is applicable to a number of commonly used ILs such as the imidazolium- and ammonium-based ILs except for those composed of acidic cations or anions.

The method was utilized to monitor the purification efficiency in the recrystallization of a typical hydrophilic IL, 1-butyl-3-methylimidazolium methanesulfonate from acetone. As seen in Figure 2, the chemical shift of water was drastically changed before and after the recrystallization. It was demonstrated that impurity acids can be almost perfectly removed by single or double recrystallization.

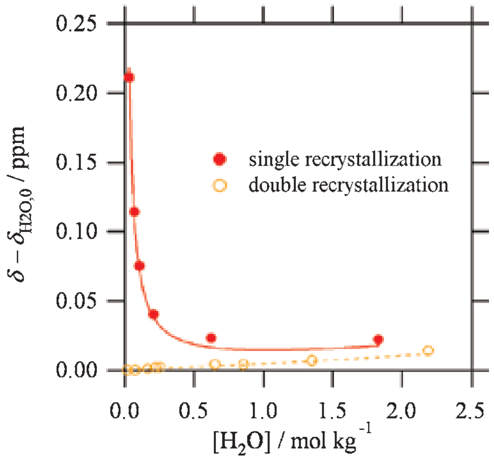

Figure 2. Plots of the chemical shift (δ-$\delta_{H2O,0}$) against [H_2O] for [bmim]$^+$[CH_3SO_3]$^-$ after single (filled circles) and double (open circles) recrystallization. The $\delta_{H2O,0}$ is the chemical shift of water in the acid-free ionic liquid in the limit of [H_2O] = 0. The ionic liquid after only single recrystalization contains the impurity acid at 1.8 mmol kg^{-1}, whereas that after double recrystallization can be regarded as perfectly pure.