Division of Environmental Chemistry
- Solution and Interface Chemistry -

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Visitors

Assoc Prof MORITA, Akihiro	Institute for Molecular Science, Japan, 25–26 January 2006
Prof KLEIN, Michael L	University of Pennsylvania, USA, 16 June 2006
Prof GANGULY, Tapan	Indian Association for the Cultivation of Science, India, 23 August 2006

Scope of Research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR and computer simulations from ambient to extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Static and dynamic NMR of endocrine disruptors, anesthetics, peptides, and proteins in model and cell membranes are also investigated.

Research Activities (Year 2006)

Presentations

In-situ NMR Spectroscopic Studies on Human Jurkat Cells, Nakahara M, Okamura E, Ninomiya K, Futaki S, Wakai C, Matubayasi N, Sugiura Y, 9th Eurasia Conference on Chemical Science, Antalya, Turk, 9–13 September.

Self-Diffusion of Supercritical Water in Extremely Low-Density Region, Nakahara M, the International Association for the Properties of Water and Steam, Witney, England, 3–8 September.

Free Energy of Solvation in the Method of Energy Representation, Matubayasi N, 16th Symposium on Thermophysical Properties, Boulder, USA, 30 July– 4 August.

Solvation Free Energy in Supercritical Water and Its Role toward Noncatalytic Reaction Control, Matubayasi N, 4th International Symposium of Molecular Thermodynamics and Molecular Simulation, Makuhari, Japan, 22–25 May.

Grants

Nakahara M, Development of Multinuclear, High-Temperature, and Diffusion Measurable NMR Probe and Molecular Analysis of Dynamics of Supercritical Aqueous Solutions, Grant-in-Aid for Scientific Research (A), 1 April 2003–31 March 2006.

Nakahara M, Free-Energy Analysis of Nanoscale Aggregates of Molecules in the Method of Energy Representation, National Research Grid Initiative Project, 1 April 2003–31 March 2008.

Nakahara M, Development of Technology for Hydrogen Production, Storage, and Transportation of Hydrogen Using Hydrothermal Reactions of Formic Acid, ENEOS Hydrogen Trust Fund, 1 October 2006–30 September 2007.

Matubayasi N, Molecular Theory of the Solvation Effect on the Structural Formation and Fluctuation of Biomolecules and their Aggregates, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2003–31 March 2008.

Matubayasi N, Toward a New Research Network

Kinetic and Equilibrium Study on the Formic Acid Decomposition in Relation to the Water-Gas-Shift Reaction

Kinetics and equilibrium are studied on the hydrothermal decarbonylation and decarboxylation of formic acid, the intermediate of the water-gas-shift (WGS) reaction, in hot water at temperatures of 170-330 °C, in order to understand and control the hydrothermal WGS reaction (Figure 1). ^{1}H and ^{13}C NMR spectroscopy is applied to analyze as a function of time the quenched reaction mixtures both in the liquid and gas phases. Only the decarbonylation is catalyzed by HCl, and the reaction is first order with respect to both $[H^+]$ and [HCOOH]. Consequently, the reaction without HCl is first and a half (1.5th) order due to the unsuppressed ionization of formic acid. The HCl-accelerated decarbonylation path can thus be separated in time from the decarboxylation. The rate and equilibrium constants for the decarbonylation are determined separately by using the Henry constant (gas solubility data) for carbon monoxide in hot water. The rate constant for the decarbonylation is 1.5×10^{-5}, 2.0×10^{-4}, 3.7×10^{-3}, and 6.3×10^{-2} mol^{-1} kg s^{-1}, respectively, at 170, 200, 240, and 280 °C on the liquid branch of the saturation curve. The Arrhenius plot of the decarbonylation is linear and gives the activation energy as 146 ± 3 kJ mol^{-1}. The equilibrium constant K_{CO} = [CO] / [HCOOH] is 0.15, 0.33, 0.80, and 4.2, respectively, at 170, 200, 240, and 280 °C. The van't Hoff plot results in the enthalpy change of $\Delta H = 58 \pm 6$ kJ mol^{-1}. The decarboxylation rate is also measured at 200-330 °C both in acidic and basic conditions. The rate is weakly dependent on the solution pH and is of the order of 10^{-4} mol kg^{-1} s^{-1} at 330 °C. Furthermore, the equilibrium constant K_{CO_2} = $[CO_2][H_2]$ / [HCOOH] is estimated to be 1.0×10^{2} mol kg^{-1} at 330 °C.

Figure 1. Reaction scheme of water-gas-shift reaction.

Slowdown of H/D Exchange Reaction Rate and Water Dynamics in Ionic Liquid: Deactivation of Solitary Water Solvated by Small Anions in 1-Butyl-3-Methyl-Imidazolium Chloride

The H/D exchange reaction (Figure 2) and the rotational dynamics of heavy water (D_2O) are studied at 50 °C in the room-temperature ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim][Cl]), in the D_2O range of 3–55 M. The initial H/D exchange rates are observed as 1×10^{-7}, 4.5×10^{-6}, 1.0×10^{-5}, 4.1×10^{-5}, 1.1×10^{-4} and 3.7×10^{-4} s^{-1}, respectively, at $[D_2O]$ of 2.8, 7.1, 8.1, 10.8, 15, and 25 M. The rate is very slow and less than 10^{-5} s^{-1} at $[D_2O]$ below ~7 M. It steeply increases to the order of 10^{-4} s^{-1} for 7 M $< [D_2O] <$ 10 M, and linearly increases with $[D_2O]$ in the more water-rich region. The intercept of the linear region at $[D_2O]$ = ~9 M is interpreted by considering that each chloride anion deactivates 1.6 equivalent water molecules due to the strong solvation (Figure 3). Correspondingly, the rotational correlation time of D_2O at $[D_2O]$ < 7 M is one order of magnitude larger than that in water-rich conditions.

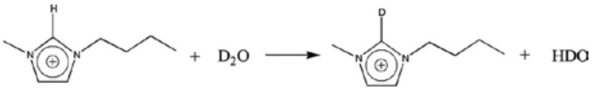

Figure 2. H/D exchange reaction scheme of [bmim] cation.

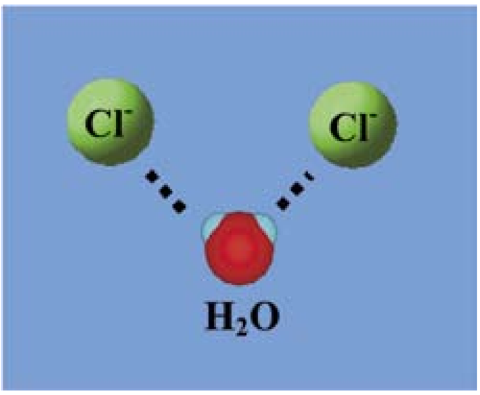

Figure 3. Schematic draw of the solvation of water by chloride anions.

between Physics and Chemistry, Grant-in-Aid for Creative Scientific Research, 1 April 2004–31 March 2006.

Okamura E, Molecular Dynamics in Lipid Rafts by High-Sensitivity, High-Resolution NMR, Grant-in-Aid for Scientific Research (C), 1 April 2005–31 March 2007.

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 2008.

Award

Matubayasi N, Young Scientist Award, The Minister of Education, Culture, Sports, Science and Technology of Japan, 11 April.