Division of Environmental Chemistry
– Solution and Interface Chemistry –

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Scope of Research

We investigate chemical phenomena in condensed phases. (1) To understand the chemical structure, property and reactions in a two-dimensional molecular aggregate, the keywords of molecular interactions and orientation are focused on, and the fluctuated molecular aggregates are investigated by using originally developed spectroscopic and theoretical techniques. (2) 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, and NMR spectroscopy.

KEYWORDS

Infrared and Raman Spectroscopy	Free Energy
Surface and Interface Chemistry	Solvation
Nano Particle and Fibril Analysis	Solution Theory

Selected Publications

Shimoaka, T.; Rikiyama, K.; Katsumoto, Y.; Hasegawa, T., Infrared Spectroscopic Study of Stereo-controlled Poly(*N*-isopropylacrylamide) with an Extended Chain Conformation Induced by Adsorption on a Gold Surface, *Anal. Bioanal. Chem*., **405,** 9411-9418 (2013).

Norimoto, S.; Morimine, S.; Shimoaka, T.; Hasegawa, T., Analysis of Surface Coverage of a Self-Assembled Monolayer of Octadecyl Silane on a Si(100) Surface by Infrared External-Reflection Spectroscopy, *Anal. Sci*., **29,** 979-984 (2013).

Wakai, C.; Shimoaka, T.; Hasegawa, T., Analysis of Hydration Process and Rotational Dynamics of Water in a Nafion Membrane Studied by ^{1}H NMR Spectroscopy, *Anal. Chem*., **85,** 7581-7587 (2013).

Takemura, K.; Burri, R. R.; Ishikawa, T.; Ishikura, T.; Sakuraba, S.; Matubayasi, N.; Kuwata, K.; Kitao, A., Free-energy Analysis of Lysozyme–triNAG Binding Modes with All-atom Molecular Dynamics Simulation Combined with the Solution Theory in the Energy Representation, *Chem. Phys. Lett*., **559,** 94-98 (2013).

Karino, Y.; Matubayasi, N., Interaction-component Analysis of the Urea Effect on Amino Acid Analogs, *Phys. Chem. Chem. Phys*., **15,** 4377-4391 (2013).

Mogami, G.; Miyazaki, T.; Wazawa, T.; Matubayasi, N.; Suzuki, M., Anion-Dependence of Fast Relaxation Component in Na−, K−Halide Solutions at Low Concentrations Measured by High-Resolution Microwave Dielectric Spectroscopy, *J. Phys. Chem. A*, **117,** 4851-4862 (2013).

Topics

Analysis of Hydration Process and Rotational Dynamics of Water in a Nafion Membrane Studied by ^{1}H NMR Spectroscopy

^{1}H NMR spectroscopy is employed to reveal the hydration process of a Nafion membrane by measuring both the chemical shift and the spin-lattice relaxation time. In a former study, the hydration process was suggested to comprise two steps: the molecular adsorption of water on the sulfonic acid groups, and wetting with liquid water. The present study has revealed the first step can further be divided into two steps. By introducing a new experimental technique, the quantitatively reliable NMR measurements of protons (^{1}H) of water involved in the polymer membrane are realized. In addition, a new analytical procedure is developed using a reciprocal concentration on a saturation-adsorption model, and the hydration is clearly revealed to have three individual steps. Both the chemical shift and the relaxation time plots against the reciprocal concentration exhibit three linear parts with apparently different slopes. Of great interest is that the initial hydration is divided into two stages: the first hydration is a very strong adsorption of water probably on the hydroxyl group of the sulfonic acid group, and the second one is a relatively weak adsorption on another site of the sulfonic acid group. The third hydration is readily assigned to excess bulk (liquid-like) water as expected. These adsorption processes are readily correlated with the rotational motion of water by converting the spin-lattice relaxation time to the rotational correlation time.
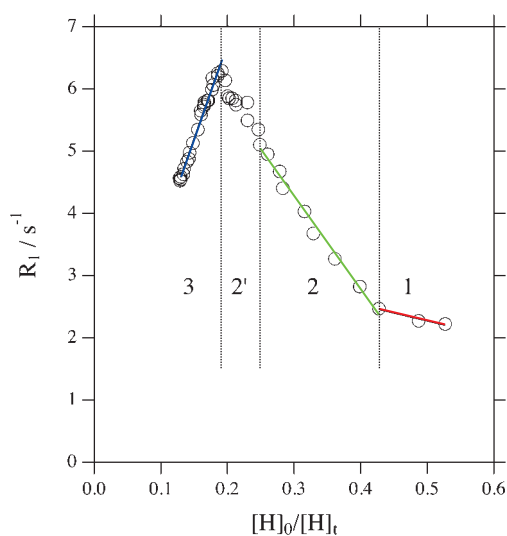
Free-Energy Analysis of Water Affinity in Polymer

Affinity of small molecule to polymer is an essential property for designing polymer materials with tuned permeability. In the present work, we develop a computational approach to the free energy ΔG of binding a small solute molecule into polymer using the atomistic molecular dynamics (MD) simulation combined with the method of energy representation. The binding free energy ΔG is obtained by viewing a single polymer as a collection of segments and employing an approximate functional constructed from distribution functions of the interaction energy between solute and the segment obtained from MD simulation. The binding of water is then examined against 9 typical polymers. The relationship is addressed between the segment size and the calculated ΔG, and a useful segment size is identified to compromise the performance of the free-energy functional and the sampling efficiency. It is found with the appropriate segment size that the ΔG convergence at a statistical error of ~ 0.2 kcal/mol is reached at ~ 4 ns of replica-exchange MD of the water-polymer system and that the mean absolute deviation of the computational ΔG from the experimental is 0.5 kcal/mol. The connection is further discussed between the polymer structure and the thermodynamic ΔG.
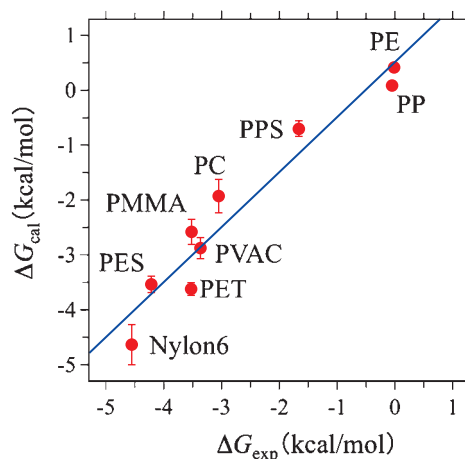

Figure 1. The spin-lattice relaxation rate (R_1) plotted against the reciprocal concentration of proton.

Figure 2. Comparison between the calculated free energies ΔG_{cal} and the experimental ones ΔG_{exp}. The solid line represents the least-square fit expressed as $\Delta G_{cal} = 1.0 \ \Delta G_{exp} + 0.5$. The error bar is expressed at 95% confidence limit (twice the standard error), and is smaller than the size of data symbol when it is not seen.