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– Solution and Interface Chemistry –

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Mr MARSALEK, Ondrej — Czech Academy of Science, Czech Republic, 25 January–31 March
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Scope of Research

The structure, dynamics, and reaction of solutions with nano-scale inhomogeneity and/or with fine tunability are investigated by NMR spectroscopy, computer simulation, and statistical-mechanical theory of solutions, 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.

KEYWORDS

Lipid Membrane
Supercritical Fluid
Ionic Liquid
Free Energy
Dynamic Inhomogeneity

Selected Publications

Yasaka Y, Wakai C, Matubayasi N, Nakahara M: Rotational Dynamics of Water and Benzene Controlled by Anion Field in Ionic Liquids: 1-butyl-3-methylimidazolium Chloride and Hexafluorophosphate, *J. Chem. Phys*, **127,** 104506 (8 pages) (2007).

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).

Takahashi H, Ohno H, Kishi R, Nakano M, Matubayasi N: Computation of the Free Energy Change Associated with One-electron Reduction of Coenzyme Immersed in Water: A Novel Approach within the Framework of the Quantum Mechanical/molecular Mechanical Method Combined with the Theory of Energy Representation, *J. Chem. Phys.*, **129,** 205103 (14 pages) (2008).

Yoshida K, Matubayasi N, Uosaki Y, Nakahara M: Scaled Polynomial Expression for Self-Diffusion Coefficients for Water, Benzene, and Cyclohexane over a Wide Range of Temperatures and Densities, *J. Chem. Eng. Data*, **55,** 2815–2823 (2010).

Karino Y, Fedorov MV, Matubayasi N: End-point Calculation of Solvation Free Energy of Amino-acid Analogs by Molecular Theories of Solution, *Chem. Phys. Lett.*, **496,** 351–355 (2010).

Dynamical Inhomogeneity of Lipid Membrane

The dynamical inhomogeneity in the lipid membrane is studied over a wide range of curvature by the solution-state ^{1}H NMR-nuclear Overhauser effect (NOE). To make possible the NOE measurement for large vesicles, the transient NOE method is combined with the spin-echo method (transient NOE-SE method) and is applied to micelle of 1-palmitoyl-lysophosphatidylcholine (PaLPC) with a diameter of 5 nm and to vesicles of dipalmitoylphosphatidylcholine (DPPC) with diameters ranging from 30 to 800 nm. The transient NOE-SE method suppresses the broad components in model-membrane signals and enables quantitative assessment of the NOE intensities even for an almost flat bilayer of ~800 nm in diameter. It is found that the NOE intensity increases with the diameter up to ~100 nm, and the model membrane is considered flat beyond ~100 nm. While the NOE between the hydrophilic choline and hydrophobic terminal methyl groups is absent for micelle as expected, its intensity is comparable to that for the neighboring group for vesicles of larger diameters. The origin of NOE signals between distant sites is revealed by MD analysis. The MD simulation is performed for the PaLPC micelle and the DPPC flat bilayer, and the time correlation function determining the NOE cross intensity is calculated. The corresponding correlation time for the DPPC flat bilayer enhances to microsecond and is shown to yield an observable NOE signal even for the hydrophilic terminal and hydrophobic terminal sites. Since the correlation time depends on the proton pairs by orders of magnitude, the NOE intensity for large vesicle is combined information of distance and dynamics and does not reflect only the distance. The correlation time in large vesicle is then determined by employing the experimental NOE intensity and the MD-based distance distribution. It is found to vary by three orders of magnitude over the proton sites in the case of large vesicles.

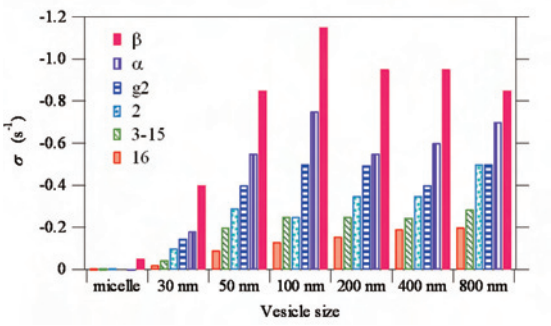

Figure 1. The vesicle size dependence of the cross relaxation rate constant σ between the γ site and the other sites at 60ºC.

Free-Energy Analysis of Hydration Effect on Protein with Explicit Solvent

Hydration is a key factor for controlling the stability and fluctuation of protein structure. In the statistical thermodynamic context, the hydration effect is quantified by the solvation free energy and is affected by specific protein-water intermolecular interactions. In the present work, the relationship between the protein conformation and the hydration effect is investigated for the equilibrium fluctuation of cytochrome *c*. To elucidate the hydration effect with explicit solvent, the solvation free energy of the protein immersed in water was calculated using the molecular dynamics simulation coupled with the method of energy representation. As shown in Figure 2, the protein intramolecular energy and the solvation free energy are found to compensate each other in the course of equilibrium fluctuation. The energy variation corresponding in magnitude to the formation/breakage of several tens of hydrogen bonds is induced and compensated by the solvent water. The correlation of the solvation free energy is further examined against the average sum of protein-water interaction and the excluded-volume part of the solvation free energy. The average sum is dominated by the electrostatic interaction and varies in proportion to the solvation free energy. The excluded-volume part has no correlation to the (total) solvation free energy and is virtually constant. The variation of the solvation free energy in response to the conformational fluctuation at equilibrium is described by the linear-response-type relationship with the protein-water interaction supplemented by an offset representing the excluded-volume effect.

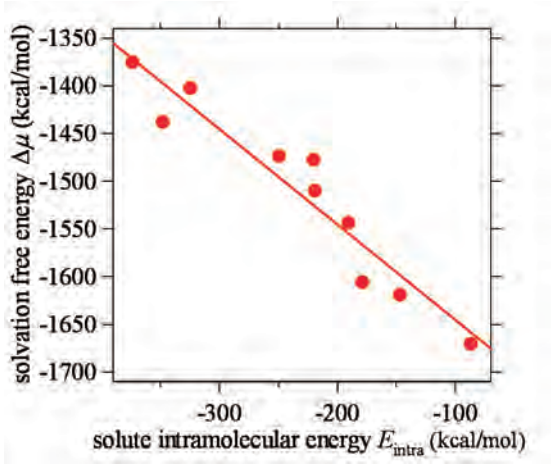

Figure 2. The solvation free energy $\Delta\mu$ of cytochrome *c* plotted against the intramolecular energy E_{intra}. The solid line represents the least-square fit and is given by $E_{intra} + \Delta\mu = -1.7\times10^3$ kcal/mol.