L1

Water-Alcohol Mixtures: What Have We Learnt from Molecular Simulations

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The wide-spread and commonly accepted explanation of the behavior of water-alcohol mixtures in terms of an enhanced structuring of water does not seem to be supported by modern diffraction experiments: Neutron scattering experiments show highly heterogeneous mixing across the entire concentration range despite apparent miscibility of both components. In the light of the yet unsettled controversy as for the origin of the observed anomalies it is understandable that overwhelming majority of molecular simulation studies have focussed on the structure with very little attention paid to the thermodynamic properties.

Using first commonly accepted realistic models (effective pairwise potentials) and simple primitive models, we report molecular simulation results for both the excess mixing and partial molar properties of water-methanol mixtures over the entire concentration range with the particular emphasis on the low concentration ends.
It is shown that:

1. Results obtained for both types of potential models are in a mutual qualitative agreement.
2. Concerning comparison with experimental data then:
    (a) realistic models give a reasonably good agreement only for volumetric properties; results for excess enthalpy are rather bad and only its sign is predicted correctly.
    (b) the qualitative trend of the partial molar volume of methanol at low concentrations (minimum) is not reproduced at all.
3. Non-ideality of the mixture results primarily from non-additivity of short-range REPULSIVE interactions.

Whereas the developed effective pairwise potential models provide a good prediction for both thermodynamic and structural properties of pure compounds, in the case of mixtures interaction models rely only on various, only purely empirical, combining rules.

To identify defects in models of water-alcohol interactions and to account directly for the water-alcohol interaction in a simple way, polarizibility of water molecules has been considered.
It turns out that this non-additive effect changes qualitatively the behavior of the mixture yielding results in qualitative agreement with experiment even for partial molar volumes.

S1

Diffusion of Hydrophobic and Hydrophilic Molecules in Water and Organic Solvents. How Are Solvations Reflected in Diffusion?

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It is of interest to examine how solvations are reflected in the diffusion processes. Some questions may be raised. Is there any difference between the effects of hydrophobic hydration and hydrophilic hydration? Is there any difference between the effects of the hydration in water and the solvation in organic solvents?

To answer these questions, we have measured translational diffusion coefficients of aromatic hydrocarbons and hydroxylic molecules in water over a wide range of temperature covering 265-433 K.[1,2] The diffusion coefficients of aromatic hydrocarbons are smaller in water than in organic solvents when compared at the same viscosity, which might reflect hydrophobic hydration. Although we expected that the hydration is sensitive to the temperature, the product, $D\eta/T$, where D is the diffusion coefficient, η is the viscosity of the solvent, and T is the temperature in K, showed very weak temperature dependence. This is in contrast to the results in ethanol, where the product, $D\eta/T$, shows significantly large temperature dependence depending upon the solute.[3]

In water, the Arhenius plots of $\ln D$ vs. $1/T$ do not show straight lines, indicating that the (apparent) activation energies decrease with increasing temperature. This is also in contrast with the result in ethanol, where the plots show straight lines. The most significant difference is that the activation energies in ethanol show significantly large dependence on the solutes whereas those in water show very weak dependence on the nature of the solutes and are close to the activation energy for the self-diffusion of water. Effects of inter- and intra-molecular hydrogen bonding interaction in organic solvents[4] and hydrophobic hydration of ions in water[5] are also discussed.

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L2

Local Structure in Supercritical Ionic Solutions as Seen by MD Simulations and EXAFS Spectroscopy

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Supercritical fluids are characterised by strong local order fluctuations and thus are challenging systems for structural studies [1]. By combining Molecular Dynamics (MD) simulations with Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy, we have elucidated the structure of the Br- hydration shell in low concentrated aqueous solutions (KBr, RbBr and CsBr) from ambient to supercritical conditions. The densities explored correspond to pressures up to 450 bar [2-3]. This combination of techniques appears to be essential for a proper analysis as in supercritical conditions the local fluctuations severely limit the validity of standard EXAFS analysis [4].

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S2

Dynamics of Liquids with Strong Coulombic Interaction

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Introduction: Structure and Dynamics of dense liquids are usually dominated by the repulsive intermolecular interaction. In particular, the interaction through the steep repulsive interaction, called "collision", plays the central role in the liquid state dynamics. However, there are some liquids which possess so strong Coulombic interaction that the intermolecular electrostatic interaction is dominant in the determination of their dynamic properties. In such cases, one often observe "anomaly" in their dynamics. We have been undertaking the study on the dynamics of liquids with strong Coulombic interaction with the aid of mode-coupling theory (MCT), and some of the results below shall be introduced in the presentation.

Compressed Water:[1] The mobility of liquid water increases with increasing density in the low-temperature, low-pressure region, which is one of the anomalous properties of liquid water compared with other molecular liquids. We calculated the dynamics of water as the function of density and pressure with MCT for molecular liquids based on the interaction-site model. The site-site correlation functions required as the input for MCT calculation are obtained by the reference interaction-site model (RISM) integral equation. We succeeded in reproducing the characteristic increase of mobility with density qualitatively, although the quantitative agreement is not so good. The analyses were performed based on the theoretical expression of the memory function in MCT, and we revealed that the friction on the dielectric mode due to the coupling between the charge- and number-density modes is responsible to the enhancement of mobility with compression.

Molten LiBr and SiO_2:[2] Molten SiO_2 is another well-known example of liquid whose mobility is increased by compression. Molten LiBr also shows the increase in the molar ionic conductivity with increasing pressure, which is less famous than the anomalies of SiO_2 and water. We calculated the dynamic properties of the two molten salts with MCT, and succeeded in the anomalous pressure dependence of ionic mobility. The analyses are performed as is the case of water, and we showed that the pressure dependence of the ionic mobility of these molten salts can be understood in the same way as compressed water.

Dynamic Hydrophobicity:[3] The dissolution of hydrophobic molecules into water leads to the retardation of the mobility of solvent water molecules, which contradicts with our naïve intuition in that weak solute-solvent interaction makes the relaxation of the solvent molecules slower. We performed MCT calculations on the water / Lennard-Jones solute mixtures using RISM structure as input, and succeeded in the characteristics of the hydrophobic slowing down of water molecules. Furthermore, we showed that both strong and weak solute-solvent interaction makes the mobility of water slower, whereas the interaction of intermediate strength makes faster, which correspond to positive, hydrophobic, and negative hydration, respectively.

Molar Conductivity Minimum of Electrolyte Solution: The molar conductivity of electrolyte solution often exhibits a minimum as the function of concentration when the dielectric constant of the solvent is low. The MCT calculation on model systems shows that the existence of the minimum can be explained without any consideration of ionic association.

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L3

Modeling of Supramolecular Structure and Permittivity of Liquids in Quasichemical Approach: Methanol from Melting Point to Critical State

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Quasichemical models [1,2] provide a unified molecular approach to describe the structure and various macroscopic properties of liquids and their mixtures. The molecular-thermodynamic formulation makes it possible to model supramolecular structure and properties of liquid systems in a wide range of the parameters of state, including supercritical region, with minimal computational demands.

We report the results [3] on modeling of the supramolecular structure and dielectric permittivity of pure fluid methanol in the temperature range from melting point to supercritical state using the Quasichemical Model of the Nonideal Associated Solution (QCNAS). Two models of supramolecular structure are considered. The first model [4] includes only chain-like aggregation, while the second one [5] takes into account both chain-like and cyclic methanol aggregates. The cyclic aggregates are necessary for describing properties of alcohol mixtures [1-5], though their role is small in pure methanol.

Dielectric permittivity and dipole correlation factor of methanol were calculated in the temperature interval 177-593 K with pressure ranging from 0.1 to 20 MPa. Both models proved quite adequate in reproducing experimental data for pure methanol but including cyclic aggregates of methanol is essential for consistency with the models for methanol mixtures [5]. The thermodynamic and structural parameters of supramolecular aggregates are reported. Distribution functions of aggregates over size and structure were evaluated in the entire temperature range and compared with experimental data. Evolution of the distribution functions of aggregates with variation the parameters of the state (temperature, pressure) are discussed.

Supramolecular aggregates with long range molecular correlations extending beyond the nearest coordination shells were revealed, including supercritical region of parameters of state.

The work was supported by Russian Funding for Basic Research (project N 07-03-01105).

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S3

Effect of the Solutes (Urea and Acetone) on the Structure of Water: A Molecular Dynamics Simulation

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keywords: Orientational order, locale structure, aqueous solutions

When analysing the effect of the solute on the structure of water in aqueous solutions using standard statistical approaches(radial distribution functions), one is faced with one principal thermodynamic problem: the changes of solvent structure occur only near the solute and averaging through all of thermodynamic ensemble diminishing all effect sometimes closely to zero. Therefore, in order to understand the effect of the solute on the structure of water, it is important to find theoretical approach for studying the local structure in aqueous solutions. The main idea is to evaluate smoothed distribution functions over physically small volume. One can then introduce the informational entropy associated with these smoothed correlation functions. For introducing of such informational entropy, two orientational parameters[1,2] measuring the extent to which a molecule of water and its four neighbors adopt a tetrahedral arrangement and the nearest neighbour distribution (nnd) approaches[3] as an indicator of a locale structure in aqueous solutions, will be used. In the nnd approach, the neighbours of a central atom are sorted by distance into the first neighbours; second neighbours, etc. Separate radial distribution functions, $p_{\alpha\beta}(n,r)$ may be defined for each set of nearest neighbours atoms β (indicated by n), and at distance r from the central atom α. These functions are less averaged and contain then more information than the corresponding $g_{\alpha\beta}(r)$ (the radial distribution of atoms β around α). In order to get information on the orientation between a probe molecule and another belonging to a class of neighbouring molecules, we also can calculate the orientational distributions, $q_{\alpha\beta}(n,r,\cos(\theta))$ as follow: for a distance r between the central atom α and an atom β belonging to a class n of neighbouring molecule, we calculate the distribution function, $\cos(\theta)$, where θ is the angle between the unit vectors along the molecular axes of the two molecules and we average over all choices of the central atoms. The analysis of the nearest radial (how molecule are distributed, on average, in their distance from a probe molecule) and orientational (the extent to which neighbouring molecules are at a specific angles with respect to each other) distributions will allow to address unambiguously the effect of the solute on the local radial and orientational structure of water. This allows to move beyond the present clichés used in the study of aqueous solutions and to avoid using nebulous terms like "structure making" and "structure breaking" to describe the effect of the solutes on the structure of water. Furthermore, to point out the changes occurring at a level of the three-dimensional network of H-bonds in aqueous solutions, the effect of the solute on the structure of water is also quantified by following the behaviour of the elasticity of hydrogen bond network upon the variation of the composition of the mixture. The elasticity of the spatial H-bond network is manifested by the tendency to preserve its initial configuration. This parameter is used as measure of hydrogen bonds network resistance to any external changes and is defined as elasticity modulus of hydrogen bonds network, introduced within the statistical theory of elasticity in the liquid state[4].
This approach is used to asses the effect of urea and acetone solutes on the structure of water.

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L4 The Raman Noncoincidence Effect of the S=O Stretching Mode of Neat Liquid Dimethyl Sulfoxide

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The magnitude of the noncoincidence effect (NCE) of the S=O stretching [ν(S=O)] vibration in liquid dimethyl sulfoxide (DMSO-$^{13}C_2$ and DMSO-$^{12}C_2$) has been determined from the separation of the anisotropic and isotropic components of the Raman band observed at around 1042 cm^{-1}. The measurements have been carried out for isotopically substituted liquid DMSO-$^{13}C_2$, in order to avoid as much as possible the overlap of the ν(S=O) band with the bands of the methyl rocking modes and with possible combination bands of lower-frequency modes. In the liquid phase of DMSO, this overlap is pronounced in the normal isotopic species DMSO-$^{12}C_2$, but much less in the isotopically substituted DMSO-$^{13}C_2$. This simplified ν(S=O) band profile observed for liquid DMSO-$^{13}C_2$ is in agreement with that provided by spectral calculations based on the extended MD/TDC/WFP method, in which the intermolecular resonant vibrational interaction between molecules of identical species is determined by the transition dipole coupling (TDC) mechanism. The observed magnitude of the NCE is in reasonable quantitative agreement with the MD/TDC/WFP result, and with the prediction obtained from Logan's analytical treatment of the NCE, which was developed within the framework of the mean-spherical approximation of the dipole-dipole interaction.

This work is supported by the grant P16372-N02 from the Austrian Science Fund.

S4

Time-Domain Theoretical Analysis of the IR, Polarized Raman, and 2D-IR Spectra of Peptide Chains in Aqueous Solution

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The profiles of the linear IR, polarized Raman, and 2D-IR spectra of the amide I mode of peptide chains in aqueous solution are analyzed theoretically by using a time-domain computational method. This method[1,2] includes both the frequency modulations induced by the interactions with solvent water molecules and the resonant vibrational couplings between peptide groups, so that the vibrational frequency crossings among peptide groups and the resultant non-adiabatic effects are taken into account in a natural way. It is shown that the negative noncoincidence effect (negative values of $\nu_{\mathrm{IR}} - \nu_{\mathrm{iso}}$ and $\nu_{\mathrm{aniso}} - \nu_{\mathrm{iso}}$) observed[3] for the amide I band of short peptide chains of alanine is consistent with the structures dominated by the polyproline II and β-type conformations obtained from MD simulations. This negative noncoincidence effect arises from resonant vibrational coupling between the amide I vibrations of peptide groups and the resultant delocalization of vibrational modes. However, the effect of this delocalization cannot be clearly seen in the 2D-IR band profiles. In contrast, in the case of a longer peptide chain in the α-helical conformation, the effect of the delocalization of vibrational modes is easily recognized in the 2D-IR band profiles, although the magnitude of the noncoincidence is small.

To see the nature of the vibrational frequency modulations and the extent of the resultant changes in the characters of the normal modes, the time correlation functions of the frequency modulations $C_{\mathrm{L}}(t)$ and the mode identity[2] $M(t)$ are calculated. As shown on the left-hand side of Fig. 1, the system proceeds halfway to complete mode mixing in ~60 fs. $C_{\mathrm{L}}(t)$ (Fig. 1, right) also decays rapidly, giving rise to a motional narrowing effect on the band profiles. The oscillatory behavior of $C_{\mathrm{L}}(t)$ in the first ~100 fs originates from the librational motions of solvent water molecules. The latter result is discussed by comparing it with the case of the OH stretching mode of liquid water.[4]

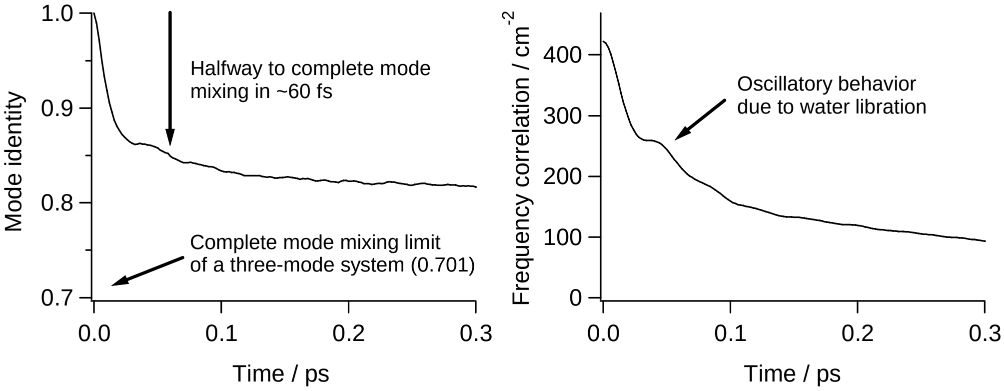

Fig. 1. The time correlation functions of the mode identity $M(t)$ (left) and the frequency modulations $C_{\mathrm{L}}(t)$ (right) calculated for the amide I mode of tetraalanine in aqueous solution at 298 K.[5]

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L5

Association and Clusterization Phenomena in Electrolyte Solutions: Statistical Mechanical Modeling

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For the last decades the progress in liquid state theory creats a new possibilities for description and interpretation of many phenomena in electrolyte solutions. In this report we present some our results connected with the application of modern liquid theory to the statistical mechanical modeling of different type of association and clusterization in electrolyte solutions. Between them we consider the revised version of ion association concept which is build on the modern statistical thermodynamics of associative fluids. Analytical solution of the associative mean sperical approximation (AMSA) and the modified version of the mean sperical approximation-the mass action law (MSA-MAL) approach for ion and ion-dipole models are used to revise the concept of ion association. In the considering approach in contrast to the traditional one both free and associated ion electrostatic contributions are taken into account and therefore the revised version of ion association concept is correct for weak and strong regimes of ion association. The capabilities of the developed approaches are illustrated by the description of thermodynamic and transport properties of electrolytes solutions in weakly polar solvents. The proposed theory is applied to explain the anomalous properties of electrical double layer in a low temperature region and for the treatment of the effect of electrolyte on the rate of intramolecular electron transfer. The revised concept of ion association in framework of ion-molecular approach is applied to describe the concentration dependences of dielectric properties of electrolyte solutions. We will also present some our result connected with the study of the influence of the ion charge on hydrated-hydrolyzed structure and dynamical properties of multivalent cations in aqueous solutions. Our investigation demonstrates a wide variety of hydrated-hydrolysed forms of cations, including aquo, hydroxo-aquo, hydroxo, oxo-hydroxo and oxo forms. Finally we will consider some aspects connected with the modeling of hydration structure of some amphiphilic molecules.

S5

Ultrafast Vibrational Dynamics of Small Ions in Solution Studied by Nonlinear Infrared Spectroscopy

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Molecular dynamics in the condensed phase are strongly affected by nature of solute-solvent interactions. In the condensed phase, the linewidth of the vibrational spectrum is broader than that in the gas phase. Vibrational line shapes contain useful information on the dynamical and static interaction with the environment. However, it always has a certain ambiguity for separating various contributions to the lineshape. Nonlinear infrared (IR) spectroscopy has been shown to be a powerful tool to investigate solute-solvent interactions and vibrational frequency fluctuations in the condensed phase. In particular, three-pulse IR photon echo measurement is a useful technique to probe the vibrational frequency fluctuations in the condensed phase. Frequency fluctuations of the solute are very sensitive to the dynamics of the surrounding environments. As shown in the previous studies, the peak position (or the first moment) of the photon echo signals is a sensitive measure for the spectral diffusion process. Time scales of the spectral diffusion process can be characterized by the correlation function of the vibrational frequency fluctuation. In this contribution, we will present the results of the vibrational dynamics of small ions in polar solvents.

A great deal of effort has been devoted to study the structural and dynamical properties of hydrogen bonded systems both in the gas and condensed phase because hydrogen bonds play an important role in many chemical and biological systems. We investigated the spectral diffusion process (solvation dynamics) of small ions, such as OCN^-, SCN^- and $Fe(CN)_6^{4-}$, in hydrogen-bonding solvents such as water and methanol. Studies on simple ions provide detailed physical origins on solute-solvent interactions and serve as a benchmark for theoretical modeling. For the anti-symmetric stretching mode of OCN^- and SCN^- in methanol, the correlation functions for both ions decay with time constants of around 100 fs and 4 ps. Three-pulse photon echo measurements for $Fe(CN)_6^{4-}$ in D_2O showed that the correlation function of the frequency fluctuations decays on <100 fs and 1.5 ps time scales. The slow decaying components of the correlation function are due to making and breaking of the hydrogen bonds between ion and solvent. Based on our results of small ions, we found that the time scales of the correlation function do not depend on the solute and are determined by the solvent, while the amplitudes of the components depend on the solute and solvent. Our results suggest that longer-range solute-solvent interaction plays an important role in the vibrational frequency fluctuations.

We have also studied the vibrational dynamics of SCN^- in various types of polar solvents (formamide, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetonitrile, and so on) because most of the time-resolved IR studies so far have been focused on the vibrational dynamics in protic solvents such as water and alcohols. In order to understand the nature of the dynamical interactions in protic solvents, it is important to compare the dynamical properties of the vibrational transitions in aprotic solvents with those in protic solvents. From the FT-IR spectra of the anti-symmetric stretching mode of SCN^-, the peak of the absorption spectrum is located at around 2056 cm^{-1}, which does not depend on the solvent used. On the other hand, the linewidth of the absorption spectrum in protic solvents is much broader than in aprotic solvents. It is shown theoretically that a shift in the vibrational frequency of this mode depends on the location and number of hydrogen bonds between SCN^- and solvent molecules. By comparing with the results of the photon echo measurements in protic solvents, we found that the fast decaying component of the correlation function is dominant in aprotic solvents, while the relative contribution of slow one is larger in protic solvents. In this presentation, we will discuss the mechanism of the frequency fluctuations of SCN^- in polar solvents.

L6

On Microscopic Interpretation of Volumetric Data

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The ultimate value of thermodynamic measurements in biomolecular studies depends on our ability to interpret measured macroscopic properties in terms of microscopic events, such as changes in particular intra- or intermolecular interactions. In this respect, volumetric measurements have been intensively used for characterizing the hydration properties of a wide range of solute classes as well as changes in hydration accompanying various processes of biological importance, e. g., conformational transitions of proteins. With enhanced sensitivity and reduced sample volumes of current instruments, microscopic interpretation of macroscopic results represents the main challenge and limitation of volumetric studies. Such interpretations can be performed only within the framework of assumed models of solute in solution preferably reinforced by computer simulations. This issue is central to even the simplest biological systems, such as amino acids and short peptides, and becomes particularly pressing when dealing with proteins and nucleic acids. I will discuss the use of some conventional approaches that are currently employed for rationalizing in terms of hydration volume, compressibility, and expansibility data on proteins and nucleic acids. I will also present volume, compressibility, and expansibility results on the binding of adamantane to β- and γ-cyclodextrins. The volumetric changes accompanying the association of adamantane with β-cyclodextrin are consistent with the release to the bulk of 20 to 25 hydrophobic waters. On the other hand, the resulting volumetric data on the binding of adamantane to γ-cyclodextrin suggest release of hydrophobic waters plus formation of a highly compressible interior cavity. Interestingly, the intrinsic coefficient of the adamantane-γ-cyclodextrin inclusion complex appears to be close to that of the interior of a globular protein.

S6

Molecular Recognition Realized by the 3D-RISM Theory

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Molecular recognition is the most important process in living systems, which is related to a variety of functions: ion transport in membrane channels, enzymatic reactions, ligand binding by protein, and so on.

The problem has been a great challenge for any theoretical method including the molecular simulations and the statistical mechanics, because it concerns the free energy of guest molecules inside and outside a host molecule, which touches the thermodynamic limit in one hand, and the inhomogeneity on the other hand.

Recently, we have found that the 3D-RISM theory, the statistical mechanics theory of molecular liquids, has a capability of "detecting" small molecules, such as water and ions, trapped in pores of protein. We could have realized the distribution of the small molecules not only around a protein, but also inside a cavity of the host molecule, just like what is observed by the X-ray or neutron diffraction measurement.

In the seminar, the latest progress made in our group regarding the molecular recognition is presented. The topics includes the selective ion-binding by human lysozime, and the proton exclusion of aquaporins.

S7

FTIR Spectroscopic Imaging Applied to Atherosclerotic Aorta

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Keywords: FTIR imaging, atherosclerosis, thoracic aorta

Atherosclerosis, one of the main causes of heart attack and stroke, consists of local deposits of fat, cells and collagen within the arterial intima and innermost media. A large number of processes contribute to the pathogenesis of atherosclerosis, although their specific role in the development of such a complex disease is not yet fully understood[1]. Enhanced transport phenomena bringing plasma-derived macromolecules, particularly low density lipoproteins (LDL), into the arterial wall can account for the occurrence of lesion-prone areas of the vasculature. Monocytes infiltrate the sub-endothelial space, differentiate into macrophages and accumulate LDL-derived cholesteryl esters and other lipids, thereby becoming the foam cells that are characteristic of early lesions. Lipid deposits have an age-dependent spatial pattern in human arteries and in animal models of the disease[2].

The *in-situ* investigation of biomedical samples, such as arteries affected by atherosclerosis, constitutes an important approach to the study of complex diseases and related processes. Fourier Transform Infrared (FTIR) imaging offers a powerful tool for biological and pharmacokinetic studies in medical specimens allowing information to be obtained on tissue structure as well as chemical composition[3]. The use of a microscope objective with a Germanium ATR crystal yields FTIR images with high spatial resolution (on a micron scale), which is particularly necessary for analysing tissue samples. Characteristic bands of proteins and lipids, respectively amide I-II and ester carbonyl stretching, are used to determine their distributions within the arterial wall. Applications of micro- and macro-ATR-FTIR imaging to rabbit thoracic aorta affected by atherosclerosis will be presented and research in this area will be discussed.

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S8

Applications of the 3D-RISM Theory of Molecular Solvation to Protein Aqueous Solution Systems

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Water plays crucial roles not only in protein structure but also in its function such as ligand recognition. At the thermodynamic or free energy level, solvent water regulates the intra-protein and intermolecular protein-ligand interactions by, for example, the hydrophobic and the dielectric screening effects. At the atomic level, each water molecule has its own role and acts as an integral component of the system. For instance, water molecules buried in the protein cavities or located at the binding interface of protein-ligand complexes maintain the specific local structures by mediating hydrogen bonds or simply filling void spaces.

Molecular simulation has been widely used for the investigation of protein structure and function in aqueous solution. In the simulation, the solvent effects are considered by using continuum solvent models or by including water molecules explicitly. The former method requires minor computational effort to calculate the solvation free energy approximately, but it can never describe the roles of individual water molecules. In contrast, the later can explain the detailed behavior of water molecules, but it requires very high computational expenses to evaluate the solvent effects at the free energy level.

The integral equation theory of molecular liquids is an alternative approach. The theory is based on statistical mechanics and therefore can deal with the solvent effects at the atomic and thermodynamic level equally. Specifically, the theory yields the atomic distribution functions of water around the protein from the intermolecular interaction potentials and calculates the thermodynamic quantities from the distribution functions. Until recently, the applications of the liquid theory had been limited to small molecular systems, but in 2004[1] we succeeded in calculating the hydration structure and thermodynamics of proteins with the most advanced theory of molecular liquids, known as the 3D-RISM theory. After that study, we have continuously applied the 3D-RISM theory to various protein aqueous solution systems in order to investigate the roles of water in protein structure and function.

Here, I will present our recent studies on protein hydration, structure, and function using the 3D-RISM theory, especially (1) molecular recognition by protein,[2-4] (2) protein folding,[5] and (3) pressure-induced structural transition of protein.[6] In Topic 1, it is demonstrated that the 3D-RISM theory has the ability to detect the binding sites of ionic and hydrophobic ligands as well as water molecules in a target protein. In Topic 2, it is argued that the hydration entropy is a substantial driving force in protein folding. In Topic 3, we will find that the penetration of water molecules into the protein interior reduces the partial molar volume of the protein and it is the trigger of the pressure-induced denaturation of protein.

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S9

Structure and Dynamics of Molecules and Ions in Room Temperature Ionic Liquids

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Recently, room-temperature ionic liquids (ILs) attract much attention as a novel and “green” reaction medium because ILs can dissolve a variety of organic solutes like supercritical fluids. There have been carried out a variety of dynamic investigations on fluorescent probes[1] and neat ILs.[2] We have reported a dynamic study on dissolved reactants.[3] In ILs, we can study water not as a solvent but as a solute or reactant.[3] For a better understanding of the water reactivity, it is necessary to elucidate the dynamic aspects of water in ILs where water is solvated by ions in contrast to dilute aqueous electrolyte solution. For obtaining the rotational correlation time τ_{2R}, it is very powerful to measure the spin-lattice relaxation time T_1 by means of NMR. As shown previously, the τ_{2R} ratio of water to benzene decreases in neutral organic solvents with increasing solvent polarity due to the attractive interaction between the solute and solvent.[4][5] Thus we can use the τ_{2R} ratio, $\tau_{W/B}$, as a measure of the strength of solvation of water (polar) and benzene (nonpolar) by ions. The fluctuating electrostatic field due to ions is very large in the short range. Therefore, the smaller anion is more important in ionic solvation than the larger organic cation. We will show the difference in the rotational dynamics between polar water and nonpolar benzene in several ILs that have different in anion size. For water, it is predicted by the hydrodynamic Stokes-Einstein-Debye (SED) law that the τ_{2R} is one order of magnitude smaller than that for benzene due to the difference (9 times) in the molecular volume. In such a nonpolar solvent as carbon tetrachloride, the τ_{2R} ratio is very small. In polar acetonitrile, the ratio becomes larger due to attractive interactions. We show that the ratio becomes close to 1 and that the smaller water rotates rather slowly when the solutes are solvated by full-charges instead of partial ones.

As a new topic, we focus on the liquid structure of ILs on the atomic level. It is of great importance to understand the liquid structure since the properties of the ionic liquid is strongly influenced by the intermolecular configurations among large organic cations that have flexible and highly anisotropic structures. We will investigate the cation-cation configuration in an ionic liquid, 1-butyl-3-methylimidazolium chloride ([bmim][Cl]). Computer simulations have showed that the liquid structure of ILs have a charge-ordering structure that is controlled by Coulombic interactions among cations and anions. To elucidate the short-range structure, we have employed here the transient ^{1}H-NOE [6] and succeeded in determing intermolecular proton-proton distances between the aromatic imidazolium cations as new information on the intermolecular configuration among cations.

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S10

Cesium Formate: A Computational Study

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ABSTRACT:
Cesium formate has a number of important and unusual properties that have made it an extremely new base fluid for many applications in the oil industry. However a major problem with this compound is that it precipitates heavily from solution, thus limiting its exploitation. In this contribution we present extensive molecular dynamics study attempting to identify the phase transition at 363 K from orthorhombic to cubic as previously reported[1]. Ab-initio methods have also been introduced to describe the cesium-formate-water interactions. Finally, attempts to characterise the dominant growth surface under vacuum, and in contact water and electrolyte solutions. Studies in the presence of various additives will also be presented. The simulations have been analysed to give molecular level information on the mechanism of crystal growth and control of inhibition under typical operating conditions, and is discussed in detail.

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$Au(CN)_2^+$ and its Solvation in Nitromethane

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Solutions containing gold in one or the other form are prominent in nanoelectronics, catalysis and cluster science. We investigated $Au(CN)_2^+$, one of the few small Au(III) ions stably solvated in nitromethane (NM). By means of computational chemistry techniques we investigate the structure of $Au(CN)_2^+$ and the NM - $Au(CN)_2^+$ potential energy surface. We derived an analytical Au^+ - CH_3NO_2 potential energy expression for use in molecular dynamical simulations The derivation of the energy surface and its properties are discussed with respect to the solvation of the gold - cyanide complex.