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Theoretical Study on the Structures and Energies of Acetic Acid Dimers in Aqueous Solution

Takakazu Nakabayashi, Hirofumi Sato, Fumio Hirata, and Nobuyuki Nishi*

Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

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The effects of hydration on the dimerization energies and structures of acetic acid dimers are studied by the reference interaction site model self-consistent-field (RISM-SCF) method. Comparisons of the RISM-SCF results are also made with those obtained from the self-consistent reaction field (SCRF) methods to examine the dielectric effects of the solvent. The RISM-SCF method predicts the marked stabilization due to solvation in the dimer structures with large dipole moments. From the decomposition analysis of the excess chemical potential, the contribution from the free carbonyl oxygen is found to be much larger than the other atoms for the stabilization of these dimers in aqueous solution. Such a stabilization in the polar dimers is not obtained from the simplest SCRF method that considers only the solute dipole.

1. Introduction

Molecular association of acetic acid has been a subject of extensive investigation for many years.[1−20] In the gas phase, acetic acid forms a centrosymmetric cyclic dimer containing two O−H···O═C hydrogen bonds[1,2] as depicted in Figure 1. In the crystalline state, on the other hand, acetic acid exists in polymer chains involving C−H···O═C and O−H···O═C hydrogen bonds,[3−5] although other carboxylic acids are known to form associated cyclic dimers similar to those that exist in the gas phase.[6] The liquid structure of acetic acid has been studied by various methods.[7−12] By analyzing neutron diffraction data, Bertagnolli has suggested that the cyclic dimer structure yields a good description of the structure of liquid acetic acid.[7] However, Monte Carlo simulations have suggested that liquid acetic acid consists mainly of the hydrogen-bonded chains, not the cyclic dimer.[10] We have recently reported the temperature dependence of the Raman spectra of acetic acid in a wavenumber region of 15−3700 cm^{-1}.[11,12] By performing ab initio molecular orbital (MO) calculations on the Raman spectra of some different cluster species of acetic acid molecules, we suggested that liquid acetic acid is predominantly composed of the hydrogen-bonded chains as the fragments of the crystalline networks.[11,12]

In aqueous solution, the assumption made in some previous publications is that the only equilibrium occurring is between the monomer and the cyclic dimer.[13−16] From the theoretical point of view, however, such a cyclic dimer with a null dipole moment is hardly stabilized in polar environment. Ng et al. have applied factor analysis to the Raman spectra of mixtures of acetic acid and water at high acid concentrations and ascribed the carbonyl stretching band envelope to a sum of contributions from acetic acid monomers, cyclic and linear dimers, and linear polymers.[17] By using dielectric constant measurements, Kaatze et al. have suggested the existence of two microphases: one is a water-rich phase and the other is an acetic acid phase.[18] The mass spectrometric analysis of clusters isolated from liquid droplets has also suggested that the acetic acid molecules preferentially form their aggregates in binary solutions of acetic acid and water.[19]

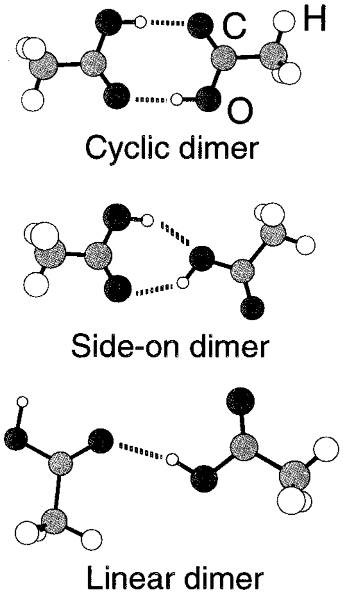

Figure 1. Structures of acetic acid dimers treated in this study.

Recently we have observed the Raman spectra of binary solutions of acetic acid and water with varying mole fraction of acetic acid.[11,20] On the basis of the coincidence between the calculated and the observed Raman spectra, we suggested that a side-on dimer, which is depicted in Figure 1, or a microphase in which this dimer structure is an elementary unit is most likely for acetic acid at high acetic acid concentrations in aqueous solution. This means that the side-on dimer with the structure generating a large dipole moment is more stable than the cyclic dimer in aqueous solution, although the cyclic dimer is quite stable in the gas phase. A linear dimer structure shown in Figure 1 is also expected to obtain marked stabilization in aqueous solution because this dimer exhibits the largest dipole moment among acetic acid dimers. However, the linear dimer structure optimized in the isolated condition[21] has one out-of plane mode with an imaginary wavenumber that leads to the dimer structure

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* Author to whom correspondence should be addressed. Fax: +81-564-54-2254. E-mail: nishi@ims.ac.jp.

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involving C−H···O═C and O−H···O═C hydrogen bonds (the dimer unit of the chain structure in the crystal).[12] This means that the linear dimer is not stable in the gas phase. Knowledge on the changes in the energies and structures of clusters on going from gaseous phase to aqueous solution is, therefore, essential for obtaining a deeper insight into the clusters existing in the solution.

There has been remarkable progress in the theories for calculating molecular properties in solutions in the last two decades. Among various methods, self-consistent reaction field (SCRF) methods based on the dielectric continuum model for solvent have been widely used in interpreting the solvent effects on the solute electronic structure.[22−25] In these methods, the solute occupies some kind of cavity surrounded by the dielectric continuous solvent. A dipole and/or multipole in the solute will induce an electric field (reaction field) in the solvent medium, which in turn will act to electrostatically stabilize the solute. SCRF models differ in the definition of the cavity and the reaction field. The simplest reaction field model (hereafter called the dipole model in this study) uses a spherical cavity and considers only the solute dipole.[23,25] This model requires only the two parameters: the solvent dielectric constant and the cavity radius. The polarizable continuum model (PCM) defines the cavity as a set of overlapping spherical atoms with the appropriate van der Waals radii.[22] This procedure can be considered to perform the multipole expansion to infinite order. A cavity defined as an isosurface of the total electron density of the solute is used in the isodensity PCM model (IPCM), which only needs two parameters as the dipole model: the dielectric constant and the isodensity value.[24,25] The SCRF methods have had great success; however, they cannot treat a microscopic solvation structure because the solvation free energy is estimated in relation to the dielectric constants, which are macroscopic properties of solvents.

The RISM-SCF method[26−30] is an ab initio self-consistent field method in quantum chemistry combined with an extended version of the reference interaction site method (RISM) in statistical mechanics of molecular liquids. This method deals with the solute−solvent interactions as the sum of site−site interactions between solute atoms and solvent molecules, and thus has an advantage in appropriately describing microscopic solute−solvent interactions. The theory has been successfully applied to a variety of chemical structures in solutions, especially in aqueous solutions.[26−30] In this article, we report the results of theoretical investigations on the dimerization energies and optimized structures of the acetic acid dimers in aqueous solution by the RISM-SCF and the dipole methods. IPCM single-point energy calculations are also performed. To our knowledge, it is the first report to perform the ab initio MO calculations for the electronic structures of the hydrogen-bonded clusters in aqueous solution along with the microscopic solvation structures around the cluster species.

2. Methods

The detailed explanations of the RISM-SCF theory have been described elsewhere.[26−30] Briefly, the solute structures are calculated from solvated Fock operators including the average electrostatic potential arising from classical solvent molecules. The solvent distributions around a solute site are determined by the extended RISM equation in which the solute-induced potential field is incorporated via partial charges on solute atoms. Both the solute electronic structure and the solvent distribution are derived simultaneously in a self-consistent manner. All the ab initio MO calculations are carried out at the Hartree−Fock (HF) level with the Huzinage−Dunning−Raffinetti double-ζ plus polarization (DZP) basis set.[31,32] Molecular geometries are fully optimized both in the gas and the solution phases using the analytical energy gradient technique.[27,30] The RISM equations are solved with the hyper netted chain (HNC) approximation.[33,34]

TABLE 1: Binding Energies[a] (in kcal/mol) of Acetic Acid Dimers in Gaseous Phase and Aqueous Solution at the HF/DZP Level

		solution		
	gas	RISM	dipole[b]	IPCM[c]
cyclic dimer	−14.37	−1.32	−12.86	−6.72
side-on dimer	−6.25	1.68	−6.79	−6.22
linear dimer	−5.55	0.32	−6.05	−8.59

[a] Binding energy is defined as the difference between twice the energy of a monomer and the energy of a dimer in each state. [b] The cavity radii employed in the dipole method are 3.38 Å for *cis*-monomer, 4.07 Å for cyclic dimer, 4.00 Å for side-on dimer, and 4.12 Å for linear dimer. [c] Single-point energy calculation.

The total energy in the RISM-SCF theory is defined as the sum of the following three energy components:[27,30] (1) the electronic energy of the solute molecule in the gas phase (E_{iso}), (2) the reorganization energy arising from the relaxation of the electronic structure and the molecular geometry upon transferring the solute from gas to aqueous solution (E_{reorg}), and (3) the excess chemical potential due to solute−solvent interaction ($\Delta\mu$). We adopt the free energy derived from the HNC closure relation for the chemical potential term in this study. [35]

The acetic acid molecules are optimized to have a C_s plane containing the heavy atoms and a methyl hydrogen at the side of the C═O group. The other two methyl hydrogens are located symmetrically above and under the carboxylic plane. A planar structure of C_s symmetry is also assumed for each dimer species. The SPC-like solvent model[36] is used to describe the solvent water in the RISM equations. The Lennard−Jones parameters for acetic acid are taken from the OPLS parameter set.[10,30] All the Lennard−Jones parameters are fixed since the van der Waals interactions remain almost unchanged during the RISM-SCF procedure. The standard combination rule is used for the determination of all the van der Waals interactions.[26] The density of water is assumed to be 1.0 g/cm^3 at a temperature of 298.15 K.

The SCRF calculations are performed by the Gaussian 94 program package[37] on a DEC workstation (AlphaStation 500). All the calculations are carried out at the HF/DZP level. The cavity radii to the dipole model are determined by means of the VOLUME keyword in the Gaussian 94 program, so that they are consistent with the molecular volumes of the optimized structures. The dielectric constant of water is assumed to be 78.39. The isosurface level of 0.0004 is used in the IPCM calculations. This value has been considered to closely reproduce solute volumes in the liquid.[24,25]

3. Results and Discussion

3.A. Binding Energies and Geometries. The calculated binding energies of the cyclic, side-on, and linear dimers are shown in Table 1. In the gas phase, it is known that the cyclic dimer is the most stable among the dimer species of acetic acid. At the HF/DZP level, the energy difference between the cyclic and side-on dimers in the gas phase is estimated to be 8.12 kcal/mol, which agrees reasonably with previous Hartree−Fock level calculations such as HF/6-31++G** (7.62 kcal/mol).[12] Force calculations for the cyclic and side-on dimers confirm convergence to the minima on the potential energy surface in the gas phase,[12] while the linear dimer is optimized to be a saddle point as mentioned earlier.

Geometry optimizations in aqueous solution are performed by the RISM-SCF and the dipole methods. In the case of the RISM-SCF method, the energy difference between the cyclic and side-on dimers is reduced to be 3.00 kcal/mol, showing that the cyclic dimer is no longer quite stable among the acetic acid dimers in aqueous solution. The difference between the cyclic and linear dimers is also markedly reduced to be 1.64 kcal/mol. Furthermore, the linear dimer is calculated to become more stable by 1.36 kcal/mol than the side-on dimer in aqueous solution. Thus the RISM-SCF method reverses the relationship between the side-on and linear dimers with respect to the binding energy. To estimate the effect of electron correlation on the binding energy, single-point energy calculations for the optimized structures are carried out at the second-order Møller−Plesset perturbation (MP2) level.[38] The binding energies in the solution are also examined with the constraint that the chemical potential term be the same as that obtained at the HF level. The MP2 calculation predicts that the energy difference between the cyclic and side-on dimers is 8.95 kcal/mol in the gas phase and 4.52 kcal/mol in the solution. Thus the change in the energy difference of the two dimers on going from the gas phase to aqueous solution is 4.43 kcal/mol, which is 0.69 kcal/mol larger than that obtained at the HF level mentioned above. This suggests that the effect of electron correlation is of little importance in the discussion of the changes in the relative energy due to solvation.

By means of the dipole method, the binding energies in aqueous solution for the cyclic, side-on, and linear dimers are calculated to be −12.86, −6.79, and −6.05 kcal/mol, respectively. This result indicates that, within the limits of the electrostatic interactions at the dipole level, the cyclic dimer is fairly stable even in aqueous solution. The dipole model predicts that the energy difference between the side-on and linear dimers remains almost unchanged on going from the gas phase to aqueous solution, which is also different from the RISM-SCF result. The difference in the binding energy between the cyclic and side-on dimers obtained by the IPCM single-point energy calculation is found to be smaller than that obtained by the RISM-SCF method. However, careful consideration is needed since the free energy of cavity formation and the dispersive interaction between the solute and solvent molecules are not treated in the IPCM procedure. The ambiguity in the definition of the isodensity level should also be taken into account. It should still be noted that the linear dimer becomes the most stable among the three dimers by the IPCM single-point energy calculation.

From the IPCM and the RISM-SCF results, the cyclic and linear dimer structures as well as the side-on dimer one are suggested in binary solutions of acetic acid and water, although vibrational frequency calculations under these models are needed to discuss whether the linear dimer is at the potential energy minimum in aqueous solution or not. The binding energy of the side-on dimer is calculated to be positive by the RISM-SCF method, which means that the dimerization to the side-on dimer cannot gain the stabilization than the twice of the hydrated energy of the monomer. A possible origin of this disagreement with the experimental results is the difference of the mole fraction. In the previous Raman studies, we used acetic acid−water mixtures with acetic acid mole fraction above 0.0075[11,20] while the assumption of the infinite dilution is required in the present calculations. Consideration of solute−solute interactions might be necessary to fully estimate the stabilization of the side-on dimer in aqueous solution.[11,17−20]

TABLE 2: Energy Components of Acetic Acid Monomer and Dimers in Aqueous Solution Computed Using the RISM-SCF Method at the HF/DZP Level

	E_{iso} (hartrees)	E_{reorg} (kcal/mol)	$\Delta\mu$ (kcal/mol)
cis-monomer	−227.8721748	3.94	0.66
cyclic dimer	−455.7672506	4.05	18.19
side-on dimer	−455.7543088	5.96	11.16
linear dimer	−455.7531901	5.52	9.54

TABLE 3: Dipole Moments (in debyes) of Acetic Acid Monomer and Dimers in Gaseous Phase and Aqueous Solution at the HF/DZP Level

		solution		
	gas	RISM	dipole	IPCM[a]
cis-monomer	1.89	2.94	2.18	2.25
cyclic dimer	0.00	0.00	0.00	0.00
side-on dimer	3.89	5.85	4.78	5.40
linear dimer	3.95	5.20	4.98	4.38

[a] Single-point energy calculation.

Table 2 collects the energy components calculated by the RISM-SCF method. Since the excess chemical potentials computed with the HNC method are known to contain systematic errors on the positive side, the total energies of all the species are higher in aqueous solution than in the gas phase. The excess chemical potential of the side-on dimer is lower by 7.03 kcal/mol than that of the cyclic dimer, indicating that the stabilization due to solvation reduces the energy difference between the two dimers in Table 1. This result is consistent with the expectation that the cyclic dimer with a null dipole moment is hardly stabilized by solute−solvent electrostatic interactions. The stabilization due to solvation in the linear dimer is calculated to be 1.62 kcal/mol greater than that in the side-on dimer.

Table 3 compares the dipole moments obtained by the RISM-SCF and the SCRF calculations. All the methods predict that the dipole moments of the side-on and linear dimers become larger on going from the gas phase to aqueous solution. The dipole moment of the side-on dimer obtained from the RISM-SCF method is larger than that obtained from the dipole method. Such a large increase in the dipole moment in the RISM-SCF method may enhance the solute−solvent electrostatic interactions and contribute the greater stabilization due to solvation in the side-on dimer. On the other hand, by means of the RISM-SCF and the IPCM methods, the linear dimer is calculated to have a smaller dipole moment than the side-on dimer, although the linear dimer becomes more stable than the side-on dimer in aqueous solution by the above two methods (Table 1). The dipole model predicts the opposite tendency: the linear dimer has a larger dipole moment than the side-on dimer and the linear dimer is not so stable as the side-on dimer. These results confirm that analyses of not only the macroscopic but also the microscopic solute and solvation structures are needed for the detailed discussion of the clusters existing in the solution.

Table 4 shows the optimized geometries characteristic of hydrogen-bonding interactions in the dimer species. The dipole model has no effect on the structure of the cyclic dimer because of its null dipole moment. Thus only the geometries obtained by the RISM-SCF method are shown as the solvated structure of the cyclic dimer. In the RISM-SCF results, the distances for the intermolecular hydrogen bonds of the cyclic and side-on dimers are calculated to be lengthened on going from the gas phase to aqueous solution. A remarkable structural change is

TABLE 4: Geometrical Parameters[a] Characteristic of Hydrogen-Bonding Interactions in Acetic Acid Dimers in Gaseous Phase and Aqueous Solution at the HF/DZP Level

	cyclic dimer		side-on dimer[b]						linear dimer[b]					
		solution[c]			solution						solution			
	gas	RISM	gas		RISM		dipole		gas		RISM		dipole	
$r_{\mathrm{C=O}}$	1.205	1.215	1.197	1.189	1.212	1.209	1.201	1.193	1.196	1.192	1.213	1.211	1.200	1.195
$r_{\mathrm{C-O}}$	1.309	1.315	1.324	1.334	1.322	1.319	1.320	1.327	1.325	1.326	1.319	1.318	1.321	1.318
$r_{\mathrm{O-H}}$	0.963	0.978	0.952	0.956	0.970	0.973	0.951	0.957	0.950	0.956	0.967	0.976	0.949	0.959
$r_{\mathrm{H\cdots O}}{}^{d}$	1.814	1.909	2.068		2.078		2.012		1.942		1.907		1.911	
$r_{\mathrm{H\cdots O}}{}^{e}$			2.128		2.143		2.223							

[a] In units of angstroms. [b] First entry is the acetic acid molecule whose $\mathrm{C{=}O}$ is the H-bond acceptor. [c] The dipole model for the cyclic dimer gives the same structure as that in gaseous phase. [d] Intermolecular $\mathrm{H{\cdots}O}$ distance for the $\mathrm{O{-}H{\cdots}O{=}C}$ hydrogen bond. [e] Intermolecular $\mathrm{H{\cdots}O}$ distance for the $\mathrm{O{-}H{\cdots}O{-}C}$ hydrogen bond.

seen in the cyclic dimer, the hydrogen-bonding distance of which is 0.095 Å longer in the solution than in the gas phase. This result indicates that the intermolecular hydrogen-bonding interactions of both the dimers are weakened effectively by the local solute−solvent interactions. The $\mathrm{C{=}O}$ and $\mathrm{O{-}H}$ bond lengths of both the dimers also become longer in the solution than in the gas phase. Since the hydrogen bonds between the solute molecules become weaker in aqueous solution as mentioned above, this result can be attributable to the hydration around these sites. The $\mathrm{O{-}H{\cdots}O{=}C}$ hydrogen bonding distance of the linear dimer becomes shorter and is nearly equal to that of the cyclic dimer in the solution. This means that the $\mathrm{O{-}H{\cdots}O{=}C}$ interaction of the linear dimer becomes stronger on going from the gas phase to aqueous solution, which contributes the stabilization of the linear dimer in the solution.

In the geometries of the side-on dimer at the dipole model, the most interesting to note is that the $\mathrm{O{-}H{\cdots}O{=}C}$ distance is shortened on going from the gas phase to aqueous solution, while the $\mathrm{O{-}H{\cdots}O{-}C}$ distance is lengthened. In other words, the $\mathrm{O{-}H{\cdots}O{=}C}$ hydrogen bond becomes stronger and the $\mathrm{O{-}H{\cdots}O{-}C}$ hydrogen bond becomes weaker by the interaction with the dielectric continuous solvent. This result is apparently different from the RISM-SCF result, in which both the hydrogen bonds become weaker in aqueous solution. The $\mathrm{O{-}H{\cdots}O{=}C}$ distance of the linear dimer is also calculated to be shortened by the dipole model. The dipole method predicts the slightly longer $\mathrm{O{-}H{\cdots}O{=}C}$ distance for the linear dimer than the RISM-SCF method. It has been known that the $\mathrm{C{\cdots}O}$ distance of the $\mathrm{C{-}H{\cdots}O}$ hydrogen bond is in the 3.0−4.0 Å distance range.[39] Since the linear dimer structure obtained from the dipole method has the $\mathrm{C{\cdots}O}$ distance of 3.779 Å, the $\mathrm{C{-}H{\cdots}O{-}C}$ interaction may affect its stability in the dielectric continuous solvent. The rest of the dimers have the longer $\mathrm{C{\cdots}O}$ distances than the $\mathrm{C{-}H{\cdots}O}$ hydrogen-bonding range. In the intramolecular bonds, all the $\mathrm{C{=}O}$ and $\mathrm{O{-}H}$ bond lengths in the solution are calculated to be only a little longer than those in the gas phase. For example, the difference in the $\mathrm{C{=}O}$ bond length of the side-on dimer between the two states is about 0.004 Å by the dipole method compared with 0.015−0.02 Å by the RISM-SCF method. This result suggests that the macroscopic dipole−dipole interaction has only minor effects on the lengths of the intramolecular bonds.

3.B. Solvation Structures. In the RISM-SCF theory, we can define the contribution of the solute atom to the solvation free energy from the decomposition of the excess chemical potential into the site−site contributions.[30] The results for the monomer and the dimer species are collected in Table 5. The contribution of each atom in this table is not the same as the solvation free energy of the atom being placed in the solvent by itself.[30] First entry for the side-on (linear) dimer is the acetic acid molecule, the carbonyl oxygen of which is hydrogen-bonded to the other acetic acid molecule. By comparing the results for the dimer species, we can readily find that the contributions from the free carbonyl oxygens in the side-on and linear dimers are much greater than the other atoms. This result indicates that solvation around the free carbonyl oxygen makes a great contribution to the stabilization of these polar dimers in aqueous solution. The sum of the contributions of the carbonyl oxygens to the excess chemical potential is 3.15 kcal/mol larger in the linear dimer than in the side-on dimer. As for the hydroxyl groups, the sum of the contributions is 3.67 kcal/mol larger in the linear dimer than in the side-on dimer, which arises mainly from the interference by the two hydrogen bonds in the side-on dimer with solvation around the constituting hydroxyl group. Unexpectedly, the free hydroxyl group in the linear dimer hardly affects the greater stabilization of the linear dimer in aqueous solution.

TABLE 5: Contributions of Solute Sites to the Excess Chemical Potential (in kcal/mol) Computed Using the RISM-SCF Method at the HF/DZP Level

solute site	*cis*-monomer	cyclic dimer	side-on dimer[a]		linear dimer[a]	
C (carbonyl)	12.60	10.99	8.11	12.17	7.02	18.88
O=	−18.08	−12.05	−10.32	−19.45	−9.73	−23.19
OH	−2.58	−0.05	−1.25	2.49	−1.53	−0.90
C ($\mathrm{CH_3}$)	6.88	9.93	9.00	9.78	9.77	6.72
H($\mathrm{CH_3}$)	0.96	0.07	0.42	0.15	0.27	0.86
H($\mathrm{CH_3}$)	0.44	0.10	0.10	−0.07	−0.05	0.74
H($\mathrm{CH_3}$)	0.44	0.10	0.10	−0.07	−0.05	0.74

[a] First entry is the acetic acid molecule whose $\mathrm{C{=}O}$ is the H-bond acceptor.

The radial distribution functions (RDF) of water hydrogen around the carbonyl oxygens calculated by the RISM-SCF method are presented in Figure 2. The results calculated for water oxygen around the hydroxyl hydrogens are shown in Figure 3. We also plot the solute−solvent RDFs within the dipole model in these figures by calculating the distances between the constituent atoms in the solute and the boundaries of the cavity. Since the solvent in the dipole model is represented by a structureless dielectric continuum beyond the cavity, the obtained functions are presumed to be written by the Heaviside function. All the RISM-SCF functions show distinct peaks representing the first solvent shell, the height of which exhibits great variety depending on the dimer configuration. It is important to notice that the position of the first peak does not change much. This is due to the domination of the repulsive interaction in the liquid state. In case of RDF from the dipole method, on the other hand, the "distance of closest approach" reflects the difference among the dimer configuration. Since the distance of closest approach between atoms should not be varied by the dimer structure, the description due to the dipole

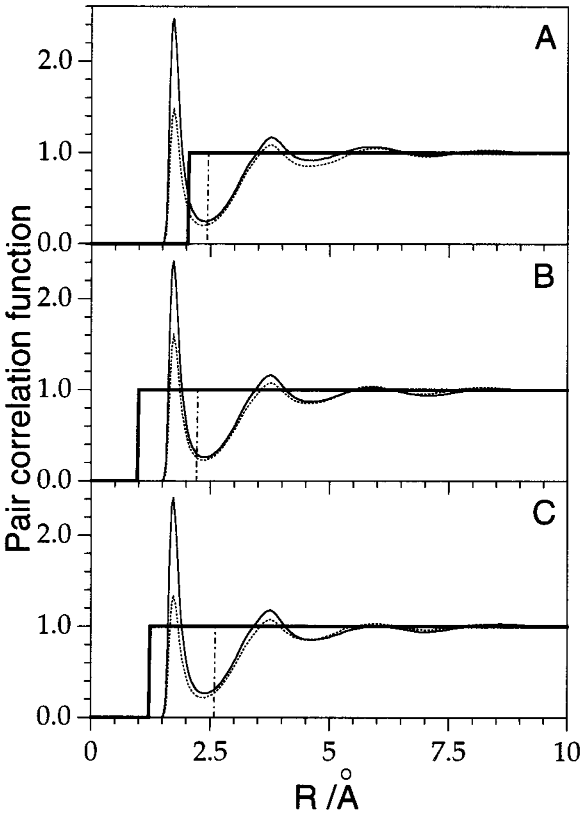

Figure 2. Radial distribution functions of water hydrogen around carbonyl oxygens of acetic acid molecules computed by the RISM-SCF and the dipole methods. In case of RDF from the dipole method, the center of mass is treated as the center of the cavity. Solid and dotted traces are obtained from the RISM-SCF method, and thick-solid and dot−dashed traces are from the dipole method. (A) Solid and thick-solid traces, *cis*-monomer; dotted and dot−dashed traces, cyclic dimer. (B) Solid and thick-solid traces, side-on dimer (the acetic acid molecule whose C═O is free); dotted and dot−dashed traces, side-on dimer (the acetic acid molecule whose C═O is the H-bond acceptor to the other acetic acid molecule). (C) Solid and thick-solid traces, linear dimer (the acetic acid molecule whose C═O is free); dotted and dot−dashed traces, linear dimer (the acetic acid molecule whose C═O is the H-bond acceptor to the other acetic acid molecule).

model is unphysical. The results represent ill-behavior of the continuum model.

In the RDFs obtained from the RISM-SCF method, the interactions between the solute and solvent molecules in the neighborhood of the first peak are important in the determination of the solvation structure. In Figure 2, the RDFs for the free carbonyl oxygen show markedly high first peaks, which indicates that the free carbonyl oxygens have the strongest interaction with water hydrogens among the carbonyl oxygens in the dimers. This result is consistent with the analysis of the decomposed excess chemical potential discussed above. Among the functions in Figure 3, the RDF for the hydroxyl hydrogen constituting the O−H···O═C bond in the linear dimer shows the lowest peak, which indicates that the strong O−H···O═C hydrogen bond fairly interferes with solvation around this hydroxyl hydrogen. No significant differences are seen among the RDFs between negative charges on the carbonyl and water oxygens in Figure 4A and those between positive charges on the hydroxyl and water hydrogens in Figure 4B. It can be hence said that the dimer configuration has only negligible effects on the repulsive interactions between the solute and solvent molecules.

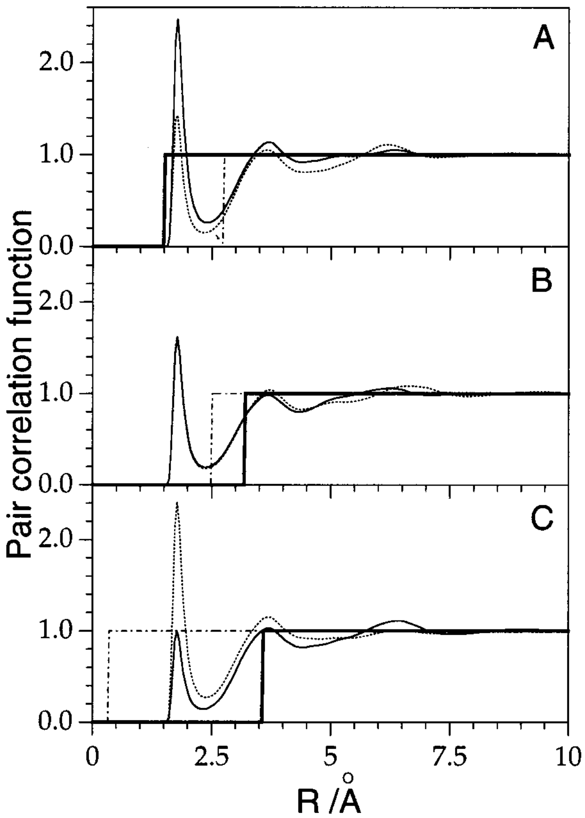

Figure 3. Radial distribution functions of water oxygen around hydroxyl hydrogens of acetic acid molecules computed by the RISM-SCF and the dipole methods. In case of RDF from the dipole method, the center of mass is treated as the center of the cavity. Solid and dotted traces are obtained from the RISM-SCF method, and thick-solid and dot−dashed traces are from the dipole method. (A) Solid and thick-solid traces, *cis*-monomer; dotted and dot−dashed traces, cyclic dimer. (B) Solid and thick-solid traces, side-on dimer (the acetic acid molecule whose C═O is free); dotted and dot−dashed traces, side-on dimer (the acetic acid molecule whose C═O is the H-bond acceptor to the other acetic acid molecule). (C) Solid and thick-solid traces, linear dimer (the acetic acid molecule whose C═O is free); dotted and dot−dashed traces, linear dimer (the acetic acid molecule whose C═O is the H-bond acceptor to the other acetic acid molecule).

4. Conclusions

We apply the RISM-SCF and the SCRF methods to investigate the electronic structures of the cyclic, side-on and linear dimers of acetic acid molecules in aqueous solution. Owing to the stabilization in the side-on dimer, the energy difference between the cyclic and side-on dimers in aqueous solution is calculated to be reduced by the RISM-SCF method; 3.0 kcal/mol in the solution compared with 8.1 kcal/mol in the gas phase. Decomposition analysis of the RISM-SCF solvation energy indicates that the hydration around the free carbonyl oxygen is of great importance for lowering the total energy of the side-on dimer in the solution. Significant stabilization is also obtained in the linear dimer that is unstable in the gas phase. Not only solvation around the free carbonyl oxygen but also the increase in the O−H···O═C hydrogen bonding interaction contributes the stabilization in the linear dimer, although solvation around the free hydroxyl group has only a minor effect on the solvation energy. In the present RISM-SCF calculations, we only discuss the enthalpic contribution for the solute term in the solvation free energy. Vibrational frequency calculations are necessary to discuss the entropic contribution of the solute. The marked stabilization in the polar dimers is not obtained from the simplest SCRF method that makes use of the spherical cavity and

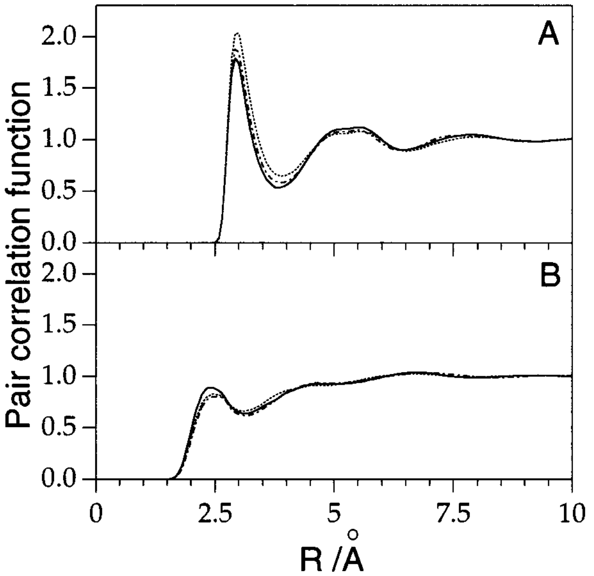

Figure 4. (A) Radial distribution functions of water oxygen around carbonyl oxygens of acetic acid molecules computed by the RISM-SCF methods. (B) Radial distribution functions of water hydrogen around hydroxyl hydrogens of acetic acid molecules computed by the RISM-SCF methods. Solid trace, cyclic dimer; dotted trace, side-on dimer (the acetic acid molecule whose C═O is free); dot−dashed trace, side-on dimer (the acetic acid molecule whose C═O is the H-bond acceptor to the other acetic acid molecule).

considers only the solute dipole. There may be the nonnegligible barrier height between solvated dimer and monomer species, since the microscopic solvation structures around the monomer molecules should be rearranged to form the solvated dimers. To provide a more definitive conclusion on this point, however, potential of mean force calculations along the hydrogen-bonding distances is essential. Finally, the present study has suggested that the RISM-SCF method is useful to obtain information on the structures of hydrogen-bonded clusters in aqueous solution. Extension to other molecular systems is an interesting and important subject for connecting cluster chemistry in gaseous phase to solution chemistry.

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