



Structural properties of hydrogen-bond network in liquid formamide-water mixtures



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ABSTRACT

Molecular dynamics simulations have been performed to investigate the structural properties of the extended hydrogen-bond (H-bond) network of liquid formamide(FA)-water(W) mixtures over the whole concentration range. Instruments of complex network analysis have been utilized to identify and quantify the structural aspects of the H-bond networks involving FA-FA, W-W, and FA-W H-bonding interactions. These include the degree distributions, the distributions of network neighborhood numbers up to the second order, and the geodesic distributions. Collectively, they provide information regarding not only the local H-bonding environment of the species but also the H-bonding environment beyond their immediate neighbors. These analyses revealed that although the connectivity patterns within the H-bond network of the mixtures are altered significantly with the composition, the degree of connectivity of the networks are well maintained. Neighborhood analysis revealed that in the water rich solution nearly all FA molecules form the H-bonded clusters of the form $[FA \cdots W \cdots W]$ and that the H-bonded cluster $[W \cdots W \cdots FA \cdots FA \cdots W \cdots W]$ is the dominant structural motif involving FA dimers. According to the geodesic analysis, population of the chain-like H-bond pathways composed of one type of molecular species increases with the increasing mole fraction of the other type of species, until the mixture reaches the equimolar composition.

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1. Introduction

The hydrogen-bond (H-bond) network is widely believed to play a key role in understanding the physical properties of several polar liquids [1–8], and their mixtures [9–11]. Numerous studies have been dedicated to the structure and dynamics of the H-bond network of bulk water [3,4,6,12–14], which is of crucial importance to understanding its highly unusual physical properties. Liquid formamide has also been shown to form an extended H-bond network, like water [8,15,16]; and yet, somewhat less attention has been paid to the properties of its H-bond network [5,17]. The formamide, $HCONH_2$, molecule contains both a carbonyl and an amino group, both of which have the ability to form strong H-bonds with H_2O . The formamide-water solution, therefore, represents an ideal model of a polar solute dissolved in a polar solvent.

The structure of the H-bond network of the liquid formamide is of particular interest since it is essentially composed of the hydrogen bonding interactions between the $C=O$ and $N-H$ groups. It is well known that this type of interaction exists in biological macromolecules such as proteins and nucleic acids [18].

Therefore, formamide is traditionally regarded as a simple model in the studies of H-bonds between peptide linkage and H-bonds between nucleotides of nucleic acids (e.g. DNA, RNA). Another major type of intermolecular interaction seen in biological macromolecules (e.g. proteins) is the hydrogen bonding between the peptide link and water, in particular, the $O-H \cdots O=C$ and $N-H \cdots O-H_2$ hydrogen-bonds. Properties of the structure of the H-bond network of formamide-water mixtures, therefore, have great potential to provide additional insights into the biological processes such as the interaction of H_2O with the proteins.

There are only a handful of experimental studies on the structural and dynamic features of the formamide-water binary solutions. A recent neutron diffraction study in combination with molecular dynamics simulations of the formamide-water mixtures reported that the distribution of the number of H-bonded neighbors does not change significantly with the formamide mole fraction and that the molecules form percolated networks at each concentration [10]. Intermolecular associations of formamide with water in an equimolar formamide-water solution were recently examined by means of neutron scattering experiments combined with density functional theory calculations [19]. Which proposed one trimeric and two tetrameric formamide-water clusters, all of which involve a cyclic component. Femtosecond dynamics of

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molecules in the formamide-water solutions was investigated by using optical-heterodyne-detected optical Kerr effect (OHD-OKE) spectroscopy, according to which water molecules substitute for formamide molecules while preserving an overall intermolecular structure very similar to that observed in pure formamide solvent [20].

Insights into the structural properties of the formamide-water solutions have been gleaned mostly from the classical statistical molecular simulations such as molecular dynamics (MD), or Monte Carlo (MC) [7,10,21–25]. Some molecular simulation studies discussed the structure of the binary solutions of water and formamide mainly in terms of radial distribution functions (RDFs), which are traditionally utilized to understand the average probability of finding a specific atom type near specified atoms; and are not quite sufficient as indicator of global structural features [21,22,24]. For example, Cordeiro et al. [24] performed Monte Carlo simulations of formamide-water mixture and reported that a formamide molecule forms three H-bonds with nearby waters based on their RDF analyses. On the other hand, some authors examined the structure of the formamide-water mixtures utilizing somewhat limited hydrogen-bond network analyses in addition to the RDF based analyses [10,23,25]. Rode et al. [23], and Elola et al. [25] for example, investigated the structural properties of the formamide-water solutions, among traditional techniques, by means of the distributions of H-bond numbers n_{HB} per molecule in the binary solutions. They both reported that there is a substitution of formamide molecules by water in the H-bonds and formation of a common H-bond network [23,25]. Regarding structure of the H-bond network of the formamide-water mixtures, only a basic understanding that is generally limited to the local H-bonding configurations in the first coordination shell of the molecular species has been obtained. Thus, there has been little discussion regarding the structural properties of the extended H-bond network beyond the immediate local environment of the species in the binary mixtures of formamide and water.

The present work utilizes a set of complex network analysis tools for the detailed description of the structural properties of the H-bond network in liquid formamide-water mixtures. Initially, the data obtained by the molecular dynamics simulations of the formamide-water mixtures were analyzed utilizing radial pair distribution functions and pair energy distributions. It was highlighted that the traditional interpretations of these distribution functions may lead to ambiguous information regarding the structural changes in the mixtures of different compositions. Thus, we employed a series of instruments of complex network analysis for the identification of the structural features in binary mixtures at various formamide mole fractions. These instruments include: (i) the distributions of molecules with different numbers of H-bonds, which yield a good representation of the local H-bond network topology; as well as (ii) the distributions of molecules having different number of molecules within their second order network neighborhood (includes the molecule itself, its immediate neighbors, and their neighbors), and (iii) the geodesic (the shortest contiguous H-bond path between any two molecules) distributions, both of which provide valuable information regarding the structure of the extended H-bond network beyond the immediate local environment of the molecular species in the liquid formamide-water mixtures.

2. Molecular dynamics simulations

Molecular dynamics trajectories were generated for liquid formamide-water mixtures, containing 0.00, 0.17, 0.33, 0.50, 0.67, 0.83, and 1.00 mol fraction of formamide (x_{FA}). Each simulation data consist of 1 ns production runs in NVE (microcanonical) ensemble

of a periodic box consisting of a total of $N = 216$ molecules, previously equilibrated for 0.5 ns in both NPT (isothermal-isobaric) and NVT (canonical) ensembles. The three-site TIP3P potential model [26] was employed for water. For the formamide molecule, the potential parameters were taken from the CHARMM General Force Field (CGenFF) [27]. Electrostatic interactions were modeled by a Coulomb potential and the long-range interaction was corrected by means of the Ewald method with precision of 10^{-6} . The van der Waals interactions were modeled by a Lennard-Jones 12-6 potential. After equilibration process, side length of each cubic simulation box reproduced the experimental densities measured at room temperature [28]. The box side length employed and the corresponding total and partial number densities for each production run are displayed in Table 1 as a function of formamide mole fraction.

All the MD simulations were performed at the target temperature of 300 K using the DL_POLY 4.07 [29] program. A 1 fs timestep was utilized and trajectories of each simulation were saved every 10 fs.

3. Results and discussion

3.1. Radial pair distribution functions

Site-site pair distribution functions, $g_{a-b}(r)$, were analyzed to gain general insight into the localized interactions, focusing mainly on the sites that participate in hydrogen bonding, in each simulated solution. Fig. 1 displays the formamide-formamide (FA-FA) $g_{a-b}(r)$ functions for O-HC and O-HT atom pairs, describing the FA structures hydrogen bonded through the *cis* (HC) and *trans* (HT) protons of FA (atom labels are shown in the scheme of FA molecule depicted in Fig. 1). Both pair distribution functions $g_{O-HC}(r)$ and $g_{O-HT}(r)$ have higher first peaks at higher FA mole fractions. However, the peak positions show negligible FA mole fraction dependence. Similarly, both distribution functions have their first minima located at around 2.7 Å, staying nearly unaffected by the change in FA mole fraction. We note that our FA-FA pair distribution functions are in good agreement with previous studies [23,25].

Water-water (W-W) $g_{a-b}(r)$ functions for O_w-O_w , O_w-H_w , and H_w-H_w atom pairs are depicted in Fig. 2. We observe significant increase in the peak heights with decreasing water mole fraction, suggesting enhanced correlation of water molecules for the lower water content mixtures. This trend is exactly opposite to that observed for the FA-FA $g_{a-b}(r)$ functions, where the peak heights decrease with decreasing FA mole fraction. The same trend (i.e. increase) in the peak heights of the water-water $g_{a-b}(r)$ functions with increasing solute content was previously observed in several studies of binary aqueous mixtures [30–34] and attributed to the structural enhancement of the water in these mixtures. However, this explanation, which is based on an interpretation of the radial distribution functions, contradicts the water structure obtained

Table 1

Total and partial number densities for the solutions studied (ρ) and the box length employed in each MD simulation (L).

x_{FA}	ρ^a (\AA^{-3})	ρ^b (\AA^{-3})	ρ_{FA}^b (\AA^{-3})	ρ_{W}^b (\AA^{-3})	L (\AA)
1.00	0.0151	0.0150	0.0150	–	24.312
0.83	0.0167	0.0165	0.0137	0.0027	23.590
0.67	0.0185	0.0183	0.0122	0.0061	22.776
0.50	0.0210	0.0207	0.0103	0.0103	21.867
0.33	0.0241	0.0237	0.0079	0.0158	20.898
0.17	0.0280	0.0279	0.0046	0.0232	19.783
0.00	0.0333	0.0339	–	0.0339	18.546

^a Experimental densities [28].

^b Densities observed after each MD equilibration.

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