Water-formamide mixtures: Topology of the hydrogen-bonded network ☆

Imre Bakó [a,*], Julianna Oláh [b], Anikó Lábas [b], Szabolcs Bálint [a], László Pusztai [c], Marie Claire Bellissent Funel [d]

[a] Institute of Organic Chemistry Research Centre for Natural Sciences, Hungarian Academy of Sciences, Magyar Tudósok körútja 2, P.O. Box 286, Budapest, Hungary
[b] Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, H-1111 Szent Gellért tér 4. Budapest, Hungary
[c] Institute for Solid State Physics and Opics, Wigner RCP of the H.A.S. H-1121, Budapest, Konkoly Thege út 29-33, Hungary
[d] Laboratoire Leon Brillouin, CEA-SACLAY 91191, Gif sur Yvette, Cedex, France

ARTICLE INFO

ABSTRACT

A neutron diffraction measurements and molecular dynamics simulations have been performed to study the hydrogen bonded structure of water-formamide mixtures. We showed that the calculated and measured total neutron diffraction radial distribution function agreed very well. After evaluation of this function, the hydrogen-bonded structure of mixtures with various compositions has been studied, and the clustering properties and the topology of the hydrogen-bonded network were investigated. The results show that these mixtures exhibit an extended range structure in solution. In water-formamide mixtures the average number of hydrogen bonded neighbors (water, formamide) and the distribution of the number of H-bonded neighbors do not change significantly as a function of the formamide mole fraction. Molecules are shown to form percolated networks at each concentration. The composition of cyclic entities in these systems is very close to being ideal; that is, these systems are microscopically homogeneous.

1. Introduction

It is known that hydrogen bonds (H-bonds) play important roles in a wide variety of complex materials, such as biological macromolecules or supramolecular systems (see, e.g. Refs. [1–12]. Amides are the simplest organic molecules that can be models of peptide bonds. Interactions between peptide groups play an essential role in shaping the structure and properties of biological systems, such as proteins and nucleic acids, as well as the behavior of many solvent systems. Hydration properties of amide groups during the folding process are leading factors for determining the secondary and ternary structure of proteins.

Formamide, H-CO-NH$_2$, is the simplest molecule containing an amide group that can represent a simplistic model of the peptide bond. The intermolecular structure of liquid formamide has been the subject of several theoretical and experimental studies (see Refs. [13–21]). It has been shown that a three-dimensional hydrogen-bonded network exists in liquid formamide, similar to that found in liquid water [14,17,21]. Additionally, it was suggested that the primitive ring distribution in liquid formamide and water are significantly different [21]; this statement was corroborated by static dielectric studies [13].

Interactions between water and formamide molecules have received a great deal of attention, too (see, e.g., Refs. [22–30]). One of the main conclusions of these studies was that, based on the structural parameters, these systems can be regarded as a prototype of an ideal mixture [22,24]. In contrast, Perera et al. revealed structural microheterogenities in aqueous amides [27]. Ladanyi et al. revealed that excess internal energy of mixing is a small positive value calculated from molecular dynamics simulations, and it agrees very well with the experimentally determined heat of mixing [31].

The structure of these systems at the molecular level can be described as a complex network. Which, in turn, may be characterized by its topological properties. Recently, we described the topology of hydrogen bonded aggregations in water [32] and pure liquid formamide [21], and we were able to detect a significant amount of structural microheterogenities in water/methanol mixtures [32].

The aim of the present study was to get new insight into the microscopic properties of formamide-water mixtures by characterizing their topological properties. First we carried out new neutron diffraction experiments on deuterated formamide-water mixtures and used it to evaluate the performance of the two interatomic potential models available for formamide in the literature [33–35]. Next, we applied graph theory adjusted for the study of hydrogen bonded networks in order to get a description of the topological properties of the H-bonded network in liquid water/formamide mixtures.

☆ Dedicated to Prof. Vojko Vlachy.
* Corresponding author.
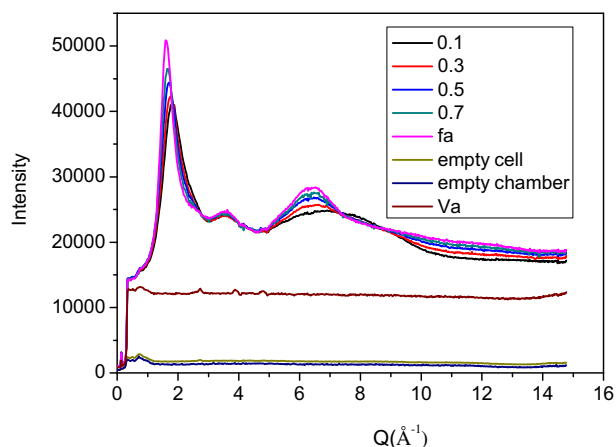E-mail address: bako.imre@ttk.mta.hu (I. Bakó).

Fig. 1. Experimental total scattering intensities for different formamide mole fraction values. Data are also given for the empty cell, empty chamber and for the vanadium bar.

2. Wide angle neutron scattering

Neutron diffraction experiments on fully deuterated liquid samples, with mole fractions of $DCOND_2$ x_{fa} = 0.1, 0.3, 0.5, 0.7 in D_2O, have been conducted on the hot-source diffractometer 7C2 of the Laboratoire León Brillouin (CEA Saclay, France). The liquids were placed in a vanadium container with diameters of 6 mm and wall thickness of 0.1 mm. The incident neutron wavelength was 0.70 Å. For standard correction and normalization procedures, additional runs (vanadium rod, cadmium rod, empty container and background) were also performed. Raw diffraction data were corrected for background, container- and sample absorption, and multiple scattering; intensities then were normalized by making use of scattering data on the vanadium rod sample. A more detailed description of the correction procedure can be found in Ref. [36–38]. Experimental total scattering intensities are given in Fig. 1, while neutron weighted total structure factors are provided in Fig. 2a (numerical data are available upon request from the authors).

The conversion of the observed interference function, $I(Q)$, to an r-space representation (i.e., the pair correlation function) is normally conducted by numerical Fourier transformation. This process leads to various inaccuracies arising from statistical fluctuations, limited Q-range and possible systematic errors in the original data sets. Here we apply a different approach to solve this problem, developed by Pusztai and McGreevy [39], called MCGR, which is an acronym for 'Monte Carlo treatment of the g(r)' function. This procedure uses an inverse approach in which the pair correlation function (total or partial) is generated numerically, and modified by a random process until its inverse Fourier transform $I(Q)$ agrees with the experimentally measured $I_{obs}(Q)$ within its errors. A more detailed description of the procedure is given in Ref. [40] and is also available from the World Wide Web [41].

The comparison of the measured total neutron structure factors for formamide-water mixture with those resulted at the end of MCGR procedure is given in Fig. 2a; agreement between MCGR model and experiment is excellent. The total radial distribution function and the corresponding water and formamide intramolecular contributions are shown in Fig. 2b.

3. Computer simulation details

We have performed classical molecular dynamics simulations in the NVT ensemble using the Nose-Hoover thermostat at an average temperature of 298 K on liquid formamide-water mixtures at formamide mole fractions of x_{fa} = 0.00, 0.10, 0.30, 0.50, 0.7, 0.90, 1.00. The simulations were performed with the six-site (i.e., 'all atom' type) OPLS [33,34] and Cordeiro [35] potentials for formamide; in both cases, SPC/E [42]

water was the solvent. Lorentz-Berthelot combining rules were applied to calculate the mixed potential terms. In all simulations the periodic cube contained 2048 molecules; side lengths of the cubes corresponded to the experimental densities) [43]. The corresponding box lengths are given in the Supplementary material. The timestep in every simulation run was 1 fs.

Short-ranged intermolecular potential interactions were truncated at half of the corresponding box-size. Periodic boundary conditions were employed and the Ewald summation was used to handle the long-range Coulomb interactions.

All simulations were performed using the DLPOLY 2.16 software [44]. After performing a 1 ns-long equilibrations, the trajectories were saved in every 1000 steps, and 10 ns of simulation times (altogether 10^4 structures for each system) were used for calculating the quantities of interest.

Average hydrogen bond number, N_{HB}, was calculated by averaging the number of hydrogen bonds over the trajectory and over all molecules.
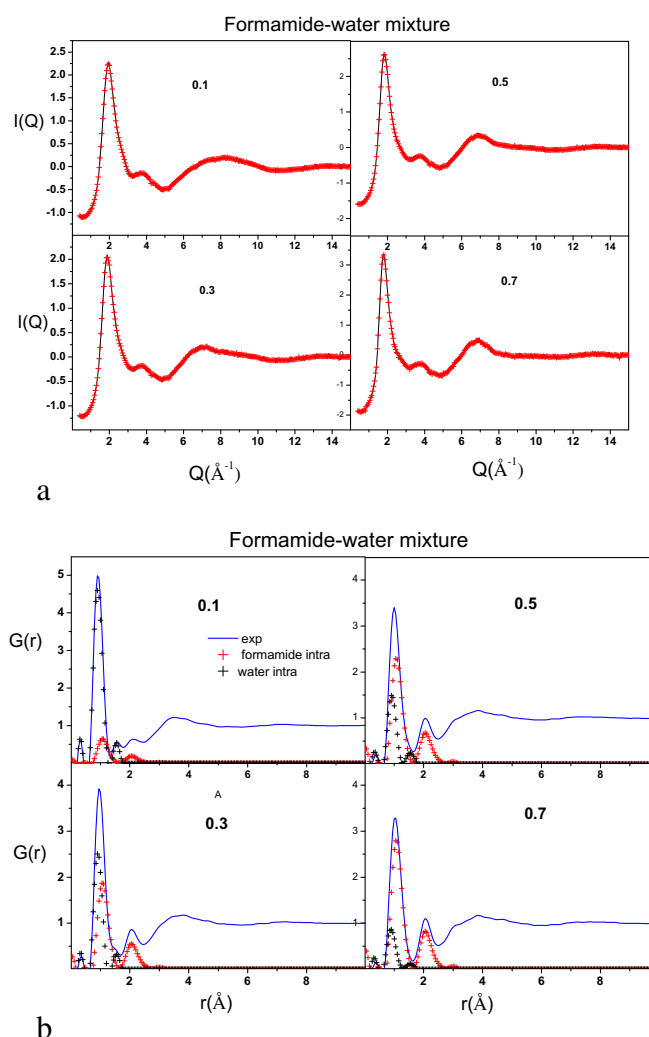

a

b

Fig. 2. a Comparison of the corrected total neutron structure functions (I(Q)) (dots) of liquid $DCOND_2/D_2O$ mixture x_{fa} = 0.10, 0.30, 0.50, 0.7 with those obtained after the MCGR procedure (full line). b. Total experimental neutron pair correlation function of liquid-liquid $DCOND_2/D_2O$ mixture x_{fa} = 0.10, 0.30, 0.50, 0. (full line) and Fourier transform of intramolecular contributions $I_M(Q)$ of water and formamide molecule to the total structure function (cross).