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The structure of water–methanol mixtures under an electric field: Ab initio molecular dynamics simulations

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ABSTRACT

Ab initio molecular dynamics simulations were employed to study the microstructure of water–methanol mixtures subject to external electric fields. The electric field has a complex effect on the hydrogen bond network in the mixtures. At low methanol concentrations the water molecules form a percolated network surrounding short chains of methanol molecules. At high concentrations the water and methanol molecules segregate forming two separate hydrogen bond networks. The application of the field affects the structural evolution of the hydrogen bond network and a surprising 'hollow channel' is formed in the methanol-rich mixtures when under moderate fields (~0.50 V/Å).

1. Introduction

It is well recognized that mixtures of methanol and water possess remarkably rich and complex structural and dynamical properties. The structural and dynamic properties of mixtures of these two molecules have been thoroughly studied both experimentally and with theoretical simulations [1–7]. The hydrogen bonding in liquid methanol is distinctly different from that in liquid water due to the presence of the hydrophobic methyl group. Previous X-ray, neutron diffraction, and Raman spectroscopy experiments have determined that liquid water has a uniform tetrahedral coordination, whereas liquid methanol forms linear hydrogen-bonded chains mixed with some ring structures [8–10]. However, there are no experimental studies providing an interpretation to these rings structures. Pure liquid water and neat methanol are two molecular systems which show high rates of proton mobility due to their hydrogen-bonded (H-bonded) network [4,11]. Meanwhile, early simulations of aqueous methanol led to the development of empirical potentials for Monte Carlo and classical molecular dynamics simulations [12–14] and also the inclusion of a dispersion-corrections and van der Waals interactions for ab initio molecular dynamics (AIMD) simulations [15–19].

Understanding the fundamental properties of water–methanol solutions is important for a wide range of chemical applications. Although methanol, in principle, may be mixed with water in any arbitrary ratio, there is experimental evidence that the mixing is incomplete at the molecular-level [5,20–22]. This is reflected in the much lower than expected entropy increase for an ideal or randomly mixed water–methanol solution. This has been attributed to the hydrophobic headgroups creating 'ice-like' structures in the surrounding water [23], or hydrophobic headgroups clustering in the solution [4]. Furthermore, previous experimental and theoretical studies indicate that at low methanol concentrations the mixture consists of two separate percolating hydrogen-bonded networks [6,24]. A recent broadband electric spectroscopy (BES) study has proposed a new picture: at dilute methanol concentrations the water molecules stabilize the chainlike methanol clusters; while at high methanol concentrations, the absence of any linear trend is observed [25]. Nevertheless, a detailed microstructural analysis of water–methanol mixtures under ambient conditions is unavailable. The application of an electric field to a molecular system may result in even more complicated scenarios. Understanding the changes to the hydrogen bonding structure induced by an applied field is crucial to areas such as electrochemistry and biology. However, as pointed out by Suresh and coworkers [26], this phenomena typically involves multiple factors including: dipole–dipole interactions and surface affects. Such complications have led to various ambiguous. Early X-ray scattering studies suggested that the water molecules are reoriented and ordered in layers near a charged surface with the H-bond networks being disrupted at the surface under an electric field of 10^9 V/m [27]. Early molecular dynamics simulations [28–32] and more recent work by Berkowitz and coworkers [33,34] determined that at high electric field strengths the H-bond network in water remains intact,

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Table 1
Parameters of the water–methanol mixtures used in this AIMD study.

Methanol mole fraction	# of water	# of methanol	# of density/ atoms (/^{3})	Supercell volume (Å^3)
0.00	48	0	0.1006	1430.0
0.20	38	10	0.0963	1807.6
0.40	29	19	0.0936	2147.5
0.60	19	29	0.0915	2525.1
0.80	10	38	0.0901	2864.9
1.00	0	48	0.0888	3242.5

although the water molecules are aligned along the direction of the field for strengths in the range of 1×10^{10}–4×10^{10} V/m. Very recently, Saitta et al. [35] using AIMD simulations reported on dissociation of water under an electric field (range 0–1 V/Å, 1.0 V/Å equals to 1×10^{10} V/m). Sun et al. [36] determined from their simulations that the H-bond structure in methanol is enhanced under a field of 1×10^{10} V/m. In contrast, Suresh and coworkers [26] suggested that the H-bond structure goes through a maximum as the field strength is increased. Thus, the understanding of the microstructural and dynamical properties of the H-bond network of either water or methanol when subjected to an electric field is not fully understood. To our knowledge there are no investigations reporting the effects of an applied electric field on water–methanol mixtures.

We have undertaken AIMD simulations on pure water, neat methanol, and water–methanol mixtures under an electric field. Without the influence of a field, we confirmed that water–methanol mixtures are indeed not ideally mixed at both low and high methanol concentrations. This is attributed to the hydrophobic alkyl group of methanol. However, when an electric field is applied, these two molecules show a dissimilar response to the field as they have different dipole moments and alignment (the dipole moments of water and methanol are 1.85 and 1.69 D, respectively). At a threshold of 0.50 and 1.0 V/Å, the methanol and water molecules, respectively, dissociate.

We found that the electric field has a complex effect on the hydrogen bond interactions in the H_2O—CH_3OH mixtures. Although the calculated hydrogen bond numbers show limited improvement upon applying an electric field, the mixtures show different hydrogen bond interactions at different concentrations. And only in methanol-rich mixtures ($X_M = 0.80$), a hollow channel structure is formed when under moderate electric field ($E = 0.50$ V/Å). Most of this long hollow channel structure is aligned along the field direction and is disrupted under a strong electric field ($E = 1.00$ V/Å) due to dissociation of the molecules. We suggest that this new found hollow channel structure may explain the reported abnormalities in the thermo-physical properties of water–methanol mixtures.

2. Methodology

Density functional theory (DFT) based AIMD simulations in the canonical ensemble (NVT) were performed as implemented in the Vienna Ab Initio Simulation Package (VASP) [37,38]. The structural parameters used in the simulations of pure water, pure methanol, and the water–methanol mixtures are collected in Table 1. For pure methanol, 48 methanol molecules were placed in a periodic tetrahedral supercell (with a size of 12.2 Å × 16.3 Å × 16.3 Å) reproducing the experimental density of 0.79 g/cm^3 at ambient conditions. For pure water, 48 water molecules were put in a periodic supercell with size of 9.3 Å × 12.4 Å × 12.4 Å, corresponding to an ambient density of 1.00 g/cm^3.

The simulations were performed using the projector augmented-wave (PAW) method and the electronic subsystem was sampled at the Γ-point of the first Brillouin zone with a plane wave cutoff of 400 eV. The generalized gradient approximation in the Perdew–Burke–Ernzerhof functional (GGA-PBE) [39] was utilized for the exchange-correlation functional. The forces were relaxed to meet the convergence criteria of 10^{-4} eV. In the molecular dynamics simulations, the supercell was heated up to 300 K via repeated velocity rescaling for 1 ps with a time step of 0.5 fs. The supercell was then equilibrated at 300 K in the NVT (canonical) ensemble for 5 ps with the same time step. In the production runs, the supercell was equilibrated at 300 K in the NVT ensemble for 15 ps. Simulations of the water–methanol mixtures were performed at four concentrations: $X_M = 0.20$, 0.40, 0.60, and 0.80 (see Table 1). The finite applied electric field ranged from 0.0 to 1.0 V/Å at an interval of 0.25 V/Å (1.0 V/Å equals to 1×10^{10} V/m).

Normally the trajectory length and system sizes in AIMD studies are limited due to computational cost. We carefully checked the literature and found that the trajectory length and system sizes in the current study are comparable to previous AIMD studies. The supercell size (for pure water, 400 atoms in a 9.3 Å × 12.4 Å × 12.4 Å tetrahedral cell) and the length of the production runs (15 ps) in current AIMD simulations are probably sufficiently long to examine the local atomic structures of well-equilibrated water–methanol mixtures. However they may not satisfy the requirement of extracting dynamical information concerning ion transport. In a future study, we will increase the trajectory length and system size to examine proton transport in these mixtures. In particular, we are currently studying the length scale of the hollow channel, which is crucial in judging the feasibility of a channel-mediated proton transport mechanism.

3. Results and discussions

3.1. Pure water and methanol

As a first step in our simulations we sought to accurately reproduce the structures of single water and methanol molecule. Each molecule was placed in a cubic cell and equilibrated at 0 K. We found that the calculated structures of both molecules are consistent with prior results. The bond distances (Å), bond angles (°) of a methanol molecule at 0 K are collected in Table 2. Our results are in good agreement with prior experimental and computational results [40–43] with the exception of the C—O bond length which is slightly (0.025) longer.

The structural parameters of neat liquid methanol and pure water at 300 K were analyzed from the AIMD simulations. Note that the intramolecular contributions of the radial distribution functions (RDFs) are not excluded in this study. The RDFs for the O—O in liquid methanol and water are shown in Figure 1. For liquid

Table 2
Calculated bond distances (Å), bond angles (°) for a single CH_3OH at 0 K by first principles methods. H_a represents in-plane hydrogen atom, H_b represents out-of-plane hydrogen atom.

Method	r (OH)	r (CO)	r (CH$_a$)	r (CH$_b$)	∠ (COH)	∠ (OCH$_a$)	∠ (OCH$_b$)
DFT-GGA (this study)	0.986	1.442	1.098	1.104	107.2	107.7	111.3
DFT-GGA [40]	0.980	1.420	–	–	111.7	111.2	112.2
DFT-GGA [41]	0.970	1.442	1.095	1.100	108.8	106.1	111.7
HF [42]	0.938	1.395	1.080	1.086	110.0	107.4	112.0
Exp. [43]	0.981	1.417	1.094	1.094	108.0	107.2	111.9