Temperature-induced changes in the hydrogen-bond network of isopropanol-water mixtures at low isopropanol concentration

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Isopropanol-water mixtures have attracted a continuous interest thanks to their anomalous behaviour in many aspects (thermodynamic and transport properties, diffusion coefficient, compressibility, viscosity). These features are reflected their non-trivial liquid-phase diagram as well. In these systems, hydrogen bonds play a fundamental role. By means of monitoring of their changes as a function of temperature can elucidate the freezing process at the molecular level.

For this purpose, we have performed a series of Molecular Dynamics simulations for isopropanol–water mixtures with 5, 10 and 20 mol% isopropanol content for reproducing X-ray diffraction data [1] at the available temperatures: 298 K and 268K (for x=0.05); 298 K, 268K and 263K (for x=0.1); 298 K, 268K, 263K and 258K (for x=0.2). For isopropanol the All-Atom Optimized Potential for Liquid Simulations (OPLS-AA) [2] has been used in each calculation. In order to find the potentials that provide the best agreement with experimental total scattering X-ray structure factors [1] we have applied two different water force field, the Extended Simple Point Charge model (SPC/E) [3] and the improved Transferable Intermolecular Potential with four Particles (TIP4P-2005) [4].

The resulting MD trajectories have been analysed to reveal the hydrogen-bond network. Two molecules are considered to be hydrogen-bonded to each other if they are found at a distance $r(O\cdots H) < 2.5$ Å, and the interaction energy is smaller than −12 kJ/mol. [5]
Average number of hydrogen bonds/molecule as a function of composition and temperature has been calculated. Fractions of ethanol molecules as H-acceptors and as H-donors in the H-bonds have been identified. Observable trends on varying the temperature have been revealed in terms of size distributions of cyclic entities. [6] Furthermore, dynamical properties have been investigated. [7]

References

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