ELSEVIER

Chemical Physics 260 (2000) 159–182

Chemical Physics

www.elsevier.nl/locate/chemphys

Intermolecular potential for benzoic acid–water based on the test-particle model and statistical mechanical simulations of benzoic acid in aqueous solutions

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Received 5 May 2000

Abstract

Structures and interaction energies of benzoic acid–water (BA–H_2O) 1:1, 1:2, 2:1 and 2:2 complexes were investigated using intermolecular potentials derived from the test-particle model (T-model). The absolute and some lowest-lying minimum energy geometries of the 1:1 and 1:2 complexes were examined using ab initio calculations with the Hartree–Fock (HF) and the second order Møller–Plesset (MP2) perturbation theories. The T-model, HF and MP2 calculations revealed that cyclic arrangements of hydrogen bonds (H-bonds) between the COOH group and H_2O represent the absolute minimum energy geometries of the 1:1 and 1:2 complexes. The results on the 2:1 and 2:2 complexes showed that the cyclic H-bonds in the dimers could be opened to allow insertion of water molecules. Based on the T-model potentials, aqueous solutions of BA and $(BA)_2$ were investigated by conducting a series of molecular dynamic (MD) simulations. It was found that, except at the solute–solute H-bonds, the hydration structures of the cyclic H-bond planar (CHP) and side-on type (SOT) dimers are not substantially different from a single BA. The atom–atom pair correlation functions ($g(R)$) derived from MD simulations suggested that, in very dilute aqueous solution, the cyclic H-bonds in the CHP and SOT dimers are not stable and can be disrupted by the solute–solvent H-bond interaction and thermal energy fluctuation.

Keywords: Ab initio; T-model; Benzoic acid; Dimer; Aqueous solution