Thermodynamics and Structure of Molecular Clusters in Supercritical Water

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The formation of small hydrogen-bonded molecular clusters in supercritical water has recently attracted significant attention. The cluster formation results in local structural and density heterogeneity in the fluid. Thus, topologically different H-bonded water clusters may even be considered as distinct chemical species. Quantitative description of the thermodynamics and structure of such clusters is important for many fundamental and practical reasons. We applied Monte Carlo and molecular dynamics computer simulations to quantitatively analyze the statistics of size, topology, and energy distributions of H-bonded water clusters over wide ranges of near- and supercritical temperatures and densities. The extent of hydrogen-bonded cluster formation in supercritical water has been explored by application of a hybrid geometric and energetic hydrogen-bonding criterion to the analysis of computer simulation results. Relative abundance and geometric and energetic characteristics of topologically different trimers, tetramers, and pentamers were examined in detail. In contrast to many *ab initio* results, our simulations demonstrate that open chain- and tree-like clusters are preferentially formed in supercritical water, while cyclic ring-like structures occur only rarely. These findings clearly indicate that not only energetic, but also entropic effects play significant role in determining the stability and abundance of particular cluster types in supercritical water. Partitioning of molecules between clusters of the same size, but topologically different structure is found to be virtually independent of temperature and density. Geometric and energetic characteristics of small hydrogen-bonded clusters in supercritical water vary only slightly with temperature and density.