

Vapor–Liquid Interfacial Properties of Mutually Saturated Water/1-Butanol Solutions

Bin Chen,^{1,2} J. Ilja Siepmann,² and Michael L. Klein¹

¹*Center for Molecular Modeling and Department of Chemistry,
University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104-6323*

²*Department of Chemistry and Department of Chemical Engineering and Materials Science,
University of Minnesota, 207 Pleasant Street SE, Minneapolis, MN 55455-0431*

Abstract

Adsorption and ordering at the vapor–liquid interfaces of *mutually saturated* water/1-butanol solutions at a temperature of 298.15 K were investigated using configurational-bias Monte Carlo simulations in the Gibbs ensemble and compared to the surface properties of neat water and 1-butanol liquids. A dense 1-butanol monolayer is observed at the surface of the water-rich phase which results in a substantial decrease of its surface tension. In contrast, there is no enrichment of water molecules at the surface of the butanol-rich phase and its surface tension is not significantly changed. Analysis of the interfacial structures reveals that these systems exhibit orientational ordering and composition heterogeneity. Analysis of the hydrogen-bonding distributions suggests that the formation of the 1-butanol monolayer is driven by an excellent match between water and the primary alcohol, that is, additional hydrogen bonds are formed between the excess free hydrogens of surface water and the excess hydrogen-bond acceptor sites of 1-butanol.