**Excess Thermodynamic Properties of Binary Liquid Mixtures of Butanol Isomers with Di-*n*-Butyl Ether at 298.15 K, 0.1 MPa**

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Binary liquid mixtures of alcohols and ethers are of importance as potential biofuels or additives for internal combustion engines,1 and have also attracted fundamental interest as model liquid systems containing one component (the alcohol) that can strongly self-associate through hydrogen bonding (HB), and one that cannot self-associate *via* HBs (ether), yet can interact strongly with the former as HB acceptor.2 The excess thermodynamic properties of these mixtures, specifically the excess molar enthalpies and volumes (*H*E and *V*E), have been extensively measured.1-3 Butanol isomer + di-*n*-butyl ether (DBE) binary mixtures, in particular, show interesting volumetric differences, with *V*E changing from negative (1- and *iso*-butanol) to positive (2- and *tert*-butanol) with increasing butanol alkyl group branching. Representative 1- and 2-butanol + DBE mixtures were studied, for the first time, by atomic-resolution classical Molecular Dynamics (MD) computer simulations. The simulations reveal decided differences in the degree of self-association of the two butanol isomers and support existing interpretations of the *H*E and *V*E in a general sense, but also suggest that more subtle differences in H-bonded topologies may contribute significantly to the anomalous volumetric properties of these mixtures.4

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| **Fig. 1.** MD computer simulation configurations of *equimolar* mixtures of 1- or 2-butanol with DBE. Ether molecules are omitted and hydroxyl (-OH) groups shown using a space-filling (red and white spheres) representation in order to highlight the differences in HB topologies. Simulation cell edges are shown in blue. |

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