Spectroscopic Quantification of Hydrogen Bonding for Improved Phase Equilibrium Models

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With the renewed interest in biorenewable materials, advances are needed in the understanding and modeling of intermolecular interactions, such as hydrogen bonding. Thermodynamic models such as SAFT, CPA and ESD have gained prominence by explicitly representing hydrogen bonding. Unfortunately, attainment of association parameters is not straight forward. Spectroscopic methods such as FTIR can provide insight; however, resulting parameters are largely dependent on the range of experiments and the method of interpretation. To address this issue, we have developed an improved method to obtain a functional relationship between concentration and absorbance, which satisfies the Beer's law expression across a range of temperatures and concentrations. The new method quantifies the entire hydroxyl stretch region over the temperature, and concentration ranges studied and provides a distribution of different hydrogen bond types in liquids. Recently, we have leveraged this spectroscopic insight to provide association parameters for an activity-coefficient-based model based on Wertheim statistical mechanics. We discuss the fitting of the TPT1, RTPT, and TPT2 theories to the spectroscopic data for several alcohols and demonstrate phase equilibria modeling. The combination of spectroscopy and thermodynamic modeling produces improved phase behavior predictions for alcohol + hydrocarbon systems and provides fundamental insight into association at the molecular level.