

Spectroscopic Quantification of Cooperative Bonding of Alcohols

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Wertheim TPT-1 theory using a single association strength for alcohols provides the basis of modern equations of state such as the SAFT, ESD and CPA equations of state. Typically, the association strength parameters are inferred via fitting of pure component density and vapor pressure data. Spectroscopic measurements of the hydroxyl stretch in solutions of various alcohol concentrations provide experimental evidence of association, but challenges of interpretation have hindered the application of spectroscopy for association parameter regression. Association causes a shifting of absorbance to lower wavenumbers and a significant increase in absorbance intensity. As temperature changes, the distribution of bonded species changes, resulting in a significant temperature dependence of the integrated area of the hydroxyl region. Using trends from quantum calculations, we developed an attenuation coefficient function that provides a scaling of the hydroxyl absorbance region.¹ After scaling, the integrated area is independent of temperature. Using curve fitting, populations for hydroxyls on the chain ends and the center of chains can be estimated independent of an association model. The method has been applied to a series of alcohols, demonstrating that two association strengths of Resummed Thermodynamic Perturbation Theory (RTPT)² are required to fit spectroscopic data.^{3,4} The populations of hydrogen bonds predicted by the model are in good agreement with the curve fits of the spectra.³ TPT-1 is incapable of fitting the spectra. For methanol and ethanol, the measurements and model are consistent with literature measurements of pure alcohol absorbance. Phase equilibria modeling with using RTPT is superior to use of TPT-1 and implements the same number of adjustable parameters. The RTPT model of infinite dilution activity coefficients and infinite dilution partial molar enthalpies approach infinite dilution differently than TPT-1 and are consistent with the limited experimental data available in the dilute region.

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