SPECTROSCOPY OF ASSOCIATING SYSTEMS: LEVERAGING MOLECULAR INSIGHT TO IMPROVE THERMODYNAMIC MODELING

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ABSTRACT

Revitalized interest in biorenewable materials has revealed some accompanying challenges. For example, many compounds of interest, such as alcohols, are polar and readily self-associate, causing them to behave in a non-ideal manner. Equations of state (EOSs) such as the statistical associating fluid theory (SAFT), cubic plus association (CPA), and Elliot-Suresh-Donohue (ESD) are attractive options for modeling because they explicitly account for hydrogen bonding. However, these EOSs are typically parameterized by fitting macroscopic pressure-volume-temperature data, a practice that ignores molecular measurements of the bonding. Advancing the predictive power of thermodynamic models for polar systems requires molecular-level awareness, which can be provided by spectroscopy.

This work implements variable-temperature infrared spectroscopy guided by insight from computational quantum mechanics to quantify the extent of hydrogen bonding in alcohol + cyclohexane systems based on the alcohol's hydroxyl stretching vibration. A new scaling technique is developed that provides for the first time a temperature-independent integrated area for the hydroxyl stretching region. For further validation of the new scaling method, the scaled infrared spectra are correlated to the nuclear magnetic resonance spectra for 1-butanol + cyclohexane and 2-propanol + cyclohexane using quantum calculations with minor empirical adjustments. The infrared measurements are used to parameterize two association constants for each binary system, which are implemented in a new activity coefficient model based on the resummed form of Wertheim's perturbation theory (RTPT). The widely used implementation of one association parameter for each binary (TPT-1) in PC-SAFT, CPA, and ESD is shown to be inadequate for fitting the spectroscopic data.

The RTPT model succeeds in recovering the hydroxyl bond type distributions from the infrared measurements. When the association constants from spectroscopy are applied to the modeling of phase equilibria, association is demonstrated to be the dominant contribution to solution non-ideality. When combined with combinatorial and residual models, RTPT provides an improved representation of experimental phase equilibria and excess enthalpies when compared to the TPT-1 model.

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CHAPTER 1: Introduction

1.1 Significance and Overarching Objective

Hydrogen bonding is a complicated molecular phenomenon which affects macroscopic vapor pressure and thermodynamic mixture properties. While not as strong as a covalent bond, the cumulative molecular attractive effects of hydrogen bonding are significant and result in non-ideal behavior at the macroscopic level. A unifying thermodynamic theory capable of bridging the microscopic and macroscopic length scales remains elusive. The challenge of leveraging a molecular understanding of association for the prediction of bulk properties has created an intellectual gap between fundamental chemistry and engineering applications.

This failure to reconcile molecular phenomena with macroscopic properties extends beyond the laboratory, affecting industry as well. Computer simulators used to design and operate separations processes struggle to model vapor-liquid equilibrium data for associating systems accurately.¹ Furthermore, the thermodynamic models underpinning these simulators suffer from limited predictive power, due in part to their reliance on fitted parameters which lack a sufficient connection to the fundamental chemistry occurring in these systems. This limitation is especially unsettling for industry, considering that these processes are often highly energy and financially intensive, constituting up to 33% of industrial operating costs.²

Because of this, hydrogen bonding is deserving of study not merely to expand fundamental understanding at the molecular level, but also with the intent of improving thermodynamic modeling capabilities. In short, a firm understanding of the molecular level is necessary to make meaningful and informed predictions of macroscopic properties.

1.2 Association: A Molecular Approach

In its most basic form, hydrogen bonding is a short-range and directional interaction that originates from the covalent bond between a proton and electronegative heteroatom. The polarization due to the large difference in electronegativity of the atoms results in the hydrogen atom having a partial positive charge and thereby facilitating interactions with neighboring molecules with electronegative atoms or unsaturated bonds.³ Hydrogen bonds are characterized by the angle created by the proton and the two electronegative atoms on either side. Stronger hydrogen bonds are correlated with increased hydrogen bond linearity.⁴

Hydrogen bonding can occur within the same molecule (*intramolecular*) or between neighboring molecules (*intermolecular*). When molecules hydrogen bond intermolecularly with other molecules of the same species, it is referred to as self-association as opposed to cross-association, which occurs between dissimilar species. Cross-association is also described as 'solvation' in the engineering literature, but the term has become less favored recently to avoid confusion with the other meanings of the term. Compounds can also be classified by their degree of participation in hydrogen-bonding. Examples are provided in Table 1-1. Hydrogen-bond-donors contain a proton that is covalently bound to an electronegative atom such as oxygen, whereas hydrogen-bond-acceptors typically contain electron lone pairs or π -electrons.

Туре	Description	Examples	
Ι	molecules with one or more donor groups and no acceptor groups	haloforms, highly halogenated compounds, acetylenes, protonated amines, heteroaromatics	
II	molecules with one or more acceptor groups and no donor groups	ketones, ethers, esters, olefins, aromatics, tertiary amines, nitriles, isonitriles	
III	molecules with both donor groups and acceptor groups	water, alcohols, phenols, inorganic and carboxylic acids, primary and secondary amines	
IV	molecules with neither donor nor acceptor groups	saturated hydrocarbons, carbon tetrachloride, carbon disulfide	

Table 1-1: Hydrogen bonding classifications (adapted from Pimentel and McClellan⁵).

For self-associating molecules of Type III, such as alcohols, hydrogen bond types can be classified according to their participation in hydrogen bond networks. Literature has identified the following hydroxyl types, which are presented in Figure 1:^{6–8} Alpha hydroxyls (α) correspond to unassociated monomers. Beta hydroxyl sites (β) participate in hydrogen bonding by accepting a hydrogen bond through the oxygen lone pairs. Like the isolated alpha hydroxyls, beta sites have an unassociated O-H bond. Gamma hydroxyls (γ) participate only as hydrogen bond donors and remain unassociated at the oxygen. Delta hydroxyls (δ) participate both as hydrogen bond donors and acceptors. Less common are eta hydroxyls (η) and zeta hydroxyls (ζ) both of which accept hydrogen bonds on each of the lone pairs. However, they differ in that eta bonds also donate a hydrogen bond at the proton.



Figure 1-1: Specific hydrogen bonding environments for alcohols and their corresponding covalent bonds. Alpha hydroxyl sites (α -black) are associated with alcohol monomers. Beta sites (β -blue) and gamma sites (γ -red) are located on the ends of polymeric chains. Beta receives a hydrogen bond whereas a gamma O-H donates a hydrogen bond. Delta hydroxyls (δ -green) receive and donate a hydrogen bond. Eta hydroxyls (η -purple) and zeta hydroxyls (ζ -orange) each receive two hydrogen bonds; however, eta differs in that it also donates a hydrogen bond.

Because of their ability to donate and receive hydrogen bonds, self-associating liquids are capable of forming complex frameworks including linear chains,⁹ rings,¹⁰ coils,¹¹ and supramolecular structures.^{12,13} The population of specific oligomers depends on the molecular structure, temperature and pressure, as well as the concentration.^{14,15} For alcohols, the most notable structure is the dimer, which early literature deemed unique from other oligomerizations. This consideration of uniqueness was rooted in the idea that the dimer was likely a cyclic structure whose polarized electron pairs enhanced the strength of subsequent additions.^{16,17} Van Ness et al. proposed that cyclic oligomerizations beyond that of the dimer were unlikely due to the fast exchange rate of hydrogen bonds,¹⁴ which occur in the order of 10⁻¹² s as reported by pump-probe infrared spectroscopic measurements.^{18,19}

Debate remains as to the prominence of linear versus cyclic structures.²⁰ Infrared experiments on ethanol in carbon tetrachloride conducted by Schwager et al. suggested that linear

structures predominate.²¹ More recent spectroscopic work performed on ethanol + cyclohexane has suggested that cyclic trimers and tetramers dominate at higher alcohol concentrations.²² Viscosity measurements provide a conflicting description and instead suggest that cyclic structures predominate in alcohols.²³ Those findings contradict the results of some molecular dynamics calculations which support chain polymerization for primary alcohols.^{24,25} Lack of a consensus indicates that experiments directed at unraveling alcohol speciation could provide meaningful clarity.

1.3 Measuring Association: Infrared Spectroscopy

1.3.1 Light and the Infrared Region

Light is an optical phenomenon possessing the characteristics of a wave and a particle, also known as a photon. We now understand that the visible light we perceive constitutes only a fraction of the entire electromagnetic spectrum, which spans from ultra-high-frequency gamma rays to low-frequency radio waves. Light is a powerful tool for the interpretation of molecular behavior. Of particular interest are light frequencies in the infrared region of the electromagnetic spectrum. This region is further subdivided into the far-infrared (14.3-50 μ m), mid-infrared (2.5-15 μ m), and near-infrared (0.7-2.5 μ m). Light absorption from the far-infrared spectrum induces excitation in the rotational states. In contrast, radiation from the mid and near-infrared region is responsible for the vibrational excitation of covalently bonded groups of electrons.²⁶ This work will focus our attention on light from the electromagnetic spectrum's mid-infrared (fundamental infrared) region. The near infrared region corresponds to overtones of the fundamental vibrations.

1.3.2 Molecular Vibrations and Infrared Absorption

From classical electrodynamics, it is understood that for a molecule to absorb radiation, two criteria must be satisfied: (1) the frequency of the vibrational oscillation must exactly match that of the incoming radiation, and (2) the vibration must be accompanied by a change in either or both the magnitude or the direction of the dipole moment.^{27,28}

The first criterion is necessary for a chemical bond to interact with the irradiating light. Like many molecular phenomena, interatomic vibrations are quantized. Absorption of a photon of the correct energy excites a vibrational mode in a molecule from the ground state to a higher vibrational quantum state. Excitation requires a photon of the same frequency as the chemical bond's vibration which therefore bridges the gap between the vibrational quantum levels matches exactly according to Bohr's frequency condition $\Delta E = hc\tilde{v}$. The light that misses this resonant condition is transmitted unchanged.

The second condition is slightly more nuanced than the first. The vibration of the bond creates a change in the molecular dipole moment and produces an alternating electric field that fluctuates at a frequency equal to the vibrational frequency. During vibration, coupling occurs between changes in the charge distribution of the bond and the oscillation of the incident infrared electromagnetic field.²⁹ This coupling allows the photons to transfer energy to the vibration increasing its amplitude. The intensity of that absorbance is directly proportional to the rate of change of the electrostatic dipole moment with the oscillatory amplitude; in general, the more significant the gradient in the dipole moment with amplitude, the more intense the absorbance. This effect is readily observed for the hydrogen bonding of the hydroxyl group which introduces a noticeable change in the dipole moment.³⁰

1.3.3 The Beer-Lambert-Bouguer Law

A quantitative understanding of the associating species is necessary for a complete description of hydrogen bonding and careful parameterization of thermodynamic models. To quantitatively utilize the absorbance spectrum of a chemical compound we need to correlate the concentration of a specific type of chemical bond with its absorbance signal. The Beer-Lambert-Bouguer law (BLBL) provides such a relationship.

Consider a sample container with parallel faces which contains an absorbing species that is being irradiated by a monochromatic source. If we neglect reflective losses at the interfacial surfaces due to differences in the refractive index, it is evident that the intensity of the incident beam (I_0) will decrease as it proceeds through the sample. The reduction in the number of photons passing through a differential slice of the sample per unit time is proportional to the number of photons available for absorption and the concentration of the absorbing species. The change in radiant power of monochromatic radiation (dP), which is absorbed at a specific level (P), can be related to the number of absorbing molecules in a slice of the sample (da) by a proportionality factor (k) via Eq. 1-1.

Rearrangement and applying the limits of integration produces Eq. 1-2 and Eq. 1-3, respectively.

$$\int_{P_0}^{P} \frac{dP}{P} = -k \int_0^{N} da \qquad \qquad \text{Eq. 1-2}$$

where:

$$P_0$$
 = the radiant power of the incident radiation
N = the number of absorbing molecules in the beam per area

$$\ln \frac{P}{P_0} = -kN$$
 Eq. 1-3

Removing the negative sign by inverting the logarithmic term leads to Eq. 1-4.

$$\ln \frac{P_0}{P} = kCl$$
 Eq. 1-4

Converting from natural to common logarithms facilitates quicker quantification of changes in orders of magnitude. In this form, *k* is replaced with the molar attenuation coefficient $\left(\epsilon, \left[\frac{dm^3}{mol \cdot cm}\right]\right)$ and the ratio of $\log \frac{P_0}{P}$ is defined as the absorbance (*A*, [*A*. *U*.]) resulting in the BLBL expression (Eq. 1-5).

$$\log \frac{P_0}{P} = A = \epsilon Cl$$
 Eq. 1-5

The power of this relationship lies in its simplicity and applicability; however, quantification of the absorbing species concentration at a particular wavenumber relies on knowledge of the sample path length and the molar attenuation coefficient. While the path length is constant for a given measurement, there is a variation in the molar attenuation coefficient as a function of wavenumber.

The ability of a particular covalent bond-type to absorb radiation of a certain wavelength is an intrinsic property and its propensity to vibrational excitation is expressed in the molar attenuation coefficient. Though peak height was originally used to quantify the molar attenuation coefficient, more recent work has suggested that peak area is a more accurate means of establishing the relationship between absorbance and concentration. This is straightforward for isolated vibrations, but the process becomes more nuanced when vibrational resonances have significant overlap, as in the case of hydrogen bonding involving hydroxyl groups. This issue will be discussed in more detail in future chapters. To summarize: Uncertainty in the attenuation coefficient has hampered quantification efforts directed at alcohol hydrogen bonding and, until recently, has impeded meaningful progress in the area.

The molar attenuation coefficient is easily determined for materials that do not selfassociate by plotting their absorbance versus concentration at a constant pathlength. The slope of such a plot is taken as the molar attenuation coefficient for that material. In the case of selfassociating materials, such as alcohols, the quantification process is not as straightforward. Hydrogen-bonding strongly influences the electronic character of covalent bonds, causing large changes in their transition dipole moments.³¹ For alcohols, this manifests as broadening and redshifting of the hydroxyl stretching frequency, accompanied by an increase in absorbance.^{14,32}

The difficulty in describing the wavenumber dependence of the molar attenuation coefficient have limited accurate quantification of the hydroxyl region. Prior works have attempted to circumvent this issue by assuming molar attenuation coefficients are constant for all oligomers. However, quantum calculations and numerous observations suggest that this assumption is likely incorrect.³³ A more fruitful method was described by Asprion et al., where equilibrium constants were simultaneously determined in conjunction with the molar attenuation coefficients for the monomer, dimer, and polymer, under the assumption of a 1,2-n association model.³⁴ However, the work herein shows that the dimer/polymer attribution of attenuation coefficients is flawed and develops a new method for quantification of hydrogen bonds and the distribution of hydrogen bond configurations.

1.4 Modeling Association

1.4.1 Activity Coefficients

Phase behavior is governed by the Gibbs energy, G, which is a combination of enthalpy, H, and entropy, S, namely G = H - TS. Hydrogen-bonding, much like a chemical reaction, contributes to both the enthalpy and entropy. The behavior of species in a mixture is determined by the chemical potential, which is a defined quantity determined by the composition derivative of the extensive Gibbs energy of a system. Analogous to potential energy for mechanical driving forces, chemical potential is an indicator of the direction of change that a system will take based on chemical driving forces. Since chemical potential is a gradient quantity, it is important to

understand that the chemical potential exists relative to a standard state, μ_A^o . The standard state is selected by the practitioner, though process design conventions typically use the pure fluid at the same temperature and pressure as the mixture. Integration of the chemical potential from the standard state to the mixture state is quantified by the activity of the species in solution, $a_i = x_i \gamma_i$, where x_i is the mole fraction of the component and γ_i is the corresponding activity coefficient.

$$(\mu_i - \mu_i^o)/(RT) = \ln x_i \gamma_i$$
 Eq. 1-6

The activity acts as a unitless "correction" measure of the chemical potential relative to the pure component when the pure standard state is used. For an ideal solution relative to the pure component standard state the mole fraction is the activity ($\gamma_i = 1$). The Gibbs energy of mixing is the Gibbs energy of the mixture relative to the mole fraction weighted Gibbs energies of the components. For an ideal solution, the Gibbs energy of mixing (ΔG_{mix}^{is}) is

$$\frac{\Delta G_{mix}^{is}}{RT} = \sum_{i} \ln x_i$$
 Eq. 1-7

The activity coefficient is influenced by phenomena such as the aggregatory behavior in alcohols. Aggregation reduces the effective number of particles in the solution so the monomer activity requires a chemical potential correction due to intermolecular interactions and the related entropy and enthalpy of association.³⁵ Capturing this non-ideal behavior is important for the design and operation of unit operations such as distillation and extraction.

1.4.2 Modeling Considerations

It is well understood that association causes deviations from ideal behavior, which is reflected in the vapor-liquid-equilibrium (VLE) data of these systems. To capture these deviations, Raoult's Law can be modified to include a fugacity coefficient (φ_i) and an activity coefficient (γ_i).

Deviations from ideal gas behavior are described by the fugacity coefficient, whereas an activity coefficient is included to capture departures from ideal solution behavior.

$$y_i \varphi_i P = x_i \gamma_i \varphi_{pure\ i}^{sat} P^{sat} \exp\left(\frac{V^L(P - P^{sat})}{RT}\right)$$
 Eq. 1-8

This work models non-idealities with a "gamma-phi" approach, which involves the modeling of the component activity coefficients. When the standard state is taken as the pure component at the same temperature and pressure as the mixture, from Eq. 1-9 and Eq. 1-10 it can be seen that the activity coefficient is related to the excess Gibbs energy per mole of the mixture (G_{Mix}^E) , where n_i and n_T are the moles of component *i* and the total number of moles, respectively.³⁶ The excess Gibbs energy is the difference between the Gibbs energy of the mixture and the Gibbs energy of an ideal solution.

$$n_T G_{Mix}^E = RT \sum_i n_i \ln(\gamma_i)$$
 Eq. 1-9

$$RT\ln(\gamma_i) = \left(\frac{\partial n_T G_{Mix}^E}{\partial n_i}\right)_{T,P,n_i(j\neq i)}$$
Eq. 1-10

Bala and Lira illustrated that a component's activity coefficient arises from the contribution of three separate terms: the combinatorial (γ_i^{comb}), the residual (γ_i^{resid}), and association (γ_i^{assoc}).³⁷ Logarithms allow the contributions to be summed as seen in Eq. 1-11.

$$\ln(\gamma_i) = \ln(\gamma_i^{comb}) + \ln(\gamma_i^{resid}) + \ln(\gamma_i^{assoc})$$
 Eq. 1-11

The combinatorial term represents non-idealities due to entropy, which arise from molecular differences in size and shape. The residual term arises from energetic non-idealities and also contains several adjustable parameters.³⁷ Finally, the association term represents non-ideal

effects ascribable to intermolecular forces such as hydrogen-bonding and is the focus of this work.³⁸ Models used to calculate the contribution of the association term to the activity coefficient fall into three categories: lattice, chemical theory, and perturbation theory. However, for the scope of this work, henceforth, discussions will be limited to the chemical and perturbation theories.

The chemical theory description of association represents hydrogen bonding with a weak reversible chemical reaction where chemically distinct aggregates coexist in chemical equilibrium within an ideally-behaving solution.³⁹ This equilibrium can be described in terms of its equilibrium constants as well as the temperature and concentration of the system.⁴⁰ However, for this approach to be used successfully, the modeler must have advanced knowledge of aggregate stoichiometries, and the equilibrium constants must be determined from experiments. This limitation was considered a disadvantage by early work, which claimed that predictions involving chemical theory were of limited quantitative use.³⁹ Despite the early criticism, the chemical theory was improved by Campbell et al. who derived expressions for the monomer mole fraction and used it to describe systems of alcohols and alkanes. By assuming that alcohols aggregate in linear chains, he was able to develop a closed-form expression for association contribution to the gamma term.⁴¹

A statistical mechanics-based description of association is provided by perturbation theory, which relates specific site-based interactions with bulk fluid behavior.⁴² One of the most popular perturbation theories involves the work of Wertheim, who developed a model for association based on the interaction between acceptor sites (A_i) and donor sites (D_j) located on repulsive cores. A hallmark achievement of Wertheim's theory was the connection between the excess Helmholtz energy of association and the concentration of non-bonded sites at equilibrium (X^{A_i}). From this relationship, the monomer density could be related to the association strength ($\Delta^{A_iD_j}$) between interacting sites. Despite its rigor, the deterministic nature of Wertheim's theory does not easily lend itself to experiments.⁴⁰ A welcomed simplification was developed by Chapman et al., who reduced Wertheim's theory to its first-order thermodynamic perturbation (TPT-1),⁴² which considers linear chains. Recently, Bala and Lira have demonstrated the equivalence of TPT-1 and chemical theory for alcohols and provided a simplified form for γ^{assoc} in terms of the fraction of non-bonded acceptor sites (X^{A_i}), monomer density (ρ_0) and solution molar density (ρ).³⁷ Their derivation assumed no excess volume, a universal packing factor, conventional mixing rules, and a van der Waals repulsive term for compressibility.

$$\ln \gamma_1^{assoc} = 2 \ln \left(\frac{X^A}{X^{A,0}} \right) - (1 - X^{A,0}) + \left(\frac{\rho}{\rho_1} \right) x_1 (1 - X^A)$$
 Eq. 1-12

$$\ln \gamma_2^{assoc} = \left(\frac{\rho}{\rho_2}\right) x_1 (1 - X^A)$$
 Eq. 1-13

1.5 Overview of this work

The introduction has reviewed the concepts of spectroscopy necessary to characterize concentrations of species and the shifts of vibrational frequencies when hydrogen bonding is present. Chapter 2 Focuses on the Beer-Lambert-Bouguer law and presents an application that can be leveraged to readily calculate sample pathlength from spectrophotometer output files. Quantification requires accurate pathlengths. In Chapter 3, a new methodology is presented to quantify hydrogen bonding by scaling the raw spectra to obtain integrated peak areas that are independent of temperature as demonstrated for 1-butanol. Chapter 4 demonstrates measurement of mid-range IR data for several alcohols and application of spectroscopy for engineering modeling by determining association strengths from published literature measurements. Due to the unavailability of the raw spectra, the methods of Chapter 3 cannot be applied, but the spectra are shown be adequately modeled with two association strengths. A new activity model based on the

RTPT method is developed and applied. In Chapter 5, spectra are collected for ethanol and 1butanol in cyclohexane. The methods of Chapter 3 are refined to provide more thorough modeling. The Resummed Thermodynamic Perturbation Theory (RTPT) is shown to represent the experimental data, not only for the overall association, but also for the distribution of hydrogen bond types in solution. In Chapter 6, additional spectra are collected spectra are collected extending the systems to seven primary alcohols, two secondary alcohols and one tertiary alcohol. The methods of Chapter 3 are further refined, and results are applied for engineering modeling. Chapter 7 demonstrates a relationship between infrared wavenumber and NMR chemical shift for the hydroxyl group and the mapping of infrared spectra to correlate the NMR spectra. Chapter 8 provides density measurements that were collected in anticipation of NMR spectroscopy that was not performed within this work due to time limitations. Chapter 9 provides overall conclusions and offers recommendations for future directions.

CHAPTER 2: A MATLAB[®] Application for Calculation of Cell Pathlength in Absorption/Transmission Infrared Spectroscopy

2.1 Preface

Fourier transform infrared spectroscopy is an established technique for the qualitative determination of organic structure. Absorption infrared spectroscopy can be employed quantitatively using Beer's law. However, reliable quantitative analysis requires that the pathlength is known within 1%. Pathlengths based on nominal spacer thickness are not sufficient for accurate work due to variances in cell assembly and thermal expansion. The "interference pattern" method provides an accurate determination of cell pathlength but requires plotting of empty cell spectra and counting of the fringes. This work provides a MATLAB[®] application with a graphical user interface implementing an interactive plot where the user selects the region for the calculation. Then the program automatically computes the cell pathlength providing a rapid determination of pathlength for practitioners.

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2.3 Introduction

Absorption infrared spectroscopy is an established instrumental method for qualitative determination of molecular functionality. Common to both academic and industrial laboratory settings, infrared spectroscopy is primarily used for qualitative identification of functional moieties via their characteristic resonance frequencies and absorbance intensities. Modern infrared spectrophotometers utilizing Fourier transforms allow for fast and efficient data collection. This technological advance has enhanced the utility of infrared spectroscopy, making it an expedient method for qualitative as well as quantitative measurements.

Vibrational excitation occurs when chemical bonds absorb photons whose frequency matches that of the bond. For this excitation to be infrared active, the magnitude of the dipole moment vector must change with oscillation. In absorption spectroscopy, the fraction of incident light absorbed by the sample at a specific wavelength is proportional to the concentration of absorbing molecules in the beam path. This relationship, which describes the interaction of light with the chemical medium at a particular frequency, is described by the Beer-Lambert-Bouguer law (Eq. 2-1)

$$A_{\widetilde{\nu},i} = \epsilon_{\widetilde{\nu},i} C_i l \qquad \text{Eq. 2-1}$$

where $\epsilon_{\tilde{\nu}}$ is the molar attenuation coefficient (known as the molar extinction coefficient in older literature), $C_{\tilde{\nu}}$ is the concentration of the chromophore and *l* is the pathlength. Provided that the molar attenuation coefficient and pathlength are known the formula can be rearranged, allowing for concentration to be calculated from an absorbance peak height or area. Harris⁴³ provides indepth discussion of the interplay of concentration, pathlength, and intensity.

Cell pathlength is typically set using lead or Teflon[®] spacers sandwiched between two salt plate windows. According to Meloan,²⁷ quantitative reliability of infrared measurements necessitates that the pathlength must be known within 1%. Because cells are often disassembled and reassembled for cleaning and polishing of windows, the pathlength can vary upon reassembly relative to calibrations and the nominal dimensions spacer dimensions provided by the manufacturers are not adequate for quantification. Further, cell pathlength may change due to thermal expansion,⁴⁴ and in-situ measurements provide the best reliability of pathlength measurement.²⁸ The pathlength should be calculated during calibration and then the attenuation coefficient is determined based on the known concentration and absorbance measurement according to Eq. 2-2.

$$\epsilon \left[\frac{dm^3}{mol \cdot cm} \right] = A_{standard} / (C_{standard} \cdot l_{calibration})$$
 Eq. 2-2

If the cell is disassembled or reassembled, the pathlength (l_{sample}) should be measured again before the sample is loaded and then the concentration is determined using Eq. 2-3.

$$C_{sample}\left[\frac{mol}{dm^3}\right] = A_{sample}/(\epsilon l_{sample})$$
 Eq. 2-3

2.4 Pathlength Measurement Using the Interference Pattern

When the cell is empty, the refractive indices are significantly different for the salt plate windows and the inert gas (nitrogen, air, etc.) in the sample cell. Thus, a measurable amount of the irradiating light is internally twice reflected at the gas/salt interfaces within the cell before exiting on the detector side. Constructive and destructive interference between the irradiating light and internally reflected light occurs at all wavelengths, resulting in maximum intensities when the wavelength of light exiting the cell is an integer multiple of twice the cell pathlength. Likewise, minimums in intensity occur when the wavelengths of exiting light are half integer multiples of twice the cell pathlength. Wavelengths lying between half and full integer multiples give rise to intermediate absorbance intensities. The resulting spectrum is comprised of successive oscillations known as an "interference pattern" which allows for the pathlength to be calculated from the span of several adjacent minima using Eq. 2-4 where *l* is the cell pathlength in centimeters, N_c is the number of complete cycles (fringes), and $\tilde{\nu}_H$, $\tilde{\nu}_L$ are the high and low wavenumbers selected for the calculation.²⁸

$$l [cm] = \frac{1}{2} \left(\frac{N_c}{\tilde{\nu}_H - \tilde{\nu}_L} \right)$$
 Eq. 2-4

2.5 The Pathlength Application

The application can be run on any operating system where MATLAB[®] is installed. No additional MATLAB[®] toolboxes are required. The code is developed for absorption spectroscopy. The cell should be clean and the windows free of surface imperfections or clouding. Before taking a scan of the empty cell a background scan should be collected to remove environmental effects. Next, the empty cell should be scanned, ideally with a dry inert gas in the sample space, and the instrument output should be saved in a .csv format with the first column containing wavenumbers and the second column containing absorbance or percent transmittance. The app will disregard any lines in the file with text.

A screenshot of the application's graphical user interface (GUI) is shown in Figure 2.1. The empty cell spectrum is loaded by clicking the *Get Data* button which opens a standard file browser allowing the practitioner to select the empty cell .csv file. After the file has loaded, the file name will be displayed as the title of the plot, e.g. in Figure 2.1, the file is Path.csv. The entire empty cell spectrum is displayed as a blue line (obscured by the smoothed red line in Figure 2.1), enabling the user to visually inspect the spectra before selecting the region to be used for the pathlength calculation. The user can vary the region of the spectrum used for the calculation by adjusting the maximum and minimum values in the *Wavenumber Window* box. Data resolution is calculated and displayed.

A smoothing filter is provided because noise in the spectra can interfere with determination of the wave minima used for counting cycles. The smoothing filter applies a quadratic spline fitted to a specified wavenumber span. Setting the smoothing span to the width of the top third of the cycle typically works well. The plot is interactive, thus clicking on the curve displays coordinates,



permitting rapid determination of a reliable span to use for smoothing.



Once the desired region has been established, and the span specified, depressing the *Calculate Pathlength* button performs the calculation and generates a value for the cell pathlength in centimeters. The smoothed spectrum is displayed as a red line. The number of fringes used in the calculation are determined automatically, eliminating tedious counting where user errors may occur. Circles appearing on the plot of Figure 2-1 denote the fringe minimums detected by the program and the x's describe complete cycles (N_c) relative to the first minimum. The first and last circle observed on the plot coincide with the wavenumber values used to perform the calculation. The calculation should be performed two to three times using different wavenumber ranges to confirm the pathlength. Values should vary by less than 0.2%.²⁸

The app is configured so that smoothing can be changed without resetting the selected wavenumber range. Noise in the spectra can cause incorrect identification of the cycle minima if the smoothing span is too small. The user can identify this behavior when viewing the circles on the calculated plot, reset the smoothing filter, and recalculate the pathlength. The complete cycles within the active plot window are used in the calculation, not the nominal wavenumbers used in the GUI to select the window.

2.6 Summary and Conclusions

The pathlength application provides a convenient method to accurately and quickly calculate the pathlength of IR cells. The app is easy to use, and the visualization of the fringe pattern provides an opportunity for the user to interactively change the selected wavenumber window and smoothing to use for the pathlength calculation. The app eliminates tedious counting where user error may occur. The pathlength app is distributed via the MATLAB[®] Central File Exchange repository at <u>https://www.mathworks.com/matlabcentral/fileexchange/77353-pathlength</u> and code is available at <u>https://www.egr.msu.edu/thermoprops/pathlength</u>. Documentation is provided with the app download for users who may need to edit the data .csv file as well as an example data file and step-by-step instructions.

CHAPTER 3: Quantitative Analysis of Infrared Spectra of Binary Alcohol + Cyclohexane Solutions with Quantum Chemical Calculations

3.1 Preface

Hydrogen bonding has profound effects on the behavior of molecules. Fourier transform infrared spectroscopy (FTIR) is commonly used to qualitatively identify hydrogen bonding moieties present in a chemical sample. However, quantitative analysis of infrared (IR) spectra is nontrivial for the hydroxyl stretching region where hydrogen bonding is most prominently expressed in organic alcohols and water. Specifically, the breadth and extreme overlap of the $\tilde{v}(OH)$ stretching bands, and the order of magnitude variability of their IR attenuation coefficients complicates the analysis. In the present work, sequential molecular dynamics (MD) simulations and quantum mechanical (QM) calculations are used to develop a function to relate the integrated IR attenuation coefficient to the vibrational frequencies of hydroxyl bands across the $\tilde{v}(OH)$ stretching region. This relationship is then used as a guide to develop an attenuation coefficient scaling function to quantitatively determine concentrations of alcohols in hydrocarbon solution from experimental IR spectra by integration across the entire hydroxyl frequency range.

The computational work presented in this chapter was the performed in majority by Aseel Bala and with support from Cesar Plascencia. Experimental measurements and identification of the functional form of the molar attenuation coefficient were contributed by the author of this work.

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3.3 Introduction

Much can be learned from a chemical sample based solely on its interactions with electromagnetic radiation. In Fourier transform infrared (FTIR) spectroscopy, light from the infrared region (10-12500 cm⁻¹) is used to excite chemical bond vibrations. Measurements can be categorized into three main wavenumber ranges: near- (4000-12500 cm⁻¹), mid- (200-4000 cm⁻¹) and far IR (10-200 cm⁻¹) with most fundamental molecular vibrations occurring in the mid-IR. Within the harmonic oscillator approximation, energy differences among the vibrations of different molecules and bonds result from differences in their bond strengths and reduced masses, leading to characteristic absorptions for specific functional groups. Incident light is absorbed when the vibrational excitation has an associated transition dipole (net dipole change upon excitation), and the absorption intensity reflects the magnitude of the transition dipole. Qualitative analysis of infrared absorption spectra enables structure elucidation of chemical compounds via their characteristic frequencies and absorbance intensities. However, since the transition dipoles are strongly modulated by the degree and topology of hydrogen bonding, the attenuation coefficients (classically known as extinction coefficients) required for accurate quantification of hydroxyl moieties from their infrared absorptions vary widely.

Quantitative analyses of IR absorption spectra can be used to gain insight into the concentration of functional groups in a solution. For example, Williams et al.⁴⁵ explored the relationship between absolute integrated intensities of the C-H stretching and bending bands of gas-phase alkanes. Comparing the results from density functional theory (DFT) calculations to

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experimental IR spectra, these authors found that the numbers of C-H bonds in the molecules studied were linearly correlated with the integrated intensities of C-H stretching and bending bands. IR has also found use in chemometrics;⁴⁶ several researchers have correlated intensities of various classes of compounds with physical characteristics of the molecules such as numbers of methylene groups,⁴⁷ molecular size⁴⁸ and degree of branching.⁴⁹

The O-H stretching bands of alcohols and carboxylic acids have been the focus of studies probing the complex effects of hydrogen bonding.^{7,8,19,50–55} In alcohols, the O-H sites absorb across a range of ~3200 cm⁻¹ to 3700 cm⁻¹, roughly displaying two overall absorption regions: a sharp high frequency band and a broader composite of several overlapping bands at lower frequency. The formation of hydrogen bonds has long been known to red-shift the O-H stretching frequency while simultaneously increasing its integrated intensity,^{56,57} a phenomenon that is easily understood in terms of differences in the vibrationally modulated dipole oscillations. In studies of supercritical and liquid methanol, Wu et al.⁵² found that an isothermal increase in density causes the integrated O-H peak area to increase and the vibrational band to shift to lower frequencies. As expected, isobaric heating has the opposite effect. Hydrogen bonding has also been studied in nozzle sprays,⁵⁸ but quantitative transference of aggregate distributions to static conditions would be speculative.

To address the challenges involved in IR analysis of hydroxyl peaks, computational tools such as molecular dynamics (MD)⁵⁹ and quantum chemical (QM) simulations^{45,50,60–65} have been used to elucidate the effects of hydrogen bonding on IR peak characteristics. MD and QM calculations offer different balances of computational expense with modeling rigor; the former can model very large systems at modest computational cost but does not completely capture the changes in electronic structure induced by hydrogen bonding which are also largely responsible

for the dipole variations that define IR absorption intensity. Interaction energies and cluster distributions are also very sensitive to the potentials chosen; indeed, in a simulation of 10 mol% CH₃OD in CCl₄ at 300K, Kwac and Geva⁶⁶ found that depending on the empirical force field, the simulated fraction of hydroxyls in monomers (denoted as α below) varied widely, from 5.4 to 18.5%, while the fraction of hydroxyls in long chains (denoted as δ below) varied from 52-75%. For these reasons, MD is often used in conjunction with QM⁶⁶⁻⁶⁹ rather than as the primary tool for hydrogen bonding investigation.

A recent development in the computational community is empirical mapping. This approach, developed by Skinner et al.^{31,70–73} for water, creates functions or "maps" relating vibrational frequencies to approximate spectra using MD calculations. In this way, one can obtain a meaningful fundamental understanding of a system's IR response without having to use excessive computational resources. Mesele and Thompson⁷⁴ extended these techniques to primary alcohols, developing several "universal" maps that relate the transition frequencies, dipole derivatives and position matrix elements to the electric field on the atoms.

In this work, we present a combined computational and experimental approach which leverages the power of simulations to address the challenges of interpreting the infrared spectra of hydroxyls. In short, we use the qualitative trends produced from large-scale simulations to develop the shape of an attenuation coefficient function for quantitative liquid phase infrared spectroscopy. We apply this technique to quantitatively analyze the entire IR hydroxyl band and to calculate the relative and absolute concentrations of hydroxyl groups in the various contexts (monomers and oligomers) existing in solution. In the discussions below, references to the hydroxyl vibrational bands pertain to the vibrations of the covalent O-H bond in a RO-H---OHR hydrogen bond, not the vibrations of the actual H---O hydrogen bond.⁵⁶ Also, the term 'formal concentration' refers to

the concentration of a given compound in solution ignoring speciation into hydrogen bonded (or other) clusters - i.e. the molecules are counted individually. The term "formal concentration" in chemistry is synonymous with "apparent concentration" used in chemical engineering.

3.4 Analysis of the O-H Stretching Band

Quantitative interpretation of infrared spectra begins with the Beer-Lambert-Bouguer law, which relates the observed absorbance of a solute to its concentration in solution according to Eq. 2-1. where $A_{\bar{v},i}$ and $C_{\bar{v},i}$ are the observed absorbance and concentration of each absorbing solute *i* respectively. The pathlength, *l*, is the thickness of sample that the light passes through and $\varepsilon_{\bar{v},i}$ is the molar attenuation coefficient, known in older literature as the absorption or extinction coefficient, of species *i*. The attenuation coefficient is a fundamental property of a molecular transition (e.g. a vibration), relating absorbance of light at a specific frequency to the compound's concentration. To simplify the application of IR spectra, $\varepsilon_{\bar{v},i}$ is usually assumed to be independent of solute concentration. In common practice with any absorption spectroscopy, solutions of known concentrations are prepared and analyzed. For a given solute absorbance, the observed peak height values are then plotted against the experimental solute concentrations of the solutions. The molar attenuation coefficient is calculated as the slope of this plot, which is ideally linear. The complication with hydroxylated analytes is that they speciate into hydrogen bonded aggregates whose absorptions and attenuation coefficients differ greatly from those of the isolated monomers.

3.5 Motivation

While research in this area is extensive, we are unaware of any work that successfully enables quantification of the entire hydroxyl IR band area for alcohols by relating the integrated area to the formal alcohol concentration. Quantification of the bond type distribution would improve understanding of bond cooperativity and effects of temperature on the cluster distributions. These are the insights needed to inform efforts to model phase equilibria.^{75–77} Indeed, in the development of engineering models for the association of an alcohol in an inert solvent, the key quantity that defines the extent of hydrogen bonding is the fraction of hydroxyl protons that remains nonbonded at equilibrium.

For alcohols, self-association by hydrogen bonding strongly shifts and broadens the observed IR bands in the -OH region, complicating quantification. Moreover, there is disagreement in the literature concerning the assignments of this region's vibrational bands to specific structural features. In early studies,^{34,51,78} vibrational bands were assigned to hydrogen bonded clusters and were distinguished based on the size of the cluster. Hall and Wood⁶ proposed that covalent O-H bond vibrations should be classified individually according to whether and how they participate in hydrogen bonding. Their categories, which we adopt here, are as follows: If the O-H moiety is isolated, neither accepting nor donating a hydrogen atom, it is classified as an α hydroxyl. If it is accepting one hydrogen atom (i.e. interacting via the lone electron pairs on its oxygen) but not donating (i.e. the O-H hydrogen has no additional close contacts), it is classified as a β hydroxyl. These and the other four hydroxyl classifications are illustrated in Figure 3-1. Throughout this work, the hydrogen-bonded molecules are referred to as oligomers, and the oligomers together with neighboring molecules not involved in the hydrogen bonded aggregate as clusters.



Figure 3-1: Classification labels of hydroxyl environments.

The motivation behind the current study is to develop a procedure capable of accurately determining the fraction of free hydroxyl protons and conduct a thorough quantitative analysis of the O-H IR bands. To develop a quantitative interpretation of IR spectra, the following procedure was followed. First, we generated hydrogen-bonding environments using MD simulations of alcohol + cyclohexane mixtures. Then, probable hydrogen bonds were identified and small clusters from the MD frames were extracted. Their hydroxyl vibrations were then evaluated for frequency and intensity using QM. Next, a variety of functional forms for the attenuation coefficient were proposed to represent the shape of the frequency-dependent absorbance intensity from the QM calculations. The proposed functional forms were then used to scale datasets of experimental IR spectra measured over various temperature and alcohol/hydrocarbon composition ranges. To evaluate the proposed functions for the attenuation coefficient, the experimental hydroxyl regions of the scaled infrared spectra were integrated, generating parity plots of measured and formal concentrations. Least squares regression of the parity plot was used to optimize the parameters of the proposed scaling function. The recommended form of the attenuation coefficient function is provided below.

3.6 Computational Methods

3.6.1 Molecular Dynamics Simulations

Molecular dynamics simulations were carried out using the AMBER 14 package.⁷⁹ The AMBER94 force field was implemented with the AM1-BCC charge method with no modifications to the force field parameters. For each concentration, a cubic box of 1-butanol and cyclohexane molecules was created using PACKMOL⁸⁰ using conditions in Table 3-1 and the energy of the system was minimized within 1500 steps. Next, the box was heated with a 40 ps NVT ensemble, using a time step of 2 fs, in two stages. The temperature was ramped up from 0 to 283.15 K during the first 9000 steps, and then equilibrated at that temperature for the 11000 steps. Next, density was equilibrated for 8 ns using an NPT ensemble at 1 bar with a time step size of 2 fs. The temperature and pressure were controlled using the Langevin thermostat (with a collision frequency of 2 fs) and Berendsen barostat respectively; both were implemented with default parameters. The 2.4 ns production NPT stage was at the same conditions as the equilibration. During the NVT and NPT simulations, periodic boundary conditions were enforced in the x,y and z coordinates. The cutoff for non-bonded interactions was set at 8 Å. Beyond 8 Å, the default AMBER long-range corrections were used; a continuum model was used for Lennard-Jones interactions and the Particle Mesh Ewald (PME) summation method was used for electrostatic interactions.

To save computational time, C-H and O-H bond lengths were constrained using the SHAKE algorithm. This method was repeated for ethanol + cyclohexane at equimolar compositions using a 10 ns NPT equilibration period and a 3 ns NPT production period. The simulation details that varied between systems are given in Table 3-1. The purpose of the runs was to provide hydrogen-bonded oligomers for the quantum calculations, and thus low temperatures

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were selected for the simulations. As shown in Table 3-1, the equilibration segments were longer than 8 ns in all cases, giving all the systems ample time to equilibrate.

System	Units	1-butanol + cyclohexane		ethanol + cyclohexane
Alcohol Mole Fraction		0.1016	0.5	0.5
Number of alcohol	26	128	168	
molecules				
Number of		220	100	160
cyclohexane molecules	230	250	128	108
Density during	$\left[\frac{1}{2}\alpha/m^{3}\right]$	785 + 2	707 + 2	760 ± 3
production	[Kg/III] / c	765 ± 5	191 ± 3	709 ± 3
Temperature	[Kelvin]	283.15	283.15	298.15
NPT Equilibration	[0	0	10
Time	[IIS]	0	0	10
NPT Production Time	[ns]	2.4	2.4	3

Table 3-1: MD simulation details of run parameters for 1-butanol + cyclohexane systems studied in this work.

* Ideal solution densities based on experimental pure component densities are 792, 802, 779 kg/m³, respectively.

The hydrogen bond criteria were defined as an O---O distance < 3.2 Å and an O-H…O bond angle $> 130^{\circ}$ which is consistent with the definition used by Jeffrey⁴ to denote strong and moderately strong hydrogen bonds. Using this definition, hydrogen bonded oligomers of various sizes were identified, and each hydroxyl was assigned a class based on the labels in Figure 3-1.

The distribution of hydroxyl types, i.e. β , γ , or δ , for 1-butanol molecules that participate in trimers during the MD simulation is shown in Figure 2 and serves as a measure of thermal equilibration. The data for Figure 2 was obtained from 589 frames collected every 40 fs in the 2.4 ps of the production run. Each molecule appeared in a trimer in about 15% of the frames. The distribution was random for the three bond types across all molecules in solution confirming that bond formation and breaking occurs randomly in the simulation.



Figure 3-2: Bond distribution from an equimolar (i.e. mole fraction 0.5 alcohol) 1-butanol + cyclohexane MD simulation presented as the number of occurrences collected from trimers using the production frames. The x-axis represents the unique identifying number of each 1-butanol molecule. The distribution demonstrates that bond breaking and formation occur at random during the simulation.

3.6.2 Quantum Mechanics Simulations

A hydrogen-bonded alcohol oligomer and its neighboring molecules, herein referred to as a cluster, were taken from frames of the MD trajectory. Specifically, all alcohol and cyclohexane molecules with atoms that fell within 5 Å of the hydrogen-bonded hydroxyl hydrogen atoms in the oligomer were retained for the QM calculation and served as explicit solvent molecules for the oligomer. All other molecules beyond this cutoff were excluded. This cutoff effectively ensured that the sampled hydroxyl environments were representative of the entire frame while minimizing the computational effort required for quantum calculations. To this end, a constrained geometry optimization was then performed on the cluster where only the -CH₂OH groups in the oligomer were allowed to relax.
Gaussian09⁸¹ was used to optimize the -CH₂OH groups of each cluster and perform frequency calculations. The chosen B3LYP⁸² method combined with the modest 6-31G* basis set⁸³⁻⁸⁵ has been shown^{60,65} to capture the effects of hydrogen bonding for a reasonable computational cost. This modest level of theory was selected to survey a large number of samples, seeking patterns of behavior, rather than absolute quantitative values. Higher level calculations on a modest subset of the systems studied confirmed the persistence of the behaviors discovered, verifying that the results were not an artifact due to this relatively low level of theory. The calculated IR frequencies and attenuation intensities for the O-H stretching vibrations were screened by first scaling⁸⁶ the frequencies of each cluster by 0.96 and then collecting all frequency and intensity pairs with a frequency above 3100 cm⁻¹. The number of collected vibrational modes was ~24,000 and ~2,600 for the ethanol + cyclohexane and 1-butanol + cyclohexane systems, respectively.

Initially, the datasets for the two alcohols were examined separately, but the patterns for these two linear primary alcohols were found to exhibit near-perfect overlap. This behavior is in accord with the exact overlap of the O-H bands in their gas-phase spectra^{87,88}. The datasets were therefore combined, plotted as intensity vs. wavenumber, and smoothed by applying a moving average with a Hann window-type and a window size of 101 cm⁻¹. Various other moving average window types were considered, but differences were minor.

For purposes of classification, vibrational motions were divided into coupled and uncoupled categories for analysis based on criteria explained below. Coupling can be substantial between functional groups that have near-degenerate vibrational frequencies and are close and suitably oriented. Hydrogen bonding represents the major mechanism of such coupling between hydroxyls on different alcohols. The classification of IR peaks to structural classes of hydrogen hydroxyls (α, β, γ , or δ) becomes complicated for strongly coupled O-H vibrations due to contributions from multiple O-H stretching displacements in a given vibrational mode of a cluster. Therefore, vibrational modes were categorized as described below, and only assigned to hydrogen bond O-H classifications for vibrations in which one O-H moiety's motions were dominant. Further, only linear clusters were considered for the vibrations analyzed; structures including η and ζ hydroxyls were neglected because they were found to occur infrequently compared to the other types of hydroxyls. Table 3-2 shows the average percentage bond distribution among the vibrations that were structurally assigned. For each bond classification, the value shown was calculated by averaging the numbers of each O-H bond type over 13,000 frames. While α, β, γ , and δ hydroxyls occurred in relatively high populations, η and ζ constitute less than 1% of the O-H bonds, on average.

	1-Butanol	+ Cyclohexane	Ethanol + Cyclohexane
Hydroxyl Type	$x_{BuOH} = 0.1$	$x_{BuOH} = 0.5$	$x_{EtOH} = 0.5$
α	41.79	20.76	23.29
β	18.54	21.34	21.23
γ	19.05	22.59	22.95
δ	20.23	34.33	31.18
η	0.27	0.72	0.95
ζ	0.12	0.27	0.39

Table 3-2: Average distribution of O-H bond types in % for three systems. Data from 13,000 frames is averaged for each system.

As further explained below, vibrational localization among the various O-H bond stretching modes in an oligomer was assessed in terms of the displacement of each O-H hydrogen atom in a given O-H mode, using the following criteria:

$$d^2 = \Delta x_H^2 + \Delta y_H^2 + \Delta z_H^2$$
 Eq. 3-1

where Δx_H , Δy_H and Δz_H are the displacements of the hydrogen atom in the x, y, and z directions respectively as reported in the quantum chemical vibrational analysis. A vibrational mode was considered to be uncoupled (isolated) if one of the O-H hydrogen atoms had a d^2 value at least 0.3 Å² greater than any other atom in the optimized geometry. If a particular stretching mode fit the criteria then the active O-H bond was classified ($a, \beta, etc.$) according to Wood and Hall's labeling scheme. Otherwise, if the motions are more evenly distributed over multiple sites, the hydroxyls in the cluster remain unclassified and are included in the analysis of coupled vibrations. The 0.3 Å² criterion used here to differentiate coupled and uncoupled vibrations is arbitrary, but does provide initial insights into the populations of bond-types that contribute to the different regions of the O-H stretching band.^{19,89–91}

3.7 Experimental Methods

Anhydrous cyclohexane (lot# SHBJ0085) and 1-butanol (lot# SHBH8917) of 99.5% and 99.8% purity, respectively, were purchased from Sigma-Aldrich. All reagents were dried in a glovebox under nitrogen atmosphere using 20% w/v Spectrum M194 3- Å 1/16" molecular sieves. Sieves were prepared by flame heating under vacuum until vessel pressure reached 11.3 Pa gauge, after which they were allowed to cool and brought to atmospheric pressure with dry house nitrogen. Sieves were added to all reagents and drying occurred for at least 72 hours before use in all cases as suggested by Williams and Lawton.⁹² All glassware was cleaned in acetone and hexane and oven dried overnight before use. Sample concentrations were prepared volumetrically assuming

ideal volumes of mixing. Temperature-dependent volumes were calculated through $V = \sum_i x_i V_i$. Excess volumes for the mixtures are less than $0.4\%^{93}$ so the use of ideal mixing volumes is well within other experimental errors. Liquid molar volume calculations used accepted experimental values from the NIST ThermoData Engine.⁹⁴ Experimental liquid density data were regressed with a polynomial over the experimental temperature range and the polynomial was used when calculating molar volumes for concentration calculations.

The temperature was monitored during the sample preparation and was taken as the average reading of two thermometers positioned near the samples. Binary samples consisting of alcohol and cyclohexane were prepared in 10-mL volumetric flasks of type A precision. Alcohol was measured using an appropriately sized Hamilton gas-tight syringe. Each concentration was independently prepared. After sample preparation, the flask was stoppered and inverted twenty times before a thirty second vortex stir to homogenize. Samples were then transferred to borosilicate scintillation vials using screw tops with a PTFE liner. Vials were wrapped in Parafilm before being removed from the glovebox.

Samples were analyzed using a JASCO FT/IR-6600 Spectrometer. The sample compartment was under a continuous house nitrogen purge. Samples were injected into the cell from a Luer lock syringe into an airtight valve system consisting of 1/16" O.D. stainless steel components that was connected to a Specac demountable heatable liquid flow cell (GS20582) with CaF₂ windows and a PTFE spacer (GS20070-0.01MM, GS20070-0.025MM, GS20070-0.1MM, and GS20070-0.5MM). The cell windows were cleaned with hexane at the end of each day and the cell apparatus was stored under house nitrogen between uses.

The cell was dried internally before use with low pressure house nitrogen with complete drying confirmed by FTIR scan. The FTIR sample compartment was purged with house nitrogen

at a flowrate of 50 ft³/hr for 30 minutes before the background scan and throughout all experimental scans. Temperatures were set by a Specac 4000 Series High Stability Temperature Controller operating a Specac electrical heating jacket (GS20730) with cooling water running through the jacket at the recommended rate of 0.5 L/min. Observed temperature variations were less than ± 0.1 °C. The sample cell's path length was measured in centimeters using the fringe interference method²⁷ depicted in Eq. 2-4.

Ethanol and 1-butanol solutions were scanned at 10 °C increments from 30-60 °C. All samples reached thermal equilibrium (constant temperature) within six minutes and were allowed to stabilize for an additional two minutes before scans. The IR method consisted of 128 background and sample scans at a resolution of 0.5 cm⁻¹. For each composition, the empty chamber background was collected at ambient temperature and was automatically subtracted from each of the sample spectra before further processing

3.8 Results and Discussion

3.8.1 Processing and Preliminary Analysis of Experimental IR Spectra

The background-subtracted IR spectra were processed as follows. The hydroxyl band region was determined to be 3049.9 to 3755.2 cm⁻¹ which is the integration range used in analyses below. The solvent bands were removed from the spectra by subtracting the concentrationweighted absorbance of neat cyclohexane at the same temperature and nominal path length as the sample. The subtraction was tuned by a factor f to eliminate residual solvent peaks in the wavenumber range 1800 – 2500 cm⁻¹ where alcohol did not absorb. The mathematical operation was a subtraction of $f \cdot \rho_{sample}^{molar} A_{cyclo}(\tilde{v}, T) l_{cyclo} / (\rho_{cyclo}^{molar} l_{sample})$ where ρ^{molar} is molar density and the adjustment was always $0.99 \le f \le 1.01$. The processed experimental IR spectra for 1-butanol in cyclohexane in the region of the hydroxyl stretching band are shown in Figure 3-3 for $x_{BuOH} = 0.0819$. As the temperature increased, peak one (~3645 cm⁻¹), peak two (~3632 cm⁻¹), and peak three (~3518 cm⁻¹) increased in absorbance while peak four (~3457 cm⁻¹) and broad peak five (~3341 cm⁻¹) diminished.



Figure 3-3: Spectra for 8.19 mol% n-butanol in cyclohexane after subtraction of the concentration-weighted contribution of cyclohexane.

While band assignment is a topic of great interest, we defer such discussion to subsequent publications. In this work, we instead conduct a quantitative analysis of the entire hydroxyl region. To this end, we begin with an investigation of the physical significance of the absorbance band area. Figure 3-4 shows the relationship between the total area under the entire O-H absorbance band and the formal concentration for four solutions at five temperatures calculated as area/pathlength $A^{I}/l = (1/l) \int A(\tilde{v}) d\tilde{v}$ where wavenumbers are in cm⁻¹, pathlength is in cm, and A^{I}/l has units of cm⁻². We refer to the calculations as 'unscaled' because, in later figures, we scale A^{I}/l using an attenuation coefficient function.



Figure 3-4: Total absorbance band area of the O-H band for 1-butanol + cyclohexane data as a function of the formal molarity. Fifty-six spectra were collected at four temperatures (30, 40, 50 and 60 $^{\circ}$ C). For a given mole fraction of 1-butanol, temperature variations affect the molarity and distribution of O-H bond moieties, with lower temperatures favoring formation of dimers and oligomers via hydrogen bonding. Lower temperatures exhibit higher areas at a given formal concentration.

It is immediately clear from Figure 3-4 that the linearity of the integrated area and concentration that is traditionally assumed for a given absorbance in the Beer-Lambert-Bouguer law does not apply for the unscaled overall hydroxyl band. Figure 4 indicates that the molar attenuation coefficient, ε , must vary strongly at different vibrational frequencies since the integrated areas for a fixed mole fraction vary with temperature due to the changes in the distribution of hydrogen bonds. As discussed below, the results of the QM/MM analysis provide key insights into this variability, resulting in relationships between absorption intensity and wavenumber.

3.8.2 Results from QM/MM

In this section, the calculated IR characteristics of the alcohol hydroxyl stretch vibrations are investigated. The simulation results for alcohol hydroxyl stretch vibrations were analyzed in three groupings: (1) a subset of uncoupled vibrations for linear oligomers of the 1-butanol + cyclohexane system; (2) a subset of uncoupled vibrations for linear oligomers of the ethanol + cyclohexane system; and (3) all O-H stretching vibrations (coupled and uncoupled and all structures including cyclics) in both the 1-butanol + cyclohexane and ethanol + cyclohexane systems. The purpose of the limited study of linear oligomers (monomers, dimers, trimers, and tetramers) is to explore the relation between hydroxyl classification (α , β , etc.) and the frequency/intensity. However, the quantitative attenuation coefficient scaling function is based on the third grouping which includes hydroxyl stretches for linear, cyclic, and branched oligomers.

Table 3-3: Number of each species and bond analyzed with QM calculations for uncoupled vibrations of 1-butanol and ethanol molecules. All species larger than a monomer have one β and one γ hydroxyl. Trimers and tetramers also possess one and two δ hydroxyls respectively. Cyclic oligomers and those with coupled vibrations are not included.

		$x_{BuOH} = 0.1$	$x_{BuOH}=0.5$	$x_{EtOH} = 0.5$	Total
	Monomer	653	366	859	1878
cies	Dimer	153	230	413	796
Spe	Trimer	53	52	236	341
	Tetramer	46	23	223	292
pe	α	653	366	859	1878
yl Ty	β	252	305	872	1429
Hydrox	γ	252	305	872	1429
	δ	145	98	682	925

Table 3-3 lists the numbers of each bond and species type analyzed for the uncoupled cases involving 1-butanol and ethanol (cases 1 and 2). The multiple representations for each hydrogen bonding type, with a wide range of vibrational frequencies and intensities are averaged in Table

3-4. Hydroxyls are included in the table only if all the vibrations of the oligomer hydroxyls are uncoupled. The reported "intensity" from Gaussian09 is the integrated intensity, *I*, in units of km/mol, which is defined by the equation:

$$I = \int_{band} \varepsilon(\tilde{\nu}) d\tilde{\nu} \qquad \qquad \text{Eq. 3-2}$$

We use *I* reported by Gaussian09 as a measure of the strength of each hydroxyl's IR absorbance (attenuation coefficient), with the understanding that it is proportional to the peak height ε_{max} , and use only the pattern of the behavior, not the absolute values.

			$\tilde{\nu}_{avg}~(\mathrm{cm}^{-1})$			I (km/mol)	
		$\begin{array}{l} x_{BuOH} = \\ 0.1 \end{array}$	$\begin{array}{l} x_{BuOH} = \\ 0.5 \end{array}$	$\begin{array}{l} x_{EtOH} = \\ 0.5 \end{array}$	$\begin{array}{l} x_{BuOH} = \\ 0.1 \end{array}$	$\begin{array}{l} x_{BuOH} = \\ 0.5 \end{array}$	$\begin{array}{l} x_{EtOH} = \\ 0.5 \end{array}$
Monomer	α	3602	3587	3589	32	54	40
Dimer	β	3601	3583	3578	52	72	69
	γ	3479	3471	3468	377	411	395
Trimer	β	3589	3572	3574	68	96	79
	γ	3418	3414	3423	464	525	497
	δ	3410	3412	3407	584	537	537
Tetramer	β	3586	3574	3574	68	88	83
	γ	3436	3426	3418	427	428	425
	δ	3387	3363	3373	629	676	651

Table 3-4: Average calculated vibrational frequencies and vibrational intensity (*I*), for uncoupled hydroxyl stretch vibrations in butanol + cyclohexane.

The clusters captured from the MD all have different arrangements, each providing a different vibrational frequency and absorption intensity. The first observation is that with an increase in the formal concentration of alcohol in the simulated box, there is a slight red shift in almost all the vibrational frequencies accompanied by an increase in intensity. In general, a red shift and increase in intensity is observed as the size of the hydrogen-bonded oligomer increases. The wavenumber shift is most prominent between dimers and larger oligomers with dimer β and

 γ hydroxyls having vibrational frequencies that are, on average, ~10 and ~50 cm⁻¹ higher than those of trimers and tetramers respectively. The trend in Table 3-4 shows the intensity increasing significantly in the order α , β , γ , δ .

Figure 3-5 plots the absorption intensity as a function of vibrational frequency for the combined data points from each of the uncoupled hydroxyl vibrations computed for the two formal 1-butanol concentrations, $x_{BuOH} = 0.1$ and $x_{BuOH} = 0.5$. For improved visual comparison with experimental data, all QM frequencies that were already scaled were also blue-shifted by 60 cm⁻¹ to center the monomer (α -type) vibrational region on the experimental maximum at 3645 cm⁻¹. When the intensity vs. wavenumber data for the two concentrations was plotted, the plots for the two concentrations overlapped, indicating that formal concentration has little effect on the $\tilde{\nu}$ -*I* relationship. Therefore, they are plotted together in Figure 3-5 and the different markers denote the four hydroxyl types studied here: α (downward triangles), β (upward triangles), γ (right-facing triangles). While the focus of the current discussion concerns 1-butanol, the same calculations for ethanol overlap as discussed below. Because the calculated points are dense, the results for each alcohol obscure the results for the other when plotted together. For clarity, background markers (x's) are plotted for ethanol in cyclohexane, and later (Figure 3-6) we show a plot for ethanol with 1-butanol in the background.



Figure 3-5: Uncoupled hydroxyl stretching frequencies for two concentrations of 1-butanol + cyclohexane mixtures (triangles) calculated from QM simulations compared to ethanol calculations (shown as x). Down, up, right, and left-pointing markers denote α , β , γ , and δ hydroxyl vibrations respectively.

From Figure 3-5, the two contexts in which the O-H hydrogen atom is free, α and β , overlap completely and are responsible for the sharp higher frequency peak in the O-H stretching region. Together, these two bond types constitute most of the free hydroxyl protons in solution, though the current analysis excludes branched oligomers such as those which include ζ hydroxyls. Significant disagreement exists in the literature concerning the α - β overlap in IR spectra. Several authors have assumed that β hydroxyl vibrations do not contribute significantly to the sharp high frequency peak, instead allocating that band entirely/predominantly to the α vibration.^{14,95,96} In these cases, it is assumed that most clusters in solution are cyclic (resulting in few β hydroxyls), that the β peak occurs at a different frequency altogether, or that the intensity of the β absorbance is significantly less than that of the α . However, consistent with more recent work in this area,^{7,97}

red-shift of β relative to α vibrations, and comparable absorption intensities for both α and β hydroxyls. Presumably, for these systems, the change in electronic structure when the oxygen atom accepts another proton only weakly affects the free hydroxyl bond strength. The next observation is that the uncoupled γ hydroxyls appear at a lower frequency and, in general, have greater integrated attenuation coefficients, (approximately 3 to 10 times that of the α and β hydroxyls).

Uncoupled δ hydroxyls follow the same pattern as the γ hydroxyls, showing additional red shifting and integrated attenuation coefficients that are, in general, 3 to 20 times that of the α and β hydroxyls). The frequency trend is easily explained by recognizing that, as the hydroxyl protons become more "shared" due to hydrogen bonding, the covalent bond is weakened. As a result, the potential energy surface describing the hydroxyl stretch becomes broader and shallower, causing the vibrational frequency of the hydroxyl to red shift. As for the intensity, it is directly proportional to the square of the transition dipole moment. Thus, the increase in intensity for hydroxyls in oligomers (β , γ , and δ hydroxyls) versus hydroxyls in monomers (α hydroxyls) arises from arrangements of the oligomers that increase the transition dipole moment relative to the transition dipole moment in a monomer. Conversely, the low intensities for the oligomers relative to the monomer can be rationalized by recognizing that certain arrangements of the oligomer can decrease the dipole moment relative to the monomer.

The most significant and least obvious finding of this work is that the relationship between the integrated attenuation coefficient of an O-H bond and its vibrational wavenumber follows a curve that is independent of the bond category. As well-articulated by an anonymous reviewer: "The system is dynamic in nature, with a range of hydrogen-bond distances and angles that are continually being made and reformed. This leads to a near continuum of net dipoles for each categorized species. The dimers, trimers, and tetramers, etc., are in a dynamic condition, and the resulting infrared spectrum is a measure of the overall averages." Previous studies in this area have recognized patterns in vibrational characteristics. For example, as early as 1956, Huggins and Pimentel⁹⁸ noted a red-shift and increase in absorption intensity with increased hydrogen bond strength. Asprion et al.³⁴ performed curve fitting of alcohol in hydrocarbon mixtures by using separate attenuation coefficients for monomer, dimer, and polymer, and found an increased red shift and an increased attenuation coefficient for each. More recently, Mesele and Thompson⁷⁴ conducted DFT calculations on neat alcohols and showed that the empirical maps that relate transition frequencies, position matrix elements, dipole derivatives and the electric field are surprisingly linear. Moreover, these relationships were identical for all four primary alcohols tested and were predicted to hold for all other alcohols.

Having independently uncovered this pattern, we further explored the vibration/intensity relation by repeating the described MD + QM procedure for an equimolar mixture of ethanol + cyclohexane at 298.15 K. As shown in Figure 3-5, the ethanol calculations (shown as x's) lie directly under the 1-butanol + cyclohexane calculations. For greater clarity, Figure 3-6 shows the ethanol + cyclohexane vibrations with butanol + cyclohexane vibrations included as x's in the background. The visual similarities between the two mixtures seen in Figure 3-5 and Figure 3-6 give an early indication that the uncovered patterns may be universal for primary alcohols.

Because inclusion of the coupled vibrations is also essential for a complete analysis of the spectra, the coupled vibrations were also collected from the QM results. Some of the coupled vibrations have small intensities, reflecting near-negligible transition dipoles. Figure 3-7 combines Figure 3-5 and Figure 3-6 but also includes the coupled vibrations and the Hann moving average calculated with a wavenumber window of 101 cm⁻¹. The coupled vibrations strongly broaden the

O-H vibrational band at low frequencies, indicating that the attenuation coefficient should become approximately constant at the low frequency end of the -OH stretching region.



Figure 3-6: Uncoupled hydroxyl stretching for an equimolar ethanol + cyclohexane mixture (triangles) calculated from QM simulations. Background x's show the 1-butanol calculations from Figure 3-5. Down, up, right, and left-pointing markers denote α , β , γ , and δ hydroxyl vibrations respectively.



Figure 3-7: Uncoupled and coupled 1-butanol and ethanol hydroxyl stretching frequencies and integrated attenuation coefficients calculated from QM simulations (left axis). Uncoupled bond vibrations of ethanol + cyclohexane and 1-butanol + cyclohexane are shown as x. Circles are coupled vibrations for both systems. Solid jagged line – Moving weighted average (Hann window, window size = 101). Solid line (right axis) – integrated attenuation function curve used to obtain parity plots from experimental data, as explained below.

3.8.3 Scaling and Further Analysis of Experimental IR Spectra

Noting the order of magnitude variations in absorption intensities calculated as a function of O-H participation in hydrogen bonding, and the resulting nonlinear behavior with concentration and temperature seen in Figure 3-4, to quantify hydroxyl spectra, a function relating attenuation coefficient to wavenumber is needed. At first, it would seem that attenuation coefficients for each category of absorbing species might need to be separately assigned. However, noting the simplicity of the patterns obtained from quantum simulations a curve that mimics the QM trends was explored as a scaling function applied to experimental data. The moving average in Figure 3-7 suggests an attenuation coefficient curve constructed from three line segments smoothed with splines at the intersections as shown in Figure 3-8. To develop the curve, seven parameters are needed: two for each line segment and one for the width of the splines. The spline widths are constrained to be the same in order to minimize the number of parameters. Of the seven parameters, six are adjusted to spectra: 1&2) the intersection of Seg1 and Seg2, (x_B , y_B); 3) the slope of Seg1, m_1 ; 4&5) the intersection of Seg2 and Seg3 (x_R , y_R); and 6) the spline width. The slope of Seg3 is fixed at zero as suggested by the moving average. It is worth noting that a polynomial function was insufficient in capturing the curve characteristics well.

Fitting of the above function to experimental data entailed dimensionless scaling of the integrated attenuation coefficient curve relative to the attenuation coefficient at 3645 cm⁻¹, $\psi(\tilde{v}) = \epsilon(\tilde{v})/\epsilon_{3645}$. At each frequency, the assumed $\psi(\tilde{v})$ was calculated and used to scale the experimental absorbance by:

$$\tilde{A}(\tilde{v}) = \frac{A(\tilde{v})}{\psi(\tilde{v})}$$
 Eq. 3-3

where \tilde{A} represents the scaled absorbance at wavenumber \tilde{v} . Following scaling, each spectrum was integrated to obtain a scaled area $\tilde{A}_{int} = \int \tilde{A}(\tilde{v})d\tilde{v}$. The integrated areas for all scaled spectra were divided by path length and plotted against alcohol molarity to check agreement with Beer's law linearity and to determine *k* (Eq. 3-4).

$$\frac{\tilde{A}_{int}}{l} = \frac{\int A(\tilde{v})/\psi(\tilde{v})d\tilde{v}}{l} = \frac{\epsilon_{3645}\int (A(\tilde{v})/\epsilon(\tilde{v})d\tilde{v}}{l} = \epsilon_{3645}\int c(\tilde{v})d\tilde{v} = kc \qquad \text{Eq. 3-4}$$

In Eq. A-1, ϵ_{3645} (APPENDIX A: Detailed Summary of Attenuation Coefficient Function) has units of length²/mol and k has units of length/mol. Using cm as length units results in ϵ_{3645}/k = 1 cm. A linear parity plot of predicted and experimental concentrations would result when the numerical values of k and ϵ_{3645} match. Iterating, while using cm as path length units and wavenumber in cm⁻¹, to obtain k with each iteration and using the value to calculate the dimensionless scaling function $\psi(\tilde{v}) = \epsilon(\tilde{v})/(k(1 \text{ cm}))$ led to convergence where $\int c(\tilde{v})d\tilde{v} =$ c/(1 cm). After convergence, the attenuation coefficient at any wavenumber could be calculated using $\epsilon(\tilde{\nu}) = \epsilon_{3645}\psi(\tilde{\nu})$. The choice of the reference frequency at 3645 cm⁻¹ for scaling was arbitrarily selected as it is the location of the maximum of the free hydroxyl peak. Specification of a different wavenumber would simply scale $\psi(\tilde{\nu})$ relative to that wavenumber. Some key values for the attenuation curve are $\epsilon_{3645} = 820 \text{ dm}^2/\text{mol}$, $\epsilon_R = 29,600 \text{ dm}^2/\text{mol}$, the slope of segment 1 is 122 cm·dm²/mol, and the slope of segment 2 is $-131 \text{ cm} \cdot \text{dm}^2/\text{mol}$. The complete function is given with more precision APPENDIX A: Detailed Summary of Attenuation Coefficient Function.



Wavenumber

Figure 3-8: Schematic of three-segment attenuation coefficient curve smoothed with splines. The text discusses the parameters used for the elements and APPENDIX A provides parameter values.

Figure 3-9 shows plots of the spectra that were scaled by applying the optimized $\psi(\tilde{v})$ to Figure 3-3 via Eq. 3-4. In the resulting scaled spectra, peaks one (~3645 cm⁻¹) and two (~3632 cm⁻¹) now dominated, while peaks three (~3518 cm⁻¹) and four (~3457 cm⁻¹) became slightly more resolved, and peak five (~3341 cm⁻¹) was diminished considerably. All peaks retained the temperature-dependent behavior observed in the unscaled spectra.



Figure 3-9: Scaled absorbance spectra for 1-butanol + cyclohexane at 8.19 mol% 1-butanol. Spectra from Figure 3-3 are scaled with $\psi(\tilde{v})$.

Across these rescaled spectra, Beer's law is now validated as evidenced by comparing calculated concentration $c = (\int \tilde{A} d\tilde{v})/(\epsilon_{3645}l)$ with formal concentration for 56 spectra at various concentrations and four temperatures in Figure 3-10. The coefficient of determination is $R^2 = 0.9993$ for the 56 spectra.



Figure 3-10: Scaled absorbance area of the O-H region for 1-butanol + cyclohexane data. Fifty-six spectra of 1-butanol in cyclohexane were collected at four different temperatures and at four pathlengths. The dashed line represents parity between experimental formal concentrations and integrated areas.

The proportionality between the integrated area across the O-H region and the formal concentration is significantly corrected in the scaled area plot in Figure 3-10 compared to that of Figure 3-4. To compensate for the effect of temperature on the density, the band areas tabulated in Table 3-5 include a thermal density correction:

$$\frac{A_{int,reported}}{l} = \frac{A_{int,experimental}}{l} \left(\frac{\rho^{ref}}{\rho_T}\right)$$
 Eq. 3-5

where ρ^{ref} and ρ_T are the mixture densities at a reference temperature (298.15 K) and the temperature of the experiment, respectively. After thermal correction, the integrated concentration response of the scaled areas is remarkably uniform regardless of temperature for all the compositions studied when the coefficient of variance between temperatures is compared as a percentage in Table 3-5. The coefficient of variance (COV) is calculated using:

$$COV = \frac{stddev}{Mean Area} = \left(\sqrt{\frac{\sum(Area - Mean Area)^2}{s - 1}}\right) / (Mean Area)$$
 Eq. 3-6

where s is the number of temperature data points at each mole fraction.

Table 3-5: Examples of integrated areas and percent coefficient of variation (COV) for the O-H absorbance and scaled absorbance.

	Nominal Cell Pathlength [cm]	T [°C]	Thermally Corrected			
Mole fraction r (1-butanol)			Unscaled		Scaled	
			Area / <i>l</i> [cm ⁻²]	COV	Area / <i>l</i> [cm ⁻²]	COV
0.2005	0.002	30	45100	11%	1558	1.1%
		40	42030		1549	
		50	38790		1537	
		60	35180		1520	
0.0819	0.010	30	16700	16%	648.0	1.1%
		40	15110		656.2	
		50	13300		660.3	
		60	11410		664.4	
0.0218	0.050	30	2609	45%	170.9	0.6%
		40	1919		172.6	
		50	1331		172.8	
		60	864.9		173.3	
0.0112	0.100	30	798.0	55%	91.20	1.1%
		40	502.5		91.92	
		50	324.5		91.91	
		60	222.8		89.81	

Figure 3-10 and Table 3-5 demonstrate that, with the scaled spectra, the Beer-Lambert-Bouguer law can be applied successfully to the entire hydroxyl absorption region permitting quantification of the hydroxyl band to determine the alcohol concentration in solution. Stated another way, the various free or H-bonded hydroxyl sites in a scaled spectrum are respectively interpreted with the same weighting, just as NMR spectra show absorbances with areas directly proportional to the amounts of the respective sites. To our knowledge, no other work has performed a comparable quantitative analysis of the O-H region due to its known complexity. Currently, work is under way to explore the analysis of experimental spectra from binary mixtures of ethanol in cyclohexane using the same method. Preliminary data indicate that the functional form of the molar attenuation coefficient observed for 1-butanol may be applied. The work presented here provides a powerful tool to map IR band absorptions to concentration in solution, effectively placing all O-H sites, regardless of their context, on a quantitatively equal footing.

3.9 Summary and Conclusions

In this work, the hydroxyl vibrational band was analyzed quantitatively for alcohol + hydrocarbon mixtures using insights from QM simulations. First, MD simulations were carried out to generate sample environments around hydroxyl groups. Then, selected clusters were further analyzed with QM calculations to gain an understanding of their vibrational spectroscopic characteristics. Evaluation of isolated vibrations on solvated linear oligomers provided insight on the relations between bonding and vibrational frequency/intensity, but coupled vibrations were included when developing the attenuation coefficient curve. Inspired by trends seen in the plots of QM calculated absorption intensities vs. wavenumbers, an attenuation coefficient scaling function was devised to normalize experimental spectra across the whole O-H region. This attenuation coefficient curve was calculated using three line segments smoothed with splines at the intersections. When experimental spectra for butanol-cyclohexane samples at various concentrations and temperatures were scaled using this effective attenuation coefficient function,

the integrated areas of the whole O-H stretching region were found to quantitatively reflect the known alcohol concentrations. Quantitation across the notoriously variable hydrogen bonding region of the infrared spectrum, historically analyzed in qualitative terms or only in local segments, represents a new and powerful tool. Ongoing work will explore extensions of this tool to additional functional groups and mixtures, and their use to gain insight into physical properties and phase behavior.

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CHAPTER 4:Parameterization of a RTPT Association Activity Coefficient Model using Spectroscopic Data

4.1 Preface

Self-associating species exhibit highly nonideal vapor-liquid phase behavior in many mixtures, which is challenging to model. The most successful models, such as the statistical associating fluid theory (SAFT) equations, are based on Wertheim's first thermodynamic perturbation theory (TPT-1). However, despite its success, the traditional TPT-1 implementations of SAFT lack the requisite flexibility to account for the cooperative effects of hydrogen bonding observed in alcohol + hydrocarbon systems. The resummed thermodynamic perturbation theory (RTPT) provides an improved representation of these systems by considering hydrogen bond cooperativity. While more robust than its TPT-1 predecessor, RTPT has only been validated against computer simulations. In this work, we develop a form of the RTPT association contribution to the activity coefficient and fit RTPT parameters to experimental spectroscopic data. The agreement between the RTPT model and experimental infrared spectroscopy data is striking despite requiring only one additional parameter compared to TPT-1. Calculated enthalpies indicate the occurrence of positive hydrogen bond cooperativity in all the systems examined. Association constants fitted to spectroscopic data are used to calculate activity coefficient contributions using a Flory combinatorial term. For completeness, regressions of vapor-liquid equilibrium data are included and utilize a non-random two-liquid (NRTL) model residual contribution.

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4.3 Introduction

Hydrogen bonding significantly influences the physical behavior of solutions. When comparing associating fluids with those of similar molecular weight and atomic constitution that do not associate, associating species have higher boiling points and enthalpies of vaporization, and exhibit strongly nonideal behavior in mixtures, which is challenging to model. Since the early 1990s, association modeling using Wertheim's statistical mechanics^{99–102} has been integrated into several equations of state (EOS), such as cubic plus association (CPA), as well as the statistical associating fluid theory (SAFT) family of equations.^{42,103,104}

The concept of hydrogen bond cooperativity has been proposed by a number of spectroscopic studies when data are available over a range of 0 to 20 mol %.^{7,105–107} Similarly, quantum mechanical calculations have shown that formation of the first hydrogen bond exhibits a smaller magnitude association constant than subsequent hydrogen bonds (positive cooperativity).^{61,108–111} Marshall and Chapman recently developed the two-constant Wertheim approach for cooperative bonding known as resummed thermodynamic perturbation theory (RTPT).¹¹² The study yielded an equation for the Helmholtz free energy and the model was compared to Monte Carlo simulations but has not yet been evaluated with experimental data. Experimental methods such as nuclear magnetic resonance (NMR) or Fourier Transform infrared (FTIR) spectroscopy are commonly used to measure the extent of hydrogen bonding.^{105,111,113,77,78,34,114,53,115} Several investigators have concluded that a more complete description of the spectroscopic data for mixtures which contain alcohols requires two association constants^{7,34,77,78,116} due to cooperative hydrogen bonding. The two-constant models also provide an improved representation of phase equilibria and multicomponent heat of mixing.^{117–120}

This work extends the RTPT model of Marshall and Chapman¹¹² to an activity coefficient model expression and to demonstrate the strength of the resulting model by comparing to infrared (IR) spectroscopic data for binary alcohol + hydrocarbon systems. To this end, we fit the association constants to IR data from literature, predict the association contribution to the activity coefficients, and demonstrate fitting of the residual contribution to phase equilibria data. This manuscript is organized as follows: First, a brief background is provided on the use of spectroscopy for the determination of association constants. Then, the TPT-1 and RTPT methods are summarized, and an overview of the methods used for solving the RTPT material balances is given. We then derive the RTPT contribution of association to activity coefficients and outline the procedures used for regressing infrared spectroscopy data and for modeling VLE data. Finally, we discuss the results of the regressions and apply the fitted RTPT model to phase equilibria data as proposed by Bala et al.¹²¹

4.4 Background

4.4.1 Hydrogen Bonding and IR Spectroscopy

Infrared spectroscopy provides quantification of hydrogen bonding by relating integrated peak areas linearly to concentration through the Beer-Lambert law using an integrated molar attenuation coefficient¹²². The fundamental stretching frequency of an alcohol's hydroxyl group, $\tilde{v}(OH)$, appears in the infrared region 3000-3800 cm⁻¹ in the form of three peaks, a sharp higher frequency peak and two broad lower frequency peaks. The absorbances are sensitive to local molecular environments making IR an ideal probe for the measurement of hydrogen bonding. The position of a particular alcohol molecule within the larger oligomer, as categorized in Figure 4-1, largely determines the frequency at which that residue's hydroxyl group will absorb.¹²² Alpha (α) hydroxyls are synonymous with unassociated monomer alcohol molecules. Located at one end of

linear aggregates are beta (β) hydroxyls which also possess a non-bonded hydroxyl proton. As recently as the early 2000s, confusion existed about whether the sharp peak that appears near 3650 cm⁻¹ included a contribution from the unbound hydroxyl group (β) at the end of linear aggregates. von Solms et al.¹¹⁵ compared monomer fractions calculated using spectroscopic data from several publications where the 3650 cm⁻¹ peak was interpreted as monomer. Current interpretations recognize that IR vibrational bands are more appropriately attributed to bonds^{7,53,89,123} as first proposed by Hall and Wood,⁶ rather than to entire hydrogen bonded species. Furthermore, it is clear today that α and β hydroxyls absorb in the same region with similar absorption intensity.¹²²

At the opposite end of hydrogen-bonded chains are gamma (γ) hydroxyls which have a bound proton and a non-hydrogen-bonded oxygen. Located between the β and γ hydroxyls are the delta-type (δ) hydroxyls which participate in two interactions; one hydrogen bond is donated at the hydroxyl proton, and one hydrogen bond is accepted at the oxygen. The participation of δ in two hydrogen bonds significantly weakens the parent covalent bond causing it to appear at lower wavenumbers (red-shifted) relative to the other bond types with a significantly larger attenuation coefficient.



Figure 4-1: Nomenclature for various bonding motifs found in alcohol solutions.

Older literature often interpreted red-shifted absorbances that appeared in response to increased hydrogen bonding in terms of associated species^{95,115} (i.e., dimer, polymer) rather than the bond types depicted in Figure 4-1. One such example from the work of Asprion et al.^{34,124} is

shown in Figure 4-2 and features a species-based evaluation. The following examples illustrate the distinction between a species-based interpretation and one established using bond types. A linear dimer contains one γ and one β hydroxyl, and both contribute to the absorbance spectrum producing two peaks instead of a single dimer peak. Similarly, a linear oligomer comprised of n alcohol residues has one γ , one β , and $(n - 2) \delta$ hydroxyls, and will contribute to peaks in each of the three vibrational regions, indicating that chains contribute to the region labeled as monomer in Figure 4-2. Finally, a cyclic aggregate without branching would contain only δ hydroxyls. The availability of integrated peak areas from the work of Asprion et al., permits the measurements to be reinterpreted in this work.



Figure 4-2: Curve fitting example from Asprion et al.,³⁴ which assigns certain regions of the infrared spectrum to aggregates of a specified size. In the figure, the absorbance (*A*) is divided by cell pathlength (*d*) and a tilde is used to denote the mole fraction of alcohol. The monomer (Mo), dimer (Di), and polymer (Po) designations are not used in this work. Reprinted from³⁴ with permission from Elsevier.

4.4.2 Wertheim's Thermodynamic Perturbation Theory

Wertheim developed a novel approach to association which relied on a material balance between acceptor and donor sites on molecules. The formation of a hydrogen bond, therefore, consumes one acceptor site and one donor site. The simplest application of Wertheim's theory is TPT-1, where bonding is determined by independent probabilities. The potential for generalized application of Wertheim's method was recognized by Chapman et al.,¹²⁵ leading to the SAFT EOS. The SAFT model uses a spherical reference fluid, modeling species as irreversibly bonded chains and modeling reversible association between species with an association constant. The resulting statistical associating fluid theory (SAFT) equation of state was extended by Gross and Sadowski who replaced SAFT's spherical molecule reference fluid with that of a hard-chain reference fluid for the dispersion contribution resulting in the perturbed-chain statistical associating fluid theory (PC-SAFT).^{103,126} The association term remains relative to a hard-sphere reference fluid. Three component-specific parameters are used in PC-SAFT to relate to the reference fluid: 1) a segment number (*m*); 2) a segment diameter (σ); and 3) a segment energy (ϵ_i/k). Each association pair requires two association parameters: 1) an effective bonding volume (κ_{ij}^{AD}); and 2) a bonding association energy (ϵ_{ij}^{AD}/k). Parameters for pure components are typically obtained by regression of pure-component saturated vapor pressure and saturated-liquid density data.

The use of bonding sites permits different bonding schemes. Typically alcohols are modeled using the 2B bonding scheme, which allocates two association sites to the host molecule; one acceptor site on the oxygen and one donor site on the hydroxyl proton.¹²⁶ The 2B scheme restricts bonding to linear chains. In the typical TPT-1 implementation, a single association constant, Δ_{ij} , is assumed for all oligomerizations with the form:

$$\Delta_{ij} = N_A d_{ij}^3 g_{ij}(d) \kappa_{ij}^{AD} \left(\exp\left(\epsilon_{ij}^{AD} / (kT)\right) - 1 \right) \right)$$
 Eq. 4-1

where Δ_{ij} in this manuscript is in cm³/mol and d_{ij} is the temperature-dependent segment pair diameter in Angstroms and Avogadro's number, N_{A_i} is included to as a unit conversion factor. The hard sphere radial distribution function at contact, $g_{ij}(d)$, is given by eq A7 of Gross and Sadowski¹⁰³, converted here to use molar density.

$$g_{ij}(d) = \frac{1}{(1-\zeta_3)} + \left(\frac{d_i d_j}{d_i + d_j}\right) \frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j}\right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3}$$
 Eq. 4-2

$$\zeta_{l} = (\pi/6)N_{A} \rho \sum_{i} x_{i} m_{i} d_{i}^{l} ; \ l \in \{2,3\}$$
 Eq. 4-3

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-3\left(\frac{\epsilon_i}{kT}\right)\right) \right]$$
 Eq. 4-4

4.4.3 The Resummed Thermodynamic Perturbation Theory

Sear and Jackson introduced a method for cooperative bonding deriving equations from statistical mechanics.¹²⁷ More recently, Marshall and Chapman provided a more rigorous derivation and demonstrated that the primary difference between RTPT framework and the final equation of Sear and Jackson's work is the temperature dependence given by the Mayer term instead of a Boltzmann term.¹¹² To our knowledge, neither approach has been compared with spectroscopic data.

In the RTPT approach, one association constant, Δ_2 , represents the bonding of an acceptor and donor site to form a dimer species. A second association constant, Δ_N , represents chain formation of *n*-mers ($n \ge 3$) and uses the same value for trimers and longer chains. Both association constants are given by the form in Eq. 4-1 but have distinct values for κ_{ij}^{AD} and ϵ_{ij}^{AD}/k . The expression for Helmholtz energy provided by Marshall and Chapman¹¹² is

$$\frac{A^{assoc}\rho}{RT} = x_1 \rho \ln \frac{\rho_o}{x_1 \rho} - 2x_1 \rho X^A + \frac{(x_1 \rho X^A)^2}{\rho_o} + x_1 \rho - \frac{\Delta c^{(o)}}{N_A \underline{V}}$$
 Eq. 4-5

As explained in APPENDIX D: Conversion of Extensive Helmholtz Energy to Molar, the notation in this work uses molar Helmholtz energy, and molar densities. The quantity $\rho_1 = x_1\rho$ is the apparent molar density of alcohol in the mixture. Here, $\rho_1 X^A = x_1\rho X^A$ is the sum of the molar densities of bonding species with unbonded acceptor site *A*, which is the apparent molar density multiplied by the fraction of acceptor sites that are unbound, X^A . The density of unbound donor sites is $x_1\rho X^D$. The density of alcohol monomer is ρ_0 where both the acceptor and donor sites are unbound. By material balance, in a binary solution of alcohol + hydrocarbon, $X^A = X^D$. Because the unbound donors and acceptors are equal in a binary mixture of alcohol + hydrocarbon, the acceptor site balances are written herein even though most discussion will refer to free hydrogens which are hydrogen bond donors.

The notation of Marshall and Chapman¹¹² is transformed in this work to accommodate empirical fitting of bonding volumes as part of the association constant, and thus we define the dimer association constant $\Delta_2 \equiv N_A f_{AB}^{(1)} \Delta$, and the *n*-mer association constant $\Delta_N \equiv N_A f_{AB}^{(2)} \Delta$, where the right-hand side is Marshall and Chapman's notation and the left-hand side is used here. Adapting notation to this work, the last term of Eq. 4-5 is

$$\frac{\Delta c^{(o)}}{N_A \underline{V}} = \frac{(x_1 \rho X^A)^2 \Delta_2}{1 + (\Delta_2 - \Delta_N) \rho_o}$$
Eq. 4-6

Note that $\Delta c^{(o)}$ is single term representing a perturbation and not an association constant. The bonding equilibrium balance equations are obtained by the derivatives of Eq. 4-5 with respect to $x_1 \rho X^A$ and ρ_o as provided by Marshall and Chapman¹¹² as eqs (17) and (18) in their work. Adapting the notation to this work, these become

$$\frac{x_1 \rho X^A}{\rho_o} - 1 = \frac{x_1 \rho X^A \Delta_2}{1 + (\Delta_2 - \Delta_N)\rho_o}$$
 Eq. 4-7

$$\frac{x_1 \rho}{\rho_o} = \left(\frac{x_1 \rho X^A}{\rho_o}\right)^2 - \frac{(\Delta_2 - \Delta_N)(x_1 \rho X^A)^2 \Delta_2}{(1 + (\Delta_2 - \Delta_N)\rho_o)^2}$$
Eq. 4-8

(see APPENDIX E: Key Material Balance Equationsfor the derivation manipulating Eq. 4-7 and Eq. 4-8). Eq. 4-7 can be rearranged to identify the contributions of α and β hydroxyls to the free site density.

$$x_1 \rho X^A = \rho_o + \frac{x_1 \rho X^A \Delta_2 \rho_o}{1 + (\Delta_2 - \Delta_N) \rho_o} = \rho_\alpha + \rho_\beta;$$

$$\rho_\beta = \frac{x_1 \rho X^A \Delta_2 \rho_o}{1 + (\Delta_2 - \Delta_N) \rho_o}$$
Eq. 4-9

4.5 Methods and Derivations

4.5.1 Comparison of RTPT with Chemical Theory

Until the late 1980s, hydrogen bonding was described exclusively using chemical theory and it continues to be used today.^{61,41,128,129} The RTPT model possesses striking similarities to the 2-constant Kretschmer-Wiebe model^{118,128}, which is not apparent by the equations provided here. A comparison is provided in the APPENDIX C: Relation of RTPT to Kretschmer-Wiebe. There are four distinct differences between the equilibrium constants in the Wertheim method of Chapman et al. compared to traditional chemical theory. First, the association constants relate the bonding energy to the equilibrium constant via the Mayer function instead of the Boltzmann function. Secondly, the Wertheim equilibrium constant exhibits a composition dependence represented by the radial distribution function. As shown in APPENDIX C: Relation of RTPT to Kretschmer-Wiebe, at a fixed temperature, if the composition dependence of the radial distribution function is omitted and a Boltzmann term is used in place of the Mayer term, the association constant reduces to an equivalent chemical theory concentration-based equilibrium constant, K_c . The third distinction from chemical theory is most important, being that the approach represents association as a site interaction rather than a chemical reaction between species. The approach uses probabilities of bonding and eliminates the need to write out all the chemical reactions between species. Finally, the fourth distinction is that the Wertheim framework can be readily extended to higher order perturbations.

4.5.2 Solution Procedure for X^A

Marshall and Chapman solved a cubic equation for monomer density ρ_o and then X^A . Here we present an iterative method that simplifies the calculation by implementing a quadratic equation instead. The monomer density is related to the free site fraction via the following quadratic equation derived in the APPENDIX E: Key Material Balance Equations.

$$\rho_0 = \frac{2x_1 \rho X^A}{1 + x_1 \rho \Delta_N X^A + \sqrt{(1 + x_1 \rho \Delta_N X^A)^2 + 4(\Delta_2 - \Delta_N)x_1 \rho X^A}}$$
Eq. 4-10

Note that fraction of monomer $\rho_0/(x_1\rho)$ remains finite even at infinite dilution of component (1) where the limiting value is unity. The fraction of sites free is shown in the APPENDIX E: Key Material Balance Equations to be

$$X^{A} = \frac{1}{1 + x_{1}\rho\Delta_{2}X^{A}/s^{2}}$$
 Eq. 4-11

$$s = 1 + (\Delta_2 - \Delta_N)\rho_0 \qquad \qquad \text{Eq. 4-12}$$

TPT-1 can be obtained from RTPT by setting $\Delta_2 = \Delta_N$, resulting in (*s* = 1) in Eq. 4-11 and Eq. 4-10 becomes $\rho_0 = x_1 \rho (X^A)^2$ after inserting Eq. 4-11.

Excess volumes for liquid systems are very small and typically ignored in many common models such as Flory's equation and Scatchard-Hildebrand. Therefore, in this work, the ideal solution density was assumed and the partial molar volume at all compositions is equivalent to the pure component molar volume. Pure component densities were regressed for experimental literature data and mixture densities and volumes were calculated using

$$\frac{1}{\rho} = \frac{x_1}{\rho_{pure,1}} + \frac{x_2}{\rho_{pure,2}}$$
 Eq. 4-13

$$\overline{V}_i = V_{pure \, i} = \frac{1}{\rho_{pure, i}}$$
Eq. 4-14

The procedure to solve iteratively for X^A uses several steps at a given apparent compositon x_1 . First, the pure component liquid densities are calculated at the experimental temperature via a polynomial fitted to experimental pure component densities. The mixture density is evaluated in Eq. 4-13 and the association constants are evaluated via Eq. 4-1, Eq. 4-2, Eq. 4-3, and Eq. 4-4.

To initialize iterative soluion to Eq. 4-10, Eq. 4-11, and Eq. 4-12, the free site fraction X^A is assumed and the monomer density is calculated by Eq. 4-10. The free site fractions are refined in Eq. 4-11 and Eq. 4-12 using the assumed value of X^A . A successive substitution reinserts X^A into Eq. 4-10, Eq. 4-11, and Eq. 4-12 until the set of values converges. The values of ρ_o and X^A can then be used in other calculations as shown in later sections.

4.5.3 VLE Methods and Derivation of the RTPT Activity Coefficient Model

Vapor-liquid equilbria (VLE) can be characterized using the gamma-phi approach where the fugacity coefficient ($\hat{\varphi}_k$) and activity coefficient (γ_k) describe the non-ideality of the vapor and liquid phases, respectively,

$$y_k \hat{\varphi}_k P = x_k \gamma_k P_k^{sat}$$
 Eq. 4-15

Traditionally, the activity coefficient combines the association contribution with a combinatorial and residual term, as seen in Eq. 4-16. The combinatorial term is entropically based

and accounts for differences in the size and shape of molecules, while the residual expression captures the energetics of molecular interactions and other remaining effects.

$$\ln \gamma_k = \ln \gamma_k^{comb} + \ln \gamma_k^{res} + \ln \gamma_k^{assoc}$$
 Eq. 4-16

Here, we use the Flory term for the combinatorial contribution

$$\ln \gamma_k^{comb} = \ln \frac{V_k}{V} + \left(1 - \frac{V_k}{V}\right)$$
 Eq. 4-17

and the NRTL is used for the residual term. For a binary mixture, this is given by:

$$\ln \gamma_{k}^{res} = x_{j}^{2} \left[\frac{\tau_{kj} G_{kj}}{\left(x_{k} G_{kj} + x_{j} \right)^{2}} + \tau_{jk} \left(\frac{G_{jk}}{x_{k} + x_{j} G_{jk}} \right)^{2} \right]; k \neq j$$

$$G_{lm} = \exp(-\alpha_{lm} \tau_{lm}); \tau_{lm} = a_{lm} + b_{lm}/T$$
Eq. 4-18

where the empirical parameters a_{lm} , b_{lm} , $\alpha_{lm} = \alpha_{ml}$ are adjusted to experimental data.

Recognizing that vapor phase deviations from an ideal gas are typically smaller than a couple of percent for the conditions used herein, we represent the fugacity coefficients using the Hayden-O'Connell equation of state.

The association contribution, $\ln \gamma_k^{assoc}$, is the key term in Eq. 4-16 and the focus of this work. As shown by Bala et al.³⁷ when the species standard states are at the same *T* an *P* as the mixture, liquid-phase activity coefficients are given by

$$\ln \gamma_k^{assoc} = \frac{1}{RT} \left(\frac{\partial \underline{A}^{assoc}}{\partial n_k} \right)_{T,P,\{n_{j\neq k}\}} \bigg|_{mix} - \frac{\underline{A}^{assoc}}{RT} \bigg|_{pure k} + \frac{P^{assoc}}{RT} \left(\frac{\partial \underline{V}}{\partial n_k} \right)_{T,P,n_{\{j\neq k\}}} - \frac{P^{assoc}}{RT} V_k$$
Eq. 4-19

$$\frac{1}{RT} \left(\frac{\partial \underline{A}^{assoc}}{\partial n_k} \right)_{T,P,\{n_{j \neq k}\}} = \ln \hat{\varphi}_k^{assoc} - Z^{assoc} \frac{\overline{V}_k}{V}$$
 Eq. 4-20

The activity coefficients are obtained by differentiation of Eq. 4-5 as summarized in APPENDIX G: Activity Coefficients. The derivations in the original paper are unnecessarily constrained to zero excess volume as explained by Bala, et al.¹³⁰ and are accordingly revised here. The formulas for a binary mixture, where component (1) is the alcohol and component (2) is the hydrocarbon, are:

$$\ln \gamma_1^{assoc} = \ln \left(\frac{\rho_o}{x_1 \rho} \frac{\rho_{pure 1}}{\rho_{o,pure 1}} \right) - (1 - X_{pure 1}^A) + x_1 (1 - X^A) \left(\frac{V_1}{V} \left(1 + \left(\frac{\partial \ln g_{11}}{\partial \ln \rho} \right)_{T, \{n_i\}} \right) - \rho \left(\frac{\partial \ln g_{11}}{\partial \rho_1} \right)_{T, \underline{V}, n_2} \right)$$
Eq. 4-21

$$\ln \gamma_2^{assoc} = x_1 (1 - X^A) \left(\frac{V_2}{V} \left(1 + \left(\frac{\partial \ln g_{11}}{\partial \ln \rho} \right)_{T, \{n_i\}} \right) - \rho \left(\frac{\partial \ln g_{11}}{\partial \rho_2} \right)_{T, \underline{V}, n_1} \right)$$
Eq. 4-22

where ρ_i represents molar density and the derivative terms are given by

$$\begin{pmatrix} \frac{\partial \ln g_{11}}{\partial \ln \rho} \end{pmatrix}_{T,\{n_{i\neq k}\}} = \frac{1}{g_{11}} \left(\frac{\zeta_3}{(1-\zeta_3)^2} + \left(\frac{d_1}{2}\right) \left(\frac{3\zeta_2}{(1-\zeta_3)^2} + \frac{6\zeta_2\zeta_3}{(1-\zeta_3)^3}\right) + \left(\frac{d_1}{2}\right)^2 \left(\frac{4\zeta_2^2}{(1-\zeta_3)^3} + \frac{6\zeta_2^2\zeta_3}{(1-\zeta_3)^4}\right) \right)$$
 Eq. 4-23

$$\rho\left(\frac{\partial \ln g_{11}}{\partial \rho_k}\right)_{T,\underline{V},\{n_{i\neq k}\}} = \frac{1}{g_{11}} \left(\frac{(n\zeta_{3,n_k})}{(1-\zeta_3)^2} + \left(\frac{d_1}{2}\right) \left(\frac{3(n\zeta_{2,n_k})}{(1-\zeta_3)^2} + \frac{6\zeta_2(n\zeta_{3,n_k})}{(1-\zeta_3)^3}\right) \qquad \text{Eq. 4-24} \\
+ \left(\frac{d_1}{2}\right)^2 \left(\frac{4\zeta_2^2(n\zeta_{2,n_k})}{(1-\zeta_3)^3} + \frac{6\zeta_2^2(n\zeta_{3,n_k})}{(1-\zeta_3)^4}\right)\right)$$

where

$$(n\zeta_{l,n_k}) \equiv n\left(\frac{\partial\zeta_l}{\partial n_k}\right)_{T,\underline{V},\{n_{i\neq k}\}} = (\pi/6)N_A\rho m_k d_k^l; \ l \in \{2,3\}$$
Eq. 4-25

To generate activity coefficients, the molar volumes, densities, and X^A are first calculated at the mixture concentration and for the pure alcohol using the method of Section 4.5.2 above. Then the radial distribution function derivatives and activity coefficients are calculated using Eq. 4-21 to Eq. 4-25.

For the binary case presented here, the form of the activity coefficient expressions can be related to those resulting from TPT-1 presented by Bala and Lira³⁷ if the general forms of the monomer and radial distribution function derivative are used. The differences of the activity coefficient expressions between RTPT and TPT-1 are in the relation between ρ_o and X^A , rather than the way that these quantities appear in the activity coefficient relations. For TPT-1, since $\rho_o = x_1 \rho (X^A)^2$, the leading logarithm term appears as

$$\ln\left(\frac{\rho_o}{x_1\rho}\frac{\rho_{pure\ 1}}{\rho_{o,pure\ 1}}\right) = \ln\left(\frac{X^A}{X^A_{pure\ 1}}\right)^2 = 2\ln(X^A/X^A_{pure\ 1})$$
Eq. 4-26

where it is written in the previous work as a sum over the acceptor and donor instead using the factor of two on the acceptor expression.

The contribution of association to the excess Helmholtz energy is derived in APPENDIX F: Excess Helmholtz Energy and is

$$\left(\frac{A^E}{RT}\right)^{assoc} = x_1 \ln\left(\frac{\rho_o}{\rho_1} \frac{\rho_{pure\ 1}}{\rho_{o,pure\ 1}}\right) + x_1 \left(X^A_{pure\ 1} - X^A\right)$$
Eq. 4-27
Eq. 4-27 can be converted to the form typically cited for TPT-1 by inserting the TPT-1 monomer density $\rho_o = x_1 \rho (X^A)^2$. For practitioners, the infinite dilution values are important. Using Eq. 4-21 to Eq. 4-25, it can be shown that the activity coefficients at infinite dilution are given by

$$\ln(\gamma_1^{assoc})^{\infty} = \ln\left(\frac{\rho_{pure\ 1}}{\rho_{o,pure\ 1}}\right) - (1 - X_{pure\ 1}^A)$$
Eq. 4-28

$$\ln(\gamma_2^{assoc})^{\infty} = \left(1 - X_{pure\ 1}^A\right) \left(\frac{V_2}{V_1} \left(1 + \left(\frac{\partial \ln g_{11}}{\partial \ln \rho}\right)_{T,\{n_i\}} \Big|_{x_2=0} \right) - \rho_1 \left(\frac{\partial \ln g_{11}}{\partial \rho_2}\right)_{T,\underline{V},n_1} \Big|_{x_2=0} \right)$$
Eq. 4-29

Note that $\ln(\gamma_1^{assoc})^{\infty}$ is independent of solvent and that $\ln(\gamma_2^{assoc})^{\infty}$ is related to the volume ratio of the components. For a strongly associating component (1) in an inert solvent (2)

$$\ln(\gamma_1^{assoc})^{\infty} \sim \ln\left(\frac{\rho_{pure\ 1}}{\rho_{o,pure\ 1}}\right)$$
 Eq. 4-30

$$\ln(\gamma_2^{assoc})^{\infty} \sim V_2/V_1$$
 Eq. 4-31

When component (1) associates strongly, $\rho_{o,pure 1}$ is a small number and thus γ_1^{assoc} becomes infinite when $X_{pure 1}^A$ goes to zero but γ_2^{assoc} has a limiting value. The radial distribution function derivatives do not cancel in $\ln(\gamma_2^{assoc})^{\infty}$ unless the pure species parameters are extremely similar, but the magnitude of the difference in terms is typically a minor contribution.

4.5.4 Parameterization of RTPT using Spectroscopic Data

To obtain association parameter values for the RTPT activity coefficient, we use spectroscopic data for alcohol + alkane systems presented by Asprion et al.^{34,124} However, we reinterpret the integrated monomer areas (see Figure 4-2) as the sum of α and β hydroxyls.

Fitting the spectroscopic data using TPT-1 requires the determination of three parameters: the integrated Beer-Lambert molar attenuation coefficient (ε_{BL}) and two parameters used to calculate Δ_{ij} : the effective association site volume (κ_{ij}^{AD}) and the association energy (ε_{ij}^{AD}). As discussed earlier, a more complete description is provided by RTPT, which uses two association constants of different values, Δ_2 and Δ_N , to account for hydrogen bond cooperativity. Our implementation of RTPT requires only one additional parameter compared to TPT-1 for a total of four parameters: the integrated molar attenuation coefficient, an association energy for the formation of the dimer (ε_2^{AD}), an association energy for oligomers comprised of three or more alcohol residues (ε_N^{AD}), and an effective association site volume (κ^{AD}) which is the same for the dimer and *n*-mer. In principle, κ^{AD} could differ for the dimer and *n*-mer, but we achieved satisfactory fits using a common value and thus cannot justify an additional parameter. For the pure component parameters used in Eq. 4-1, we selected the PC-SAFT values from the work of Gross and Sadowski¹²⁶ which are included in Table 4-1.

Component	m_i	σ_i [Å]	$\frac{\epsilon_i}{k}[K]$	
methanol	1.52550	3.23	188.90	
ethanol	2.38270	3.1771	198.24	
1-propanol	2.99970	3.2522	233.40	
2-propanol	3.09290	3.2085	208.42	
1-butanol	2.75150	3.6139	259.59	
1-pentanol	3.62600	3.4508	247.28	
1-hexanol	3.51460	3.6735	262.32	
phenol	3.09089	3.4438	315.03	
<i>n</i> -hexane	3.05760	3.7983	236.77	
cyclohexane	2.53030	3.8499	278.11	

Table 4-1: PC-SAFT molecular parameters used in this work.

To establish a relationship between absorbance and concentration, the Beer-Lambert law in Eq. 4-32 is used.

$$A^{I} = \varepsilon_{BL} lC = \varepsilon_{BL} lx_{1} \rho X^{A}$$
 Eq. 4-32

In this equation, A^{I} is the integrated absorbance, ε_{BL} is the integrated molar attenuation coefficient, l is the optical cell pathlength (instead of the variable d used by Asprion), and C is the analyte concentration. Asprion's tabulated A^{I}/l values for 'monomer' were reinterpreted as unbound hydrogens ($\alpha + \beta$). The integrated molar attenuation coefficient was obtained by rearranging the Beer-Lambert expression as seen in Eq. 4-33. In this form the concentration, or equivalently, the molar density of unbonded hydroxyl protons, was expressed as $x_1\rho X^A$ as described earlier.

$$\varepsilon_{BL} = \frac{(A^I/l)}{x_1 \rho X^A}$$
 Eq. 4-33

The regression procedure for the association parameters was carried out as follows. First, at each experimental composition, a value of A^I/l was obtained from Asprion's data. Then, using guessed parameter values for the association constants, a corresponding value for the free site density, $x_1\rho X^A$, was calculated using methods of Section 4.5.2. Next, we calculated the value of ε_{BL} . In other studies, ε_{BL} is sometimes determined from dilute measurements where association is insignificant³⁴, but that approach requires arbitrary selection of the dilute range. Instead, we used a two-stage regression. During *stage-1*, each isotherm (T_j) was regressed individually by adjusting parameters to minimize the objective function in Eq. 4-34, which fits a value of $\overline{\varepsilon}_{BL,j}$ and one or two Δ values for TPT-1 or RTPT, respectively.

$$obj = \sum_{i=1}^{data} \left(\left(\frac{(A^{I}/l)}{x_{1}\rho X^{A}} \right)_{i} - \overline{\varepsilon}_{BL,j} \right)^{2}$$
 Eq. 4-34

Here, $\overline{\varepsilon}_{BL,j}$ is the mean value of the integrated molar attenuation coefficient across the composition range for data at a single temperature. Once this stage is complete, this value is averaged again for the three temperatures studied to obtain the parameter, $\overline{\varepsilon}_{BL,s1}$. During *stage-2*, the mean value of the *stage-1* integrated molar attenuation coefficient ($\overline{\varepsilon}_{BL,s1}$) was fixed for each solute-solvent pair and replaced $\overline{\varepsilon}_{BL,j}$ in Eq. 4-34 while optimizing the κ^{AD} , ϵ_2^{AD} and ϵ_N^{AD} for all temperatures. Details of the regressions are provided by flowsheets in the APPENDIX H: Regression Flow Diagram.

Regression of parameters for the Mayer form of the association constant presents challenges like the well-studied Boltzmann/Arrhenius form. The pre-exponential and exponential parameters in Eq. 4-1 are strongly interacting, and the implicit use of infinite temperature as a reference temperature is problematic for regression. The proper way to obtain parameters and confidence intervals is through the use of a reference temperature near the experimental temperatures.^{131,132} Without the use of a reference temperature, the asymptotic confidence interval for κ^{AD} spanned zero which is unphysical. Instead, a modified form of the association constants, given in Eq. 4-35 and Eq. 4-36, was used which included a temporary parameter (p) and a temporary reference temperature (T_r) which was set to 313.05 K.

$$\Delta_2 = N_A d^3 g_{11}(d) p \exp\left(\frac{\epsilon_N^{AD}}{kT_r}\right) \left(\exp\left(\frac{\epsilon_2^{AD}}{kT}\right) - 1\right)$$
 Eq. 4-35

$$\Delta_N = N_A d^3 g_{11}(d) p \exp\left(\frac{\epsilon_N^{AD}}{kT_r}\right) \left(\exp\left(\frac{\epsilon_N^{AD}}{kT}\right) - 1\right)$$
 Eq. 4-36

Values for $p, \epsilon_2^{AD}, \epsilon_N^{AD}$ were obtained by regression after which we calculated $\kappa^{AD} = p \exp(\epsilon_N^{AD}/(kT_r))$. Because the κ^{AD} and Δ values are dependent on temporary parameters, the 95% confidence interval for these quantities were determined by the bootstrap (replacement by

resampling) method¹³³, which involved calculating and sorting the values from 1000 bootstrap fitting trials and selecting the 25th and 975th values as the lower and upper bounds of the confidence interval, respectively. Due to the interacting parameters and nonlinearity, the optimum parameters are not centered in the confidence intervals.

4.6 **Results and Discussion**

The primary goal of this work is to provide the derivation and implementation of an association term that is consistent with the framework of RTPT as introduced by Marshall and Chapman. In this section, we begin by demonstrating that TPT-1 is incapable of representing the infrared data. The publication of this work¹³⁴ included incorrect parameter values due to a coding error that was discovered after publishing the work. The figures and tables in this chapter are revised from the publication to provide results from the correct parameter values. The plots are indistinguishable, and the values of $\epsilon_{(2 \text{ or } N)}^{AD}$ are nearly the same but the κ^{AD} values are noticeably different.

4.6.1 Comparison of TPT-1 with RTPT

To compare the TPT-1 and RTPT models, a *stage-1* regression was performed, and a representative result featuring ethanol + cyclohexane is displayed in Figure 4-3. The inclusion of one additional association energy term in RTPT for the formation of *n*-mers provides excellent representation of the absorption while TPT-1 lacks the flexibility to capture the curvature of the experimental data for ethanol above 2 mol%. Similar trends were observed in the other primary alcohols as well as 2-propanol and phenol. Furthermore, the integrated molar attenuation coefficients obtained from the RTPT *stage-1* regression shows a smaller coefficient of variation (3%) compared to TPT-1 (\geq 18%), which additionally exhibits an unexpectedly strong temperature dependence (Figure 4-4). As part of a final effort to fit the data using TPT-1, we performed a *stage-*

2 regression of TPT-1 using the average $\overline{\epsilon}_{BL,s1}$ obtained from the *stage-1* regression of RTPT. This also resulted in an unsatisfactory fit as seen in Figure 4-5. Therefore, all subsequent regressions were performed with RTPT.



Figure 4-3: Stage-1 regression using RTPT and TPT-1 for ethanol + cyclohexane binary system. RTPT fits the data well (–), while TPT-1 (– –) is unable to replicate the curvature of the experimental data.



Figure 4-4: Average integrated molar attenuation coefficients, $\overline{\varepsilon}_{BL,all,j}$, which resulted from the stage-1 regression of ethanol + cyclohexane data using TPT-1 and RTPT.



Figure 4-5: Stage-2 regression of TPT-1 (–) using stage-1 RTPT integrated molar attenuation coefficient for ethanol + cyclohexane system demonstrating inability of TPT-1 to fit the data as explained in the text.

Stage-2 regression was performed on each solute-solvent pair as seen in Figure 4-6 to Figure 4-10, where Figure 4-10 presents an example of a satisfactory fit with RTPT for 1-hexanol + cyclohexane. A complete list of parameters obtained from the regressions as well as their 95% confidence intervals are presented in Table 4-2. The regressed values are coupled to the pure component parameters summarized in Table 4-1, and should not be directly transferred to other pure component parameters.



Figure 4-6: RTPT fit compared to spectroscopic data with parameters regressed using the twostage method for the systems of ethanol + n-hexane (left) and ethanol + cyclohexane (right) at three temperatures.



Figure 4-7: RTPT fit compared to spectroscopic data with parameters regressed using the twostage method for the systems of 1-propanol + n-hexane (left) and 2-propanol + n-hexane (right) at three temperatures.



Figure 4-8: RTPT fit compared to spectroscopic data with parameters regressed using the twostage method for the systems of 1-butanol + n-hexane (left) and 1-hexanol + cyclohexane (right) at three temperatures.



Figure 4-9:RTPT fit compared to spectroscopic data with parameters regressed using the twostage method for the systems of 1-pentanol + n-hexane (left) and phenol + n-hexane (right) at three temperatures.



Figure 4-10:RTPT fit compared to spectroscopic data with parameters regressed using the twostage method for the systems of 1-hexanol + n-hexane (left) and 1-hexanol + cyclohexane (right) at three temperatures.

	-	К	^{AD} , [cm ³ /mol]	$\epsilon_2^{AD}/k, \mathrm{[K]}$		ϵ_N^{AD}/k , [K]	
Solute	Solvent	Value	95% C.I.	Value	95% C.I.	Value	95% C.I.
methanol	<i>n</i> -hexane	6.413E-02	2.586E-02 - 1.745E-01	1568	1241 - 1834	2435	2141 - 2697
	cyclohexane	8.264E-01	1.383E-01 - 1.632E+00	659.7	349.3 - 1221	1693	1500 - 2226
ethanol	<i>n</i> -hexane	1.606E-01	6.234E-02 - 4.710E-01	1355	1041 - 1647	2220	1907 - 2502
	cyclohexane	3.153E-03	8.299E-04 - 9.722E-03	2320	2021 - 2659	3341	3000 - 3739
1-propanol	<i>n</i> -hexane	1.049E-02	4.238E-03 - 2.306E-02	2117	1851 - 2412	2930	2689 - 3202
2-propanol	<i>n</i> -hexane	1.388E-02	6.356E-03 - 3.260E-02	2111	1860 - 2317	2849	2590 - 3078
1-butanol	<i>n</i> -hexane	4.087E-02	2.041E-02 - 7.603E-02	1528	1334 - 1701	2425	2237 - 2634
	cyclohexane	1.884E-02	6.401E-03 - 3.932E-02	1801	1554 -2149	2630	2408 - 2938
1-pentanol	<i>n</i> -hexane	8.840E-03	3.393E-03 - 2.490E-02	2244	1947 - 2517	2984	2679 - 3271
1-hexanol	<i>n</i> -hexane	1.996E-02	1.227-02 - 3.190E-02	1817	1683 - 1966	2659	2520 - 2804
	cyclohexane	1.262E-02	8.164E-03 - 2.021E-02	1903	1770 - 2044	2741	2603 - 2876
phenol	<i>n</i> -hexane	6.549E-02	3.534E-02 - 1.605E-01	1668	1390 - 1865	2289	1612 - 2369

Table 4-2: Regressed association parameters using RTPT and the two-stage regression method.

Values presented in Table 4-2 for the association parameters and those presented in a later section (Table 4-3) are slightly different than published values due to an error in calculating the preexponential term. This error has been addressed and all values presented in this document have been corrected.

4.6.2 Delta Comparison with Solvent Trends

To better understand the influence of the inert solvent on association, RTPT Δ -values were calculated for each of the binary pairs at 298.15 K at an alcohol mole fraction of one. A plot of Δ_2 and Δ_N versus carbon chain length is provided in Eq. 4-11 and Eq. 4-12 for the first six primary alcohols. The results of the error analysis are included to convey the bootstrap 95% confidence intervals. We encountered some challenges with regressing the methanol data, which is reflected in the deviation of the parameter values and confidence intervals from trends observed in the other systems. A more detailed discussion of these challenges is provided later. The Δ values associated with the formation of the *n*-mer were larger in magnitude than the corresponding dimer value in all cases. This is consistent with the understanding of positive cooperability which postulates that, once the first hydrogen bond has formed, subsequent hydrogen bonds become more energetically favorable, hence $\Delta_N \gg \Delta_2$.^{110,111,119}

The solvent appears to have a minimal effect on Δ_2 as the data from both solvents is clustered around a mean value near 1024 cm³/mol. Except for 1-pentanol the value of Δ_2 appears relatively constant and virtually independent of solvent. The Δ_N values displayed a less consistent trend than those obtained for Δ_2 . Values obtained in *n*-hexane are generally larger than those obtained in cyclohexane. Average values are 15710 cm³/mol and 16630 cm³/mol for solvents *n*hexane and cyclohexane, respectively. Δ_N increases by about 20% between 1-propanol and 1hexanol when *n*-hexane is the solvent. Based on these results, solvent interactions appear to have a greater influence on the formation of oligomers larger than dimers.





Figure 4-11: Δ_2 versus carbon chain length with error bars for primary alcohols methanol through 1-hexanol in cyclohexane and *n*hexane at 298.15 K and pure alcohol concentration.

Figure 4-12: Δ_N versus carbon chain length with error bars for primary alcohols methanol through 1-hexanol in cyclohexane and *n*hexane at 298.15 K and pure alcohol concentration.

The methanol + alkane systems show an unusual trend in regressed parameters compared to larger alcohols: the κ^{AD} value is relatively large and the $\epsilon_{2 \text{ or } N}^{AD}$ values are relatively small. Figure 4-13 shows a decrease in the free hydrogen A^{I}/l values between 8 and 14 mol%; this trend was observed for both methanol systems. Similar behavior was observed for both ethanol systems and 1-butanol + *n*-hexane at high concentrations, though the decrease in the latter was minimal. As the concentration of hydroxyls is increased, the $\tilde{\nu}(OH)$ region becomes congested with overlapping absorbances from several types of hydrogen bonds thereby making definitive assignment difficult. This issue is not uncommon and has been addressed by Meijer¹³⁵, Barlow et al.,¹³⁶ and Wandschneider et al.⁶¹ who note that in these situations the problem is under-constrained and comparable fits can be obtained from several different interpretations depending on the initial guess. We attribute the decrease in the A^{I}/l values to the absorbance peak fitting procedure when subtracting the overlap of the γ (designated by Asprion as dimer) and (δ) (designated by Asprion as polymer) with the free hydrogen ($\alpha + \beta$) peak resulting in an underestimation of the free hydrogen population. This is a possible explanation for the challenges encountered in fitting the methanol systems and the unusual values of regressed κ^{AD} and $\epsilon_{2 \text{ or } N}^{AD}$ compared to other systems. These observations highlight an opportunity to revisit the partitioning of the hydroxyl region in future spectral measurements using the scaling methods of Bala et al.¹²²



Figure 4-13: RTPT fit compared to spectroscopic data with parameters regressed using the twostage method for the systems of methanol + n-hexane (left) and methanol + cyclohexane (right) at three temperatures. Poor quality data for is observed at high alcohol concentrations for both solvents, resulting in inferior model parameters.

4.6.3 Enthalpy of Positive Cooperativity

To better understand the thermodynamics of association, the enthalpies of association for the dimer (ΔH_2) and *n*-mer (ΔH_N) were calculated using $\Delta_{2 \text{ or } N}$ values obtained from *stage-2* of the RTPT regression and the van't Hoff relation.

$$\Delta H_{2 \text{ or } N} = R \frac{d \ln \Delta_{2 \text{ or } N}}{d \left(\frac{1}{T}\right)}$$
 Eq. 4-37

To provide a basis for comparison, all enthalpies were calculated using $\Delta_{2 \text{ or } N}$ values at 298.15 K and pure alcohol composition. Table 4-3 summarizes the results and shows that the dimer association enthalpy is about 70-75% of the *n*-mer value. The average enthalpy for the formation of a dimer across all systems studied was -16.6 kJ/mol. This value is 6.9 kJ/mol smaller in magnitude than the average *n*-mer enthalpy of -23.6 kJ/mol. The calculated enthalpies do not show a clear trend with carbon number.

Comparison with literature must be made against chemical theory approaches that use two concentration-based association constants (K_c) since no other experimental RTPT fits exist. To our knowledge, the only work meeting this criteria for primary alcohols is Kretchmer and Wiebe¹²⁰ who modeled alcohol vapors using dimers and tetramers. They reported values of -16.7 kJ/mol for ΔH_2 and values of -92.4, -84.1, and -94.6 kJ/mol for cyclic hydrogen-bonded tetramers of methanol, ethanol, and 2-propanol, respectively. Subtracting their dimer value from a tetramer and dividing the remainder by the three remaining bonds results in average *n*-mer enthalpies, ΔH_N , of (-92.4-(-16.7))/3 = -25.3, -22.5, and -26.0 kJ/mol per hydrogen bond, respectively. These values are consistent with the average dimer value of -16.6 kJ/mol and *n*-mer value of -23.6 kJ/mol per hydrogen bond presented in this work. These findings further highlight the differences between the hydrogen bonds of dimers and those formed in higher-order oligomers.

		298.15 K , $x_{alcohol} = 1$			
Solute	Solvent	$-\Delta H_2$	$-\Delta H_N$	$-\Delta H_2$	
bolute	Sorvent	[kJ/mol]	[kJ/mol]	$-\Delta H_N$	
methanol	<i>n</i> -hexane	15. <u>3</u> 7	22. <u>5</u> 2	0.683	
	cyclohexane	8.4 <u>2</u> 7	16. <u>3</u> 9	0.514	
ethanol	<i>n</i> -hexane	13. <u>3</u> 8	20. <u>4</u> 7	0.654	
	cyclohexane	21. <u>2</u> 9	29. <u>7</u> 7	0.715	
1-propanol	<i>n</i> -hexane	19. <u>58</u>	26. <u>3</u> 2	0.744	
2-propanol	<i>n</i> -hexane	19. <u>6</u> 0	25. <u>7</u> 3	0.762	
1-butanol	<i>n</i> -hexane	14. <u>7</u> 2	22. <u>0</u> 9	0.666	
	cyclohexane	16. <u>9</u> 4	23. <u>8</u> 0	0.712	
1-pentanol	<i>n</i> -hexane	20. <u>4</u> 8	26. <u>6</u> 2	0.769	
1-hexanol	<i>n</i> -hexane	16. <u>9</u> 0	23. <u>8</u> 8	0.708	
	cyclohexane	17. <u>6</u> 2	24. <u>5</u> 6	0.717	
phenol	<i>n</i> -hexane	15. <u>4</u> 0	20. <u>5</u> 2	0.750	

Table 4-3: Enthalpies of association based on extrapolation to purity.

4.6.4 Activity Coefficient Contributions

After fitting association parameters to the spectroscopic data, the association contribution to the activity coefficients can be calculated using Eq. 4-21 and Eq. 4-22. This contribution can then be combined with the residual and combinatorial contributions using Eq. 4-16 to complete the activity coefficient calculation. For the mixtures studied here, the activity coefficient is dominated by the

association contribution and the combinatorial contribution is minor. To illustrate the importance of the association effects, we omit the residual term entirely for the mixtures shown in this section and predict the activity coefficient using the association parameters shown in Table 4-2 for γ^{assoc} and Flory's model for γ^{comb} .

Figure 4-14 shows an excellent prediction of the activity coefficients for the system 1hexanol + cyclohexane using only the association and combinatorial contributions. For this system, the combinatorial contribution is so small that it is not discernable when plotted relative to the association contribution, thus only the sum of the contributions is plotted. The prediction of the activity coefficient from only the association contribution is striking; no empirical adjustment of a residual contribution is included. Because the activity coefficient represents the behavior of the mixture relative to the pure species, the infinite dilution activity coefficient for alcohol is dependent on the extent of hydrogen bonding in the pure alcohol (Eq. 4-28). The predicted behavior of the activity coefficients for the associating component are of particular interest in Figure 4-14. The 1-hexanol infinite dilution activity coefficient is approached with a slope that decreases in magnitude as infinite dilution is approached as illustrated by the inset plot. Clearly, the infinite dilution value is not approached asymptotically from below but rather from the side, and the slope change occurs below about 2 mol% alcohol (inset of Figure 4-14).



Figure 4-14: Activity coefficient data at 70 °C for the system of 1-hexanol + cyclohexane overlaid with the predicted activity coefficients resulting from the sum of the RTPT association term and the Flory combinatorial. Experimental data is from Svoboda et al.¹³⁷

The change of slope is due to the smaller association constant of the dimer compared to the *n*-mer and cannot be modeled with a TPT-1 single association constant which approaches infinite dilution with a large magnitude slope.

The association and combinatorial contributions are displayed alongside experimental data in Figure 4-15 for the methanol + cyclohexane system. For this system, the combinatorial contribution is discernable on the plot, but still minor. While the representation of the experimental data is satisfactory for most of the mole fractions, there is a noticeable overprediction of the infinite dilution value for methanol. We believe that this behavior is attributable to the challenges discussed previously regarding the spectroscopic data for this system. The decrease in tabulated absorbance above 8 mol% reported for this system effectively depresses the calculated values of X^A as mole fraction increases, leading to an overrepresentation of the degree of hydrogen bonding when extrapolated to pure alcohol. This leads to an overprediction of the activity coefficient at infinite dilution. Similar behavior occurs in the ethanol systems and thus uncertainties for these systems may be larger than the reported confidence intervals. Because the concentration of hydroxyls is more significant for shorter alcohols, hydrogen bonding is more prominent compared to longer alcohols at the same alcohol mole fraction, and interference from the γ and δ hydroxyls in the absorbance spectra appears at lower mole fractions for a given temperature in these systems, complicating accurate determination of monomer.



Figure 4-15: Contributions to the overall activity coefficient (–) for methanol (blue) + cyclohexane (black) system at 55 °C compared to the data of Morachevskii.¹³⁸ The solid line is the sum of the combinatorial term (– –) and predicted association term (– –). Infinite dilution values were calculated by linearly regressed data provided by Lazzaroni et al.¹³⁹ and denoted with red symbols.

4.6.5 Extension to Vapor Liquid Equilibrium

For chemical process design, accurate representation of phase equilibria data is critical. The association contribution of Eq. 4-16 is dominant but some adjustment is necessary for precise modeling. The residual term is small but integral to precise process engineering modeling. Asprion et al.¹¹⁷ selected the UNIQUAC method for accurate fitting. In this work, we demonstrate that the combination of RTPT with the NRTL residual model results in precise fitting of experimental data over industrially relevant temperature ranges. Figure 12 demonstrates fitting for the system 1hexanol + cyclohexane, and Figure 4-17 demonstrates fitting for 1-butanol + cyclohexane. The vapor phase virial coefficient Hayden-O'Connell parameter, η , used for regression is 2.2 for 1-butanol and 1-hexanol. The non-randomness parameter, α_{ij} , was set to 0.3 for both systems. The residual adjustment is minor in both cases and the fits over the temperature ranges are excellent using only a small temperature-independent NRTL contribution, representing a correction to the combinatorial contribution at infinite temperature. The temperature dependence of the VLE data is captured entirely by the association contribution predicted from the spectroscopic fits, and no temperature-dependent residual contribution is needed.



Figure 4-16: Results of Aspen regression using association parameters obtained from experimental infrared data of Asprion for 1-hexanol + cyclohexane. Experimental data are from Svoboda et al.¹³⁷



Figure 4-17: Regression results for 1-butanol + cyclohexane system using the association parameters obtained from the data of Asprion. Experimental data are from Smirnova and Kurtunina.¹⁴⁰

4.7 Summary and Conclusions

This work derives a form of the association contribution to the activity coefficient that is consistent with the resummed thermodynamic perturbation of Wertheim's theory developed by Marshall and Chapman. RTPT accounts for positive cooperativity in hydrogen bonding and expresses association effects using two constants, one for the formation of a dimer and another for all subsequent bonds formed. Further, we reinterpret Asprion's spectroscopic measurements in terms of hydrogen bonding motifs and evaluate the RTPT and TPT-1 thermodynamic models. RTPT provides a better description of the data when compared to TPT-1 using only one additional fitted parameter. The regression resulted in the prediction of enthalpy which averages -16.6 kJ/mol for dimer and subsequent hydrogen bonds have an average per bond enthalpy of -23.6 kJ/mol. Both enthalpies are consistent with values of Kretschmer and Weibe. The association constants for the dimer are found to be approximately 1024 cm³/mol in both *n*-hexane and cyclohexane at 298.15 K. The average association constants for *n*-mer are 15710 cm³/mol and 16630 cm³/mol for solvents *n*-hexane and cyclohexane, respectively. The Δ_N exhibits a 20% increase between 1-propanol and 1-hexanol when *n*-hexane is the solvent but are independent of carbon number in cyclohexane. A form for the association activity coefficient was derived in a manner consistent with RTPT. Furthermore, the parameters obtained from the regression were used to satisfactorily predict activity coefficients and phase behavior for selected binary alcohol + hydrocarbon systems. Examination of the experimental spectroscopic data for three systems exhibit a decrease in absorbance at concentrations above 8 mol%, suggesting that uncertainty beyond the statistical results is probable, and improved methods of curve fitting are required for future measurements.

4.8 Acknowledgements

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CHAPTER 5:Infrared Quantification of Ethanol and 1-Butanol Hydrogen Bonded Hydroxyl Distributions in Cyclohexane

5.1 Preface

Quantifying the mid-range infrared hydroxyl stretch absorbance region has traditionally been a challenge due to the wavenumber dependence of the attenuation coefficient. Interpretation often assigns a single attenuation coefficient to each type of hydrogen-bonded aggregate. This work leverages a recently developed technique of scaling hydroxyl stretching absorbances in the mid-infrared region with a continuous attenuation coefficient function that produces integrated areas, which directly correlate to hydroxyl concentrations. After scaling, the hydroxyl absorbance is fitted with five curves, of which four are dominant. These four curves represent unique hydroxyl configurations and translate to specific aggregate structures. The technique is applied to ethanol and 1-butanol. The resulting population distributions of hydrogen-bonded hydroxyl configurations are compared with the resummed thermodynamic perturbation theory (RTPT) model for linear chains as a function of concentration and temperature. The model is demonstrated to capture the critical features of the distributions.

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5.3 Introduction

Given its broad importance in the chemical and biological sciences, hydrogen bonding has been the subject of many notable works over the century since its recognition.^{4,5,142} Yet, despite great strides in mapping its molecular behavior, a complete and predictive understanding of the bulk effects of hydrogen bonding remains elusive. Quantification and characterization of the specific hydrogen-bonded aggregates are needed to test theoretical knowledge and practical applications such as modeling the phase equilibria of liquid mixtures. For associating compounds such as alcohols, effective representation of phase equilibria necessitates accounting for hydrogen bonding, typically in the form of association parameters. These model parameters depend strongly on the chemical and physical interactions of the molecules, motivating quantitative spectroscopic analysis to probe them.¹¹⁵

For thermodynamic modeling of an associating substance, a fundamental property is the extent of its association at equilibrium. For alcohols, this can be expressed in the fraction of hydroxyls that remain unbonded (i.e., not involved in hydrogen bonding).¹¹⁵ Different techniques, including nuclear magnetic resonance (NMR), near-infrared spectroscopy (NIR), and mid-infrared spectroscopy (MIR), have been used to assess this 'monomer fraction'. The application of NMR is limited for quantification due to its long measurement timescale, which collapses all hydroxyl resonances to a single chemical shift value. Thus, essential details are unavailable via NMR as the chemical shifts of individual hydrogen-bonded clusters (dimers and oligomers) are unknown. As for NIR spectroscopy, while the measurement timescale is appropriate the spectra show heavily overlapped vibrational overtone bands, which are difficult to analyze.¹⁴³

Mid-infrared spectroscopy (henceforth, IR) remains one of the most popular spectroscopic methods for studying the self-association of alcohols^{14,34,54,105,106,123,144–147} since it provides a high

level of detail in the $\tilde{v}(OH)$ stretch region. However, in an IR spectrum of a sample containing alcohol molecules in monomeric and aggregated arrangements, correctly assigning the constituent absorbances among the fundamental $\tilde{v}(OH)$ bands has proved challenging. More problematic is that quantitative analysis of all resonances in the overall hydroxyl region (3000-3750 cm⁻¹) has been hampered by an inability to determine the wavelength dependence of the molar attenuation coefficient. The hydroxyl region is also strongly temperature-dependent, diminishing confidence in the peak integration necessary to quantify unbonded hydroxyls. To address this issue, Bala et al.¹²² introduced a wavelength-dependent molar attenuation coefficient function with a form based on trends computed via quantum chemical simulations. The function was then optimized and refined using variable concentration and temperature experimental data to provide a temperatureindependent integrated hydroxyl absorbance. The present work aims to apply curve-fitting to the absorbances in the scaled spectra to obtain populations of specific hydroxyl types from the alcohol's $\tilde{v}(OH)$ absorbance. Further, we compare the experimental populations with predictions from Marshall and Chapman's resummed thermodynamic perturbation theory (RTPT),^{112,134} which captures essential features of the observed hydroxyl distributions.

5.4 Background

There are many infrared-active vibrational modes present in alcohols; however, the most useful mode for the study of alcohol self-association is the hydroxyl stretching vibration, $\tilde{v}(OH)$, which appears in the 3000 to 3750 cm⁻¹ region of the IR spectrum. The effect on this covalent bond upon forming a hydrogen bond is readily observed. Specifically, participation in a hydrogen bond redistributes the electron density within the O-H bond, thereby lowering and broadening its absorption frequency and increasing its infrared attenuation constant. Even small changes in alcohol concentration or measurement temperature result in significant variations among the free

and hydrogen-bonded hydroxyl populations in the landscape of the $\tilde{v}(OH)$ region. This sensitivity to association makes it an ideal reporter for quantifying the monomer fraction. IR enables the various hydrogen bonded O-H sites to be categorized and enumerated according to their positions within a particular oligomer.^{7,53,89,123} This approach was first proposed by Hall and Wood⁶ and has led to the definition of the distinct hydrogen-bonded hydroxyl configurations shown in Figure 5-1: alpha (α), beta (β), gamma (γ), and delta (δ).¹⁰⁶ Lastly, eta (η), and zeta (ζ) hydroxyls are also present in alcohol-containing solutions and have been identified in molecular dynamics simulations.¹⁴⁸



Figure 5-1: Hydroxyl types observed in liquid alcohols. The number of hydrogen bonds received by the oxygen (Oⁱ) and donated by the proton (H^j) for each hydroxyl type is denoted in superscript.

When alcohol is dilute (less than approximately 0.2 mol%) in a non-hydrogen-bondforming (inert) solvent such as cyclohexane, the alcohol spectra exhibit a sharp singlet near 3640 cm⁻¹ with a low wavenumber shoulder. As the concentration of alcohol is increased, dimers begin to form, producing β and γ hydroxyls. The β hydroxyls (O¹H⁰ as shown in Figure 5-1, where the superscripts indicate the number of participations in hydrogen bonds) are located at the terminus of a hydrogen-bonded chain and receive a hydrogen bond at the oxygen while the hydroxyl proton remains free. A γ hydroxyl is located on the chain end opposite of β and consists of a nonhydrogen-bonded oxygen attached to a hydrogen-bonded proton (O^0H^1). Molecular dynamics and quantum mechanics simulations^{106,122} of alcohol clusters indicate that the frequency of α and β hydroxyls appear in the same wavenumber region of the infrared spectrum and contribute to the sharper peak at ~3640 cm⁻¹ while γ hydroxyls are visible near 3500 cm⁻¹.

As the concentration of alcohol is increased further, the γ absorbance increases, and a broad peak emerges in the absorbance spectra centered near 3325 cm⁻¹ as the population of chains increases. The δ hydroxyls, which appear in the center of chains, contribute to this broad absorbance; their resonance is the most red-shifted relative to the non-bonded α sites. In linear oligomers, δ hydroxyls are hydrogen-bonded at the oxygen and the hydrogen (O¹H¹), an arrangement that significantly polarizes the electron density within the parent O-H bond. In addition, δ hydroxyls feature a broad Gaussian-like¹⁴⁹ distribution of frequencies since each covalent bond is weakened to a different extent depending on their position or geometric orientation within the "floppy" hydrogen-bonded chain.

Collectively, the $\tilde{v}(OH)$ region is sensitive to subtle changes in hydrogen bonding induced by altering the alcohol concentration or sample temperature. Temperature is a measure of the average kinetic energy of the molecules. Thus, an increase in temperature indicates that more alcohol molecules are able to escape the hydrogen bonding potential. This manifests as a decrease in δ hydroxyls coupled with a concurrent increase in the 'free peak' produced by α and β hydroxyls.

Positively cooperative hydrogen bonding occurs due to the polarization of the O-H bond, allowing the hydroxyl proton to become a more favorable hydrogen bond donor. Partial charges within the dimer are stabilized by adding a monomer to form a trimer. This significant difference in the bonding interaction of the dimer relative to other oligomerizations has been noted by other researchers^{7,61,105–107} and warrants special consideration through the use of two association parameters; one describing the effects of dimer formation and a second to other capture the formation of larger oligomers.

5.5 Methods

5.5.1 Infrared Measurements

Anhydrous ethanol, 1-butanol, and cyclohexane were obtained from Sigma-Aldrich at purities of 99.5%, 99.8%, and 99.5%, respectively. Ethanol and 1-butanol were stored over activated 3 Å molecular sieves for at least 72 h before use, and no further purification was performed. Solutions of alcohol + cyclohexane were prepared volumetrically using type-A glassware and Hamilton gas-tight syringes in a glovebox under a nitrogen atmosphere. Experimental concentrations were calculated by assuming ideal solution behavior, which neglects the excess volume of mixing. Pure component molar densities for mixing solutions were calculated using a second-order polynomial fitted to pure component data from the NIST ThermoData Engine.¹⁵⁰ The coefficient of determination was higher than 0.99 for all components.

Infrared spectra were collected in absorbance mode using a Jasco FT/IR-6600 spectrophotometer equipped with a Ge/KBr beam splitter and DLaTGS detector. Before the background spectrum was collected, the sample compartment was purged with nitrogen for 30 min. The nitrogen purge was maintained for all subsequent measurements. All measured spectra, including the background, were collected using 128 scans at 2 cm⁻¹ resolution using a Specac demountable liquid flow cell (model GS20582) equipped with CaF₂ windows. Cell temperature was controlled with a Specac electrically heated jacket and model 4000 high stability temperature controller in 10 °C increments from 30 to 60 °C with an uncertainty of +/- 0.05 °C. Cold tap water was supplied to the heating jacket at the manufacturer's recommended flow rate of 500 mL/min.

The sample was introduced to the flow cell using an external valve system that connected the sample syringe with a Luer-lock fitting, preventing the introduction of environmental moisture.

Teflon spacers were selected to produce absorbances of ≤ 1 A.U. in the region 3050 cm⁻¹ to 3800 cm⁻¹. The pathlength must be known within 1% to relate the absorbance reliably to concentration.²⁷ As such, the manufacturer-provided nominal spacer thickness dimensions were of inadequate precision. Instead, pathlengths were calculated for each sample using a MATLAB[®] application¹⁵¹ based on the fringe interference spectrum of the empty cell taken over a 300 cm⁻¹ interval.

5.5.2 MD/QM Simulations and Scaling Methods

To guide the interpretation and curve fitting of the spectra, we selected peak locations to represent the key hydroxyl types found in molecular dynamics simulations. In our previous work,¹²¹ clusters were extracted from molecular dynamics simulations and analyzed using quantum mechanical simulations at the B3LYP level of theory with the 6-31G* basis set to interrogate the infrared vibrations associated with the O-H bond. Other details regarding the molecular dynamics and quantum mechanics simulations are provided by Bala et al.^{121,122}

After removing solvent absorbance, spectra are often fitted with curves for the different hydroxyl configurations where each curve or wavenumber range is assigned a single attenuation coefficient.^{34,106,149} A major development from our previous work is the Beer's law scaling of the mid-range IR absorption spectra to obtain temperature-independent integrated hydroxyl absorbances for ethanol and 1-butanol at concentrations of up to 20 mol% alcohol in cyclohexane.¹²² The scaling applies a function that changes with wavenumber, whose shape was developed from trends in quantum chemical calculations and refined empirically using multiple concentration and temperature spectra. This scaling compensates for the significant increase in

attenuation coefficient displayed by the lower frequency hydrogen-bonded species. The scaled spectra are analyzed via curve-fitting, and their integrated absorptions are compared quantitatively.

5.5.3 Spectra Preprocessing and Regression of Molar Attenuation Coefficient

Previously, we reported on spectra for 1-butanol up to 20 mol% in cyclohexane;¹²² this work includes two additional concentrations: 25 mol% and 30 mol%. Ethanol solutions up to 30 mol% in cyclohexane were prepared, but evaporative losses prevented measurements at 60 °C at concentrations above 10 mol% ethanol. Because concentration changes due to thermal expansion of solutions, we use mole fraction to quantify composition in reported results. The collected spectra were subjected to a series of preprocessing steps before the molar attenuation coefficient was regressed. Baseline correction and the subtraction of absorption signals attributable to the cyclohexane in the region of interest – $\tilde{v}(3050 \text{ cm}^{-1} \text{ to } 3800 \text{ cm}^{-1})$ – were performed using methods detailed elsewhere.¹⁵² Additional spectra adjustments, such as smoothing, were not performed at any point. The overall hydroxyl region was scaled using methods presented by Bala et al.¹²² and summarized in Section 5.5.2. Parity plots comparing measured and correlated concentrations for both alcohols and the scaling constants are available in APPENDIX K: Parity Plots.

5.5.4 Curve-Fitting

The absorbance profile of liquid phase vibrations combines characteristics of a gas-phase Lorentzian shape and the Gaussian character exhibited by solids.¹³⁵ To account for these features, a product pseudo-Voigt shape was chosen for three reasons: the model has a physical basis¹³⁵; it contains fewer parameters than a sum-Voigt profile, and it is commonly applied to spectra obtained from the liquid phase.¹⁵³ The form of Eq. 5-1 was adapted from Kruger et al.¹⁵⁴ and requires four fitted parameters: peak height (*H*), peak center ($\tilde{\nu}_0$), Gaussian width (W_G), and Lorentzian width (W_L).

$$A = \frac{H}{1 + W_L^2 (\tilde{v}_i - \tilde{v}_0)^2} \cdot exp \left(-W_G^2 (\tilde{v}_i - \tilde{v}_o)^2\right)$$
Eq. 5-1

Within a single temperature, the scaled spectra were fitted with six product pseudo-Voigt curves: five for the $\tilde{v}(OH)$ region hydroxyls (α , β , γ , δ , and unassigned) and one for the $\tilde{v}(CH)$ region. The curve-fitting process began with the most dilute alcohol samples and proceeded to higher alcohol concentrations. Optimized parameters from each regression were used as the initial values for the next highest concentration of alcohol.

To isolate the hydroxyl absorption, the pseudo-Voigt curve associated with the alcohol's alkyl group $\tilde{v}(CH)$ was subtracted from the spectrum. This band was centered in the region of ~2950 cm⁻¹ and extended into the low-frequency region of the broad $\tilde{v}(OH)$. It became visible only after subtracting the absorbance of the solvent.

Curve areas were restricted to positive values and optimized simultaneously by a nonlinear least-squares method. Integration of the curve fit areas was achieved using a trapezoidal Riemann sum of the fitted curve with 2 cm^{-1} intervals over the range of 3050 cm⁻¹ to 3800 cm⁻¹.

5.5.5 Modeling Hydrogen Bonding with RTPT

Conflicting theories exist in the literature regarding the relative prominence of chains and rings in alcohols.¹⁵⁵ Here, we consider a model for cooperative bonding limited to linear chains. Recently, the Wertheim resummed thermodynamic perturbation theory (RTPT) developed by Marshall and Chapman¹¹² has been shown to agree with infrared spectroscopic measurements from Asprion.^{34,134} RTPT considers cooperative bonding, distinguishing between association strengths for the first hydrogen bond between two monomers to form a dimer (Δ_2) and association strengths for subsequent hydrogen bonds in an oligomer (Δ_N). Association strengths (Δ_n) are similar to concentration-based equilibrium constants but include composition dependence. The molar or

number density of chains of length *i* in solution is related to the molar or number densities of the constituent species,

$$\rho_i = \Delta_n \rho_{i-1} \rho_\alpha \qquad \qquad \text{Eq. 5-2}$$

which represents the addition of monomer, α , to a chain of length i - 1, and Δ_n depends on whether a dimer, $\Delta_n = \Delta_2$ or an n-mer, $\Delta_n = \Delta_N$, is formed. The sum of molar densities for α hydroxyls and β hydroxyls divided by the molar density of alcohol in the solution produces the fraction of non-bonded hydroxyl protons, $X^D = N_{\alpha+\beta}/N_a$ where N_a represents the number of alcohol molecules. The RTPT model uses a balance on proton acceptor and proton donor sites to calculate the densities of hydroxyl configuration. The association model used here assumes a 2B bonding scheme¹⁵⁶ for the hydroxyl, which translates to one proton acceptor site (A) on the oxygen and one proton donor site (D) attributed to the hydroxyl proton. When alcohol is the only associating species, for the RTPT model, the density of acceptor sites equals the density of donor sites ρ^D = ρ^A and the fraction of nonbonded donor sites is equivalent to the fraction of non-bonded sites $X^D = X^A$. The total density of donor sites is related to the fraction of non-bonded donor sites via $\rho^D = x_a \rho X^D$ where x_a is the mole fraction of alcohol, and ρ is the molar density of the mixture. Wertheim statistical mechanics models hydrogen bonding association strengths using adjustable parameters for the bonding volume (κ^{AD}), which represents the volume of a square well site on a molecule, and the square-well depth, ϵ^{AD}/k . In this work we regress a single value for the bonding volume for dimers and oligomers, and we regress two bonding energies, ϵ_2^{AD}/k or ϵ_N^{AD}/k , in the Mayer f-function according to

$$\Delta_{2 \text{ or } N} = N_A d^3_{aa} g_{aa}(d) \kappa^{AD} \left(\exp\left(\frac{\epsilon^{AD}_{2 \text{ or } N}}{kT}\right) - 1 \right)$$
 Eq. 5-3

where the subscripts *aa* denote the bonding between two alcohol molecules. The association strength is often expressed in molecular units, but here we use molar units (volume/mole). To convert molecular parameters into molar units, the expression includes Avogadro's constant (N_A). The compositional dependence of $\Delta_{2 \text{ or } N}$ is ascribed to the variation in the hard-sphere radial distribution function at contact ($g_{aa}(d)$), which depends on the solution packing fraction (ζ_l) and the temperature-variant segment diameter of the associating fluid (d_{aa}). The effect of temperature on the segment diameter is calculated via Eq. 5-6 using a segment diameter (σ_i) and the depth of the pair potential (ϵ_i/k) for each species present in the solution. The pure component parameters used for this regression are from PC-SAFT as fitted to pure component data by Gross and Sadowski¹²⁶ and are provided in Table 5-1.

$$g_{ij}(d) = \frac{1}{(1-\zeta_3)} + \left(\frac{d_i d_j}{d_i + d_j}\right) \frac{3\zeta_2}{(1-\zeta_3)^2} + \left(\frac{d_i d_j}{d_i + d_j}\right)^2 \frac{2\zeta_2^2}{(1-\zeta_3)^3}$$
Eq. 5-4

$$\zeta_l = (\pi/6) N_A \, \rho \sum_i x_i m_i d_i^l \; ; \; l \in \{2,3\}$$
 Eq. 5-5

$$d_i = \sigma_i \left[1 - 0.12 \exp\left(-3\left(\frac{\epsilon_i}{kT}\right)\right) \right]$$
 Eq. 5-6

Killian et al. demonstrated that Δ_2 and Δ_N are related to the fraction of non-bonded hydroxyl protons (X^A) through the monomer density (ρ_{α}) according to Eq. 5-7.¹³⁴

$$\rho_{\alpha} = \frac{2x_a \rho X^A}{1 + x_a \rho \Delta_N X^A + \sqrt{(1 + x_a \rho \Delta_N X^A)^2 + 4(\Delta_2 - \Delta_N)x_a \rho X^A}}$$
Eq. 5-7

The fraction of free hydroxyls is simultaneously related to the monomer density using Eq. 5-8 and Eq. 5-9.

$$X^{A} = \frac{1}{1 + x_{a}\rho\Delta_{2}X^{A}/s^{2}}$$
 Eq. 5-8

$$s = 1 + (\Delta_2 - \Delta_N)\rho_\alpha \qquad \qquad \text{Eq. 5-9}$$

 $\frac{\epsilon_i}{k}$, [K] **σ**_i, [Å] Component m_i Ethanol 2.3827 3.1771 198.24 1-Butanol 2.7515 3.6139 259.59 Cyclohexane 2.5303 3.8499 278.11

Table 5-1: PC-SAFT pure component parameters.

5.6 **Results and Discussion**

5.6.1 Frequency Distributions of Hydrogen Bonds from QM Calculations

The MD and QM simulations for ethanol + cyclohexane (50 mol% ethanol) and 1-butanol + cyclohexane (10 & 50 mol% 1-butanol) mixtures provide the distribution of vibrational frequencies for α , β , γ , and δ hydroxyls shown in Figure 5-2. Findings from the two binary systems are plotted together because separate plots showed no discernable differences between them. The vibrations of each hydroxyl type were binned in 5 cm⁻¹ wide bins and normalized and the resulting lines were smoothed with a 7-bin moving average and normalized to display the relative populations for each hydroxyl type as a function of wavenumber. These processing steps were carried out to refine the shape of the distributions and display relative information about them more clearly. The peak heights should not be used to compare hydroxyl types because the sample size is insufficient to reflect the quantitative distribution at the simulated concentrations. However, the peak shapes provide some qualitative information and a relative description of the vibrational frequencies of different hydroxyl types. In agreement with other studies,^{7,52,59,60,157} Figure 5-2 demonstrates that α and β hydroxyls appear at the same frequency and show significant overlap,

confirming that the β -hydroxyl contribution to the sharp high-frequency O-H peak should not be ignored. These calculations provide a supporting basis for assigning peak areas to specific hydroxyl configurations.



Figure 5-2: Smoothed normalized distributions of hydroxyl types from QM simulations of 1butanol + cyclohexane, and ethanol + cyclohexane mixtures. Vibrational frequencies of hydroxyl types based on sample size (*n*) for α (n=1878), β (n=1430), γ (n=1430), and δ (n=927) hydroxyls are binned in 5 wavenumber bins and smoothed with a 7-bin moving average.

5.6.2 Assigning Curves to Specific Hydroxyl Configurations

The assignment of the curve-fit areas to specific hydroxyl types was inspired by the distributions observed in the MD/QM analysis, as shown in Figure 5-3. In keeping with the recommendations of Meier¹³⁵, a minimum number of curves were used to partition the $\tilde{\nu}(OH)$ region. As a result of the scaling process, the integrated $\tilde{\nu}(OH)$ curves are equal to the concentration of hydroxyl groups with units of molarity.¹²²



Figure 5-3: Raw infrared spectrum of 20 mol% 1-butanol in cyclohexane at 30 °C (left). Beer's law scaled and curve-fit infrared absorbance spectrum for 20 mol% 1-butanol in cyclohexane at 30 °C (right). Scaling reduces the contribution of the delta hydroxyls around 3350 cm⁻¹ relative to the non-hydrogen-bonded-hydroxyl-proton absorbance near 3640 cm⁻¹. The scaled peak areas are directly proportional to concentration.

Since the resonances of α and β hydroxyls are similar,¹²² their individual contributions to the peak area cannot be readily discerned from the absorbance spectra. In addition, absorbances from the stable anti and gauche rotamers of ethanol¹⁵⁸ and 1-butanol¹⁵⁹ also appear in this region (~3645 cm⁻¹). The barrier to rotation is low for the C-O axis and is easily surmounted at ambient temperature,¹⁶⁰ further complicating definitive α/β band assignment.¹⁴⁹ In the following sections, we will refer to the concentration of α and β hydroxyls collectively as the sum of non-hydrogenbonded hydroxyl protons.^{105,106} The γ and δ hydroxyls appear at lower wavenumbers relative to the non-hydrogen-bonded hydroxyl protons. Additionally, a minor curve was required to fill out the spectrum; since we could not attribute it with confidence, it is listed as unassigned. The area of the unassigned curve is small compared to others – typically less than 1% of the total area for both alcohols - and was therefore omitted when allocating integrated areas to specific hydroxyl configurations. Additionally, occurrences of η and ζ in our molecular simulations of alcohol +
cyclohexane mixtures were less than 1%, even for mixtures of up to 50 mol% alcohol.¹²¹ Therefore the fitting of additional peaks to the spectra was not justify. The influence of the alcohol $\tilde{\nu}(CH)$ can be observed on the right, centered near 2950 cm⁻¹ (Figure 5-3).

In addition to curve areas, we also collected metrics on the curves. The variation in peak center with respect to concentration and temperature for ethanol and 1-butanol in cyclohexane are shown in Figure 5-4. The peak centers of α and β vary insignificantly with concentration and temperature, which is to be expected since the absorbance band is narrow. However, there is a shift in the peak centers for the γ and δ hydroxyls in both alcohol systems. The shift is most pronounced below 10 mol% for the γ hydroxyls and below 5 mol% for the δ hydroxyls and the unassigned hydroxyls for both alcohols. In both instances, the peak centers shift to lower wavenumbers with increasing concentration. Similar behavior was reported by Asprion et al.³⁴ at low alcohol concentrations. The peak centers also monotonically shifted to lower wavenumbers as the temperature decreased within a particular mole fraction though this shift is less pronounced.



Figure 5-4: Location of peak center for ethanol (left) and 1-butanol (right) in cyclohexane as a function of mole fraction and experimental temperature. The groupings are (left to right) (α +

 β) = black/blue, (γ) = orange, (unassigned) = cyan, and (δ) = green at temperatures 30 °C (\diamond), 40 °C (\circ), 50 °C (Δ), and 60 °C (\Box).

5.6.3 Hydroxyl Populations – Temperature and Concentration Effects

It is well understood that temperature profoundly affects the extent of hydrogen bonding.¹⁴³ Higher temperatures represent an increase in kinetic energy of the molecules in the system, which decreases their participation in hydrogen bonding. The effect of temperature and alcohol concentration on the hydrogen bond populations is evident in Figure 5-5. For a fixed mole fraction, temperature increases induced a reduction in δ hydroxyl concentration for both alcohols. The population change was quantifiable since the total integrated hydroxyl area was independent of temperature.¹²² This reduction in δ hydroxyls was offset by an increase in the concentration of non-hydrogen-bonded hydroxyls ($\alpha + \beta$) and γ hydroxyls. For example, the dissociation of one of the hydrogen bonds in a trimer produces a new α hydroxyl at the expense of a δ hydroxyl. Dissociation of a δ hydroxyl in the middle of a chain would produce a β hydroxyl and a γ hydroxyl.



Figure 5-5: Hydroxyl populations for ethanol (top row) and 1-butanol (bottom row) at 30 $^{\circ}$ C (lefthand column) and 50 $^{\circ}$ C (righthand column). The provided dashed lines connect the data and aid the observation of trends.

Like temperature, variation in alcohol concentration resulted in significant changes to the hydroxyl populations. Below 1 mol% alcohol, the contribution of the δ hydroxyls was modest. Yet, as the solution became more concentrated in alcohol, the population of δ hydroxyls became

significant, increasing with alcohol concentration and becoming the most prominent type in the solution above approximately 3-5 mol% alcohol at 30 °C and above approximately 7-8 mol% alcohol at 60 °C.

5.6.4 Regression and Statistics

The association energies and bonding volume for Eq. 5-3 are regressed using the X^A data simultaneously at all temperatures. The regression minimized the objective function $\sum_{datum i} \left[\frac{X_i^A(model) - X_i^A(experimental)}{X_i^A(experimental)} \right]^2$. Since the majority of the uncertainty in the peak area occurs at low concentrations of alcohol where complete subtraction of the solvent is most difficult, this type of objective function places more emphasis on the higher alcohol concentrations where the overall magnitude of X^A was smaller.

Since the pre-exponential and exponential terms of Eq. 5-3 are strongly coupled, an intermediate variable *p* was regressed using Eq. 5-10 and Eq. 5-11 which are modified from Eq. 5-3 to include a reference temperature (T_{ref}) .¹³¹ A value $T_{ref} = 298.15$ K was selected as it falls near the experimental range yet is not an explicitly measured temperature.¹³⁴ Following regression, κ^{AD} values were obtained via Eq. 5-12.

$$\Delta_2 = N_A d_{aa}^3 g_{aa}(d) \left(p \cdot exp\left(\frac{\epsilon_N^{AD}}{kT_{ref}}\right) \right) \left(exp\left(\frac{\epsilon_2^{AD}}{kT}\right) - 1 \right)$$
 Eq. 5-10

$$\Delta_N = N_A d_{aa}^3 g_{aa}(d) \left(p \cdot exp\left(\frac{\epsilon_N^{AD}}{kT_{ref}}\right) \right) \left(exp\left(\frac{\epsilon_N^{AD}}{kT}\right) - 1 \right)$$
 Eq. 5-11

$$\kappa^{AD} = p \cdot \exp\left(\frac{\epsilon_N^{AD}}{k T_{ref}}\right)$$
Eq. 5-12

To provide the 95% confidence interval for the parameters, bootstrapping (replacement by resampling) was employed.¹³³ The regression was performed 1000 times using randomly sampled experimental data. Once sorted, the 25th and 975th values were selected as the lower and upper limits of the confidence interval, respectively. A summary of fitted parameters, along with the respective 95% confidence interval, is given in Table 5-2. A similar analysis using the Δ_2 and Δ_N values is provided in Table 5-3.

System	κ^{AD}	(95% C.I.)	$rac{\epsilon^{AD}_{dimer}}{k}$, [K]	(95% C.I.), [K]	$rac{\epsilon_{nmer}^{AD}}{k}$, [K]	(95% C.I.), [K]
Ethanol	1.12E-02	5.347E-03 to 2.180E-02	2115	1877- 2355	2847	2634-3076
1-Butanol	1.49E-03	8.586E-04 to 2.443E-03	2715	2545- 2884	3330	3174-3499

Table 5-2: RTPT association constant regression values.

Results of the regression can be seen in Figure 5-6. The fraction of non-hydrogen-bonded hydroxyl protons increases with temperature for both alcohols, and lower alcohol concentrations correlate with higher values of X^A . These trends make physical sense as β hydroxyls comprise a more significant percentage of smaller chains, and alcohol molecules increasingly prefer to remain unassociated in situations where they are highly diluted and at higher temperatures. Interestingly, the approach to $X^A = 1$ from higher to lower alcohol mole fractions is not asymptotic, and the data moves from an upward concavity to a downward concavity near 1 mol% as seen in the bottom row plots of Figure 5-6 and also observed by Asprion et al.³⁴

Figure 5-7 provides a depiction of the residual values calculated as $X^A_{model} - X^A_{experimental}$. The largest deviation values occur in the dilute range at alcohol concentrations less than ~4 mol %. While the magnitudes of the residuals are most significant in this concentration range, when considered on a percentage basis, they constitute less than 4%. The scatter in the dilute region occurs because overall areas are small, and the resulting areas are sensitive to baseline adjustments and the removal of cyclohexane signals from the hydroxyl stretching absorbance. However, as seen in the lower row plots of Figure 5-6, this region exhibits a noticeable change in slope as the alcohol becomes more dilute and X^A approaches one.



Figure 5-6: (Top) Fraction of non-hydrogen-bonded hydroxyl protons from curve-fitting the infrared spectra overlayed by the X^A values obtained by regression of the resummed thermodynamic perturbation theory (RTPT) constants to all four experimental temperatures for

ethanol (left) and 1-butanol (right). (Bottom) Enlargement of top plots to show behavior in the dilute region for ethanol (left) and 1-butanol (right).

 X^A change rapidly, with the largest overprediction occurring at the highest temperatures. In the interval of 10 mol% to 30 mol%, the model tended to underpredict X^A for both alcohols by 0.01-0.02, and the most considerable deviations occur at the higher temperatures of 50°C and 60°C.



Figure 5-7: Residual values from regression calculated using $(X^{A}(model) - X^{A}(experimental))$.



Figure 5-8: Superimposed X^A data for ethanol and 1-butanol in conjunction with the RTPT model.

When the experimental values of X^A are superimposed in Figure 5-8, it is difficult to discern the subtle differences between ethanol and 1-butanol, particularly when the concentration of alcohol is less than 10 mol%. Janeček and Paricaud,¹⁴⁸ using molecular simulation, observed similarities in X^A vs. x_a for a series of alcohols, consistent with Figure 5-8, suggesting that $\rho\Delta$ values may be the same for all alcohols. While a model assuming the same $\rho\Delta$ values may be a valid first approximation, the confidence intervals for the fitted energy parameters do not overlap, so we present an analysis using the individual fits.

5.6.5 Comparison with Previous Work

Since RTPT has only recently been applied to experimental data, comparisons with other works over sufficient concentration and temperature ranges are limited and typically involve chemical theory.^{7,54,75,78} Recently, we demonstrated¹³⁴ the application of RTPT to the data of Asprion et al.³⁴ and Table 4-2 contains those parameters. The association constants which correspond with those parameters at 298.15 K are summarized in Table 5-3 in the rows labelled 'Asprion' for comparison with this work. Fits to Asprion's data provides dimer constants that are

smaller compared to the current work and *n*-mer constants that are larger. The publication for this chapter¹³⁴ presents the refitted values listed in for ethanol and 1-butanol. The published manuscript for Chapter 4 listed incorrect parameter values as explained and corrected in Chapter 4.

Alcohol	Temperature	Δ ₂ ,[cm ³ /mol]	(95% C.I.), [cm ³ / mol]	Δ _N ,[cm ³ /mol]	(95% C.I.), [cm ³ / mol]	ref.
	30 °C	772.02	646.89 -	8629.8	8330.1 -	This
		.,	904.54	002/10	8956.8	Work
		420 17	257.52 -	12454	11789 -	Asprion
Ethanol -		429.17	744.25	12434	13131	
	60 °C	270.24	335.81 -	5.81 - 3229.0 -	3229.0 -	This
		579.24	433.37	3413.0	3559.8	Work
		198.41	116.29 –	1252 5	3695.0 -	Acmion
			349.73	4233.3	4910.2	Asprion
1-Butanol —		1361.6	1218.1 -	10362	10115 -	This
	20 °C		1519.9		10610	Work
	30 C	041 01	674.25 -	12007	12434	A
		841.21	1015.4	13007	13465	Asprion
	60 °C	561 25	505.32 -	3418.0	3418.0 -	This
		301.55	619.93	5558.9	3678.9	Work
		454 12	369.30 -	5407 5	4856.8 -	۰ ·
		434.15 529.0	529.08	5982.4	Asprion	

Table 5-3: RTPT association constants for pure alcohol. The rows labeled 'Asprion' are fits to the data of Asprion et al.³⁴ as explained in the text.

RTPT predictions of $\alpha + \beta$ hydroxyl concentrations obtained from the data of Asprion are plotted in conjunction with experimental data and modeling results of this work in Figure 5-9. Parameters obtained from fitting the data of Asprion et al.³⁴ result in lower $\alpha + \beta$ concentrations at all temperatures and the difference between the two sets becomes most noticeable above 2 mol% alcohol.



Figure 5-9: Experimental concentration of $\alpha + \beta$ hydroxyls overlayed with predictions of the RTPT model using association parameters from this work (- -) and modified parameters from the reinterpreted work of Asprion et al.¹³⁴ (··) for ethanol (left) and 1-butanol (right) at temperatures 60 °C (green), 50 °C (red), 40 °C (blue), and 30 °C (black).

While the parameters obtained from the reinterpretation of Asprion's data are similar in magnitude to those obtained in this work it is important to discuss some differences in approach between our current method and our reinterpretation of Asprion's work, where we utilized a table of integrated areas - obtained from the assignment of five pseudo-Voigt curves - as the basis for our analysis. When curve-fitting is undertaken using unscaled spectra (Figure 5-3 left), modeling the lower wavenumber hydroxyl absorbances requires tall, broad curves, which in turn produce significant overlap with the $\alpha + \beta$ region and may contribute to a lower free-end contribution. Examining the integrated free-end absorbance areas after curve fitting, some of the data of Asprion et al.³⁴ and Reilly et al.⁵³ show a plateau or maxima in the free-end values, which occurs at high alcohol concentrations, low temperatures, or with short alcohols. By scaling before curve fitting in this work, smaller peaks are needed to fit absorbance in the γ and δ region, resulting in less overlap of peak tails with the free-end region. Even where plateaus or maxima are not observed in Asprion's skimmed data, we believe that the differences in data processing explain the larger

values of X^A obtained in this work at high concentrations. We do not observe maxima in our values of X^A using the scaling method applied above.

Since the pseudo-Voigt profile is a symmetric function, an additional complication is introduced, which impacts the relationship between integrated area and concentration. Recently we observed via quantum mechanics calculations and experimental data regression that the molar attenuation coefficient increases continuously for the fundamental hydroxyl region as a function of decreasing wavenumber. Therefore, curve-fitting infrared data prior to scaling with Beer's law would require using asymmetric peaks to account for the continuous wavenumber dependence of the molar attenuation coefficient. In principle, a linear function could be multiplied by the pseudo-Voigt function.

5.6.6 Experimental and Modeled Hydroxyl Populations

If hydroxyls are assumed to aggregate in linear chains, the monomer density (ρ_{α}) can be used in conjunction with Δ_2 and Δ_N to calculate the populations of each unique hydroxyl type. Eq. 16 of the supplemental material of Killian et al.¹³⁴ is

$$x_{\alpha}\rho X^{A} = \rho_{\alpha} + \frac{\Delta_{2}\rho_{\alpha}^{2}}{1 - \Delta_{N}\rho_{\alpha}}$$
 Eq. 5-13

Recognizing that the density of non-hydrogen-bonded hydroxyl protons results from either α or β hydroxyls, the second term on the right represents the β hydroxyls. Because every linear chain with a β -hydroxyl on one end must have a γ -hydroxyl on the opposing end, then

$$\rho_{\gamma} = \rho_{\beta} = \frac{\Delta_2 \rho_{\alpha}^2}{1 - \Delta_N \rho_{\alpha}}$$
 Eq. 5-14

The overall balance is given in APPENDIX E: Key Material Balance Equations.

$$x_{\alpha}\rho = \rho_{\alpha} + \frac{2\Delta_{2}\rho_{\alpha}^{2}}{1 - \Delta_{N}\rho_{\alpha}} + \frac{\Delta_{2}\Delta_{N}\rho_{\alpha}^{3}}{(1 - \Delta_{N}\rho_{\alpha})^{2}}$$
 Eq. 5-15

Recognizing that the second term on the right is the sum $(\rho_{\beta} + \rho_{\gamma})$, then, the final term is ρ_{δ} where

$$\rho_{\delta} = \frac{\Delta_2 \Delta_N \rho_{\alpha}^3}{(1 - \Delta_N \rho_{\alpha})^2}$$
 Eq. 5-16

Using the fit of non-hydrogen-bonded $\alpha + \beta$ hydroxyls represented by X^A in Figure 5-6, the parameters provide a model of the distribution of the hydroxyl type populations. The concentrations from Figure 5-5 are replotted in Figure 5-10 as fractions of alcohol appearing in a particular hydroxyl type, along with the RTPT model predictions. The fraction of alcohol in monomer α hydroxyls decreases with increasing alcohol concentration. For ethanol and 1-butanol, the experimental fraction of γ hydroxyls increases up to 5 mol% alcohol and then remains relatively constant. The fraction of δ hydroxyls increases most rapidly at alcohol concentrations less than 10 mol% for both alcohols.



Figure 5-10: Fraction of alcohol molecules involved in specific types of hydrogen-bonding overlayed with the resummed thermodynamic perturbation theory (RTPT) predictions for ethanol (top row) and 1-butanol (bottom row) at 30 $^{\circ}$ C (lefthand column) and 50 $^{\circ}$ C (righthand column).

The RTPT predictions tend to underestimate the fraction of γ hydroxyls and overestimate the fraction of δ hydroxyls at all temperatures, as seen in Figure 5-10. At 50°C, the underprediction of the γ hydroxyls is more apparent, as is the overprediction of the δ hydroxyls. The presence of cyclic species would shift the distribution from γ to δ hydroxyls that are already over-predicted. A possible explanation is branching due to ζ and η hydroxyls. Because the oxygen atom of these

configurations accepts two protons, the number of γ hydroxyls increases at each branch point relative to a linear chain with one γ hydroxyl. Since δ hydroxyls are the most prevalent configuration, then the formation of an η or ζ hydroxyl would likely come at the expense of a δ . Paolantoni et al.¹²³ report evidence of branching in pure 1-octanol using IR, and Janeček and Paricaud¹⁴⁸ report branching in molecular simulations. However, the ability of the RTPT linear chain model to capture the key features is striking.

5.6.7 Enthalpies

There are several considerations when determining the strength of a hydrogen bond, namely the donor and acceptor strength and its immediate environment. Since the polarity of the solvent plays a significant role in the strength of a hydrogen bond, enthalpies obtained in one medium often do not translate to another diluent. An indirect comparison can be made using the fitted association constants. Enthalpies of association for the dimer $(-\Delta H_2)$ and the *n*-mer $(-\Delta H_N)$ can be calculated using their respective association constants and the van't Hoff relation as expressed in Eq. 5-17. The values are provided in Table 5-4 and compared to values obtained by refitting data of Asprion et al.³⁴

$$\Delta H_{2 \text{ or } N} = R \, \frac{d \ln \Delta_{2 \text{ or } N}}{d \left(\frac{1}{T[K]}\right)}$$
 Eq. 5-17

For ethanol, enthalpy values obtained from this work were ~7% and ~14% different for the dimer and *n*-mer, respectively, when compared to our fit of the same system from Asprion et al.¹³⁴ For 1-butanol, the enthalpies differed by ~37% and ~23% for the dimer and *n*-mer, respectively. Calculations performed by Wandschneider et al.⁶¹ using B3LYP demonstrated that cooperativity accounted for roughly 7 kJ/mol, which is similar to the difference between ΔH_2 and ΔH_N seen in the experimental values.

	$x_{\text{alcohol}} = 1 \text{ and } 25 ^{\circ}\text{C}$				
System	$-\Delta H_2, \left[\frac{kJ}{mol}\right]$	$-\Delta H_N, \left[\frac{kJ}{mol}\right]$	$\frac{-\Delta H_2}{-\Delta H_N}$	Source	
Ethanol +	19.6	25.7	0.76	This work	
Cyclohexane	21.3	29.8	0.72	fit Asprion	
1-Butanol +	24.5	29.6	0.83	This work	
Cyclohexane	16.9	23.8	0.71	fit Asprion	

Table 5-4: Hydrogen-bonding enthalpies for ethanol and 1-butanol in cyclohexane compared to values from fitting data of Asprion et al.³⁴

While the enthalpies derived from RTPT appear reasonable, we sought an alternative means of determining the enthalpy to better evaluate our results. Hare and Sorensen¹⁶¹ detailed a method of calculating the hydrogen bond dispersion energy from Raman intensities. More recently, Paolantoni et al.¹²³ adapted this approach to infrared and leveraged it to calculate the enthalpy associated with a hydroxyl transitioning from an α/β to other bonding configurations (γ or δ). This method relies on the assumption that the absorbance peak heights in the hydroxyl region follow a Boltzmann distribution. Calculation of $\Delta H_{2 \text{ or } N}$ from the slope of the integrated experimental hydroxyl populations were performed via Eq. 5-18. This approach is independent of the thermodynamic model.

The method was applied to each mole fraction and are plotted in Figure 5-11. We are less confident in the enthalpy values below 5 mol% alcohol since neither the γ or δ populations are significant in this range, and we have therefore omitted them from the plot. For ΔH_2 the enthalpies for both systems generally increase with increasing alcohol concentration and are mostly clustered between 3-10 kJ/mol, which is near the 7 kJ/mol suggested by Paolantoni et al.¹²³ for 1-octanol. The increase in enthalpy with respect to increasing alcohol concentration is less pronounced for ΔH_N and both alcohols appear to reach similar values near 31 kJ/mol which is roughly 13% different than the value obtained by Paolantoni et al.¹²³ for 1-octanol (27.2 kJ/mol).



Figure 5-11: Calculated ΔH_2 and ΔH_N derived from the relationship of Paolantoni et al. using integrated peak areas.

5.6.8 Average Oligomer Chain Length

A valuable attribute of RTPT is that the average oligomer size (n_{ave}) can be calculated using Eq. 5-19, provided the assumption of linear association.¹⁵⁶ This calculation produces the tandem plots seen in Figure 5-12. The average chain length increases at lower temperatures and higher alcohol concentrations for ethanol and 1-butanol. The increase in oligomer size with increasing concentration is most apparent at 30 °C. At 40 °C to 60 °C, the change in oligomer length occurs most rapidly at alcohol concentrations less than 10 mol%. A global maximum in the average chain length was not predicted from the model for either alcohol for any of the compositions studied here.

$$n_{\rm ave} = 1/X^A \qquad \qquad \text{Eq. 5-19}$$

Since the X^A values for both alcohols are similar, and we plotted them together in Figure 5-8; it is not surprising that the calculated average chain lengths are also very similar. This similarity occurs despite the apparent differences in the regressed thermodynamic parameters as well as the Δ_2 and Δ_N values. The small discrepancy in chain length between ethanol and 1-butanol never exceeds one in the concentration ranges examined.



Figure 5-12: Variation in the average oligomer size (n_{ave}) as a function of alcohol composition and temperature for ethanol and 1-butanol superimposed with the prediction from the RTPT model over the entire experimental concentration range (left) and with emphasis on the dilute region (right). Experimental values are used, and the average aggregate size is greater at higher alcohol concentrations and lower temperatures.

5.7 Summary and Conclusions

Infrared spectra of the hydroxyl stretching region for ethanol + cyclohexane and 1-butanol + cyclohexane were collected at 30 °C, 40 °C, 50 °C, and 60 °C. The spectra were scaled so that the integrated peak area was proportional to concentration. The scaled spectra were curve-fit to partition the $\tilde{v}(OH)$ region into the four principal hydroxyl configurations (α , β , γ , and δ), but we were unable to justify additional curves for η and ζ hydroxyls. Since it is difficult to conclusively

separate α and β contributions due to rotational isomerism about the C-O-H bond, they were combined and regressed collectively as the fraction of non-hydrogen-bonded hydroxyl protons (X^A) to obtain association parameters for the resummed thermodynamic perturbation theory (RTPT), which assumes linear oligomerizations without branching. X^A was similar between the two alcohols at concentrations less than 10 mol % alcohol and the values for both alcohols were sigmoidal in shape when plotted as a function of mole fraction. We compared RTPT model predictions with the curve-fit experimental hydroxyl populations and observed good agreement, which is consistent with the dominance of linear oligomers in the concentration region examined. The current work provides higher values of X^A above 2 mol% when compared to refit data of Asprion et al.,³⁴ which utilized the $\alpha + \beta$ interpretation of the high frequency peak.

Hydrogen bond cooperativity was observed for alcohols ethanol and 1-butanol in cyclohexane, and that is reflected in the enthalpy values, which are lower for the dimer than the *n*-mer in both cases. Calculated enthalpies are comparable to other works investigating the phenomenon of positive cooperativity in self-associating alcohols and fall within the commonly accepted range of hydrogen bonding enthalpies (17 to 34 kJ/mol). The regressed association parameters facilitate calculation of the distribution of aggregate lengths present in the binary system using X^A . The average chain length was calculated for both alcohols and was found to be within one unit for all investigated concentrations.

5.8 Acknowledgments

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CHAPTER 6:Modeling Phase Equilibria Using Infrared Spectroscopy

6.1 Introduction

The ability to correlate the molecular properties of materials to their phase equilibria in mixtures remains an ongoing modeling challenge for industry.¹ Interest in climate responsible feedstocks has increased the need to model the polar biorenewable compounds. The thermodynamic behavior of these highly polar compounds is governed by strong intermolecular interactions such as hydrogen bonding or electrostatic interactions involving permanent or fixed dipoles which contribute to the highly non-ideal behavior of these materials. To correctly describe or predict the complex phase behavior of these systems, the attractive contribution of association to the system non-ideality must be explicitly represented. This is the approach taken by the most modern equations of state (EOS) such as Statistical Associating Fluid Theory (SAFT), Elliot, Suresh, and Donohue (ESD) and Cubic Plus Association (CPA). However, parameterization of the association term remains challenging.

Spectroscopic techniques such as nuclear magnetic resonance (NMR) spectroscopy^{77,155,162} and Fourier transform infrared spectroscopy^{34,61,114,117,149,163} (FTIR) have emerged as the two most popular means of probing intermolecular interactions. However, spectroscopic interpretation is not straightforward. Numerous investigators have interpreted the NMR chemical shift of the hydroxyl resonance as an indicator of the extent of hydrogen bonding. However, attributing the observed chemical shift into its constituent contributions requires that the chemical shift of all hydroxyl protons be known for each type of hydrogen bond. Unfortunately, this is practically impossible because the only bonding configuration for which the shift can be measured directly is the free alcohol at infinite dilution. Often, shifts of the bonded species are adjustable parameters fitted along with an assumed association scheme.

Similar controversy has surrounded infrared measurements. To quantify the concentrations of specific oligomers the Beer-Lambert law must be invoked which necessitates knowledge of the molar attenuation coefficient for a particular bond configuration and a specific frequency. In the past this was achieved in a fashion analogous to the NMR measurements where an association model was assumed, and the equilibrium constants and molar attenuation coefficients were regressed along to the spectra using molar attenuation coefficients as adjustable parameters³⁴ or a scaling was implemented of the temperature dependence of the integrated areas on either side of a isosbestic point.¹¹⁴ Recently the work of Bala et al.¹²² applied trends implied by quantum mechanics calculations to develop a functional form of the molar attenuation coefficient with a wavelength dependency that decouples the association model from the fitting of attenuation constants.

More recently, this work was extended by Killian et al.¹⁶⁴ to ethanol and 1-butanol in cyclohexane and the populations of specific hydrogen-bond configurations were determined from the scaled infrared absorbance of the hydroxyl region. These populations enabled the parameterization of association constants for the resummed thermodynamic perturbation theory (RTPT) of Marshall and Chapman¹¹² by fitting the fraction of non-bonded hydroxyl protons (X^A). This marked the first time that X^A from spectroscopic data had been used to parameterize RTPT and demonstrated that two association constants were required to correctly describe hydrogen bonding cooperativity. In this work we build upon our previous contributions and present results for 10 alcohols in cyclohexane.

The fitted RTPT model is used to calculate activity coefficients and model phase equilibria as demonstrated by Killian et. al.¹³⁴ Insight from infinite dilution activity coefficients guides the

parameter selection, and the resulting model improves the representation of phase equilibria and the excess enthalpy.

6.2 Background

6.2.1 Thermodynamic Perturbation Theory of Wertheim

For purposes of engineering thermodynamic modeling, simplified, robust approaches capable of representing the complex hydrogen bonding molecular interactions are essential. Among the most popular approaches are rooted in the work of Wertheim which describes association as an interaction between acceptor and donor sites assigned to the molecules. The interaction between acceptor and donor sites is governed by an association strength (Δ_{ij}). The association strength differs from an equilibrium constant because it can include a composition dependence due to changes in packing fraction. Several forms exist for Δ_{ij} with the most common being those of PC-SAFT (Eq. 6-1) and ESD (Eq. 6-2) which differ in the pure component values need to parameterize the radial distribution function (g_{ij}).

$$\Delta_{ij} \left[\frac{cm^3}{mol} \right] = N_A d(\sigma)^3 g_{ij} \kappa_{ij}^{AD} \left(exp\left(\frac{\epsilon_{ij}^{AD}}{kT} \right) - 1 \right)$$
 Eq. 6-1

$$\Delta_{ij} \left[\frac{cm^3}{mol} \right] = g_{ij} \kappa_{ij}^{AD} \left(exp\left(\frac{\epsilon_{ij}^{AD}}{kT} \right) - 1 \right)$$
 Eq. 6-2

Both models have similar forms for the association strength which requires two association parameters are required per Δ_{ij} : an effective bonding volume (κ_{ij}^{AD}) and a bonding association energy $\left(\frac{\epsilon_{ij}^{AD}}{k}\right)$. In addition, the PC-SAFT and ESD models differ in the molecular size parameters and their implementation for the g_{ij} . While the full implementation of RTPT regardless of model affords the flexibility of using up to four parameters, we previously demonstrated¹⁶⁴ that that bonding volumes can be set equal ($\kappa_2^{AD} = \kappa_N^{AD}$) while adjusting the energy parameters independently.

6.3 Methods and Modeling

6.3.1 Sample Preparation and Measurement

Materials were purchased from Sigma-Aldrich at the purity listed in Table 6-1. Reagents were used without purification and were stored over activated 3 Å molecular sieves in a glovebox for at least two weeks prior to use.

Table 6-1: Chemical source and purity.

Name	Item	Purity	Anhydrous	Supplier
methanol	322415-100ML	99.8%	yes	Sigma-Aldrich
ethanol	459836-100ML	99.5%	yes	Sigma-Aldrich
1-propanol	279544-100ML	99.7%	yes	Sigma-Aldrich
1-butanol	281549-100ML	99.8 %	yes	Sigma-Aldrich
1-pentanol	138975-100ML	99.1%	no	Sigma-Aldrich
1-hexanol	471402-100ML	99.1%	yes	Sigma-Aldrich
2-propanol	278475-100ML	99.5 %	yes	Sigma-Aldrich
2-butanol	294810-100ML	99.5%	yes	Sigma-Aldrich
i-butanol	294829-100ML	99.5%	yes	Sigma-Aldrich
t-butanol	471712-100ML	99.5%	yes	Sigma-Aldrich
cyclohexane	227048-100ML	99.5%	yes	Sigma-Aldrich

Solutions were prepared in a glove box under a nitrogen atmosphere to preclude the introduction of moisture. Because excess molar volumes in these systems are typically less than 0.5% (see APPENDIX T: Excess Volume Comparison), samples were prepared assuming ideal solution behavior and the partial molar volume of each component was assumed to be equal to the pure component molar volume at all concentrations (Eq. 6-3). Pure component molar volume was obtained via regression of a polynomial to experimental data from the NIST database¹⁵⁰ and

$$\overline{V_i} = V_{pure \ i} = \frac{1}{\rho_{pure \ i}}$$
Eq. 6-3

$$\frac{1}{\rho} = \frac{x_1}{\rho_{pure\ c1}} + \frac{x_2}{\rho_{pure\ c2}}$$
 Eq. 6-4

mixture densities were obtained via Eq. 6-4. In these equations, ρ is molar density. Measurements were performed at 30 °C, 40 °C, 50 °C, and 60 °C for all systems except for methanol + cyclohexane which was measured at 20 °C, 30 °C, 40 °C, and 50 °C.

6.3.2 Beer-Lambert-Bouguer Law Scaling and Quantification of X^A

The methods of scaling developed by Bala et al.¹²² was used, except that a refined fitting method was implemented. In the original work, two regressions were nested: an outer non-linear loop regressed the scaling parameters except for the absorption coefficient at 3645 cm⁻¹; a nested linear regression determined the absorption coefficient at 3645 cm⁻¹. In the refined method, and single non-linear regression is performed using the objective function is

$$OBJ = \sum_{\substack{all \ C_i \ at \\ all \ T}} \left(k_{mean} - \frac{A_{scaled,i}}{C_i} \right)^2$$
Eq. 6-5

where $k_{mean} = \left(\sum_{i} \frac{A_{scaled,i}}{C_{i}}\right)/n_{i}$. $A_{scaled,i}$ is the alcohol stretch integrated area after scaling, C_{i} is the alcohol concentration, the index *i* runs over all concentrations and temperatures, and n_{i} is the number of measurements. During regression, the value of ϵ_{B}^{f} of Figure 3-8 was constrained to a value of 1 while $\tilde{v}_{B}, \tilde{v}_{R}, \epsilon_{R}$, the spline width and the slope of segment 1 were varied. After regression, the value is assigned, $\epsilon_{B}^{f} = k_{mean}$. Parameter values for the attenuation functions are summarized in APPENDIX R: Attenuation Function Parameters.



Figure 6-1: Functional form of the integrated molar attenuation coefficient optimized for each alcohol (left) required to obtain agreement between integrated hydroxyl absorbance area and alcohol concentration (right).

The curve-fitting methodology of Killian et al.¹⁶⁴ was implemented to obtain experimental X^A values representing the fraction of nonhydrogen bonded protons for ten alcohol + cyclohexane binary and the values of X^A are summarized in APPENDIX S: Tabulated X^A Values.

6.3.3 Association Parameter Regression using the Fraction of non-Bonded Hydroxyl Protons

The advantage of the RTPT association model compared to the TPT-1 model is the description of cooperative self-association. The RTPT approach implements a different enthalpy of formation of the dimer compared to other oligomers. This difference results in two unique

association strengths; one for the dimer and one for all successive oligomerizations. Recently we demonstrated¹³⁴ how the fraction of non-bonded hydroxyls (X^A) can be related to the dimer (Δ_2) and n-mer (Δ_N) association constants through the molar density of monomer (ρ_0) as seen in Eq. 6-6 and Eq. 6-7. The equations are simultaneously solved iteratively using the adjustable parameters ϵ_{ij}^{AD} and κ_{ij}^{AD} to optimize the association strengths to fit the experimental values of X^A versus composition data at all experimental temperatures. Regression used previously published methods.¹⁶⁴

$$\rho_0 = \frac{2x_1 \rho X^A}{1 + x_1 \rho \Delta_2 X^A + \sqrt{(1 + x_1 \rho \Delta_N X^A)^2 + 4(\Delta_2 - \Delta_N)x_1 \rho X^A}}$$
Eq. 6-6

$$X^{A} = \frac{(\rho_{0}(\Delta_{2} - \Delta_{N}) + 1)^{2}}{\rho_{0}^{2}(\Delta_{2}^{2} - \Delta_{N}^{2}) + \Delta_{2}(-2\rho_{0}^{2}\Delta_{N} + 2\rho_{0} + \rho x_{1}X^{A}) - 2\rho_{0}\Delta_{N} + 1}$$
 Eq. 6-7

6.3.4 Modeling of Phase Equilibria

The relationship between a liquid and its vapor can be represented using the gamma-phi corrections to Raoult's law (Eq. 6-8) where non idealities of the liquid and vapor phases are described using an activity coefficient (γ_i) and fugacity coefficient (ϕ_i), respectively.

$$y_i \phi_i P = x_i \gamma_i P_i^*$$
 Eq. 6-8

Commonly, nonidealities represented by the activity coefficient are attributed to three contributions: combinatorial, residual, and association. The association term encompasses the non-idealities introduced by molecular aggregation. The combinatorial term is used to describe the entropic effects resulting from mixing components of differing molecular size and shape. Finally, the residual term considers molecular energetics as well as compensating for any remaining non-idealities which are otherwise not accurately represented. The parameters in for the residual term are regressed to experimental phase equilibria data and excess enthalpy data.

6.3.5 Modeling the Association Contribution

In this work we utilize the RTPT form of the association contribution.¹³⁴ For the selfassociating component, the association contribution of the activity coefficient (γ_1^{assoc}) takes the form of Eq. 6-9. For the non-associating component (γ_2^{assoc}) the equation takes the form of Eq. 6-10.

$$\ln \gamma_1^{assoc} = \ln \left(\frac{\rho_o}{x_1 \rho}\right) + x_1 (1 - X^A) \left(\frac{V_1}{V}\right) - \ln \left(\frac{\rho_{o,pure \, 1}}{\rho_{pure \, 1}}\right) - (1 - X^A_{pure \, 1})$$
Eq. 6-9

$$\ln \gamma_2^{assoc} = x_1 (1 - X^A) \left(\frac{V_2}{V}\right)$$
 Eq. 6-10

The infinite dilution forms of these expressions are shown in Eq. 6-11 and Eq. 6-12 for the associating and non-associating component, respectively.

$$\ln(\gamma_1^{assoc})^{\infty} = \ln\left(\frac{\rho_{pure\ 1}}{\rho_{o,pure\ 1}}\right) - (1 - X_{pure\ 1}^A)$$
Eq. 6-11

- -

$$\ln(\gamma_2^{assoc})^{\infty} = \left(1 - X_{pure\ 1}^A\right) \left(\frac{V_2}{V_1}\right)$$
Eq. 6-12

6.3.6 *Experimental Limiting Activity Coefficients*

The infinite dilution activity coefficient provides significant insight about bounds for deviations from ideality for the activity coefficient (partial molar excess Gibbs energy) and the partial molar excess enthalpy. The infinite dilution activity coefficient is closely related to the solvation Gibbs energy and provides an experimental measurement of that property.¹⁶⁵ Equally important to capturing the correct limiting value of the activity coefficient is replicating the temperature dependence via the partial molar enthalpies. Consideration of these bounds is required to keep model results in a range of experimental behavior.

We were interested in the trends exhibited by the limiting activity coefficients for each alcohol + cyclohexane pair. Selected data from the collection of Lazzaroni et al.¹³⁹ are plotted below in Figure 6-2 along with the corresponding 95% confidence interval. Plots for cyclohexane and 2-propanol are in APPENDIX N: Limiting Activity Coefficient Regressions. Previously we reported that the association contribution is dominant especially at low concentrations of alcohol. Conceptually, this dominance occurs because the infinite dilution activity coefficient quantifies the solvation in the mixed state relative to the pure standard state. Because alcohol molecules are significantly hydrogen bonded in the pure liquid, and nonbonded at infinite dilution, the large difference in X^A creates a large association contribution to the infinite dilution activity coefficient.



Figure 6-2: Linear regression of the natural logarithm of the limiting activity coefficient data of Lazzaroni et al.¹³⁹ with respect to inverse temperature for methanol (upper-left), ethanol (upper-right), 1-butanol (middle-left), 1-pentanol (middle-right), 1-hexanol (lower-left), and 2-propanol (lower-right) in cyclohexane.

Eq. 6-13 provides the relation between the infinite dilution activity coefficient and the infinite dilution partial molar excess enthalpies $(\overline{H}_i^{E,\infty})$. Values were calculated according using the slope of the line of best fit (b_{reg}) through the a plot of $\ln \gamma^{\infty}$ versus 1/T. For primary alcohols with available infinite dilution activity coefficients in cyclohexane, calculated values of $(\overline{H}_i^{E,\infty})$ are displayed in Figure 6-3. The experimental limiting partial molar excess enthalpy values for the alcohols have a mean value of approximately 20 kJ/mol.

$$\overline{H}_{i}^{E,\infty} = R\left(\frac{\partial(\ln\gamma_{i}^{\infty})}{\partial(1/T)}\right)_{P,\{n_{i}\neq i\}} = Rb_{reg}$$
 Eq. 6-13



Figure 6-3: Limiting partial molar enthalpies for primary and secondary alcohols in cyclohexane and cyclohexane in primary and secondary alcohols at 318.15 K. Values were calculated according to Eq. 6-13.

6.3.7 Modeling the Combinatorial and Residual Contributions

The combinatorial contribution was represented with modified Flory's (Eq. 6-14) and the binary form of NRTL was utilized for the residual term (Eq. 6-13). For Eq. 6-16, the empirical

parameters a_{ij} , b_{ij} are adjusted to the experimental *P*-*xy*, *T*-*xy*, and H^E data. The alpha values $\alpha_{ij} = \alpha_{ji}$ were set to 0.3 for both components except for the methanol + n-hexane system where $\alpha_{ij} = \alpha_{ji} = 0.25$.

$$\ln \gamma_i^{comb} = \ln \left[\left(\frac{\rho_{soln}}{\rho_i} \right)^{\frac{2}{3}} \right] + 1 - \left(\frac{\rho_{soln}}{\rho_i} \right)^{\frac{2}{3}}$$
Eq. 6-14

$$\ln \gamma_{i}^{resid} = x_{j}^{2} \left[\frac{\tau_{ij} G_{ij}}{\left(x_{i} G_{ij} + x_{j} \right)^{2}} + \tau_{ji} \left(\frac{G_{ji}}{x_{i} + x_{j} G_{ji}} \right)^{2} \right]; i \neq j$$
 Eq. 6-15

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}); \tau_{ij} = a_{ij} + b_{ij}/T$$
 Eq. 6-16

6.4 **Results and Discussion**

6.4.1 Regression of X^A

Regression of the association parameters also requires a selection of the method to represent g_{ij} . Three models were considered: PC-SAFT, ESD, and g_{ij} = constant. For the PC-SAFT method, various parameters have been used in literature for segment reference diameter, σ , dispersion energy, ϵ , and segment number m. Parameters of Gross and Sadowski, Tamouza et al. and NguyenHuynh and coworkers are shown in Figure 6-4^{126,166-168} The values for m and σ are quite different, but the molecular size md^3 calculated at 298.15 K (Figure 6-4 lower left) are very similar, a trend noted by Bala et al.¹³⁰ The values of Gross and Sadowski were used for methanol. Two values are presented for ethanol. The values shown by the red squares with white x are the recommended values, but these do not fit a systematic trend and therefore the group contribution method of NguyenHuynh et al. was applied. Note that both sets of ethanol parameters result in a very similar molecular volume. The value has a very minor effect on the segment diameter, d, and molecular size. PC-SAFT parameters are summarized in along with the selected ESD parameters.¹⁶⁹ The X^A used in the regression are provided in APPENDIX F: Tabulated X^A values.



Figure 6-4: Segment numbers, segment diameters, dispersion energies and molecular size from NguyenHuynh, Gross and Sadowski, and Tamouza et al. as described in the text.^{126,166–168}

Parameter	m	σ (Å ³)	ϵ/k [K]	b (cm ³ /mol)
Methanol	1.5255	3.230	188.9	19.962
Ethanol	1.7464	3.567	280.03	24.743
1-Propanol	2.1326	3.6605	275.288	30.005
1-Butanol	2.5188	3.7162	272.391	35.762
1-Pentanol	2.905	3.7533	270.4	40.732
1-Hexanol	3.2912	3.7798	268.921	46.45
Cyclohexane	2.5303	3.8499	278.11	35.030

Table 6-2: PC-SAFT and ESD parameters used for the radial distribution function at contact.

The infinite dilution values for the activity coefficients are closely related with the value of X^A in pure alcohol as shown by Eq. 6-11. The X^A data were regressed with both PC-SAFT and ESD models using experimental pure component volumes and the ideal volume of mixing. The resulting infinite dilution activity coefficient values obtained for each component are plotted in Figure 6-5. Both models give alcohol infinite dilution activity coefficients for the association contribution that are larger than the experimental infinite dilution value for 1-propanol through 1-hexanol. The ESD model gives values too high for all the alcohols. Considering only the infinite dilution association contribution for cyclohexane, the PC-SAFT model is acceptable. Also plotted in the figure are the values resulting from $g_{ij} = 1$ for the radial distribution at contact, implemented by using Eq. 6-2 an approach which has been used in the GCA-EOS¹⁷⁰, and by Hao and Chen.¹⁷¹ As noted by Bala and Lira,³⁷ this approximation becomes mathematically equivalent to traditional chemical theory when combined with the original Flory equation for the combinatorial contribution.

Because the RTPT model is sensitive to the choice of the radial distribution function at contact, we applied $g_{ij} = 1$ resulting in the values given by the black circles of Figure 6-5. This approach maximizes the transferability of RTPT since a numerically equivalent association

contribution can be obtained for any model which adopts the fitted parameters when the density and temperature are identical.



Figure 6-5 Comparison on experimental infinite dilution activity coefficients with values obtained by fitting the PC-SAFT and ESD radial distribution at contact using experimental pure component densities.

Regressing Eq. 6-2 using $g_{ij} = 1$, the statistically optimal parameter for regression of the X^4 data fails to accurately capture the limiting value of the excess enthalpy for the alcohol. As seen in Figure 6-6 (bottom) for the 1-butanol + cyclohexane system, the slope of the modeled values is steeper than the corresponding experimental values. Therefore, the residual term would need to be negative to counter this behavior. This was observed for all the binary systems and the partial molar excess enthalpy for each component is plotted in Figure 6-7 and are ~5-7 kJ/mol larger for each alcohol than those calculated from the infinite dilution activity coefficients (Figure 6-3). Therefore, using the statistically optimal values would require an exothermic residual contribution to counteract the endothermic overprediction of the excess enthalpy by the association term. Commonly, the residual contribution to the excess enthalpy is expected to be endothermic for a

dispersion interaction of dissimilar molecules. The values for cyclohexane were slightly smaller than the experimental values by approximately 1 kJ/mol.



Figure 6-6: Regression of X^A with unconstrained parameter values for 1-butanol in cyclohexane (top). Experimental¹⁷² and modeled molar enthalpy ascribed to the association contribution which results from unconstrained parameters for 1-butanol + cyclohexane system at 318.15 K (lower).



Figure 6-7: Limiting partial molar enthalpies for alcohol + cyclohexane systems at 318.15 K. Values were calculated using the statistically optimal parameter set for the regression of X^A .

To meet the need for representing the experimental excess enthalpy, the n-mer value was constrained to $\epsilon_N^{AD}/k = 2500$ K, resulting in a compromise of the quality of the X^A (Figure 6-8). As a result, the residual contribution was positive across the entire composition range. The reason for the need to constrain the enthalpy is not currently known.

During regression, unconstrained regression of a separate κ_2^{AD} was considered. However, a strong correlation was noted upon the corresponding value of ϵ_2^{AD}/k . For the resulting fits, we anecdotally noted that the value of Δ_2 was similar from the various fits. Thus, in keeping with our previous work the κ^{AD} terms were set equal to one-another ($\kappa_2^{AD} = \kappa_N^{AD}$).¹³⁴ Thus, even with the second association strength in the model, only two association parameter values are fitted, like TPT-1. Confidence intervals were determined using the bootstrap methods with 1000 trials and a reference temperature of 298.15 K as explained in the previous work.¹⁶⁴


Figure 6-8: Comparison of unconstrained (--) versus $\frac{\epsilon_N^{AD}}{k} = 2500 \text{ K}$ constrained (-) regression of X^A data for 1-hexanol + cyclohexane.

6.4.2 Association Parameters

Association parameters obtained from the constrained X^A regression are presented in Table 6-3 and the corresponding Δ_2 and Δ_N are plotted in Figure 6-10 at 318.15 K. The plots include the 95% confidence limits from the bootstrap method. The bonding volume and bonding energy are strongly correlated and for determination of uncertainty of association strength, the lower/upper limit of each parameter should not be used together to determine the lower/upper limit of the association energy. Instead, the pairs of optimized parameters from each bootstrap fitting trial were used together to calculate association strengths at 318.15 K for each trial, which were subsequently sorted and then the 95% confidence limits were determined from the 25th and 975th values.

Alcohol	κ^{AD} , $\left[\frac{cm^3}{mol}\right]$	95% CI	$rac{\epsilon_2^{AD}}{k}$, [K]	95% CI	$rac{\epsilon_N^{AD}}{k}$, $[K]$
methanol	2.5327	2.3794 - 2.6688	1677.2	1529.0-1814.3	2500
ethanol	1.8410	1.8011 -1.8762	1676.2	1598.1 – 1761.8	2500
1-propanol	2.0550	1.9863 - 2.1184	1699.6	1623.3 - 1768.5	2500
1-butanol	2.0527	1.9950 - 2.1044	1767.5	1721.0 - 1812.8	2500
i-butanol	1.9592	1.8655 - 2.0301	1817.1	1718.1 – 1890.2	2500
1-pentanol	2.2745	2.1802 - 2.3599	1434.7	1311.4 – 1551.5	2500
1-hexanol	2.2657	2.2029 - 2.3241	1759.6	1674.2 - 1831.4	2500
2-propanol	2.2756	2.1693 - 2.3505	1614.0	1528.0 - 1690.0	2500
2-butanol	1.6536	1.6019 – 1.7097	1723.9	1634.2 - 1801.5	2500
t-butanol	1.3283	1.2876 - 1.3612	1948.1	1874.3 - 2017.4	2500

Table 6-3: Association parameters and 95% confidence interval obtained from constrained optimization.



Figure 6-9: Association parameter comparison with 95% confidence interval for κ^{AD} (left) and $\frac{\epsilon_2^{AD}}{k}$ (right).



Figure 6-10: Delta comparison with 95% confidence interval for the dimer (left) and the n-mer (right) at 318.15 K.

6.4.3 Mapping RTPT onto TPT-1

Mapping of the fitted RTPT association contribution to TPT-1 is of interest for two reasons: 1) the mapping provides an engineering approximation to mimic the association behavior of the fit to the spectroscopic data because most engineering association models are coded using TPT-1 and this mapping provides transfer of the spectroscopically determined association contribution for use in existing code; and 2) the method permits demonstration of the benefits of using RTPT by comparing similar magnitude contributions when the $\ln \gamma_{alcohol}^{assoc,\infty}$ values from the two methods are nearly the same.

Using RTPT parameters obtained from regression of the experimental infrared data, γ^{∞} values were generated between 290 – 420 K for both the alcohol and non-hydrogen-bonding solvent cyclohexane. Then, TPT-1 κ^{AD} and ϵ^{AD}/k were regressed simultaneously for both components to obtain values that minimized the error between TPT-1 predicted and RTPT generated limiting activity coefficients according to Eq. 6-17.

$$OBJ = \sum_{species i} \sum_{temperature j} \left(\ln \gamma_i^{\infty, assoc, RTPT} - \ln \gamma_i^{\infty, assoc, TPT1} \right)_j$$
 Eq. 6-17

A graphical example of this is provided in Figure 6-11 for ethanol + cyclohexane. Note that the alcohol infinite dilution activity coefficient is fitted better than the cyclohexane activity coefficient because the objective function favors fitting of the larger activity coefficient. Similar plots are available in APPENDIX O: Mapping RTPT onto TPT-1 for the other binary systems. TPT-1 parameters obtained from this mapping process are available in Table 6-4. The association energy for TPT-1 is larger than either RTPT association energy.



Figure 6-11: Mapping the RTPT predicted limiting activity coefficients to the two-parameter form of TPT-1 for ethanol and cyclohexane.

Table 6-4: TPT-1	association para	ameters obtaine	ed by mapping	from RTPT	limiting	activity
coefficients.						

Compound	$\kappa^{AD},$	ϵ^{AD} [K]	
Compound	[cm ³ /mol]	k '[IX]	
methanol	0.064448	3633.50	
ethanol	0.92537	2670.94	
1-propanol	0.91623	2704.14	
1-butanol	0.84923	2723.85	
1-pentanol	0.67127	2816.11	
1-hexanol	0.80767	2763.15	
i-butanol	0.83051	2716.96	
2-propanol	0.94781	2724.52	
2-butanol	0.59068	2762.06	
t-butanol	0.54158	2725.75	



Figure 6-12: Comparison of X^A regression for TPT-1 (--) and RTPT (-) for 1-hexanol + cyclohexane system.

A comparison of TPT-1 and RTPT for the 1-hexanol + cyclohexane system is shown in Figure 6-12. While TPT-1 may match the RTPT limiting activity coefficients to an acceptable degree, it is unable to capture the curvature of the experimental X^A data in the dilute or concentrated alcohol region, and calculated values of X^A do not match the values from spectroscopy. This mismatch may affect mixture calculations with components with other association sites where the bond populations are more important for the statistics of cross associations.

For comparisons of the models with phase equilibria and excess enthalpy, the TPT-1 association parameters were used to repeat regressions that had been conducted for RTPT. The same data and weights were used and thus the comparisons reflect the abilities of the models fitted to the same data using the same $g_{ij} = 1$.

6.4.4 Regressed Phase Behavior and Excess Enthalpy

The following values of the Hayden-O'Connell parameters were used for the vapor phase nonidealities are summarized in Table 6-5: Summary of Hayden-O'Connell parameters used for

phase equilibria regression. In some cases, parameters were estimated based on trends in existing values.

Alcohol	η	Alcohol	η
Methanol	1.63	1-Hexanol	2.2
Ethanol	1.4	2-Propanol	1.32
1-Propanol	1.4	2-Butanol	1.75
1-Butanol	2.2	Isobutanol	1.9
1-Pentanol	2.2	t-Butanol	1.0

Table 6-5: Summary of Hayden-O'Connell parameters used for phase equilibria regression.

Selected results demonstrating the ability of RTPT and comparing to TPT-1 are available in Figure 6-13 to Figure 6-16 and the remaining systems are available in this APPENDIX P: Phase Equilibria and Excess Enthalpy.

One improvement of RTPT relative to TPT-1 is that the bubble line slope is larger in magnitude over a wider composition range as seen in the 1-propanol, t-butanol, and methanol systems, and more closely matches the experimental data. This behavior occurs because the association contribution to the activity coefficient is relatively flat as infinite dilution of the alcohol is approached as shown in Figure 6-17 (bottom left). This extends the composition range of the large value of the activity coefficient.

A second advantage of RTPT becomes apparent when considering the excess enthalpy. The overall shape and temperature dependence of the excess enthalpy is improved when RTPT is used. An inadequate temperature dependence from TPT-1 is evident even though the association energy is larger than either association energy of RTPT.

Of particular interest is the behavior of the limiting values of the excess enthalpy and activity coefficients which is demonstrated in Figure 6-17. Experimental excess enthalpy data

exhibits a pronounced rollover below 1 mol% alcohol for 1-butanol. This subtlety is captured by RTPT. The RTPT model also reproduces the crossover of the values from the two temperatures at low mole fractions.



Figure 6-13: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior (left)¹⁷³ and H^E (right)¹⁷⁴ for 1-propanol in cyclohexane.

For the methanol + cyclohexane system in Figure 6-16, the TPT-1 model has been previously noted to have difficulty fitting the liquid-liquid upper critical solution temperature and the excess enthalpy simultaneously.¹³⁰ Similar challenges are encountered with RTPT, and for this work we favored the fit of excess enthalpy for both models. The improvement in representation of excess enthalpy is significant for RTPT.



Figure 6-14: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{140,175}$ and H^E (right)¹⁷² for 1-butanol in cyclohexane.



Figure 6-15: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{176,177}$ and H^E (right)¹⁷⁸ for t-butanol in cyclohexane.



Figure 6-16: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{179,180}$ and H^E (right)^{181,182} for methanol in cyclohexane.



Figure 6-17: Limiting excess enthalpy data¹⁷² for 1-butanol + cyclohexane system at 298.14 and 318.14 K overlayed with the RTPT regression results (top). Activity coefficient data¹⁷² for 1-butanol + cyclohexane system at 318.14 K overlayed with the RTPT regression results in the dilute region (bottom left) and across the composition range with combinatorial and residual contributions (bottom right).

Component i	Component j	a _{ij}	b _{ij}	a _{ji}	b _{ji}	$\alpha_{ij} = \alpha_{ji}$
Methanol	Cyclohexane	-2.7704	1182.16	0.91635	-444.28	0.3
Methanol	n-Hexane	-0.57056	657.24	-0.78994	-95.841	0.25
Ethanol	Cyclohexane	0.76289	251.46	-0.87517	5.3007	0.3
1-Propanol	Cyclohexane	2.7896	-563.00	-2.1271	486.91	0.3
1-Butanol	Cyclohexane	1.8510	-383.49	-1.6993	431.18	0.3
1-Pentanol	Cyclohexane	3.2920	-615.50	-2.3097	470.99	0.3
1-Hexanol	Cyclohexane	3.1474	-520.49	-2.1549	402.07	0.3
i-Butanol	Cyclohexane	2.9990	-378.95	-1.9335	280.44	0.3
2-Propanol	Cyclohexane	3.5046	-658.62	-2.6118	553.51	0.3
2-Butanol	Cyclohexane	3.4572	-514.31	-2.4332	423.13	0.3
t-Butanol	Cyclohexane	0.23868	473.92	-0.83368	-63.126	0.3

Table 6-6: NRTL residual contribution parameters obtained via regression.

6.4.5 Analysis of Ternary System

Extension of binary interactions to multicomponent mixtures is important for industrial modeling. The ternary system of methanol + n-hexane + cyclohexane was predicted using parameters obtained from binary regressions of methanol + cyclohexane and methanol + n-hexane. Since methanol + n-hexane was not measuring using infrared the association parameters from methanol + cyclohexane were used. Individually, these systems are challenging to represent given the liquid-liquid phase split which occurs in both binary systems and the sensitivity of the liquid-liquid region to temperature. Furthermore, infrared measurements were performed only to ~10 mol% methanol since higher concentrations would have resulted in a liquid-liquid phase split. As seen in Figure 6-16 RTPT can accurately represent the LLE and the temperature dependence of the ternary binodal if the temperatures are not within 4 K of the upper critical solution temperatures

of the constituent binaries. The slope of the tie lines of the ternary is well matched by RTPT (Figure 6-18).



Figure 6-18: RTPT representation of ternary LLE in methanol + n-hexane + cyclohexane system at 293.15 K (left) and 303.15 K (right).¹⁸³

6.4.6 The Shape of the Contributions to the Excess Enthalpy

Analogous to the activity coefficient, the H^E can be subdivided into association, combinatorial, and residual contributions as presented in Figure 6-19. The remaining systems are available in APPENDIX P: Phase Equilibria and Excess Enthalpy. The total excess enthalpy shows a slight asymmetry where the apex is shifted to lower alcohol mole fractions. In all cases examined the association contribution is strongly skewed to the lefthand side of the diagram contributing significantly at dilute concentrations of alcohol and seems to be responsible for the overall asymmetry. The magnitude of the combinatorial contribution is insignificant. However, another interesting observation considers the shape of the residual contribution which is symmetric for most of the systems.



Figure 6-19: Contributions to H^E for i-butanol (upper left), 1-pentanol (upper right), 2-propanol (lower left), and 1-hexanol (lower right) in cyclohexane at 318.15 K.

6.4.7 Analysis of Residual Contribution

Taken individual the a_{ij}/a_{ji} , b_{ij}/b_{ji} , and α_{ij}/α_{ji} parameters, it is difficult to discern behavior trends. Using the rightmost expression in Eq. 6-16 we see that τ_{ij} and τ_{ji} can be calculated from the *a* and *b* values. This can in turn be used to evaluate the contribution of the NRTL residual to γ_i^{∞} ; calculated via Eq. 6-18 and Eq. 6-19. Generally, the residual contribution to the limiting activity coefficient decreased for both components as the size of the alcohol carbon chain increased though the values for the cyclohexane are more scattered.

$$\ln \gamma_1^{resid,\infty} = \tau_{ij} \cdot \exp(-\alpha_{ij}\tau_{ij}) + \tau_{ji}$$
 Eq. 6-18

$$\ln \gamma_2^{resid,\infty} = \tau_{ji} \cdot \exp(-\alpha_{ji}\tau_{ji}) + \tau_{ij}$$
 Eq. 6-19



Figure 6-20: Contribution of the NRTL residual term to the limiting activity coefficient for alcohols in cyclohexane (solid) and cyclohexane in alcohols (open) calculated at 318.15 K.



Figure 6-21: Ratio of Δ_N/Δ_2 values for primary (square), branched primary (diamond) secondary (circle), and tertiary (triangle) alcohols in cyclohexane at 318.15 K.

The ratio of the association constants $\left(\frac{\Delta_N}{\Delta_2}\right)$ at 318.15 K is shown in Figure 6-21. The n-mer association constant is ~10-15 times that of the dimer for primary alcohols except for 1-pentanol. The value of the ratio varies with temperature. Both secondary alcohols are not easily differentiated from their primary analogs. The deviation of the 1-pentanol ratio from the other systems is apparent and warrants further investigation.

6.5 Summary and Conclusions

This chapter confirms and extends conclusions of previous work where we demonstrated that two association parameters are needed to model spectroscopic data and the association term is the dominant contribution to solution nonideality.

The statistically optimum parameters result in infinite dilution partial molar enthalpies that are 5-7 kJ/mol too large. Thus, the value $\epsilon_N^{AD}/k = 2500 K$ was used and two association parameters (κ^{AD} and ϵ_2^{AD}/k) were adjusted. While the values of the association parameters are unique for each alcohol, the values of Δ_2 and Δ_N are similar for primary alcohols. Future work may show that a reasonable approximation is to use a universal value for all shorter chain primary alcohols. The association strengths for 2propanol were like those for primary alcohols, while the association strengths for 2-butanol were smaller.

The ratio of association constant of the n-mer was found to be roughly ten to twelve times greater than the dimer for primary alcohols at 318.15 K suggesting that formation of the dimer is the most difficult step thermodynamically. To obtain agreement with experimental excess enthalpies we utilized literature measurements of the infinite dilution activity coefficients to provide a realistic boundary on the parameter optimization. This constraint improved the representation of the excess enthalpy while still providing an acceptable regression of the infrared data and partial molar excess enthalpy and allowed for a positive NRTL residual contribution. Despite the asymmetry of the excess enthalpy, it was found that the residual contribution was symmetric for many of the systems.

The shape of RTPT activity coefficients and partial molar enthalpies has a slope that decreases in magnitude as infinite dilution of the alcohol is approached. The shape improves the fitting of VLE and excess enthalpy.

As an engineering approximation, TPT-1 can be fitted to infinite dilution activity coefficients predicted by RTPT. The resulting TPT-1 does not match the fraction of non-bonded hydroxyls obtained from the infrared measurements, and thus should not be regarded as representing the bonding distributions in solution. The temperature dependence of RTPT is superior to TPT-1. RTPT can replicate the limiting behavior of the excess enthalpy and the activity

coefficients. However, TPT-1 provides a first approximation with an engineering application where the level of detail provided by RTPT is not required.

Because of the use of $g_{ij} = 1$ for both RTPT and the mapped fitting of TPT-1, the resulting association model is independent of other pure component parameters and should be transferable to any engineering model. Only two association parameters were fitted for both models.

CHAPTER 7:Relation of Hydroxyl NMR Chemical Shift to Infrared Vibrational Frequency

7.1 Introduction

Spectroscopy is an important experimental method for probing hydrogen bonding interactions. Both mid-range infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) spectroscopy have been used to investigate hydrogen bonding. However, each technique is accompanied by unique strengths and limitations. Recently, we have been refining spectroscopic techniques for studying alcohols in hydrocarbons for improvement of engineering models^{121,122,164} and this work focuses on two alcohols systems. Understanding of alcohol mixtures provides a base for furthering understanding in more complex systems.¹⁹⁶

Quantifying hydrogen bonding for small alcohols using IR at concentrations above 30 mol% is challenging since the absorbance of the hydroxyl group exceeds one absorbance unit. NMR is more accommodating for high alcohol concentrations and with a coaxial sample tube can be used to measure pure alcohol. NMR's ability to measure more concentrated samples is offset by the level of detail which the measurement can provide. For alcohols dissolved in a nonpolar solvent the lifetime of a hydrogen bond is much shorter than the measurement timescale of NMR, thus the chemical shift of the hydroxyl proton is an average of a many shielding environments present in the sample. The diversity of environments experienced by hydroxyl protons in the solution collapses to a single chemical shift. Mid-range infrared measurements occur on a timescale sufficient to capture different environments, and the resulting spectra can be used to calculate the populations of hydroxyl types.¹⁶⁴

While the two methods rely on fundamentally different phenomena (magnetic moment relaxation for NMR and transition dipole moment for IR), properly interpreting the measurements of a single sample should lead the researcher to the same quantification of bonding. Quantum

calculations provide both a predicted chemical shift and vibrational stretch for hydroxyl bonds in selected environments. The integrated area in the scaled IR vibrational spectra is temperature-dependent, and one method of characterizing modulations in hydrogen bonding configurations uses the correlation of integrated areas on either side of a naturally occurring isosbestic point using difference spectra relative to a reference temperature.^{106,123} Recently, we have demonstrated that the IR spectra can be scaled to provide a temperature-independent integrated area under the hydroxyl region.¹²² This work demonstrates that the scaled and integrated absorbance signal of an alcohol's hydroxyl group can be mapped using quantum calculations as a guide to correlate the NMR shift at any concentration and temperature.

7.2 Background

Hydroxyl configurations in hydrogen bonds are characterized by Greek letters.¹⁶⁴ An unbonded hydroxyl is denoted as α . A hydroxyl accepting a proton on the oxygen with a free proton and labeled β . A hydroxyl donating a proton with an unbonded oxygen is denoted γ . A hydroxyl accepting a single proton and donating a proton is δ . Gutowsky and Saike¹⁹⁷ proposed that the observed chemical shift of a hydroxyl proton relative to tetramethylsilane (TMS) can be related to the fraction of the free and complexed species in the system. For hydrogen bonding alcohols in an inert solvent this relationship takes the form of Eq. 7-1⁷⁷ where δ_{obs}^{NMR} , δ_{fends}^{NMR} , δ_{cyclic}^{RMR} , and δ_{chain}^{NMR} are the observed chemical shift, the chemical shift of the free-hydroxyls (α/β), the chemical shift of all members of a cyclic species, and the chemical shift of the non-free-end molecules in a linear chain, respectively. In the notation of Gutowski and Saike used in this equation, the $\delta_i^{NMR}s$ represent the NMR shifts, not the hydroxyl labeling. The concentration of monomers (α hydroxyls), cyclic aggregates of size *i* and linear clusters of length *i*, and the total concentration of alcohol are denoted as C_M , C_i^c , C_i^l , and C_{alc} , respectively.

$$\delta_{obs}^{NMR} = \frac{C_M}{C_{alc}} \delta_{fends}^{NMR} + \sum_{i=2}^{\infty} \left[\left(\frac{nC_i^c}{C_{alc}} \right) \delta_{cyclic}^{NMR} + \left(\frac{C_i^l}{C_{alc}} \right) \delta_{fends}^{NMR} + \left((i-1) \frac{C_i^l}{C_{alc}} \right) \delta_{chain}^{NMR} \right] \quad \text{Eq. 7-1}$$

One important assumption is that the chemical shifts are fixed constants for each hydroxyl configuration. A second assumption is that there is no change in volume upon formation of a hydrogen bond. Recently, we have developed a new method to quantify bond configurations using mid-range IR spectroscopy which provides an opportunity to evaluate the use of constants for each hydroxyl configuration.¹⁶⁴ Previous chapters indicate that hydrogen bonded hydroxyls present a range of wavenumbers in the infrared spectrum that can be attributed to a near-continuum of species which reflect overlapping frequency distributions of the bond configurations. This behavior is supported by the quantum chemical calculations of Bala¹²¹ for ethanol + cyclohexane and 1-butanol + cyclohexane and provides the inspiration for the relationship proposed here. A scaling of the IR spectra provides temperature-independent integrated areas of the hydroxyl stretch region, permitting quantification of the total hydroxyl content in solution,¹²² and after curve-fitting, the distribution of configurations for primary alcohols is modeled satisfactorily by the assumption of linear chains and two association strengths.¹⁶⁴ This work provides a method to map from the broad hydroxyl distribution at a given concentration to a single value for the NMR shift.

7.3 Methods

7.3.1 Mapping Overview

Bala performed quantum calculations for hydroxyl configurations that were sampled from classical molecular dynamics simulations.¹²¹ The IR stretching frequency and NMR shift were calculated using the B3LYP level of theory and 6-31G* basis set. Though the above is a simple approximation, higher levels of theory exhibit the same trends.¹²² Configurations were calculated

and plotted in Figure 7-1. Also shown in the figure are the bond configurations identified for each hydroxyl.



Figure 7-1: Quantum calculation results from $Bala^{121}$ demonstrating the relationship between the hydroxyl proton chemical shift and the hydroxyl infrared absorbance frequency for 1butanol + cyclohexane and ethanol + cyclohexane. The second-degree polynomial function of best fit relating these two quantities is represented by the dashed line which serves as the initial value for the optimization.

The mapping process overview is illustrated in Figure 7-2. Scaling has been performed as described previously,¹⁶⁴ and it should be noticed that the ordinate is subsequently normalized using division with the sample concentration. Because the normalized area under the scaled spectra is independent of temperature, the fractional area for a subset of wavenumbers is related to the fraction of hydroxyls in that wavenumber range. IR spectra in the lower figure can be mapped to an NMR shift using Figure 7-1. Selecting a finite wavenumber range provides an integrated area that can be mapped by using the average wavenumber for the finite wavenumber range. By summing the contributions weighted by the fractional area, a single value is obtained for the NMR shift of the solution.



Figure 7-2: Schematic providing a visual description of the method being proposed herein. Fractional areas produced by integration of the scaled infrared spectra and multiplied by the corresponding mapping function value and summed for all wavenumber intervals to produce a single chemical shift value.

7.3.2 Mapping Implementation

High quality NMR data are obtained from Bala¹²¹ and Karachewski et. al⁷⁷. Because the NMR data are not available at the same temperatures and concentrations as the infrared measurements, modified Akima interpolation was used on the experimental NMR data to replicate the mole fractions and temperatures used in our infrared experiments.

Since the QM calculations require scaling, we optimized the mapping relationship using the polynomial coefficients as the initial guess. The mapping equation was allowed to shift in the y-direction by values optimized according to the objective function calculated as obj = $\sum_{i}^{n} ((\delta_{calculated,i} - \delta_{measured,i})/\delta_{measured,i})^{2}$. Values for the mapping function are $\delta^{NMR} =$ $-2.511E - 05\tilde{v}_{ave}^{2} + 0.1581\tilde{v} - 243.10 + offset$.

7.4 Results

IR data are available up to approximately 30 mol% alcohol to keep the absorbance below two, and thus the mapping is limited to this composition range. For the 1-butanol + cyclohexane system the mapping function was optimized for each temperature (Figure 7-3 top) using the y-direction shift required to achieve the best fit (Figure 7-3 bottom left). The NMR shift changes by about 4 ppm over the concentration range while the optimized offset increases by only 0.12 ppm with increasing temperature over the 30 °C range. For the 2-propanol + cyclohexane system a single offset was regressed to all temperatures simultaneously (Figure 7-4 Top).

7.5 Discussion

It is impressive that such a simple relation between IR and NMR can produce such results. In the course of this work, we also considered a linear relation for the mapping function, but the polynomial provided better mapping. The mapping function derived based on 1-butanol and ethanol was applied to NMR data for both 1-butanol and 2-propanol. We note that the polynomial function has a maximum near 3100 cm⁻¹ but is essentially flat in this region. Improvements may be possible via a broader range of species for the mapping function and particularly more calculations for larger oligomers which exhibit vibrations at the lowest wavenumbers. Study of a broader range of alcohols is also suggested. While the shape of the mapping function may be improved, we hypothesize that refinements will have similar shape to the one presented. The mapping process requires that the alcohol hydroxyl region in the infrared spectra is scaled prior to mapping. The success of the mapping is further evidence of the validity of the scaling method.

Another observation from Figure 7-1 is that the γ bonds on one end of a chain should have a different average NMR shift value compared to δ bonds. Much of the distribution of γ bonds is obscured in Figure 7-1 and the original work should be consulted for more detail.¹²² Both the β and α hydroxyls should be considered as unbonded. When curve fitting the scaled IR spectra up to about 30 mol% the peak centers are nearly constant,¹⁶⁴ suggesting that an average shift value may be possible to propose for each alcohol configuration when fitting NMR data rather than using adjustable constants for hydroxyl configurations. By reducing the adjustable constants, it may be possible to increase confidence in the association constants used to fit the NMR shifts. More work is required to evaluate the mapping function to evaluate whether it is appropriate for a wider class of alcohols and cyclic structures. The MD simulations of primary alcohols show minimal cyclic structures.^{122,148}



Figure 7-3: Interpolated experimental NMR data for 1-butanol in cyclohexane (o) overlayed with the regressed values of the optimized mapping function for each temperature (--) (top). Vertical shift of mapping function that was required to produce an optimized result as a function of temperature (bottom left). Absolute error between calculated and experimental values (bottom right).



Figure 7-4: Interpolated experimental NMR data for 2-propanol in cyclohexane (o) overlayed with the values from the regressed mapping function (--) (top). Absolute error between calculated and experimental values (bottom).

7.6 Conclusions

This work provided a mapping relationship between the chemical shift of an alcohol hydroxyl proton and its wavenumber absorbance using quantum calculations to guide development. This mapping function was optimized using experimental infrared and NMR data for the systems 1-butanol + cyclohexane and 2-propanol + cyclohexane.

CHAPTER 8: Densities of Selected Deuterated Solvents

8.1 Preface

Deuterated organic solvents are used frequently in modern nuclear magnetic resonance (NMR) experiments; however, the densities of these liquids are seldom available for conditions outside 298.15 K. To address this shortcoming, we collected density data for twelve common NMR solvents, including dichloromethane-d₂, toluene-d₈, pyridine-d₅, ethanol-d₆, tetrahydrofuran-d₈, dimethyl sulfoxide-d₆, benzene-d₆, acetone-d₆, methanol-d₄, cyclohexane-d₁₂, acetonitrile-d₃, and chloroform-d. Temperature-dependent liquid density values for dichloromethane-d₂, toluene-d₈, pyridine-d₅, dimethyl sulfoxide-d₆, ethanol-d₆, and tetrahydrofuran-d₈ were reported for the first time. Our measurements provide an expanded temperature range for benzene-d₆, chloroform-d, methanol-d₅, cyclohexane-d₁₂, acetonitrile-d₃, and acetone-d₆, for which some literature values were available. The coefficient of isobaric thermal expansivity and molar volume of each component was calculated, and the latter quantity was compared with its protiated form.

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Densities of Selected Deuterated Solvents

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8.3 Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a versatile analysis technique for the chemical, biological, and engineering sciences. Modern NMR spectrometers utilize increasingly

powerful magnets to probe the intricacies of molecular structure and behavior. Deuterated solvents are typically used to solubilize analytes since 2 H locks the spectrometer and produces a signal that is unobtrusive to that of a ¹H nucleus. When leveraging NMR to probe intermolecular interactions or evaluate molecular diffusion,¹⁹⁸ knowledge of the relationship between temperature and density for the analyte and the solvent is necessary. Unfortunately, deuterated solvent density information is limited near ambient temperatures or unavailable, even for the most frequently encountered perdeutero solvents. In this work, we report density for twelve deuterated NMR solvents, including dichloromethane- d_2 , toluene- d_8 , pyridine- d_5 , ethanol- d_6 , tetrahydrofuran- d_8 , and dimethyl sulfoxide- d_6 , benzene- d_6 , acetone- d_6 , methanol- d_4 , cyclohexane- d_{12} , acetonitrile- d_3 , and chloroform-d at atmospheric pressure and temperatures between 273.15 K and 368.15 K. Temperature-dependent liquid densities and isobaric thermal expansivities are reported for the first time over this temperature interval for dichloromethane- d_2 , toluene- d_8 , pyridine- d_5 , dimethyl sulfoxide-d₆, ethanol-d₆, and tetrahydrofuran-d₈. Our measurements provide an expanded temperature range for benzene-d₆,¹⁹⁹⁻²⁰³ chloroform-d,²⁰³⁻²⁰⁶ methanol-d₅,^{207,208} cyclohexane d_{12} ,^{209,210} acetonitrile- d_3 ,^{211,212} and acetone- d_6 .²¹³

8.4 Experimental Methods

8.4.1 Components

The solvent suppliers, purity, and deuteration percentages are listed in Table 8-1. Materials were received in sealed glass ampoules and were used without further purification, except for chloroform-d, which was stored over activated 3 Å molecular sieves for two weeks prior to measurement. The molecular sieves were activated by heating in a kiln for five days at 975 K before cooling to room temperature under a vacuum. Molecular masses were obtained for each deuterated compound from the NIST Chemistry WebBook,¹⁵⁰ except for tetrahydrofuran-d₈, which

was calculated from its protiated form using Eq. 8-1 where the molecular mass of the hydrogencontaining analog (M_H) was added to the product of the number of deuterium (N_D) and the difference in molar mass between hydrogen and deuterium ($\Delta_{\rm DH}$) taken as 1.006277 g/mol.

$$M_D = M_H + N_D(\Delta_{DH})$$
 Eq. 8-1

Compound	Manufacturer	% atom D	% Purity, (Method)	% Water, (Method)	M/[g/mol]
acetone-d ₆	Isotec	99.96%			64.1161
acetonitrile-d ₃	Aldrich	99.5%			44.0704
benzene-d ₆	Cambridge Isotope	99.95%*	100%, (GC/MS ^b)*	0.0059%, (KF ^c)*	84.1488
chloroform-d	Laboratories Sigma-Aldrich	99.82%*	100%, (GC ^a)*	0.0018%, (KF ^c)*	120.3840
cyclohexane-d ₁₂	Sigma-Aldrich	99.6%*	99%, (GC ^a)*	0.00%, (KF ^c)*	96.2334
dichloromethane-d ₂	Cambridge Isotope Laboratories	99.965%*	100%, (GC/MS ^b)*	0.0042%, (KF ^c)*	86.945
dimethyl sulfoxide-d ₆	Aldrich	99.93%*	99.96%, (GC ^a)*	0.0058%, (KF ^c)*	84.170
ethanol-d ₆	Sigma-Aldrich	99.7%*	99%, (GC ^a)*	0.0304%, (KF ^c)*	52.1054
methanol-d ₄	Sigma-Aldrich	99.981%*	99.9%, (GC ^a)*	0.0014%, (KF ^c)*	36.0665
pyridine-d ₅	Aldrich	99%			84.1307
tetrahydrofuran-d ₈	Sigma-Aldrich	99.82%*		0.01%, (KF ^c)*	80.155
toluene-d ₈	Sigma-Aldrich	99.80%*	100%, (GC ^a)*	0.0022%, (KF ^c)*	100.1877

Table 8-1: Compound specifications.

^a Gas chromatography

^b Gas chromatography-mass spectrometry

^c Karl Fischer titration

* information obtained from the manufacturer's certificate of analysis

8.4.2 Calibration and Measurements

Measurements were performed using an Anton-Parr DMA45 vibrating tube densimeter, calibrated in five-degree increments from 278.15 K to 368.15 K using ultrapure Milli-Q[®] water and Drierite[®]-desiccated air at atmospheric pressure. Accepted densities for water were obtained from the NIST Chemistry WebBook, SRD 69.¹⁵⁰ Air density was calculated using equation Eq. 8-2 at atmospheric pressure for each experimental temperature expressed in units of Kelvin. Eq. 8-2 was obtained from the densimeter instrument documentation. The atmospheric pressure (*P*)

was monitored throughout the calibration with a NIST-Traceable[®] barostat, which had an expanded measurement uncertainty with 0.95 level of confidence of U(P) = 0.62 hPa. Constants *A* and *B* were computed for each temperature using Eq. 8-3 and Eq. 8-4, respectively, where τ is the experimental period of oscillation.

A 12 L Thermo Fisher Scientific A25 bath served as the reservoir for a 50% (v/v) mixture of water and ethylene glycol, which flowed to the densimeter at a rate of 20 L/min via a Thermo Fischer Scientific AC200 immersion circulator. Heat loss between the reservoir and the densimeter was minimized by encapsulating the lines with 1-inch-thick pipe insulation, which provided an approximate *R*-Value of 6.1. The bath temperature sensor was calibrated using a NIST-traceable calibrated Hart Scientific 1510 platinum resistance probe and 1529-R display. The circulating fluid temperature was measured at the entrance to the densimeter, and it differed by less than 0.05 K from the bath setpoint temperature. The measurements are reported at the bath temperature with a standard uncertainty of u(T) = 0.05 K. Analyte density was calculated via Eq. 8-5 using the measured period of oscillation, the calibration constants *A* and *B*, and the bath setpoint temperature.

$$\rho_{air} \left[\frac{g}{cm^3} \right] = \frac{0.0012930}{1 + 0.00367 * (T[Kelvin] - 273.15)} \left(\frac{P[MPa]}{0.101325} \right)$$
Eq. 8-2

$$A\left[\frac{\sec^2 \text{cm}^3}{\text{g}}\right] = \frac{\tau_{water}^2 - \tau_{air}^2}{\rho_{water} - \rho_{air}}$$
Eq. 8-3

$$B[\sec^2] = \tau_{air}^2 - (A \cdot \rho_{air})$$
 Eq. 8-4

$$\rho_{sample} \left[\frac{g}{cm^3} \right] = \frac{\tau_{sample}^2 - B}{A}$$
 Eq. 8-5

Analytes were transferred from their primary container to a stoppered Schlenk flask in a glovebox under a nitrogen atmosphere to minimize moisture contamination. The freeze-pump-thaw method was used to dislodge dissolved gasses from the sample. Once the sample was frozen using liquid nitrogen, a vacuum was applied until the vessel's pressure was less than 3.33 Pa. This process was repeated three times, after which the contents of the flask were brought to atmospheric pressure with dry nitrogen.

Measurements were systematically performed in five-degree increments, which spanned the analyte's melting point or 273.15 K to its boiling point or 368.15 K at atmospheric pressure. Following degassing, 0.7 cm³ of the sample was transferred by pipette into the densimeter's inlet. After the circulator reached the desired temperature, the sample was allowed to thermally equilibrate for five minutes before the period of oscillation was recorded. Values were calculated as the arithmetic mean of twenty periods. After a set of measurements for a particular compound were completed, the sample chamber was cleaned with ethanol and dried with pressurized air produced by the densimeter's built-in pump. Upon completion of the measurements, the density of Milli-Q[®] water was remeasured at each temperature. The check resulted in identical density values as the calibration, demonstrating reproducibility.

8.4.3 Regression of Protiated Solvent Data for Comparison

Specific density data were collected from NIST Chemistry WebBook¹⁵⁰ for the protiated form of each analyte. Accepted values were regressed over the experimental temperature range using a second-order polynomial. The regression coefficients were then used with the experimental temperatures to calculate the specific density for the protiated components to compare with our measured values. Coefficients for these expressions can be found in the APPENDIX W: Protiated Molar Density Regression Coefficients.

8.5 Results

Densities $(\rho/(g/cm^3))$ for all measured perdeutero compounds are available in Table 8-2 and Table 8-3 along with their respective combined expanded uncertainty $U(\rho)$. To estimate the impact of purity on the measured density values a contaminant with a molecular mass 12 g/mol less than the deuterated compound was assumed in all cases. For compounds where the purity was not listed a conservative estimate of 99% was assumed which led to a larger $U(\rho)$. Sample purity was found to be the most significant contribution to the uncertainty of the density values. To gauge the effect of percent deuteration on the measured density values, the ratio of molecular weight of the completely protiated species to the molecular weight of the completely deuterated analog was used. Detailed calculations of $U(\rho)$ are provided in APPENDIX X: Uncertainty Analysis Equations and APPENDIX Y: Uncertainty Analysis Data.

T/[V]	cyclohexane-	toluene-d ₈	benzene-d ₆	tetrahydrofuran-d ₈	pydridine-d5	chloroform-d
<i>I</i> /[K]	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	<i>⊳</i> /[g/cm ³]
278.15		0.9602		1.0088	1.0635	1.5311
283.15	0.9032	0.9551	0.9609	1.0029	1.0581	1.5216
288.15	0.8978	0.9500	0.9551	0.9968	1.0528	1.5122
293.15	0.8924	0.9450	0.9493	0.9908	1.0475	1.5027
298.15	0.8870	0.9400	0.9436	0.9847	1.0421	1.4932
303.15	0.8815	0.9348	0.9379	0.9785	1.0368	1.4838
308.15	0.8760	0.9296	0.9319	0.9721	1.0313	1.4737
313.15	0.8705	0.9246	0.9262	0.9660	1.0261	1.4640
318.15	0.8650	0.9194	0.9204	0.9597	1.0207	1.4544
323.15	0.8593	0.9143	0.9145	0.9533	1.0153	1.4444
328.15	0.8536	0.9089	0.9085	0.9469	1.0098	1.4344
333.15	0.8479	0.9037	0.9026	0.9405	1.0043	
338.15	0.8421	0.8984	0.8966		0.9988	
343.15	0.8363	0.8932	0.8906		0.9933	
348.15		0.8879	0.8846		0.9878	
353.15		0.8824			0.9822	
358.15		0.8770			0.9766	
363.15		0.8716			0.9712	
368.15					0.9655	
$U(\rho)$	0.0022	0.0003	0.0003	0.0029	0.0031	0.0004

Table 8-2: Specific densities of perdeutero compounds at 1.013 MPa^a (Part I).

^a Temperature standard uncertainty is u(T) = 0.05 K. A coverage factor of k = 1.96 was used to estimate the combined expanded uncertainties for each component density $U(\rho)$.

	aaatana d	dichloromethane-	athenal d	acetonitrile-	mathanald	dimethyl
<i>T</i> /[K]	acetone-d ₆	d_2	etnanoi-d5	d ₃	methanol-d4	sulfoxide-d ₆
	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$	$\rho/[g/cm^3]$
278.15	0.9034	1.3868	0.9100	0.8569	0.9088	
283.15	0.8972	1.3775	0.9052	0.8512	0.9035	
288.15	0.8909	1.3683	0.9003	0.8454	0.8982	
293.15	0.8845	1.3590	0.8955	0.8396	0.8928	
298.15	0.8782	1.3495	0.8906	0.8338	0.8875	1.1837
303.15	0.8717	1.3401	0.8857	0.8280	0.8821	1.1783
308.15	0.8653	1.3304	0.8806	0.8221	0.8767	1.1727
313.15	0.8588	1.3208	0.8757	0.8163	0.8714	1.1674
318.15	0.8522		0.8707	0.8104	0.8659	1.1620
323.15	0.8456		0.8656	0.8044	0.8604	1.1565
328.15	0.8388		0.8603	0.7983	0.8547	1.1510
333.15			0.8550	0.7922	0.8491	1.1455
338.15			0.8497	0.7861	0.8433	1.1400
343.15			0.8442			1.1345
348.15			0.8387			1.1291
353.15			0.8330			1.1235
358.15						1.1181
363.15						1.1127
368.15						1.1073
$U(\rho)$	0.0032	0.0004	0.0040	0.0044	0.0006	0.0003

Table 8-3: Specific densities of perdeutero compounds at 1.013 MPa^a (Part II).

^a Temperature standard uncertainty is u(T) = 0.05 K. A coverage factor of k = 1.96 was used to estimate the combined expanded uncertainties for each component density $U(\rho)$.

8.6 Discussion

8.6.1 Density Comparison with Literature

A second-order polynomial was used to correlate the temperature dependency of the measured specific densities using Eq. 8-6, where the temperature is expressed in units of Kelvin. The regression coefficients are provided in Table 8-4.

$$\rho\left[\frac{g}{cm^3}\right] = C_1 T^2 + C_2 T + C_3$$
 Eq. 8-6

For the six solvents with temperature-dependent literature data, a graphical comparison of literature values with those from this work are presented in Figure 8-1, Figure 8-2, and Figure 8-3. Values for acetonitrile-d₃ were obtained from figure 4 of Sassi et al.²¹¹ using WebPlotDigitizer²¹⁴ open source software. For benzene-d₆ this work agrees with Dixon and Schiessler¹⁹⁹ and Dymond et al.²⁰⁰ within 0.03% and within 0.3% of other data. For chloroform-d, values from this work are approximately 0.1% to 0.16% higher than literature. For cyclohexane-d₁₂ this work agrees within 0.05% with Matsuo and van Hook,²⁰⁹ and is up to 0.4% higher than other literature values. Methanol-d₄ densities are withing 0.02% of Bender and van Hook,²⁰⁷ and are up to 0.7% higher than Kudryavtsev, et al.²⁰⁸ For acetone-d₆ our density values are approximately 1.2% higher than those reported by Szydlowski et al.,²¹³ for unknown reasons. Acetonitrile-d₃ densities from this work vary systematically and are as much as 0.35% lower to 0.05% higher than values presented by Sassi et al.²¹¹. In summary, the current data agree within 0.4% with at least one other researcher for five of the six systems where literature data are available.
	$C_{I} [g/cm^{3}K^{2}] /10^{-6}$	$C_2 [g/cm^3K] /10^{-3}$	$C_3 [g/cm^3]$	\mathbb{R}^2
ethanol-d ₆	-1.18 <u>3</u> 3	-0.275 <u>8</u> 6	1.07 <u>8</u> 1	0.999 <u>9</u> 7
chloroform-d	-1.25 <u>0</u> 5	-1.17 <u>4</u> 4	1.95 <u>4</u> 5	0.999 <u>9</u> 9
pyridine-d ₅	-0.366 <u>7</u> 7	-0.850 <u>9</u> 8	1.32 <u>8</u> 5	0.999 <u>9</u> 9
toluene-d ₈	-0.502 <u>2</u> 1	-0.718 <u>7</u> 5	1.19 <u>8</u> 9	0.999 <u>9</u> 9
dichloromethane-d ₂	-1.21 <u>2</u> 8	-1.16 <u>9</u> 6	1.80 <u>6</u> 0	0.999 <u>9</u> 8
benzene-d ₆	-0.530 <u>8</u> 5	-0.836 <u>8</u> 3	1.24 <u>0</u> 3	0.999 <u>9</u> 9
cyclohexane-d ₁₂	-0.842 <u>0</u> 9	-0.586 <u>4</u> 3	1.13 <u>6</u> 7	0.999 <u>9</u> 9
acetone-d ₆	-1.04 <u>4</u> 3	-0.656 <u>8</u> 3	1.16 <u>6</u> 9	0.999 <u>9</u> 9
methanol-d4	-0.731 <u>2</u> 6	-0.637 <u>5</u> 2	1.14 <u>2</u> 6	0.999 <u>9</u> 8
acetonitrile-d ₃	-0.732 <u>4</u> 5	-0.727 <u>5</u> 7	1.11 <u>5</u> 9	0.999 <u>9</u> 9
dimethyl sulfoxide-d ₆	-0.00255 <u>6</u> 2	-1.09 <u>1</u> 9	1.50 <u>9</u> 5	0.999 <u>9</u> 9
tetrahydrofuran-d ₈	-0.906 <u>1</u> 2	-0.689 <u>0</u> 8	1.27 <u>0</u> 6	0.999 <u>9</u> 9

Table 8-4: Specific density regression coefficients.

*underbar indicates the last significant digit



Figure 8-1: Comparison of experimental data with literature values from this work (t.w.) denoted by (\blacksquare) and literature for benzene-d₆ (left) ^{199–203} and chloroform-d (right).^{203–206} The percent deuteration is reported in parenthesis unless it was not listed (NL) by the author(s).



Figure 8-2: Comparison of experimental data with literature values from this work (t.w.) denoted by (\blacksquare) and literature for acetone-d₆ (left) ²¹³ and methanol-d₅ (right).^{207,208}



Figure 8-3: Comparison of experimental data with literature values from this work (t.w.) denoted by (\blacksquare) and literature for cyclohexane-d₁₂ (left)^{199,210} and acetonitrile-d₃(right).²¹¹ The percent deuteration is reported in parenthesis unless it was not listed (NL) by the author(s).

8.6.2 Prediction of Density for Perdeutero Compounds and Molar Volume Comparison

As early as 1936, McClean and Adams²⁰³ discussed estimating a deuterated liquid's density using the density of its protiated analog. Based on the assumption that the molar volume of hydrogen and deuterium forms were equal, they derived the form of Eq. 8-7 where $(\rho_{D,calculated})$ is the estimated specific density of the deuterated compound, (ρ_H) is the specific density of the protiated compound, (N_D) is the number of deuterium atoms per molecule, (Mw_H) is the molecular mass of the hydrogen analog, and (Δ_{DH}) is the difference in atomic mass between hydrogen and deuterium, taken as 1.006277g/mol. We have subsequently modified the original expression to account for the fraction of hydrogen atoms in the sample that have been replaced by deuterium (ξ) .

The modified McClean/Adams expression was used to predict specific densities at each experimental temperature using the ξ -values listed in the second column of Table 8-5. The mean percentage error (MPE) was calculated for each component using Eq. 8-8 where (n_T) is total number of measurements performed across the temperature range. The results are provided in the third column of Table 8-5.

$$\rho_{D,calculated} \left[\frac{g}{cm^3} \right] = \rho_H [1 + (\xi N_D \Delta_{DH}) / M_WH]$$
 Eq. 8-7

$$MPE = \left(\frac{100\%}{n_T}\right) \sum_{i=1}^{n_T} \frac{\left|\rho_{D,measured,i} - \rho_{D,calcualted,i}\right|}{\rho_{D,measured,i}}$$
Eq. 8-8

Interestingly, the modified McClean/Adams relation provides an acceptable estimation of specific density for many of the components. MPE values are less than 0.45% for all compounds except acetone- d_6 which exhibited a MPE of ~1.3%. Generally, compounds that contained more deuterium atoms were associated with a larger MPE. The difference in mass between hydrogen and deuterium is responsible for most of the increase in specific density from protiated compounds to their deuterated isotopologues.

Compound	Fraction of Deuterated Atoms (ξ)	Mean Percentage Error	
acetone-d ₆	0.9996	1.339%	
acetonitrile-d ₃	0.995	0.0389%	
benzene-d ₆	0.9996	0.257%	
chloroform-d	0.9982	0.131%	
cyclohexane-d ₁₂	0.996	0.258%	
dichloromethane-d ₂	0.9996	0.161%	
dimethyl sulfoxide-d ₆	0.9993	0.259%	
ethanol-d ₆	0.997	0.278%	
methanol-d ₄	0.99981	0.207%	
pyridine-d ₅	0.99	0.231%	
tetrahydrofuran-d ₈	0.9982	0.403%	
toluene-d ₈	0.9980	0.258%	

Table 8-5: Error analysis of the modified McClean/Adams formula.

The absence of complete agreement between measurement and prediction suggests that we reexamine the volumetric effects of deuterium substitution (molar volume isotope effect), which were neglected in the modified McClean/Adams relationship. These effects are best illustrated by comparing the molar volumes of a deuterated species $(V_{M,D})$ with its protiated analog $(V_{M,H})$ as seen in Figure 8-4 to Figure 8-9. The subplots illustrate the percent difference in molar volume between protiated and deuterated which was calculated according to Eq. 8-9 using the average molar volume as the basis for the calculation.

% Difference =
$$100\% \left(\frac{2 * |V_{M,D} - V_{M,H}|}{V_{M,D} + V_{M,H}} \right)$$
 Eq. 8-9

The molar volume of all measured components increases with rising temperature, a pattern consistent with the behavior of protiated liquids. Molar volumes became more similar at higher temperatures for benzene/benzene-d₆, cyclohexane/cyclohexane-d₁₂, tetrahydrofuran/tetrahydrofuran-d₈, toluene/toluene-d₈, pyridine/pyridine-d₅, methanol/methanold₄, ethanol/ethanol-d₆, and dimethyl sulfoxide/dimethyl sulfoxide-d₆. Acetone/acetone-d₆ and chloroform/chloroform-d exhibited the opposite trend as a greater discrepancy in molar volumes was observed at higher temperatures. A consistent trend was not observed for acetonitrile/acetonitrile-d₃ and dichloromethane/dichloromethane-d₂. Generally, differences between protiated and deuterated molar volumes were less than 0.45% across the temperature region, except for acetone/acetone-d₆, in which the protiated form differed from the deuterated form by as much as 1.38%.

Deuterium substitution decreases the zero-point vibrational energy of the C-D bond relative to a C-H bond. This decrease in energy produces a C-D bond which is roughly 0.005 Å shorter than a comparable C-H bond.^{215–217} Incidentally, intermolecular forces such as hydrogen bonding are strengthened, leading to decreased intermolecular distances.²¹⁸ Collectively, these effects produce a smaller molar volume for the deuterated material in the materials studied here, except for acetonitrile-d₃, whose slight percent difference does not provide a definitive conclusion.



Figure 8-4: Comparison of protiated and deuterated molar volumes for acetone/acetone- d_6 (left) and acetonitrile/acetonitrile- d_3 (right).



Figure 8-5: Comparison of protiated and deuterated molar volumes for benzene/benzene- d_6 (left) and chloroform/chloroform-d (right).



Figure 8-6: Comparison of protiated and deuterated molar volumes for cyclohexane/cyclohexane-d₁₂ (left) and dichloromethane/dichloromethane-d₂ (right).



Figure 8-7: Comparison of protiated and deuterated molar volumes for dimethyl sulfoxide/dimethyl sulfoxide- d_6 (left) and ethanol/ethanol- d_6 (right).



Figure 8-8: Comparison of protiated and deuterated molar volumes for methanol/methanol-d₄ (left) and pyridine/pyridine-d₅ (right).



Figure 8-9: Comparison of protiated and deuterated molar volumes for tetrahydrofuran/tetrahydrofuran- d_8 (left) and toluene/toluene- d_8 (right).

8.6.3 Isobaric Thermal Expansivity

Isobaric thermal expansivity (α_P) describes the volumetric response of a substance to changes in temperature at constant pressure. Isobaric thermal expansivity can be measured

$$\alpha_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P$$
 Eq. 8-10

experimentally^{219,220}; however, it is more common to calculate it indirectly using specific density data according to Eq. 8-10; yet, obtaining meaningful values from the indirect method necessitates a particular approach. Historically α_P has been calculated using the derivative of an imposed fit of ρ (*T*) data (i.e. a polynomial), yet recent work has shown that this approach produces α_P -values which exhibit an imprecise temperature dependence.²²¹ Rather, the partial differential should be evaluated using the central difference method according to Eq. 8-11, where the change in the experimental density is assessed numerically over a temperature interval (ΔT) of 5 K.^{221–223} At the low and high-temperature ρ (*T*) endpoints, α_P was calculated using the forward (Eq. 8-12) or backward (Eq. 8-13) single-sided difference method, respectively. Experimental values of density were used when applying these formulas.

$$\alpha_P[K^{-1}] = -\frac{1}{\rho(T)} \left(\frac{\rho(T + \Delta T) - \rho(T - \Delta T)}{2\Delta T} \right)$$
Eq. 8-11

$$\alpha_P[K^{-1}] = -\frac{1}{\rho(T)} \left(\frac{\rho(T + \Delta T) - \rho(T)}{\Delta T} \right)$$
 Eq. 8-12

$$\alpha_P[K^{-1}] = -\frac{1}{\rho(T)} \left(\frac{\rho(T) - \rho(T - \Delta T)}{\Delta T} \right)$$
Eq. 8-13

Calculated values of the coefficient of isobaric thermal expansivity from the experimental density data are depicted in Figure 8-10. The α_P increases with temperature and was regressed

using Eq. 8-14. Polynomial coefficients are presented in Table 8-6 and values of the coefficient of isobaric thermal expansivity from the resulting polynomial are plotted in as hashed lines in Figure 8-10. This chapter's appendix demonstrates that values calculated from analytically differentiating the density polynomial are imprecise near the ends of the experimental temperature range.

$$\alpha_P[\mathbf{K}^{-1}] = C_4 T^2 + C_5 T + C_6$$
 Eq. 8-14



Figure 8-10: Temperature dependency of the coefficient of isobaric thermal expansion (left) dichloromethane- d_2 (square), chloroform-d (diamond), cyclohexane- d_{12} (pentagon), benzene- d_6 (circle), toluene- d_8 (triangle), pyridine- d_5 (inverted triangle), (right) acetone- d_6 (square), acetonitrile- d_3 (diamond), dimethyl sulfoxide- d_6 (pentagon), methanol- d_4 (circle), ethanol- d_6 (triangle), and tetrahydrofuran- d_8 (inverted triangle).

	C4 [K ⁻³]	C ₅ [K ⁻²]	C ₆ [K ⁻¹]	\mathbf{D}^2
	/10 ⁻⁸	/10 ⁻⁵	/10 ⁻³	K
ethanol-d ₆	3.77 <u>9</u> 3	-1.96 <u>9</u> 4	3.61 <u>2</u> 7	0.992
chloroform-d	1.54 <u>1</u> 3	-0.604 <u>4</u> 9	1.71 <u>7</u> 3	0.978
pyridine-d5	1.03 <u>4</u> 0	-0.484 <u>8</u> 7	1.55 <u>5</u> 4	0.980
toluene-d ₈	0.836 <u>9</u> 4	-0.305 <u>5</u> 7	1.25 <u>2</u> 6	0.976
dichloromethane-d ₂	-0.276 <u>3</u> 5	0.514 <u>4</u> 8	0.114 <u>6</u> 4	0.950
benzene-d ₆	1.69 <u>4</u> 0	-0.803 <u>5</u> 2	2.11 <u>4</u> 9	0.979
cyclohexane-d ₁₂	2.72 <u>7</u> 6	-1.34 <u>9</u> 4	2.82 <u>6</u> 2	0.995
acetone-d ₆	3.62 <u>7</u> 7	-1.73 <u>9</u> 8	3.41 <u>6</u> 1	0.997
methanol-d ₄	4.10 <u>4</u> 3	-2.20 <u>8</u> 8	4.14 <u>3</u> 1	0.992
acetonitrile-d ₃	1.87 <u>3</u> 2	-0.771 <u>7</u> 8	2.03 <u>1</u> 0	0.991
dimethyl sulfoxide-d ₆	-0.908 <u>9</u> 1	0.684 <u>0</u> 2	-0.312 <u>5</u> 4	0.820
tetrahydrofuran-d8	0.900 <u>1</u> 0	-0.200 <u>8</u> 8	1.04 <u>6</u> 9	0.988

Table 8-6: Isobaric thermal expansivity regression coefficients.

*underbar indicates the last significant digit

8.7 Summary and Conclusions

Density values were measured for twelve deuterated solvents commonly encountered in NMR spectroscopy. Temperature-dependent specific densities of dichloromethane-d₂, toluene-d₈, pyridine-d₅, ethanol-d₆, tetrahydrofuran-d₈, and dimethyl sulfoxide-d₆ were reported for the first time at near ambient temperatures. Comparisons were made for benzene-d₆, acetone-d₆, methanol-d₄, cyclohexane-d₁₂, acetonitrile-d₃, and chloroform-d, for which there were some literature values available. Across the temperature range used in this study, all compounds exhibited decreasing specific density in response to temperature increases. The coefficient of isobaric thermal expansivity was calculated and found to increase with temperature for all components.

8.8 Acknowledgements

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CHAPTER 9: Conclusions and Future Directions

9.1 Conclusions

This work has resulted in several significant findings.

- 1. A functional form of the mid-range infrared attenuation was developed for scaling spectra that resulted in temperature-independent integrated areas for the hydroxyl stretch. The attenuation function differs in magnitude by approximately a factor of 30 for strongly bonded hydroxyls relative to free hydroxyls. This is the first method proposed for conversion of the hydroxyl stretch region to obtain a temperature-independent integrated area.
- 2. The scaling of the IR spectra does not require an assumed association model for quantification of hydroxyl region.
- 3. The scaled IR spectra can be mapped to NMR spectra using a mapping function based on quantum calculations, as further evidence of the validity of the scaling method.
- 4. All alcohols in this study exhibited similar attenuation functions.
- 5. Curve fitting of the hydroxyl region can be achieved by use of four primary peaks and one minor peak for hydroxyls, and one peak to subtract the -CH overlap. Two of the hydroxyl peaks represent the α and β hydroxyls and the other peaks represent the γ and δ hydroxyls.
- 6. The scaled spectra permit quantification of the fraction of non-hydrogen bonded hydroxyls, X^A by the fraction of the peak areas for the α and β hydroxyls relative to the total hydroxyl area. This analysis is independent of any association model for the first time.
- 7. The values of X^A vs. alcohol mole fraction are very similar for the homologous series of alcohols from ethanol to hexanol, inclusive up to 30 mol% alcohol.

- 8. Behavior of X^A for secondary alcohols compared to primary alcohol was inconclusive, with 2-propanol showing behavior like the primary alcohols, but 2-butanol showing less bonding.
- 9. Two association strengths are necessary for fitting of the infrared spectra.
- 10. Hydrogen bond type distributions from curve fitting the scaled spectra using four principal hydroxyl peaks are well-represented by the of the RTPT model over the temperature range of 30-60 °C.
- 11. An activity coefficient model was developed based on the RTPT model.
- 12. The fits of the spectra using the RTPT model were implemented as the association contribution in the NTRL-PA methodology, resulting in improved representation compared to TPT-1 for the dilute alcohol region and improved temperature dependence of the enthalpy of mixing. By constraining the bonding energy of the n-mer to ϵ_N^{AD}/k =2500 K, the same number of adjustable parameters are used compared to TPT-1 with improved results.
- 13. Mapping of RTPT to TPT-1 was demonstrated to permit approximate modeling of alcohols using existing phase equilibria code which is primarily coded using TPT-1.
- 14. Molar densities of deuterated solvents are within about one percent of the density of the nondeuterated form with the only exception being acetone-d₆. Quantification will be useful for future variable temperature NMR studies.

9.2 Future work

There are numerous avenues of research that would be extensions of the work presented in this dissertation, and they are briefly summarized in the points below with some of the accompanying challenges.

- 1. The approaches presented in this work could be applied to additional alcohol systems. The number of secondary and tertiary alcohol systems in this study was small, and primary alcohols investigated did not exceed six carbons. Longer alcohols would have a lower hydroxyl concentration and with an increase in carbon chain length of the alcohol the competition between associative and dispersive interactions would become more significant. Like the systems examined in this work a similar investigation could be undertaken for diol compounds. Other non-hydrogen bond forming solvent could also be explored.
- 2. An extension of the infrared scaling methods would involve primary, secondary, and tertiary amines. Like alcohols, amines self-aggregate and differences in infrared absorbance due to these aggregates has been well documented in literature occurring in the neighborhood of 3300 cm⁻¹. NMR data is present for amine systems in cyclohexane for comparison.²²⁴
- 3. The current work utilizes 2B (one acceptor site and one donor site) description of the hydroxyl which ignores the influence of rings and branching and assumes equality between the number of acceptor and donor sites. It is not unreasonable to assume that the smaller chain alcohols such as methanol and possibly ethanol would likely see an improvement by using a hydroxyl model which assigns two acceptor sites to the oxygen and one donor site to the proton (3B model). More fundamentally, the free electron pairs on the oxygen are not held in energetically identical orbitals. However, this extension would require derivation of cooperative bonding in a more general way, considering that our current RTPT model assumes that the number of acceptor and donor sites are equal. This line of reasoning could be extended to water which has additional complications compared to

methanol. Not only is it known to form up to four hydrogen bonds (4C model -2 acceptor sites and 2 donor sites) but it is difficult to dissolve in a non-hydrogen bond forming solvent for purposes of infrared measurements. This reduces solvent candidates to polar aprotic solvents such as acetonitrile which can cross associate with water.

- 4. The generalization of RTPT to multicomponent system would be powerful. Another important direction involves cross association such as between a ketone and alcohol. The carbonyl absorbance is well resolved in the infrared region. Incorporation of a ketone would be an accessible addition since it only serves as an acceptor and could likely be represented with a single association site. A similar argument could be made for a nitrile
- 5. The relationship between the hydroxyl stretching frequency and the NMR chemical shift of the hydroxyl proton would benefit from additional NMR data. Preliminary findings suggest that the form of the relationship is valid and does not vary significantly between primary and secondary alcohols. Ideally, the NMR measurements should be performed at temperatures and compositions that are near those measured in the infrared so that minimal interpolation is needed.
- 6. From an engineering modeling perspective, there would be value in exploring the feasibility of one set of association parameters for all the primary alcohols from methanol to 1-hexane.

BIBLIOGRAPHY

- (1) Lira, C. T.; Elliott, J. R.; Gupta, S.; Chapman, W. G. Wertheim's Association Theory for Phase Equilibrium Modeling in Chemical Engineering Practice. *Ind. Eng. Chem. Res.* in press. https://doi.org/10.1021/acs.icer.2c02058.
- (2) Kontogeorgis, G. M.; Folas, G. K. *Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories*; Wiley: Hoboken, N.J., 2010.
- (3) Yoshida, Z.; Ishibe, N.; Ozoe, H. Intermolecular Hydrogen Bond Involving a .Pi. Base as the Proton Acceptor. X. Hydrogen Bonding of Phenol with Acetylenes and Allenes. *J. Am. Chem. Soc.* **1972**, *94* (14), 4948–4952. https://doi.org/10.1021/ja00769a026.
- (4) Jeffrey, G. A. An Introduction to Hydrogen Bonding; Oxford University Press, 1997.
- (5) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*, 2nd Edition.; A Series of Books in Chemistry; W.H. Freeman and Company: San Francisco, 1960.
- (6) Hall, A.; Wood, J. L. Origin of the Structure of the OH Stretching Band of Some Phenols in Solution. Spectrochim Acta A Mol Biomol Spectrosc 1967, 23 (10), 2657–2667. https://doi.org/10.1016/0584-8539(67)80157-0.
- (7) Choperena, A.; Painter, P. An Infrared Spectroscopic Study of Hydrogen Bonding in Ethyl Phenol: A Model System for Polymer Phenolics. *Vib. Spectrosc.* 2009, *51* (1), 110–118. https://doi.org/10.1016/j.vibspec.2008.11.008.
- (8) Ohta, K.; Tominaga, K. Vibrational Population Relaxation of Hydrogen-Bonded Phenol Complexes in Solution: Investigation by Ultrafast Infrared Pump–Probe Spectroscopy. *Chemical Physics* 2007, 341 (1), 310–319. https://doi.org/10.1016/j.chemphys.2007.07.025.
- (9) Singh, L. P.; Richert, R. Watching Hydrogen-Bonded Structures in an Alcohol Convert from Rings to Chains. *Phys. Rev. Lett.* **2012**, *109* (16), 167802. https://doi.org/10.1103/PhysRevLett.109.167802.
- (10) Zimmermann, D.; Häber, T.; Schaal, H.; Suhm, M. A. Hydrogen Bonded Rings, Chains and Lassos: The Case of t-Butyl Alcohol Clusters. *Molecular Physics* 2001, 99 (5), 413–425. https://doi.org/10.1080/00268970010017009.
- (11) Yagai, S.; Kubota, S.; Saito, H.; Unoike, K.; Karatsu, T.; Kitamura, A.; Ajayaghosh, A.; Kanesato, M.; Kikkawa, Y. Reversible Transformation between Rings and Coils in a Dynamic Hydrogen-Bonded Self-Assembly. *J. Am. Chem. Soc.* 2009, *131* (15), 5408–5410. https://doi.org/10.1021/ja9005892.
- Račkauskaitė, D.; Bergquist, K.-E.; Shi, Q.; Sundin, A.; Butkus, E.; Wärnmark, K.; Orentas,
 E. A Remarkably Complex Supramolecular Hydrogen-Bonded Decameric Capsule Formed

from an Enantiopure C2-Symmetric Monomer by Solvent-Responsive Aggregation. J. Am. Chem. Soc. 2015, 137 (33), 10536–10546. https://doi.org/10.1021/jacs.5b03160.

- (13) Hecksher, T.; Jakobsen, B. Communication: Supramolecular Structures in Monohydroxy Alcohols: Insights from Shear-Mechanical Studies of a Systematic Series of Octanol Structural Isomers. J. Chem. Phys. 2014, 141 (10), 101104. https://doi.org/10.1063/1.4895095.
- (14) Van Ness, H. C.; Van Winkle, J.; Richtol, H. H.; Hollinger, H. B. Infrared Spectra and the Thermodynamics of Alcohol-Hydrocarbon Systems. J. Phys. Chem. 1967, 71 (5), 1483– 1494. https://doi.org/10.1021/j100864a046.
- (15) Kirsch, J. L.; Coffin, D. R. Infrared and Nuclear Magnetic Resonance Studies of Hydrogen Bonding in Aliphatic Alcohol Systems. J. Phys. Chem. 1976, 80 (22), 2448–2451. https://doi.org/10.1021/j100563a003.
- (16) Bellamy, L. J.; Pace, R. J. Hydrogen Bonding by Alcohols and Phenols—I. The Nature of the Hydrogen Bond in Alcohol Dimers and Polymers. *Spectrochimica Acta* **1966**, *22* (3), 525–533. https://doi.org/10.1016/0371-1951(66)80083-8.
- (17) Cohen, A. D.; Reid, C. Hydrogen Bonding by NMR. *The Journal of Chemical Physics* **1956**, 25 (4), 790–791. https://doi.org/10.1063/1.1743072.
- (18) Woutersen, S.; Emmerichs, U.; Bakker, H. J. A Femtosecond Midinfrared Pump–Probe Study of Hydrogen-Bonding in Ethanol. *The Journal of Chemical Physics* **1997**, *107* (5), 1483–1490. https://doi.org/10.1063/1.474501.
- (19) Mazur, K.; Bonn, M.; Hunger, J. Hydrogen Bond Dynamics in Primary Alcohols: A Femtosecond Infrared Study. J. Phys. Chem. B 2015, 119 (4), 1558–1566. https://doi.org/10.1021/jp509816q.
- (20) Ludwig, R. The Structure of Liquid Methanol. *ChemPhysChem* **2005**, *6* (7), 1369–1375. https://doi.org/10.1002/cphc.200400663.
- (21) Schwager, F.; Marand, E.; Davis, R. M. Determination of Self-Association Equilibrium Constants of Ethanol by FTIR Spectroscopy. J. Phys. Chem. 1996, 100 (50), 19268–19272. https://doi.org/10.1021/jp9613448.
- (22) Balanay, M. P.; Kim, D. H.; Fan, H. Revisiting the Formation of Cyclic Clusters in Liquid Ethanol. J. Chem. Phys. **2016**, 144 (15), 154302. https://doi.org/10.1063/1.4945809.
- (23) Thomas, L. H. 371. Viscosity and Molecular Association. Part V. The Association Model, and Hydrogen-Bond Enthalpies. *Journal of the Chemical Society (Resumed)* **1963**, 1995–2002.
- (24) Lehtola, J.; Hakala, M.; Hämäläinen, K. Structure of Liquid Linear Alcohols. J. Phys. Chem. B 2010, 114 (19), 6426–6436. https://doi.org/10.1021/jp909894y.

- (25) Jindal, A.; Vasudevan, S. Geometry of OH…O Interactions in the Liquid State of Linear Alcohols from Ab Initio Molecular Dynamics Simulations. *Phys. Chem. Chem. Phys.* 2020, 22 (12), 6690–6697. https://doi.org/10.1039/D0CP00435A.
- (26) Ewing, G. W. Instrumental Methods of Chemical Analysis; McGraw-Hill: New York, 1969.
- (27) Meloan, C. *Elementary Infrared Spectroscopy*; Macmillan Pub. Co.: Collier Macmillan: New York, NY, 1963.
- (28) Potts, W. J. Chemical Infrared Spectroscopy: Volume 1, Techniques; John Wley & Sons, 1963.
- (29) Silverstein, R. M.; Webster, F. X.; Kiemle, D. J.; Bryce, D. L. Spectrometric Identification of Organic Compounds, Eighth edition.; Wiley: Hoboken, NJ, 2015.
- (30) Vinogradov, S. N.; Linnell, R. H. *Hydrogen Bonding*; Van Nostrand Reinhold: New York, 1971.
- (31) Schmidt, J. R.; Corcelli, S. A.; Skinner, J. L. Pronounced Non-Condon Effects in the Ultrafast Infrared Spectroscopy of Water. *The Journal of Chemical Physics* 2005, *123* (4), 044513. https://doi.org/10.1063/1.1961472.
- (32) Coggeshall, N. D. Electrostatic Interaction in Hydrogen Bonding. *The Journal of Chemical Physics* **1950**, *18* (7), 978–983. https://doi.org/10.1063/1.1747822.
- (33) Tolbin, A. Yu.; Pushkarev, V. E.; Tomilova, L. G. A Mathematical Analysis of Deviations from Linearity of Beer's Law. *Chemical Physics Letters* 2018, 706, 520–524. https://doi.org/10.1016/j.cplett.2018.06.056.
- (34) Asprion, N.; Hasse, H.; Maurer, G. FT-IR Spectroscopic Investigations of Hydrogen Bonding in Alcohol-Hydrocarbon Solutions. *Fluid Phase Equilib.* **2001**, *186* (1–2), 1–25. https://doi.org/10.1016/s0378-3812(01)00363-6.
- (35) Anslyn, E. V.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science: Sausalito, CA, 2006.
- (36) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE Journal* 1975, 21 (1), 116–128. https://doi.org/10.1002/aic.690210115.
- (37) Bala, A. M.; Lira, C. T. Relation of Wertheim Association Constants to Concentration-Based Equilibrium Constants for Mixtures with Chain-Forming Components. *Fluid Phase Equilib.* 2016, 430, 47–56. https://doi.org/10.1016/j.fluid.2016.09.015.
- (38) Elliott, J. R.; Lira, C. T. *Introductory Chemical Engineering Thermodynamics*, Second edition.; Prentice-Hall international series in the physical and chemical engineering sciences; Prentice Hall: Upper Saddle River, NJ, 2012.

- (39) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. de. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Pearson Education, 1998.
- (40) Economou, I. G.; Donohue, M. D. Chemical, Quasi-Chemical and Perturbation Theories for Associating Fluids. *AIChE J.* **1991**, *37* (12), 1875–1894. https://doi.org/10.1002/aic.690371212.
- (41) Campbell, S. W. Chemical Theory for Mixtures Containing Any Number of Alcohols. *Fluid Phase Equilib.* **1994**, *102* (1), 61–84. https://doi.org/10.1016/0378-3812(94)87091-8.
- (42) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New Reference Equation of State for Associating Liquids. *Ind Eng Chem Res* **1990**, *29* (8), 1709–1721. https://doi.org/10.1021/ie00104a021.
- (43) Harris, D. C. *Quantitative Chemical Analysis*, 7th edition.; W. H. Freeman: New York, 2006.
- (44) Amunson, K. E.; Anderson, B. A.; Kubelka, J. Temperature Effects on the Optical Path Length of Infrared Liquid Transmission Cells. *Appl Spectrosc* 2011, 65 (11), 1307–1313. https://doi.org/10.1366/11-06405.
- (45) Williams, S. D.; Johnson, T. J.; Sharpe, S. W.; Yavelak, V.; Oates, R. P.; Brauer, C. S. Quantitative Vapor-Phase IR Intensities and DFT Computations to Predict Absolute IR Spectra Based on Molecular Structure: I. Alkanes. *Journal of Quantitative Spectroscopy* and Radiative Transfer 2013, 129, 298–307. https://doi.org/10.1016/j.jqsrt.2013.07.005.
- (46) Kumar, N.; Bansal, A.; Sarma, G. S.; Rawal, R. K. Chemometrics Tools Used in Analytical Chemistry: An Overview. *Talanta* 2014, 123, 186–199. https://doi.org/10.1016/j.talanta.2014.02.003.
- (47) Jones, R. N. The Intensities of the Infra-Red Absorption Bands of n-Paraffin Hydrocarbons. *Spectrochimica Acta* **1957**, *9* (3), 235–251. https://doi.org/10.1016/0371-1951(57)80137-4.
- (48) Wexler, A. S. Infrared Determination of Structural Units in Organic Compounds by Integrated Intensity Measurements: Alkanes, Alkenes and Monosubstituted Alkyl Benzenes. *Spectrochimica Acta* **1965**, *21* (10), 1725–1742. https://doi.org/10.1016/0371-1951(65)80085-6.
- (49) Řeřicha, R.; Jarolímek, P.; Horák, M. Determination of the Degree of Branching in Alkanes by Infrared Spectroscopy. II. Variation of the Intensity of the Antisymmetrical Stretching Vibration Bands of C-H Bonds in CH₃ and CH₂ Groups. *Collect. Czech. Chem. Commun., CCCC* **1967**, *32* (5), 1903–1912. https://doi.org/10.1135/cccc19671903.
- (50) Murdoch, K. M.; Ferris, T. D.; Wright, J. C.; Farrar, T. C. Infrared Spectroscopy of Ethanol Clusters in Ethanol–Hexane Binary Solutions. *The Journal of Chemical Physics* 2002, *116* (13), 5717–5724. https://doi.org/10.1063/1.1458931.

- (51) Tucker, E. E.; Becker, E. D. Alcohol Association Studies. II. Vapor Pressure, 220-MHz Proton Magnetic Resonance, and Infrared Investigations of Tert-Butyl Alcohol Association in Hexadecane. J. Phys. Chem. 1973, 77 (14), 1783–1795. https://doi.org/10.1021/j100633a012.
- (52) Wu, X.; Chen, Y.; Yamaguchi, T. Hydrogen Bonding in Methanol Studied by Infrared Spectroscopy. *Journal of Molecular Spectroscopy* **2007**, *246* (2), 187–191. https://doi.org/10.1016/j.jms.2007.09.012.
- (53) Reilly, J. T.; Thomas, A.; Gibson, A. R.; Luebehusen, C. Y.; Donohue, M. D. Analysis of the Self-Association of Aliphatic Alcohols Using Fourier Transform Infrared (FT-IR) Spectroscopy. *Ind. Eng. Chem. Res.* 2013, 52 (40), 14456–14462. https://doi.org/10.1021/ie302174r.
- (54) Coggeshall, N. D.; Saier, E. L. Infrared Absorption Study of Hydrogen Bonding Equilibria. *J. Am. Chem. Soc.* **1951**, *73* (11), 5414–5418. https://doi.org/10.1021/ja01155a118.
- (55) Choperena, A.; Painter, P. Hydrogen Bonding in Polymers: Effect of Temperature on the OH Stretching Bands of Poly(Vinylphenol). *Macromolecules* 2009, 42 (16), 6159–6165. https://doi.org/10.1021/ma900928z.
- (56) Sheppard, N. Infrared Spectroscopy and Hydrogen Bonding Band-Widths and Frequency Shifts. In Hydrogen Bonding: Papers Presented at the Symposium on Hydrogen Bonding Held at Ljubljana, 29 July–3 August 1957; Hadži, D., Ed.; Pergamon, 1959; pp 85–105. https://doi.org/10.1016/B978-0-08-009140-2.50013-0.
- (57) Liddel, U.; Becker, E. D. Infra-Red Spectroscopic Studies of Hydrogen Bonding in Methanol, Ethanol, and t-Butanol. *Spectrochimica Acta* **1957**, *10* (1), 70–84. https://doi.org/10.1016/0371-1951(57)80165-9.
- (58) Laksmono, H.; Tanimura, S.; Allen, H. C.; Wilemski, G.; Zahniser, M. S.; Shorter, J. H.; Nelson, D. D.; McManus, J. B.; Wyslouzil, B. E. Monomer, Clusters, Liquid: An Integrated Spectroscopic Study of Methanol Condensation. *Phys. Chem. Chem. Phys.* 2011, *13* (13), 5855. https://doi.org/10.1039/c0cp02485f.
- (59) Andanson, J.-M.; Soetens, J.-C.; Tassaing, T.; Besnard, M. Hydrogen Bonding in Supercritical Tert-Butanol Assessed by Vibrational Spectroscopies and Molecular-Dynamics Simulations. *The Journal of chemical physics* 2005, *122* (17), 174512. https://doi.org/10.1063/1.1886730.
- (60) Doroshenko, I.; Pogorelov, V.; Sablinskas, V.; Balevicius, V. Matrix-Isolation Study of Cluster Formation in Methanol: O–H Stretching Region. *Journal of Molecular Liquids* 2010, 157 (2–3), 142–145. https://doi.org/10.1016/j.molliq.2010.09.003.
- (61) Wandschneider, D.; Michalik, M.; Heintz, A. Spectroscopic and Thermodynamic Studies of Liquid N-Butanol+n-Hexane and +cyclohexane Mixtures Based on Quantum Mechanical Ab Initio Calculations of n-Butanol Clusters. J. Mol. Liq. 2006, 125 (1), 2–13. https://doi.org/10.1016/j.molliq.2005.11.011.

- (62) Hansen, P. E.; Spanget-Larsen, J. On Prediction of OH Stretching Frequencies in Intramolecularly Hydrogen Bonded Systems. *Journal of Molecular Structure* 2012, 1018, 8–13. https://doi.org/10.1016/j.molstruc.2012.01.011.
- (63) Koné, M.; Illien, B.; Laurence, C.; Graton, J. Can Quantum-Mechanical Calculations Yield Reasonable Estimates of Hydrogen-Bonding Acceptor Strength? The Case of Hydrogen-Bonded Complexes of Methanol. *The Journal of Physical Chemistry A* 2011, *115* (47), 13975–13985. https://doi.org/10.1021/jp209200w.
- (64) Ohno, K.; Shimoaka, T.; Akai, N.; Katsumoto, Y. Relationship between the Broad OH Stretching Band of Methanol and Hydrogen-Bonding Patterns in the Liquid Phase. J. Phys. Chem. A 2008, 112 (32), 7342–7348. https://doi.org/10.1021/jp800995m.
- (65) Spanget-Larsen, J.; Hansen, B. K. V.; Hansen, P. E. OH Stretching Frequencies in Systems with Intramolecular Hydrogen Bonds: Harmonic and Anharmonic Analyses. *Chemical Physics* **2011**, *389* (1–3), 107–115. https://doi.org/10.1016/j.chemphys.2011.09.011.
- (66) Kwac, K.; Geva, E. A Mixed Quantum-Classical Molecular Dynamics Study of the Hydroxyl Stretch in Methanol/Carbon Tetrachloride Mixtures: Equilibrium Hydrogen-Bond Structure and Dynamics at the Ground State and the Infrared Absorption Spectrum. J. Phys. Chem. B 2011, 115 (29), 9184–9194. https://doi.org/10.1021/jp204245z.
- (67) Staib, A.; Borgis, D. A Quantum Multi-Mode Molecular Dynamics Approach to the Vibrational Spectroscopy of Solvated Hydrogen-Bonded Complexes. *Chemical Physics Letters* **1997**, *271* (4), 232–240. https://doi.org/10.1016/S0009-2614(97)00470-3.
- (68) Ghosh, M. K.; Lee, J.; Choi, C. H.; Cho, M. Direct Simulations of Anharmonic Infrared Spectra Using Quantum Mechanical/Effective Fragment Potential Molecular Dynamics (QM/EFP-MD): Methanol in Water. J. Phys. Chem. A 2012, 116 (36), 8965–8971. https://doi.org/10.1021/jp306807v.
- (69) Wang, J.; Boyd, R. J.; Laaksonen, A. A Hybrid Quantum Mechanical Force Field Molecular Dynamics Simulation of Liquid Methanol: Vibrational Frequency Shifts as a Probe of the Quantum Mechanical/Molecular Mechanical Coupling. *The Journal of Chemical Physics* **1996**, *104* (18), 7261–7269. https://doi.org/10.1063/1.471439.
- (70) Corcelli, S. A.; Skinner, J. L. Infrared and Raman Line Shapes of Dilute HOD in Liquid H2O and D2O from 10 to 90 °C. J. Phys. Chem. A 2005, 109 (28), 6154–6165. https://doi.org/10.1021/jp0506540.
- (71) Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L. Combined Electronic Structure/Molecular Dynamics Approach for Ultrafast Infrared Spectroscopy of Dilute HOD in Liquid H2O and D2O. *The Journal of Chemical Physics* 2004, *120* (17), 8107–8117. https://doi.org/10.1063/1.1683072.
- (72) Auer, B.; Kumar, R.; Schmidt, J. R.; Skinner, J. L. Hydrogen Bonding and Raman, IR, and 2D-IR Spectroscopy of Dilute HOD in Liquid D₂O. *Proceedings of the National Academy of Sciences of the United States of America* **2007**, *104* (36), 14215–14220.

- (73) Gruenbaum, S. M.; Tainter, C. J.; Shi, L.; Ni, Y.; Skinner, J. L. Robustness of Frequency, Transition Dipole, and Coupling Maps for Water Vibrational Spectroscopy. J. Chem. Theory Comput. 2013, 9 (7), 3109–3117. https://doi.org/10.1021/ct400292q.
- Mesele, O. O.; Thompson, W. H. A "Universal" Spectroscopic Map for the OH Stretching Mode in Alcohols. J. Phys. Chem. A 2017, 121 (31), 5823–5833. https://doi.org/10.1021/acs.jpca.7b05836.
- (75) Kretschmer, C. B.; Wiebe, R. Thermodynamics of Alcohol-Hydrocarbon Mixtures. J. Chem. Phys. **1954**, 22 (10), 1697–1701. https://doi.org/10.1063/1.1739878.
- (76) Deng, D.; Li, H.; Yao, J.; Han, S. Simple Local Composition Model for 1H NMR Chemical Shift of Mixtures. *Chemical Physics Letters* 2003, 376 (1), 125–129. https://doi.org/10.1016/S0009-2614(03)00996-5.
- (77) Karachewski, A. M.; McNiel, M. M.; Eckert, C. A. A Study of Hydrogen Bonding in Alcohol Solutions Using NMR Spectroscopy. *Ind. Eng. Chem. Res.* **1989**, *28* (3), 315–324. https://doi.org/10.1021/ie00087a010.
- (78) Whetsel, K. B.; Lady, J. H. Self-Association of Phenol in Nonpolar Solvents. In *Spectrometry of Fuels*; Friedel, R. A., Ed.; Plenum Press: New York, 1970; pp 259–279.
- (79) Case, D. A.; Babin, V.; Berryman, J. T.; Betz, R. M.; Cai, Q.; Cerutti, D. S.; Cheatham III, T. E.; Darden, T. A.; Duke, R. E.; Gohlke, H.; Goetz, A. W.; Gusarov, S.; Homeyer, N.; Janowski, P.; Kaus, J.; Kolossváry, I.; Kovalenko, A.; Lee, T. S.; LeGrand, S.; Luchko, T.; Luo, R.; Madej, B.; Merz, K. M.; Paesani, F.; Roe, D. R.; Roitberg, A.; Sagui, C.; Salomon-Ferrer, R.; Seabra, G.; Simmerling, C. L.; Smith, W.; Swails, J.; Walker, R. C.; Wang, J.; Wolf, R. M.; Wu, X.; Kollman, P. A. AMBER 14, 2014.
- (80) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *Journal of Computational Chemistry 30* (13), 2157–2164. https://doi.org/10.1002/jcc.21224.
- (81) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 09, 2013.

- (82) Becke, A. D. Density-Functional Thermochemistry. V. Systematic Optimization of Exchange-Correlation Functionals. *The Journal of Chemical Physics* **1997**, *107* (20), 8554– 8560. https://doi.org/10.1063/1.475007.
- (83) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *The Journal of Chemical Physics* **1971**, *54* (2), 724–728. https://doi.org/10.1063/1.1674902.
- (84) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self—Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian—Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *The Journal of Chemical Physics* 1972, 56 (5), 2257–2261. https://doi.org/10.1063/1.1677527.
- (85) Hariharan, P. C.; Pople, J. A. The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies. *Theoretica Chimica Acta* **1973**, *28*, 213–222. https://doi.org/10.1007/BF00533485.
- (86) NIST Computational Chemistry Comparison and Benchmark Database; NIST Standard Reference Database Number 101; Release 19, April 2018, Editor: Russell D. Johnson III; Http://Cccbdb.Nist.Gov/; DOI:10.18434/T47C7Z.
- (87) 1-Butanol (NIST Chemistry WebBook, SRD 69). NIST Chemistry WebBook, SRD 69. https://webbook.nist.gov/cgi/cbook.cgi?ID=71-36-3&Type=IR-SPEC&Index=QUANT-IR,1 (accessed 2020-02-12).
- (88) *Ethanol (NIST Chemistry WebBook, SRD 69)*. NIST Chemistry WebBook, SRD 69. https://webbook.nist.gov/cgi/cbook.cgi?ID=C64175&Type=IR-SPEC&Index=29#Refs (accessed 2020-02-12).
- (89) Shinokita, K.; Cunha, A. V.; Jansen, T. L. C.; Pshenichnikov, M. S. Hydrogen Bond Dynamics in Bulk Alcohols. J. Chem. Phys. 2015, 142 (21), 212450. https://doi.org/10.1063/1.4921574.
- (90) Zheng, R.; Sun, Y.; Shi, Q. Theoretical Study of the Infrared and Raman Line Shapes of Liquid Methanol. *Phys. Chem. Chem. Phys.* 2011, 13 (6), 2027–2035. https://doi.org/10.1039/C0CP01145B.
- (91) Torii, H. Time-Domain Calculations of the Infrared and Polarized Raman Spectra of Tetraalanine in Aqueous Solution. J. Phys. Chem. B 2007, 111 (19), 5434–5444. https://doi.org/10.1021/jp070301w.
- (92) Williams, D. B. G.; Lawton, M. Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants. J. Org. Chem. 2010, 75 (24), 8351–8354. https://doi.org/10.1021/jo101589h.
- (93) González, B.; Calvar, N.; Domínguez, Á.; Tojo, J. Dynamic Viscosities of Binary Mixtures of Cycloalkanes with Primary Alcohols at T=(293.15, 298.15, and 303.15)K: New

UNIFAC-VISCO Interaction Parameters. *The Journal of Chemical Thermodynamics* **2007**, *39* (2), 322–334. https://doi.org/10.1016/j.jct.2006.06.008.

- (94) NIST Standard Reference Database 103a, NIST ThermoData Engine, Pure Components, Https://Www.Nist.Gov/Mml/Acmd/Trc/Thermodata-Engine/Srd-Nist-Tde-103a. https://www.nist.gov/mml/acmd/trc/thermodata-engine/srd-nist-tde-103a.
- (95) Fletcher, A. N.; Heller, C. A. Self-Association of Alcohols in Nonpolar Solvents. J. Phys. Chem. **1967**, 71 (12), 3742–3756. https://doi.org/10.1021/j100871a005.
- (96) Shinomiya, K.; Shinomiya, T. An Equilibrium Model of the Self-Association of 1- and 3-Pentanols in Heptane. *The Chemical Society of Japan* **1990**, *63*, 1093–1097.
- (97) Kontogeorgis, G. M.; Tsivintzelis, I.; von Solms, N.; Grenner, A.; Bøgh, D.; Frost, M.; Knage-Rasmussen, A.; Economou, I. G. Use of Monomer Fraction Data in the Parametrization of Association Theories. *Fluid Phase Equilibria* 2010, 296 (2), 219–229. https://doi.org/10.1016/j.fluid.2010.05.028.
- (98) Huggins, C. M.; Pimentel, G. C. Systematics of the Infrared Spectral Properties of Hydrogen Bonding Systems: Frequency Shift, Half Width and Intensity. J. Phys. Chem. 1956, 60 (12), 1615–1619. https://doi.org/10.1021/j150546a004.
- (99) Wertheim, M. S. Fluids with Highly Directional Attractive Forces.1. Statistical Thermodynamics. *Journal of Statistical Physics* 1984, 35 (1–2), 19–34. https://doi.org/10.1007/bf01017362.
- (100) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. 2. Thermodynamic Perturbation-Theory and Integral-Equations. *Journal of Statistical Physics* 1984, 35 (1–2), 35–47. https://doi.org/10.1007/bf01017363.
- (101) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. 4. Equilibrium Polymerization. *Journal of Statistical Physics* **1986**, 42 (3–4), 477–492. https://doi.org/10.1007/bf01127722.
- (102) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. 3. Multiple Attraction Sites. *Journal of Statistical Physics* 1986, 42 (3–4), 459–476. https://doi.org/10.1007/bf01127721.
- (103) Gross, J.; Sadowski, G. Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules. *Ind. Eng. Chem. Res.* **2001**, *40* (4), 1244–1260. https://doi.org/10.1021/ie0003887.
- (104) Gross, J.; Sadowski, G. Modeling Polymer Systems Using the Perturbed-Chain Statistical Associating Fluid Theory Equation of State. *Ind. Eng. Chem. Res.* 2002, *41* (5), 1084–1093. https://doi.org/10.1021/ie010449g.
- (105) Gupta, R. B.; Brinkley, R. L. Hydrogen-Bond Cooperativity in 1-Alkanol + n-Alkane Binary Mixtures. *AIChE Journal* **1998**, *44* (1), 207–213. https://doi.org/10.1002/aic.690440122.

- (106) Palombo, F.; Sassi, P.; Paolantoni, M.; Morresi, A.; Cataliotti, R. S. Comparison of Hydrogen Bonding in 1-Octanol and 2-Octanol as Probed by Spectroscopic Techniques. J. Phys. Chem. B 2006, 110 (36), 18017–18025. https://doi.org/10.1021/jp062614h.
- (107) Maes, G.; Smets, J. Hydrogen Bond Cooperativity: A Quantitative Study Using Matrix-Isolation FT-IR Spectroscopy. J. Phys. Chem. 1993, 97 (9), 1818–1825. https://doi.org/10.1021/j100111a017.
- (108) Umer, M.; Leonhard, K. Ab Initio Calculations of Thermochemical Properties of Methanol Clusters. J. Phys. Chem. A 2013, 117 (7), 1569–1582. https://doi.org/10.1021/jp308908j.
- (109) Umer, M.; Albers, K.; Sadowski, G.; Leonhard, K. PC-SAFT Parameters from Ab Initio Calculations. *Fluid Phase Equilib.* 2014, 362, 41–50. https://doi.org/10.1016/j.fluid.2013.08.037.
- (110) Kar, T.; Scheiner, S. Comparison of Cooperativity in CH…O and OH…O Hydrogen Bonds. *J. Phys. Chem. A* **2004**, *108* (42), 9161–9168. https://doi.org/10.1021/jp0485461.
- (111) Dominelli-Whiteley, N.; Brown, J. J.; Muchowska, K. B.; Mati, I. K.; Adam, C.; Hubbard, T. A.; Elmi, A.; Brown, A. J.; Bell, I. A. W.; Cockroft, S. L. Strong Short-Range Cooperativity in Hydrogen-Bond Chains. *Angew. Chem. Int. Ed.* **2017**, *56* (26), 7658–7662. https://doi.org/10.1002/anie.201703757.
- (112) Marshall, B. D.; Chapman, W. G. Resummed Thermodynamic Perturbation Theory for Bond Cooperativity in Associating Fluids. J. Chem. Phys. 2013, 139 (21), 214106. https://doi.org/10.1063/1.4834637.
- (113) Brinkley, R. L.; Gupta, R. B. Hydrogen Bonding with Aromatic Rings. *Aiche Journal* 2001, 47 (4), 948–953. https://doi.org/10.1002/aic.690470417.
- (114) Palombo, F.; Paolantoni, M.; Sassi, P.; Morresi, A.; Cataliotti, R. S. Spectroscopic Studies of the "Free" OH Stretching Bands in Liquid Alcohols. *Journal of Molecular Liquids* 2006, *125* (2–3), 139–146.
- (115) von Solms, N.; Michelsen, M. L.; Passos, C. P.; Derawi, S. O.; Kontogeorgis, G. M. Investigating Models for Associating Fluids Using Spectroscopy. *Ind. Eng. Chem. Res.* 2006, 45 (15), 5368–5374. https://doi.org/10.1021/ie051341u.
- (116) Haskell, R. W.; Hollinger, H. B.; Van Ness, H. C. Chemical Model as Applied to Associated Liquid Solutions. Ethanol-Heptane System. J. Phys. Chem. 1968, 72 (13), 4534–4543. https://doi.org/10.1021/j100859a028.
- (117) Asprion, N.; Hasse, H.; Maurer, G. Application of IR-Spectroscopy in Thermodynamic Investigations of Associating Solutions. *Fluid Phase Equilib.* 2003, 205 (2), 195–214. https://doi.org/10.1016/S0378-3812(02)00181-4.

- (118) Nagata, I.; Ogasawara, Y. Prediction of Ternary Excess Enthalpies from Binary Data. *Thermochimica Acta* **1982**, *52* (1–3), 155–168. https://doi.org/10.1016/0040-6031(82)85193-9.
- (119) Hofman, T. Thermodynamics of Association of Pure Alcohols. *Fluid Phase Equilibria* **1990**, *55* (1–2), 39–57. https://doi.org/10.1016/0378-3812(90)85003-S.
- (120) Kretschmer, C. B.; Wiebe, R. Pressure-Volume-Temperature Relationships of Alcohol Vapors². J. Am. Chem. Soc. **1954**, 76 (9), 2579–2583. https://doi.org/10.1021/ja01638a082.
- (121) Bala Ahmed, A. M. Fundamental Studies and Engineering Modeling of Hydrogen Bonding. Ph.D. Thesis, Michigan State University, East Lansing, MI, 2018.
- (122) Bala, A. M.; Killian, W. G.; Plascencia, C.; Storer, J. A.; Norfleet, A. T.; Peereboom, L.; Jackson, J. E.; Lira, C. T. Quantitative Analysis of Infrared Spectra of Binary Alcohol + Cyclohexane Solutions with Quantum Chemical Calculations. J. Phys. Chem. A 2020, 124 (16), 3077–3089. https://doi.org/10.1021/acs.jpca.9b11245.
- (123) Paolantoni, M.; Sassi, P.; Morresi, A.; Cataliotti, R. S. Infrared Study of 1-Octanol Liquid Structure. *Chem. Phys.* 2005, 310 (1–3), 169–178. https://doi.org/10.1016/j.chemphys.2004.10.027.
- (124) Asprion, N. Anwendung Der Spektroskopie in Thermodynamischen Untersuchungen Assoziierender Lösungen, Dissertation, C,. Ph.D. Thesis, 1996.
- (125) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT Equation-of-State Solution Model for Associating Fluids. *Fluid Phase Equilibria* **1989**, *52*, 31–38. https://doi.org/10.1016/0378-3812(89)80308-5.
- (126) Gross, J.; Sadowski, G. Application of the Perturbed-Chain SAFT Equation of State to Associating Systems. *Ind. Eng. Chem. Res.* **2002**, *41* (22), 5510–5515. https://doi.org/10.1021/ie010954d.
- (127) Sear, R. P.; Jackson, G. Thermodynamic Perturbation Theory for Association with Bond Cooperativity. J. Chem. Phys. **1996**, 105 (3), 1113–1120. https://doi.org/10.1063/1.471955.
- (128) Acree, W. *Thermodynamic Properties of Nonelectrolyte Solutions*; Academic Press Inc.: Orlando, 1984.
- (129) Apelblat, A. Erratum to "The Concept of Associated Solutions in Historical Development. Part 1. The 1884-1984 Period." J. Mol. Liq. 2007, 130 (1-3), 133-162. https://doi.org/10.1016/j.molliq.2006.09.001.
- (130) Bala, A. M.; Liu, R.; Peereboom, L.; Lira, C. T. Applications of an Association Activity Coefficient Model, NRTL-PA, to Alcohol-Containing Mixtures. *Ind. Eng. Chem. Res.* in press. https://doi.org/10.1021/acs.icer.2c01415.

- (131) Himmelblau, D. M. *Process Analysis by Statistical Methods*; John Wiley & Sons, Inc: New York, NY, 1970.
- (132) Dolan, K. D.; Yang, L.; Trampel, C. P. Nonlinear Regression Technique to Estimate Kinetic Parameters and Confidence Intervals in Unsteady-State Conduction-Heated Foods. *Journal* of Food Engineering 2007, 80 (2), 581–593. https://doi.org/10.1016/j.jfoodeng.2006.06.023.
- (133) Mishra, D. K.; Dolan, K. D.; Yang, L. Bootstrap Confidence Intervals for the Kinetic Parameters of Degradation of Anthocyanins in Grape Pomace: Bootstrap Confidence Intervals for Kinetic Parameter Estimation. J. Food Process Eng 2011, 34 (4), 1220–1233. https://doi.org/10.1111/j.1745-4530.2009.00425.x.
- (134) Killian, W. G.; Bala, A. M.; Lira, C. T. Parameterization of a RTPT Association Activity Coefficient Model Using Spectroscopic Data. *Fluid Phase Equilib.* 2022, No. 554, 113299. https://doi.org/10.1016/j.fluid.2021.113299.
- (135) Meier, R. J. On Art and Science in Curve-Fitting Vibrational Spectra. Vib Spectrosc 2005, 39 (2), 266–269. https://doi.org/10.1016/j.vibspec.2005.03.003.
- (136) Barlow, S. J.; Bondarenko, G. V.; Gorbaty, Y. E.; Yamaguchi, T.; Poliakoff, M. An IR Study of Hydrogen Bonding in Liquid and Supercritical Alcohols. J. Phys. Chem. A 2002, 106 (43), 10452–10460. https://doi.org/10.1021/jp0135095.
- (137) Svoboda, V.; Holub, R.; Pick, J. Liquid-Vapour Equilibrium. XLVII. The System Cyclohexane-1-Hexanol. *Collect. Czech. Chem. Commun.* **1971**, *36* (6), 2331–2338. https://doi.org/10.1135/cccc19712331.
- (138) Morachevsky, A. G. Investigation of Solution-Vapor Equilibrium in the Benzene-Cyclohexane-Methylalcohol System. Vestn. Leningr. Univ., 12, Ser. Fiz. Khim. 1957, 1, 118–126.
- (139) Lazzaroni, M. J.; Bush, D.; Eckert, C. A.; Frank, T. C.; Gupta, S.; Olson, J. D. Revision of MOSCED Parameters and Extension to Solid Solubility Calculations. *Industrial & Engineering Chemistry Research* 2005, 44 (11), 4075–4083. https://doi.org/10.1021/ie049122g.
- (140) Smirnova, N. A.; Kurtynina, L. M. Thermodynamic Functions of Mixing for a Number of Binary Alcohol-Hydrocarbon Solutions. *Zh. Fiz. Khim.* **1969**, *43*, 1883.
- (141) Marshall, B. D.; Haghmoradi, A.; Chapman, W. G. Resummed Thermodynamic Perturbation Theory for Bond Cooperativity in Associating Fluids with Small Bond Angles: Effects of Steric Hindrance and Ring Formation. *The Journal of Chemical Physics* 2014, 140 (16), 164101. https://doi.org/10.1063/1.4871307.
- (142) Pauling, L. *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry*, 3. ed., 17. print.; Cornell Univ. Press: Ithaca, NY, 2010.

- (143) Czarnecki, M. A. Effect of Temperature and Concentration on Self-Association of Octan-1-Ol Studied by Two-Dimensional Fourier Transform Near-Infrared Correlation Spectroscopy. J. Phys. Chem. A 2000, 104 (27), 6356–6361. https://doi.org/10.1021/jp000407q.
- (144) Asprion, N.; Hasse, H.; Maurer, G. Thermodynamic and IR Spectroscopic Studies of Solutions with Simultaneous Association and Solvation. *Fluid Phase Equilibria* 2003, 208 (1–2), 23–51. https://doi.org/10.1016/S0378-3812(02)00317-5.
- (145) Becker, E. D. Infrared Studies of Hydrogen Bonding in Alcohol-Base Systems. *Spectrochim Acta* **1961**, *17* (4), 436–447. https://doi.org/10.1016/0371-1951(61)80095-7.
- (146) Frohlich, H. Using Infrared Spectroscopy Measurements To Study Intermolecular Hydrogen Bonding: Calculating the Degree of Association, Equilibrium Constant, and Bond Energy for Hydrogen Bonding in Benzyl Alcohol and Phenol. J. Chem. Educ. 1993, 70 (1), A3. https://doi.org/10.1021/ed070pA3.
- (147) Iwahashi, M.; Hayashi, Y.; Hachiya, N.; Matsuzawa, H.; Kobayashi, H. Self-Association of Octan-1-Ol in the Pure Liquid State and in Decane Solutions as Observed by Viscosity, Self-Diffusion, Nuclear Magnetic Resonance and near-Infrared Spectroscopy Measurements. *Faraday Trans.* **1993**, 89 (4), 707. https://doi.org/10.1039/ft9938900707.
- (148) Janeček, J.; Paricaud, P. Size Distribution of Associated Clusters in Liquid Alcohols: Interpretation of Simulation Results in the Frame of SAFT Approach. J. Chem. Phys. 2013, 139 (17), 174502. https://doi.org/10.1063/1.4827107.
- (149) Sassi, P.; Palombo, F.; Cataliotti, R. S.; Paolantoni, M.; Morresi, A. Distributions of H-Bonding Aggregates in Tert-Butyl Alcohol: The Pure Liquid and Its Alkane Mixtures. J. Phys. Chem. A 2007, 111 (27), 6020–6027. https://doi.org/10.1021/jp071609q.
- (150) Linstrom, P. NIST Chemistry WebBook, NIST Standard Reference Database 69, 1997. https://doi.org/10.18434/T4D303.
- (151) Killian Jr., W. G.; Storer, J. A.; Killian Sr., W.; Lira, C. T. A MATLAB Application for Cell Pathlength in Absorption Transmission Spectroscopy. *Spectroscopy* **2020**, *35* (8), 26– 28.
- (152) Peter R. Griffiths; James A. de Haseth. Fourier Transform Infrared Spectrometry, 2nd ed.; Chemical Analysis: A Series of Monographs on Analytical Chemistry and It's Applications; John Wiley & Sons, Inc, 2007.
- (153) Bradley, M. Curve Fitting in Raman and IR Spectroscopy. Application Note, 50733; Thermo Fischer, Madison, WI, USA, 2007.
- (154) Kruger, F. J.; Schwarz, C. E.; du Preez, L. J.; Burger, A. J. Monomer Fraction Data of Dilute Alcohol/Acetone Systems Measured with Transmission Fourier Transform Infrared Spectroscopy. *Fluid Phase Equilib.* 2015, 400, 87–94. https://doi.org/10.1016/j.fluid.2015.05.010.

- (155) Karachewski, A. M.; Howell, W. J.; Eckert, C. A. Development of the AVEC Model for Associating Mixtures Using NMR Spectroscopy. *AIChE J.* **1991**, *37* (1), 65–73. https://doi.org/10.1002/aic.690370106.
- (156) Huang, S. H.; Radosz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Ind. Eng. Chem. Res.* 1990, 29 (11), 2284–2294. https://doi.org/10.1021/ie00107a014.
- (157) Vaskivskyi, Ye.; Doroshenko, I.; Chernolevska, Ye.; Pogorelov, V.; Pitsevich, G. Spectroscopic Studies of Clusterization of Methanol Molecules Isolated in a Nitrogen Matrix. Low Temperature Physics 2017, 43 (12), 1415–1419. https://doi.org/10.1063/1.5012794.
- (158) Bakke, J. M.; Bjerkeseth, L. H. Rotational Isomerism around the C–O Bond in Saturated Acyclic Alcohols—Assignment of the Experimental IR Hydroxyl Stretch Bands Using Semiempirical MO and Ab Initio Calculations. J. Mol. Struct. 1997, 407 (1), 27–38. https://doi.org/10.1016/S0022-2860(96)09726-8.
- (159) Czarnecki, M. A.; Wojtków, D.; Haufa, K. Rotational Isomerism of Butanols: Infrared, near-Infrared and DFT Study. *Chem. Phys. Lett.* **2006**, *431* (4), 294–299. https://doi.org/10.1016/j.cplett.2006.09.096.
- (160) van der Maas, J. H.; Lutz, E. T. G. Structural Information from OH Stretching Frequencies Monohydric Saturated Alcohols. *Spectrochim Acta Part A: Molecular Spectroscopy* **1974**, *30* (10), 2005–2019. https://doi.org/10.1016/0584-8539(74)80047-4.
- (161) Hare, D. E.; Sorensen, C. M. Raman Spectroscopic Study of Dilute HOD in Liquid H2O in the Temperature Range – 31.5 to 160 °C. J. Chem. Phys. 1990, 93 (10), 6954–6961. https://doi.org/10.1063/1.459472.
- (162) Eckert, C. A.; McNiel, M. M.; Scott, B. A.; Halas, L. A. NMR Measurements of Chemical Theory Equilibrium Constants for Hydrogen-Bonded Solutions. *AIChE J.* 1986, *32* (5), 820–828. https://doi.org/10.1002/aic.690320512.
- (163) Kwaśniewicz, M.; Czarnecki, M. A. The Effect of Chain Length on Mid-Infrared and Near-Infrared Spectra of Aliphatic 1-Alcohols. *Appl Spectrosc* 2018, 72 (2), 288–296. https://doi.org/10.1177/0003702817732253.
- (164) Killian, W. G.; Bala, A. M.; Norfleet, A. T.; Peereboom, L.; Jackson, J. E.; Lira, C. T. Infrared Quantification of Ethanol and 1-Butanol Hydrogen Bond Distributions in Cyclohexane. Spectrochim Acta A Mol Biomol Spectrosc In press. https://doi.org/10.1016/j.saa.2022.121837.
- (165) Roese, S. N.; Heintz, J. D.; Uzat, C. B.; Schmidt, A. J.; Margulis, G. V.; Sabatino, S. J.; Paluch, A. S. Assessment of the SM12, SM8, and SMD Solvation Models for Predicting Limiting Activity Coefficients at 298.15 K. *Processes* 2020, 8 (5), 623. https://doi.org/10.3390/pr8050623.

- (166) Tamouza, S.; Passarello, J.-P.; Tobaly, P.; de Hemptinne, J.-C. Application to Binary Mixtures of a Group Contribution SAFT EOS (GC-SAFT). *Fluid Phase Equilibria* 2005, 228–229, 409–419. https://doi.org/10.1016/j.fluid.2004.10.003.
- (167) NguyenHuynh, D.; Mai, C. T. Q. Application of the Modified Group Contribution PC-SAFT to Carboxylic Acids and Their Mixtures. *Ind. Eng. Chem. Res.* 2019, 58 (20), 8923–8934. https://doi.org/10.1021/acs.iecr.9b02052.
- (168) NguyenHuynh, D. Correlation and Prediction of Liquid–Liquid Equilibria for Alcohol/Hydrocarbon Mixtures Using PC-SAFT Equation of State at High Pressure up to 150 MPa. *Fluid Phase Equilibria* 2016, 425, 206–214. https://doi.org/10.1016/j.fluid.2016.06.002.
- (169) Elliott, J. R.; Diky, V.; Knotts, T. A.; Wilding, W. Vincent. *The Properties of Gases and Liquids*, 6th ed.; McGraw-Hill Education, 2022.
- (170) Damaceno, D. S.; Perederic, O. A.; Ceriani, R.; Kontogeorgis, G. M.; Gani, R. Improvement of Predictive Tools for Vapor-Liquid Equilibrium Based on Group Contribution Methods Applied to Lipid Technology. *Fluid Phase Equilibria* 2017. https://doi.org/10.1016/j.fluid.2017.12.009.
- (171) Hao, Y.; Chen, C. Nonrandom Two-liquid Activity Coefficient Model with Association Theory. *AIChE J* 2021, 67 (1), e17061. https://doi.org/10.1002/aic.17061.
- (172) French, H. T. Thermodynamic Functions for the Systems 1-Butanol, 2-Butanol, Andt-Butanol + Cyclohexane. J Solution Chem **1983**, 12 (12), 869–887. https://doi.org/10.1007/BF00643927.
- (173) Kurihara, K.; Uchiyama, M.; Kojima, K. Isothermal Vapor–Liquid Equilibria for Benzene + Cyclohexane + 1-Propanol and for Three Constituent Binary Systems. J. Chem. Eng. Data 1997, 42 (1), 149–154. https://doi.org/10.1021/je9602475.
- (174) Löwen, B.; Schulz, S. Excess Molar Enthalpies of Cyclohexane + N-Alcohols at 283.15, 298.15, 323.15, 343.15 and 363.15 K and at a Pressure of 0.4 MPa. *Thermochimica Acta* **1995**, 265, 63–71. https://doi.org/10.1016/0040-6031(94)02510-U.
- (175) Voňka, P.; Svoboda, V.; Strubl, K.; Holub, R. Liquid-Vapour Equilibrium. XLVI. System Cyclohexane-1-Butanol at 50 and 70 °C. *Collect. Czech. Chem. Commun.* 1971, *36* (1), 18–34. https://doi.org/10.1135/cccc19710018.
- (176) Triday, J. Q.; Veas, C. Vapor-Liquid Equilibria for the System Cyclohexane-Tert-Butyl Alcohol. J. Chem. Eng. Data **1985**, 30 (2), 171–173. https://doi.org/10.1021/je00040a011.
- (177) Buchowski, H.; Bartel, L. Vapor Pressure and Excess Gibbs Function If Carbinols-Cyclohexane Mixtures. *Polish Journal of Chemistry* **1978**, *52* (2417).
- (178) Veselý, F.; Dohnal, V.; Valentová, M.; Pick, J. Concentration and Temperature Dependence of Heats of Mixing of 1-Butanol, 2-Butanol, and 2-Methyl-2-Propanol with Cyclohexane.

Collect. Czech. Chem. Commun. **1983**, 48 (12), 3482–3494. https://doi.org/10.1135/cccc19833482.

- (179) Marinichev, A. N.; Susarev, M. P. Liquid-Vapor Equilibrium in the System Methanol– Cyclohexane at 35, 45, and 55 C and 760 Mm Hg. *Zh. Prikl. Khim.(Leningrad)* **1965**, *38*, 1619–1621.
- (180) Katayama, H. Liquid–Liquid Equilibria of Two Ternary Systems: Methanol–Cyclohexane Including 1,3-Dioxolane or 1,4-Dioxane in the Range of 277.79–308.64 K. *Fluid Phase Equilib.* **1999**, *164* (1), 83–95. https://doi.org/10.1016/S0378-3812(99)00241-1.
- (181) Dai, M.; Chao, J.-P. Heats of Mixing of the Partially Miscible Liquid System Cyclohexane
 + Methanol. *Fluid Phase Equilib.* 1985, 23 (2), 315–319. https://doi.org/10.1016/0378-3812(85)90014-7.
- (182) Gmehling, J.; Krentscher, B. *ELDATA: The International Electronic Journal of Physico-Chemical Data* **1995**, *1*, 181–190.
- (183) Góral, M.; Oracz, P.; Warycha, S. Vapour–Liquid Equilibria: XIII. The Ternary System Cyclohexane–Methanol–Hexane at 303.15 K. *Fluid Phase Equilibria* **1998**, *152* (1), 109– 120. https://doi.org/10.1016/S0378-3812(98)00383-5.
- (184) Nagai, Y.; Isii, N. Studies on Volatility of Fuels Containing Ethyl Alcohol. *Proceedings of the Imperial Academy* **1935**, *11* (1), 23–25. https://doi.org/10.2183/pjab1912.11.23.
- (185) Stokes, R. H.; Adamson, M. Thermodynamic Functions for the System Ethanol + Cyclohexane from Vapour Pressures and Enthalpies of Mixing. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73* (0), 1232–1238. https://doi.org/10.1039/F19777301232.
- (186) Moreau, A.; Martín, M. C.; Chamorro, C. R.; Segovia, J. J. Thermodynamic Characterization of Second Generation Biofuels: Vapour–Liquid Equilibria and Excess Enthalpies of the Binary Mixtures 1-Pentanol and Cyclohexane or Toluene. *Fluid Phase Equilibria* 2012, *317*, 127–131. https://doi.org/10.1016/j.fluid.2012.01.007.
- (187) Veselý, F.; Dohnal, V.; Brich, Z. Excess Enthalpies of 1-Hexanol or 1-Octanol + Cyclohexane. International Data Service Selected Data on Mixtures Ser. A 1987, No. 15, 179–182.
- (188) Nagata, I.; Ohta, T.; Uchiyama, Y. Excess Gibbs Free Energies for Binary Systems. Isopropyl Alcohol with Benzene, Cyclohexane, Methylcyclohexane. J. Chem. Eng. Data 1973, 18 (1), 54–59. https://doi.org/10.1021/je60056a011.
- (189) Storonkin, A. V.; Morachevskii, A. G. Liquid-Vapor Equilibrium in the Benzene+cyclohexane +isopropyl Alcohol System. *Zhurnal Fizicheskoi Khimii* 1956, 30 (6), 1297–1307.

- (190) Haase, R.; Tillmann, W. Mixing Properties of the Liquid System 2-Propanol + Cyclohexane. Zeitschrift für Physikalische Chemie 1995, 189 (1), 81–88. https://doi.org/10.1524/zpch.1995.189.Part_1.081.
- (191) Veselý, F.; Uchytil, P.; Zábranský, M.; Pick, J. Heats of Mixing of Cyclohexane with 1-Propanol and 2-Propanol. *Collect. Czech. Chem. Commun.* **1979**, 44 (10), 2869–2881. https://doi.org/10.1135/cccc19792869.
- (192) Gierycz, P.; Kosowski, A.; Swietlik, R. Vapor–Liquid Equilibria in Binary Systems Formed by Cyclohexane with Alcohols. *J. Chem. Eng. Data* **2009**, *54* (11), 2996–3001. https://doi.org/10.1021/je900050z.
- (193) Nataraj, V.; Rao, M. R. Isobaric Vapor-Liquid Equilibrium Data for the Binary Systems Benzene-Cyclohexane, Benzene-Isobutanol, and Cyclohexane-Isobutanol. *Indian J. Technol.* **1967**, *5*, 212–215.
- (194) Vittal Prasad, T. E.; Reddi Prasad Naidu, B.; Madhukiran, D.; Prasad, D. H. L. Boiling Temperature Measurements on the Binary Mixtures of Cyclohexane with Some Alcohols and Chlorohydrocarbons. J. Chem. Eng. Data 2001, 46 (2), 414–416. https://doi.org/10.1021/je000139p.
- (195) Belousov, V. P.; Kurtynina, L. M.; Kozulyaev, A. A. VII. Mischungswärme Des Cyclohexans Mit Propanol, n-Butanol, Isobutanol Und Dekanol. *Fiz. Khim.* **1970**, 163–166.
- (196) Böhmer, R.; Gainaru, C.; Richert, R. Structure and Dynamics of Monohydroxy Alcohols— Milestones towards Their Microscopic Understanding, 100 Years after Debye. *Physics Reports* 2014, 545 (4), 125–195. https://doi.org/10.1016/j.physrep.2014.07.005.
- (197) Gutowsky, H. S.; Saika, A. Dissociation, Chemical Exchange, and the Proton Magnetic Resonance in Some Aqueous Electrolytes. *The Journal of Chemical Physics* 1953, 21 (10), 1688–1694. https://doi.org/10.1063/1.1698644.
- (198) Li, D.; Kagan, G.; Hopson, R.; Williard, P. G. Formula Weight Prediction by Internal Reference Diffusion-Ordered NMR Spectroscopy (DOSY). J. Am. Chem. Soc. 2009, 131 (15), 5627–5634. https://doi.org/10.1021/ja810154u.
- (199) Dixon, J. A.; Schiessler, R. W. Synthesis and Properties of Deuterocarbons. Benzene-D6 and Cyclohexane-D12. J. Am. Chem. Soc. **1954**, 76 (8), 2197–2199.
- (200) Dymond, J. H.; Glen, N.; Robertson, J.; Isdale, J. D. (P, ρ, T) for {(1-x)C6H6 + XC6D6} and {(1-x)C6H6 + XC6F6} in the Range 298 to 373 K and 0.1 to 400 MPa. J. Chem. Thermodyn. 1982, 14 (12), 1149–1158. https://doi.org/10.1016/0021-9614(82)90038-6.
- (201) Ingold, C. K.; Raisin, C. G.; Wilson, C. L. 212. Structure of Benzene. Part II. Direct Introduction of Deuterium into Benzene and the Physical Properties of Hexadeuterobenzene. J. Chem. Soc. **1936**, 915–925.

- (202) Klit, A.; Langseth, A. Über die darstellung von deuteriobenzol. Z. Phys. Chem. (Leipzig) **1936**, 176A (1), 65–80.
- (203) McClean, A.; Adams, R. Succinic-α-D2, α'-D2 Acid and Its Derivatives. J. Am. Chem. Soc. 1936, 58 (5), 804–810.
- (204) Handa, Y. P. Molar Excess Volumes of Acetonitrile + Chloroform and of Acetonitrile + Deuterochloroform. *J. Chem. Thermodyn.* **1977**, *9* (2), 117–120. https://doi.org/10.1016/0021-9614(77)90076-3.
- (205) Rabinovich, I. B.; Lobashov, A. A.; Kucheryavyi, V. I. A Negative Isotope Effect in the Viscosity of Deutero Compounds. *Russ. J. Phys. Chem.* **1960**, *34* (10), 1046–1047.
- (206) Breuer, F. W. Chloroform-d (Deuteriochloroform)1. J. Am. Chem. Soc. **1935**, 57 (11), 2236–2237. https://doi.org/10.1021/ja01314a058.
- (207) Bender, T. M.; Alexander van Hook, W. Molar Volumes of CH3OH, CH3OD, and CD3OD, and Apparent or Excess Molar Volumes for (Methanol-OH + Water), (Methanol-OD + Deuterium Oxide), and (Methanol-OH + Methanol-OD), at 288.15, 298.15, and 313.15 K. *J. Chem. Thermodyn.* **1988**, 20 (9), 1109–1114. https://doi.org/10.1016/0021-9614(88)90118-8.
- (208) Kudryavtsev, S. G.; Strakhov, A. N.; Ershova, O. V. Volume Properties of Deuterated Water-Methanol Systems at 278-318 K. *Russ. J. Phys. Chem.* **1986**, *60* (9), 1319–1321.
- (209) Matsuo, S.; Van Hook, W. A. Isothermal Compressibility of Benzene, Deuteriobenzene (C6D6), Cyclohexane, and Deuteriocyclohexane (c-C6D12), and Their Mixtures from 0.1 to 35 Mpa at 288, 298, and 313 K. J. Phys. Chem. 1984, 88 (5), 1032–1040. https://doi.org/10.1021/j150649a037.
- (210) Nikolaev, P. N.; Rabinovich, I. B.; Gal'perin, V. A.; Tsvetkov, V. G. Isotopic Effect in the Heat Capacity and Compressibility of Perdeuterocyclohexane. *Zh. Fiz Khim* **1966**, *40* (5), 586–590.
- (211) Sassi, P.; Morresi, A.; Paliani, G.; Cataliotti, R. S. Differences in the Dynamic Properties of Liquid CH3CN and CD3CN above 40 °C Revealed by Rayleigh–Brillouin Scattering Spectroscopy. J. Raman Spectrosc. 1999, 30 (7), 501–506. https://doi.org/10.1002/(SICI)1097-4555(199907)30:7<501::AID-JRS402>3.0.CO;2-2.
- (212) Schroeder, J.; Schiemann, V. H.; Sharko, P. T.; Jonas, J. Raman Study of Vibrational Dephasing in Liquid CH3CN and CD3CN. J. Chem. Phys. 1977, 66 (7), 3215–3226. https://doi.org/10.1063/1.434296.
- (213) Szydlowski, J.; Gomes de Azevedo, R.; Rebelo, L. P. N.; Esperança, J. M. S. S.; Guedes, H. J. R. Deuterium Isotope Differences in 2-Propanone, (CH3)2CO/(CD3)2CO: A High-Pressure Sound-Speed, Density, and Heat Capacities Study. *J. Chem. Thermodyn.* 2005, 37 (7), 671–683. https://doi.org/10.1016/j.jct.2004.11.001.

- (214) Rohatgi, A. WebPlotDigitizer, 2021. https://automeris.io/WebPlotDigitizer.
- (215) Bartell, L. S.; Roskos, R. R. Isotope Effects on Molar Volume and Surface Tension: Simple Theoretical Model and Experimental Data for Hydrocarbons. J. Chem. Phys. 1966, 44 (2), 457–463. https://doi.org/10.1063/1.1726709.
- (216) Bates, F. S.; Keith, H. D.; McWhan, D. B. Isotope Effect on the Melting Temperature of Nonpolar Polymers. *Macromolecules* 1987, 20 (12), 3065–3070. https://doi.org/10.1021/ma00178a021.
- (217) Van Hook, W. A. Isotope Effects in Condensed Phases, the Benzene Example. Influence of Anharmonicity; Harmonic and Anharmonic Potential Surfaces and Their Isotope Independence. Molar Volume Effects in Isotopic Benzenes. J. Chem. Phys. 1985, 83 (8), 4107–4117. https://doi.org/10.1063/1.449842.
- (218) Scheiner, S.; Čuma, M. Relative Stability of Hydrogen and Deuterium Bonds. J. Am. Chem. Soc. **1996**, 118 (6), 1511–1521. https://doi.org/10.1021/ja9530376.
- (219) Pruzan, P.; Minassian, L. T.; Figuiere, P.; Szwarc, H. High Pressure Calorimetry as Applied to Piezothermal Analysis. *Rev. Sci. Instrum.* **1976**, *47* (1), 66–71. https://doi.org/10.1063/1.1134493.
- (220) Randzio, S. L.; Grolier, J. E.; Quint, J. R. An Isothermal Scanning Calorimeter Controlled by Linear Pressure Variations from 0.1 to 400 MPa. Calibration and Comparison with the Piezothermal Technique. *Rev. Sci. Instrum.* **1994**, 65 (4), 960–965. https://doi.org/10.1063/1.1144926.
- (221) Cerdeiriña, C. A.; Tovar, C. A.; González-Salgado, D.; Carballo, E.; Romaní, L. Isobaric Thermal Expansivity and Thermophysical Characterization of Liquids and Liquid Mixtures. *Phys. Chem. Chem. Phys.* 2001, *3* (23), 5230–5236. https://doi.org/10.1039/B104891K.
- (222) Zúñiga-Moreno, A.; Galicia-Luna, L. A. Densities, Isothermal Compressibilities, and Isobaric Thermal Expansivities of Hexan-2-Ol, Octan-1-Ol, and Decan-1-Ol from (313 to 363) K and Pressures up to 22 MPa. J. Chem. Eng. Data 2007, 52 (5), 1773–1783. https://doi.org/10.1021/je700145e.
- (223) Daridon, J.-L.; Nasri, D.; Bazile, J.-P. Computation of Isobaric Thermal Expansivity from Liquid Density Measurements. Application to Toluene. J. Chem. Eng. Data 2021, 66 (10), 3961–3976. https://doi.org/10.1021/acs.jced.1c00634.
- (224) Murphy, R. A.; Davis, J. C. Proton Magnetic Resonance Study of Hydrogen Bonding in Aliphatic Secondary Amines. J. Phys. Chem. 1968, 72 (9), 3111–3116. https://doi.org/10.1021/j100855a006.

APPENDIX A: Detailed Summary of Attenuation Coefficient Function

Refer to Figure 3-8 of the chapter for a schematic indicating location of the variables. The integrated attenuation coefficient function is represented by three lines with the intersections smoothed with cubic splines. The fitted/constrained parameters are indicated below using superscript f. The fitted function is expressed in terms of lines and splines for convenience. Wavenumbers are in cm⁻¹ and the attenuation coefficient is in dm²/mol. Equations for the attenuation coefficient curve and coefficients are:

Line Segment One

$$\epsilon = m_1^{\dagger} \tilde{\nu} + b_1 \qquad \qquad \text{Eq. A-1}$$

Line Segment Two

$$\epsilon = m_2 \tilde{v} + b_2$$
 Eq. A-2

$$m_2 = \frac{\epsilon_R^{\dagger} - \epsilon_B^{\dagger}}{\tilde{v}_R^{\dagger} - \tilde{v}_B^{\dagger}}$$
 Eq. A-3

Line Segment Three $(m_3^{f} = 0)$

$$\epsilon = \epsilon_R^{\dagger}$$
 Eq. A-4

Splines are determined by $(\tilde{v}_{1}, \tilde{v}_{2}) = \tilde{v}_{B}^{\dagger} \pm \Delta^{\dagger}$ and $(\tilde{v}_{3}, \tilde{v}_{4}) = \tilde{v}_{R}^{\dagger} \pm \Delta^{\dagger}$, and the corresponding y value determined from the appropriate line.

Spline One

$$c_1 = m_2 * (\tilde{\nu}_1 - \tilde{\nu}_2) - (\epsilon_1 - \epsilon_2)$$
 Eq. A-5
$$d_1 = -m_1 * (\tilde{\nu}_1 - \tilde{\nu}_2) + (\epsilon_1 - \epsilon_2)$$
 Eq. A-6

$$t_1(\tilde{\nu}) = \frac{\tilde{\nu} - \tilde{\nu}_2}{\tilde{\nu}_1 - \tilde{\nu}_2}$$
 Eq. A-7

$$\epsilon = \left(1 - t_1(\tilde{\nu})\right)\epsilon_2 + t_1(\tilde{\nu})\epsilon_1 + t_1(\tilde{\nu})\left(1 - t_1(\tilde{\nu})\right)\left(\left(1 - t_1(\tilde{\nu})\right)c_1 + t_1(\tilde{\nu})d_1\right) \quad \text{Eq. A-8}$$

Spline Two

$$c_2 = -(\epsilon_3 - \epsilon_R^{\dagger})$$
 Eq. A-9

$$d_2 = -m_2 * (\tilde{\nu}_3 - \tilde{\nu}_4) + (\epsilon_3 - \epsilon_R^{\dagger})$$
 Eq. A-10

$$t_2(\tilde{\nu}) = \frac{\tilde{\nu} - \tilde{\nu}_4}{\tilde{\nu}_3 - \tilde{\nu}_4}$$
 Eq. A-11

$$\epsilon = (1 - t_2(\tilde{v}))\epsilon_R^{\dagger} + t_2(\tilde{v})\epsilon_3 + t_2(\tilde{v})(1 - t_2(\tilde{v}))((1 - t_2(\tilde{v}))c_2 + t_2(\tilde{v})d_2)$$
Eq. A-12

Parameters are provided with up to eight significant digits because calculations of the attenuation coefficient curve involve taking the differences of large numbers. Parameter values are:

- $m_1^{\text{f}} = 121.51223 \text{ cm} \cdot \text{dm}^2/\text{mol}$ $b_1 = -443631.92 \text{ dm}^2/\text{mol}$
- $m_2 = -130.83618 \text{ cm} \cdot \text{dm}^2/\text{mol}$ $b_2 = 477672.97 \text{ dm}^2/\text{mol}$
 - $m_3^{f} = 0 \text{ cm} \cdot \text{dm}^2/\text{mol}$ $b_3 = \tilde{v}_R^{f} = 29639.512 \text{ dm}^2/\text{mol}$
 - $\tilde{\nu}_R^{\dagger} = 3424.3849 \text{ cm}^{-1}$ $\epsilon_R^{\dagger} = 29639.512 \text{ dm}^2/\text{mol}$
 - $\tilde{v}_B^{\dagger} = 3650.9240 \text{ cm}^{-1}$ $\epsilon_B^{\dagger} = 5.140849 \text{E-3 dm}^2/\text{mol}$

 $\epsilon_{3645} = 819.56086 \text{ dm}^2/\text{mol}$

 $\Delta^{\rm f}=8.3506~{\rm cm}^{-1}$

APPENDIX B: Processing of Spectra

Infrared spectra were collected using the following method. (1) The infrared spectrometer was switched on and allowed to warm up for thirty minutes and house nitrogen was fed to the sample chamber at 50 ft³/hr. The house nitrogen purge was continued at this rate for all experiments. (2) A background was taken consisting of 128 scans at 0.5 cm⁻¹ resolution. This spectrum was automatically removed from all subsequent measurements. (3) The temperaturecontrolled cell was removed from the glovebox and was positioned within the sample chamber. (4) Cooling water was supplied from the tap to the cell at a flow rate of 0.5 L/min. Sample supply lines from the cell were connected to a Luer lock three-way valve system operated outside the sample chamber. The cell temperature probe and thermal regulation cables were attached to the cell and the temperature controller which was located outside the sample chamber. The sample chamber lid was closed. (5) The cell was heated to 100 °C and maintained for five minutes before being cooled to 30 °C. House nitrogen was supplied to the cell throughout this process to purge trace moisture from the system. (6) The absorbance of empty cell was measured at 30 °C with 128 scans at 0.5 cm⁻¹ resolution under a constant nitrogen purge. (7) Sample was removed from the glove box and transferred to a 5 mL glass syringe with a Luer lock fitting. The syringe was connected to the valve system and the three-way valve was adjusted so that the nitrogen purge was stopped, and sample could be injected. Sample was injected until it was observed in the outlet collection container. The outlet value remained open to maintain atmospheric pressure within the cell. (8) The sample thermally equilibrated for ten minutes before its absorbance was collected using 128 scans at 0.5 cm⁻¹ resolution. This was done at each of the four experimental temperatures. (9) When multiple samples were evaluated within the same day, the sample was forced from the cell using nitrogen and steps (5)-(8) were repeated. At the end of each day the cell

was disassembled, and the windows were rinsed with hexane. The windows and cell body were stored under nitrogen between uses.

Three observations were made regarding the absorbance spectra: (OB1) Solvent subtraction based on calculated concentration was insufficient for removing the solvent contribution to the solution spectrum; (OB2) It was observed that cyclohexane absorbance varied with lot number; (OB3) Despite the careful sample and cell handling, trace contamination caused small sharp peaks between 3600 cm⁻¹ and 3940 cm⁻¹ which were time and temperature invariant on a given day. OB1 was addressed in the manuscript. OB2 was addressed by ensuring that the solvent spectra used for subtraction was consistent with the lot number used for constructing the solution.

The origin of OB3 was not identified but could be due to impurities in the house nitrogen because the contaminant peaks were sharp as expected for a gas phase impurity. OB3 was present spectra with small pathlengths and was remedied by quantifying the effect of the contamination in the following way. The empty cell spectrum was fitted with a decaying sine wave in the region of the contamination. Subtracting the empty cell spectrum from the sine wave fit, provided a 'noise' spectrum, which was weighted to subtract from the sample spectrum. This method successfully removed the effects of the contamination from the sample spectra.

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APPENDIX C: Relation of RTPT to Kretschmer-Wiebe

The equations for 2-K Kretchmer-Wiebe are presented by Nagata and Ogasawara¹¹⁸ and Acree¹²⁸ without derivation. The model is derived by Bala¹²¹ and called the 2-K CLAM model in the thesis as an extension of the Kretschmer-Wiebe which Bala calls the 1-K CLAM model. We provide an illustration of the similarities of 2-K Kretchmer-Wiebe model with Marshall and Chapman¹¹² resummed perturbation theory RTPT. To illustrate similarities with RTPT, we convert the notation of Bala and Marshall/Chapman to use the notation of this manuscript. Recognize the notational differences which are presented in Table C-1:

	This work	Marshall ¹¹²	Bala ¹²¹
Alcohol density	$x_{alc}\rho$	ρ	C _{alc}
Alcohol Monomer concentration	$ ho_o$	$ ho_o$	C _M
Dimer Association constant	Δ_2	$f^{(1)}_{AB}\Delta$	<i>K</i> _{<i>C</i>,2}
N-mer Association	Δ_N	$f^{(2)}_{AB}\Delta$	K _{C,Nmer}

Table C-1: Notational differences between this work and that of other authors.

To derive the 2-K Kretchmer-Wiebe model using the chemical theory approach, we start with an apparent mole balance written in terms of concentration by dividing both sides by total volume, *V*,

$$\frac{n_{alc}}{\underline{V}} = \frac{n_{alc,o} + 2n_{alc,2} + 3n_{alc,3} + \cdots}{\underline{V}}$$
Eq. C-1

$$x_{alc}\rho = \rho_o + 2\rho_{alc,2} + 3\rho_{alc,3} + \dots = \rho_o + \sum_{i=2}^{\infty} i\rho_{alc,i}$$
 Eq. C-2

To simplify notation, monomers and dimers are designated with o and D subscripts respectively, and all subsequent oligomers are referred to by the number of alcohol molecules they contain. Defining two equilibrium constants, one for the formation of dimers and another for all subsequent oligomers (note that by assuming volume does not change with association, the molar volume for an oligomer is a multiple of the monomer molar volume, $V_{alc,N} = NV_{alc,o}$):

$$\Delta_2 = \frac{\rho_{alc,2}}{\rho_o^2} = \frac{\Phi_{alc,2}/2V_{alc,o}}{\left(\Phi_{alc,o}/V_{alc,o}\right)^2} = \frac{1}{2} \frac{\Phi_{alc,2}}{\Phi_{alc,o}^2} V_{alc,o} = K_{C,2_(KW)} V_{alc,o}$$
Eq. C-3

$$\Delta_N = \frac{\rho_{alc,N}}{\rho_{alc,(N-1)}\rho_o} = \frac{(N-1)}{N} \frac{\Phi_{alc,N}}{\Phi_{alc,N-1}\Phi_{alc,o}} V_{alc,o} = K_{C,N_{-}(KW)} V_{alc,o} \quad \text{for} \quad N > 2 \quad \text{Eq. C-4}$$

where the volume fraction notation provides mapping to the Kretschmer-Wiebe equilibria and $K_{C,2_(KW)}$ and $K_{C,N_(KW)}$ are the Kretschmer-Wiebe association constants. $V_{alc,o}$ is the same as the pure alcohol molar volume. Excess volume is assumed to be negligible. For the last equality of Eq. C-3 and Eq. C-4, the composition dependence of the Wertheim Δ and the minor differences between the Mayer and Arrhenius temperature dependence must be disregarded. Combining Eq. C-3 and Eq. C-4 and rearranging yields

$$\rho_{alc,N} = \Delta_2 \Delta_N^{N-2} \rho_o^N \qquad \text{for } N > 1 \qquad \text{Eq. C-5}$$

Eq. C-5 can be substituted into the mole balance in Eq. C-2, and rearrangement of Eq. C-6 results in equation Eq. C-7.

$$\rho_{alc} = \rho_o + \sum_{N=2}^{\infty} N \Delta_2 \Delta_N^{N-2} \rho_o^N = \rho_o + 2\Delta_2 \rho_o^2 + 3\Delta_2 \Delta_N \rho_o^3 + \cdots$$
 Eq. C-6

$$x_{alc}\rho = \rho_o \left(1 + 2\Delta_2 \rho_o + \frac{\Delta_2}{\Delta_N} \{ 3(\Delta_N \rho_o)^2 + 4(\Delta_N \rho_o)^3 + \dots \} \right)$$
 Eq. C-7

Recognizing an opportunity to use a converging series for the inner braces, Eq. C-7 can be written as the closed form of the complete series with subtraction of the first two terms that do not appear in the braces.

$$x_{alc}\rho = \rho_o \left(1 + 2\Delta_2 \rho_o + \frac{\Delta_2}{\Delta_N} \left(\frac{1}{(1 - \Delta_N \rho_o)^2} - 1 - 2\Delta_N \rho_o \right) \right)$$
Eq. C-8

$$x_{alc}\rho = \rho_o \left(1 + \frac{\Delta_2}{\Delta_N} \left(\frac{1}{(1 - \Delta_N \rho_o)^2} - 1 \right) \right)$$
Eq. C-9

Bala shows that the equation written in terms of $K_{C,2} = K_{C,2}(KW)V_{alc,o}$ and $K_{C,N} = K_{C,N}(KW)V_{alc,o}$, writing in terms of volume fractions, $x_{alc}\rho V_{alc,o} = \Phi_{alc}$ and $\rho_o V_{alc,o} = \Phi_o$

$$\Phi_{alc} = \Phi_o \left(1 + \frac{K_{C,2}}{K_{C,N}} \left(\frac{1}{\left(1 - K_{C,N} \Phi_o / V_{alc,o} \right)^2} - 1 \right) \right)$$
Eq. C-10

Bala shows this can be solved for any apparent concentration $x_{alc}\rho$ as a cubic equation in monomer volume fraction, Φ_o .

We now show that Eq. C-9 is the same as Marshall and Chapman eq (20) respecting the approximations set forth. Converting notation, Chapman eq. (20) is

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \frac{2\rho_o\Delta_2(1-\rho_o\Delta_N)}{(1-\rho_o\Delta_N)^2} + \frac{\rho_o^2\Delta_2\Delta_N}{(1-\rho_o\Delta_N)^2}$$
Eq. C-11

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \frac{2\rho_o\Delta_2}{(1-\rho_o\Delta_N)^2} - \frac{2\rho_o^2\Delta_2\Delta_N}{(1-\rho_o\Delta_N)^2} + \frac{\rho_o^2\Delta_2\Delta_N}{(1-\rho_o\Delta_N)^2}$$
Eq. C-12

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \frac{2\rho_o\Delta_2}{(1-\rho_o\Delta_N)^2} - \frac{\rho_o^2\Delta_2\Delta_N}{(1-\rho_o\Delta_N)^2}$$
Eq. C-13

Adding and subtracting $1/\Delta_N$ results in equation Eq. C-14.

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \Delta_2 \left(\frac{2\rho_o - \rho_o^2 \Delta_N}{(1 - \rho_o \Delta_N)^2} + \frac{1}{\Delta_N} - \frac{1}{\Delta_N} \right)$$
Eq. C-14

Creating common denominators for the first to terms in parenthesis

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \Delta_2 \left(\frac{\Delta_N (2\rho_o - \rho_o^2 \Delta_N)}{\Delta_N (1 - \rho_o \Delta_N)^2} + \frac{1 - 2\rho_o \Delta_N + \rho_o^2 \Delta_N^2}{\Delta_N (1 - \rho_o \Delta_N)^2} - \frac{1}{\Delta_N} \right)$$
Eq. C-15

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \Delta_2 \left(\frac{1}{\Delta_N (1 - \rho_o \Delta_N)^2} - \frac{1}{\Delta_N}\right)$$
 Eq. C-16

$$\frac{x_{alc}\rho}{\rho_o} = 1 + \frac{\Delta_2}{\Delta_N} \left(\frac{1}{(1 - \rho_o \Delta_N)^2} - 1 \right)$$
 Eq. C-17

This equation matches Eq. C-9. The RTPT model and the 2-K Kretschmer-Wiebe model are distinctly different in the way that they are derived and the details of the association constants, but the similarities are striking. The RTPT model has a small composition dependence of the association constant and the Mayer term for temperature-dependence instead of the Arrhenius term typically used for the chemical theory approach. Certainly, the Wertheim framework has capability for higher order perturbations, but the forms are very similar at this level of Wertheim theory except for the details of the association constants.

APPENDIX D: Conversion of Extensive Helmholtz Energy to Molar

The notation of Wertheim^{99–102} uses extensive variables and most publications that begin from the Helmholtz energy continue the use of extensive variables and number density. However, in engineering, particularly with equations of state, the use of intensive properties is predominant. In this section we provide the conversion of the extensive Helmholtz energy to use molar properties. We demonstrate the conversion for the resummed thermodynamic perturbation theory (RTPT) derived by Marshall and Chapman^{112,141} as an extension of Wertheim's original TPT-1 model. The current conversion is applied to a binary system in which component (1) has one hbond acceptor and one h-bond donor, referred to as the 2B scheme, and component (2) has no sites.

To distinguish between number and molar properties, specifically density, we use a tilde accent to denote the former and no ornaments to denote the latter. Density in this work always represents an intensive particle density or molar density, not the reciprocal of extensive volume. Therefore, $\tilde{\rho} = N/\underline{V}$ and ρ have units of particles/length³ and mol/length³ respectively and $\tilde{\rho} = N_A\rho$. The molar density of associating component (1) is given by $\rho_1 = x_1\rho$ whether mixed or pure, whereas V_1 represents only the pure molar volume of component (1). Finally, the density of the monomer species of the associating species (1) is denoted by ρ_0 . An underbar denotes extensive quantities, such as the extensive volume \underline{V} , except in the case of number of molecules, N, and number of moles, n. All other symbols used in this work are consistent with those of Marshall and Chapman.^{112,141}

For the alcohol component (1) with associating sites *A* and *B* in a nonbonding solvent, the Helmholtz energy in extensive units is written

$$\frac{\underline{A}^{assoc}}{\underline{V}k_{B}T} = \frac{\underline{A}^{assoc}\tilde{\rho}}{Nk_{B}T} = \frac{\underline{A}^{assoc}\rho}{k_{B}T}$$

$$= \tilde{\rho}_{1}\ln\frac{\tilde{\rho}_{o}}{\tilde{\rho}_{1}} - \tilde{\sigma}_{\Gamma-A} - \tilde{\sigma}_{\Gamma-B} + \frac{\tilde{\sigma}_{\Gamma-A}\tilde{\sigma}_{\Gamma-B}}{\tilde{\rho}_{o}} + \tilde{\rho}_{1} - \frac{\Delta c^{(o)}}{\underline{V}}$$
Eq. D-1

which has units of $(\text{length})^{-3}$. Here, $\sigma_{\Gamma-i}$ is the sum of the densities of bonding species with unbonded site (*i*). The term $\Delta c^{(o)}$ is the associative contribution to the fundamental graph sum. Dividing by N_A converts to molar densities,

$$\frac{A^{assoc}\rho}{RT} = x_1\rho\ln\frac{\rho_o}{\rho_1} - \sigma_{\Gamma-A} - \sigma_{\Gamma-B} + \frac{\sigma_{\Gamma-A}\sigma_{\Gamma-B}}{\rho_o} + \rho_1 - \frac{\Delta c^{(o)}}{N_A \underline{V}}$$
Eq. D-2

which has units of molar density.

For the 2B case here where only component (1) associates, the sites are typically designated as an acceptor site (A) and donor site (D). X^A and X^D are the fraction of the respective sites that are unbonded, which are equal in the case of one associating species in an inert solvent. The density of unbonded sites is $\sigma_{\Gamma-A} = \sigma_{\Gamma-B} = x_1 \rho X^A = x_1 \rho X^D$ so we can simplify

$$\frac{A^{assoc}\rho}{RT} = \rho_1 \ln \frac{\rho_o}{\rho_1} - 2\sigma_{\Gamma-A} + \frac{(\sigma_{\Gamma-A})^2}{\rho_o} + x_1\rho - \frac{\Delta c^{(o)}}{N_A \underline{V}}$$
Eq. D-3

$$\frac{A^{assoc}\rho}{RT} = x_1 \rho \ln \frac{\rho_o}{x_1 \rho} - 2x_1 \rho X^A + \frac{(x_1 \rho X^A)^2}{\rho_o} + x_1 \rho - \frac{\Delta c^{(o)}}{N_A \underline{V}}$$
Eq. D-4

The notation of Marshall and Chapman¹¹² is transformed in this work to accommodate empirical fitting of bonding volumes as part of the association constant and thus we define the dimer association constant $\Delta_2 \equiv N_A f_{AB}^{(1)} \Delta$, and the *n*-mer association constant $\Delta_N \equiv N_A f_{AB}^{(2)} \Delta$, where the right-hand side is Marshall and Chapman notation and the left-hand side is used here. This work implements the PC-SAFT form of the association constant,

$$\Delta_{(2 \text{ or } N)} = d^3 g(d) \kappa_{(2 \text{ or } N)} (\exp\left(\frac{\epsilon_{(2 \text{ or } N)}^{AD}}{(kT)}\right) - 1)$$
 Eq. D-5

where *d* is the alcohol temperature-dependent segment diameter and the radial distribution function g(d) depends on *d*, composition, and density. The variables $\kappa_{(2 \text{ or } N)}$ and $\epsilon_{(2 \text{ or } N)}^{AD}$ are adjusted to experimental data. Converting the notation of Marshall and Chapman, the last term of Eq. D-3 produces

$$\frac{\Delta c^{(o)}}{N_A \underline{V}} = \frac{(\sigma_{\Gamma-A})^2 \Delta_2}{1 + (\Delta_2 - \Delta_N)\rho_o} = \frac{(x_1 \rho X^A)^2 \Delta_2}{1 + (\Delta_2 - \Delta_N)\rho_o}$$
Eq. D-6

where Δ_2 and Δ_N have units of length³/mol. Also, from Eq. D-4

$$\frac{A^{assoc}}{RT} = x_1 \ln \frac{\rho_o}{x_1 \rho} - \frac{2x_1 \rho X^A}{\rho} + \frac{(x_1 \rho X^A)^2}{\rho_o \rho} + x_1 - \frac{\Delta c^{(o)}}{N_A \underline{V} \rho}$$
Eq. D-7

The extensive number density derivative of Eq. D-1 is common in Wertheim statistics publications, which is equivalent to the molar density derivative of Eq. D-2. Note that differentiation of Eq. D-2 with a molar density is equivalent to multiplying Eq. D-2 by N_A to obtain equation (1) and then differentiating with $d\tilde{\rho} = N_A d\rho$. Consideration of Eq. D-3 together with Eq. D-6 as a $f(T, \rho_1, \rho_0, \sigma_A)$ provides a powerful way to extract the equilibrium relations by using the lumped variables. Gibbs energy is obtained from the density derivative of Eq. 4-36

$$\frac{1}{RT} \left(\frac{\partial (A^{assoc} \rho)}{\partial \rho} \right)_T = \frac{\rho}{RT} \left(\frac{\partial A^{assoc}}{\partial \rho} \right)_T + \frac{A^{assoc}}{RT} = \frac{A^{assoc} + (PV)^{assoc}}{RT}$$

$$= \frac{G^{assoc}}{RT}$$
Eq. D-8

The association contribution to the chemical potential of component (k) is obtained with the derivative

$$\mu_k^{assoc} = \left(\frac{\partial(nA)}{\partial n_k}\right)_{T,\underline{V},\{n_{j\neq k}\}} = \frac{\underline{V}}{\underline{V}} \left(\frac{\partial(nA)}{\partial n_k}\right)_{T,\underline{V},\{n_{j\neq k}\}} = \left(\frac{\partial(A\rho)}{\partial \rho_k}\right)_{T,\underline{V},\{n_{j\neq k}\}}$$
Eq. D-9

By the expansion rule,

$$\begin{split} \mu_{1}^{assoc} &= \left(\frac{\partial (A^{assoc}\rho)}{\partial \rho_{1}}\right)_{T,\underline{V},\{n_{j\neq1}\}} \\ &= \left(\frac{\partial (A^{assoc}\rho)}{\partial \rho_{1}}\right)_{T,\underline{V},\{n_{j\neq1}\},\rho_{o},\sigma_{A}} + \left(\frac{\partial (A^{assoc}\rho)}{\partial \rho_{o}}\right)_{T,\underline{V},\{n_{j}\},\sigma_{A}} \left(\frac{\partial \rho_{o}}{\partial \rho_{1}}\right)_{T,\underline{V}} \quad \text{Eq. D-10} \\ &+ \left(\frac{\partial (A^{assoc}\rho)}{\partial \sigma_{\Gamma-A}}\right)_{T,\underline{V},\{n_{j}\},\rho_{o}} \left(\frac{\partial \sigma_{\Gamma-A}}{\partial \rho_{1}}\right)_{T,\underline{V}} \end{split}$$

But chemical reaction equilibrium requires that the derivative with respect to ρ_o and the derivative with respect to $\sigma_{\Gamma-A} = x_1 \rho X^A$ to be zero because they involve reacting species. These derivatives provide relations for the chemical potentials of sites and monomer as influenced by the apparent density. Though the component apparent density is determined by composition, temperature and pressure, the minimization of the Helmholtz energy at a certain apparent density occurs when the derivatives with respect to reacting species ρ_o and σ_A are zero. Thus, the only nonzero term is first term on the right-most side

$$\frac{\mu_{1}^{assoc}}{RT} = \ln \hat{\varphi}_{1}^{assoc} = \frac{1}{RT} \left(\frac{\partial (A^{assoc} \rho)}{\partial \rho_{1}} \right)_{T,\underline{V},\{n_{j\neq 1}\}}$$

$$= \frac{1}{RT} \left(\frac{\partial (A^{assoc} \rho)}{\partial \rho_{1}} \right)_{T,\underline{V},\{n_{j\neq 1}\},\rho_{0},\sigma_{A}}$$
Eq. 0-11

APPENDIX E: Key Material Balance Equations

The chemical equilibria balance equations are obtained by the derivatives of Eq. D-3 with respect to $\sigma_{\Gamma-A}$ and ρ_o as provided by Marshall and Chapman¹¹² as equation (17) and (18) in that work. Recognizing the density of free acceptor sites hosted by component (1) is $\sigma_{\Gamma-A} = x_1 \rho X^A$, then

$$\frac{x_1 \rho X^A}{\rho_o} - 1 = \frac{x_1 \rho X^A \Delta_2}{1 + (\Delta_2 - \Delta_N)\rho_o}$$
 Eq. E-1

$$\frac{x_1 \rho}{\rho_o} = \left(\frac{x_1 \rho X^A}{\rho_o}\right)^2 - \frac{(\Delta_2 - \Delta_N)(x_1 \rho X^A)^2 \Delta_2}{(1 + (\Delta_2 - \Delta_N)\rho_o)^2}$$
 Eq. E-2

Eq. E-2 provides a material balance. Eq. E-1 can be rearranged to identify the contributions of α (monomer) and β hydroxyls to the free site density (note $\rho_{\alpha} = \rho_{o}$ and for the 2B bonding scheme $\rho_{\beta} = \rho_{\gamma}$)

$$x_1 \rho X^A = \rho_o + \frac{x_1 \rho X^A \Delta_2 \rho_o}{1 + (\Delta_2 - \Delta_N) \rho_o} = \rho_\alpha + \rho_\beta;$$

Eq. E-3
$$\rho_\beta = \frac{x_1 \rho X^A \Delta_2 \rho_o}{1 + (\Delta_2 - \Delta_N) \rho_o}$$

An alternative arrangement of Eq. E-1 is found by combining the terms with $x_1 \rho X^A$ using a common denominator and simplifying to give

$$\frac{x_1 \rho X^A}{1 + (\Delta_2 - \Delta_N)\rho_o} = \frac{\rho_o}{1 - \Delta_N \rho_o}$$
 Eq. E-4

Noting the appearance of the left side of Eq. E-4 we can write Eq. E-1 as

$$\frac{x_1 \rho X^A}{\rho_o} = 1 + \frac{\Delta_2 \rho_o}{1 - \Delta_N \rho_o}$$
 Eq. E-5

Squaring Eq. E-5 replaces the first term of Eq. E-2 and squaring Eq. E-4 to insert into the second term of Eq. E-2 results in equation (20) of Marshall and Chapman¹¹² which is

$$x_1 \rho = \rho_o + \frac{2\Delta_2 \rho_o^2}{1 - \Delta_N \rho_o} + \frac{\Delta_2 \Delta_N \rho_o^3}{(1 - \Delta_N \rho_o)^2}$$
 Eq. E-6

The monomer can be determined by recognizing that Eq. E-6 is a cubic in ρ_o . Instead, we present an iterative method that is solved simultaneously with X^A . The fraction of sites (of a single type, *i.e.* acceptor or donor sites) bound is found by difference between Eq. E-6 and Eq. E-5 multiplied by ρ_o to give

$$x_1 \rho (1 - X^A) = \frac{\Delta_2 \rho_o^2}{(1 - \Delta_N \rho_o)^2}$$
 Eq. E-7

Inserting the square of Eq. C-14 into the right-side results in a key equality

$$(1 - X^{A}) = \frac{x_{1}\rho\Delta_{2}(X^{A})^{2}}{(1 + (\Delta_{2} - \Delta_{N})\rho_{o})^{2}}$$
Eq. E-8

Defining for convenience

$$s = 1 + (\Delta_2 - \Delta_N)\rho_o \qquad \qquad \text{Eq. E-9}$$

we can rearrange Eq. E-8 to the more useful form

$$X^{A} = \frac{s^{2}}{s^{2} + x_{1}\rho\Delta_{2}X^{D}} = \frac{1}{1 + x_{1}\rho\Delta_{2}X^{D}/s^{2}}$$
 Eq. E-10

where we have now indicated the distinction of donors and acceptors. The donors and acceptor can be exchanged in the equation $(X^D = X^A)$ since they are equal for the system type considered here, and the similarity of Eq. E-10 with the 2B-TPT-1 is obvious where s = 1. A final key expression results from solving the following quadratic obtained by rearranging Eq. E-5

$$(\Delta_2 - \Delta_N)\rho_o^2 + (1 + x_1\rho\Delta_N X^A)\rho_o - x_1\rho X^A = 0$$
 Eq. E-11

and solving for the physically meaningful root gives

$$\rho_o = \frac{2x_1 \rho X^A}{1 + x_1 \rho \Delta_N X^A + \sqrt{(1 + x_1 \rho \Delta_N X^A)^2 + 4(\Delta_2 - \Delta_N)x_1 \rho X^A}}$$
 Eq. E-12

This monomer density is determined by solving Eq. E-12 simultaneously with Eq. E-10 using successive substitution. A trial value of X^A is used to generate ρ_o in Eq. E-12, which is used to calculate *s* and X^A from Eq. E-10 and the iteration is continued until convergence is obtained.

APPENDIX F: Excess Helmholtz Energy

The excess Helmholtz energy can be obtained by

$$\left(\frac{A^{E}}{RT}\right)^{assoc} = \frac{A^{assoc}}{RT} - x_1 \frac{A^{assoc}_{pure \, 1}}{RT} - x_2 \frac{A^{assoc}_{pure \, 2}}{RT}$$
Eq. F-1

Combining Eq. D-6, Eq. D-7, and Eq. E-1

$$\frac{A^{assoc}}{RT} = x_1 \ln \frac{\rho_o}{\rho_1} - \frac{2\sigma_{\Gamma-A}}{\rho} + \frac{\sigma_{\Gamma-A}^2}{\rho_o \rho} + x_1 - \frac{\sigma_{\Gamma-A}}{\rho} \left(\frac{\sigma_{\Gamma-A}}{\rho_o} - 1\right)$$
Eq. F-2

$$\frac{A^{assoc}}{RT} = x_1 \ln \frac{\rho_o}{\rho_1} - \frac{\sigma_{\Gamma-A}}{\rho} + x_1 = x_1 \ln \frac{\rho_o}{\rho_1} + x_1(1 - X^A)$$
 Eq. F-3

Note by Eq. E-12 that ρ_o/ρ_1 is always finite as ρ_1 approaches zero with a limiting value of unity.

$$\frac{\rho_o}{\rho_1} = \frac{2X^A}{1 + \rho_1 \Delta_N X^A + \sqrt{(1 + \rho_1 \Delta_N X^A)^2 + 4(\Delta_2 - \Delta_N)\rho_1 X^A}}$$
Eq. F-4

Thus

$$\left(\frac{A^{E}}{RT}\right)^{assoc} = x_{1} \ln \frac{\rho_{o}}{\rho_{1}} + x_{1}(1 - X^{A}) - x_{1} \ln \frac{\rho_{o,pure\,1}}{\rho_{pure\,1}} - x_{1}(1 - X^{A}_{pure\,1})$$
 Eq. F-5

$$\left(\frac{A^E}{RT}\right)^{assoc} = x_1 \ln\left(\frac{\rho_o}{\rho_1} \frac{\rho_{pure \ 1}}{\rho_{o,pure \ 1}}\right) + x_1 \left(X^A_{pure \ 1} - X^A\right)$$
Eq. F-6

APPENDIX G: Activity Coefficients

The derivation here is modified from the original publication where some of the steps were restricted to $V^E = 0$ and $\overline{V}_k = V_k$. As shown by Bala et al.,¹³⁰ using a standard state as the pure species at the same *T* and *P* as the mixture, the liquid phase activity coefficients are given by

$$\ln \gamma_k^{assoc} = \frac{1}{RT} \left(\frac{\partial \underline{A}^{assoc}}{\partial n_k} \right)_{T,P,\{n_{j\neq k}\}} \Big|_{mix} - \underline{A}^{assoc} \Big|_{pure k} + \frac{P^{assoc}}{RT} \left(\frac{\partial \underline{V}}{\partial n_k} \right)_{T,P,n_{\{j\neq k\}}} - \frac{P^{assoc}}{RT} V_k$$
Eq. G-1

$$\frac{1}{RT} \left(\frac{\partial \underline{A}^{assoc}}{\partial n_k} \right)_{T,P,\{n_{j\neq k}\}} = \ln \hat{\varphi}_k^{assoc} - Z^{assoc} \frac{\overline{V}_k}{V}$$
Eq. G-2

Note that P^{assoc} in the last term of Eq. G-1 uses the system contribution because the standard state is at the system pressure. Combining these two equations and recognizing that the partial molar volume terms cancel

$$\ln \gamma_k^{assoc} = \ln \hat{\varphi}_k^{assoc} - \underline{A}^{assoc} \Big|_{pure \, k} - \frac{P^{assoc}}{RT} V_k$$
 Eq. G-3

Using Eq. 0-11 and applying to Eq. D-3 and recognizing that g_{11} is the radial distribution function for component 1 association

$$\ln \hat{\varphi}_{k}^{assoc} = \ln \frac{\rho_{o}}{\rho_{1}} - \left(\frac{\partial \left(\Delta c^{(o)} / (N_{A} \underline{V})\right)}{\partial \rho_{1}}\right)_{T, \underline{V}, \{n_{j \neq 1}\}, \rho_{o}, \sigma_{A}}$$
Eq. G-4

$$\left(\frac{\frac{\partial \left(\Delta c^{(o)}/(N_{A}\underline{V}\right)}{\partial \rho_{1}}\right)}{\Gamma,\underline{V},n_{j\neq1},\rho_{o},\sigma_{A}}} = \frac{\sigma_{\Gamma-A}^{2}\Delta_{2}\left(\frac{\partial \ln g_{11}}{\partial \rho_{1}}\right)_{T,\underline{V},\{n_{j\neq1}\}}}{1+(\Delta_{2}-\Delta_{N})\rho_{o}} \qquad \text{Eq. G-5} \\ -\frac{\sigma_{\Gamma-A}^{2}\Delta_{2}(\Delta_{2}-\Delta_{N})\rho_{o}\left(\frac{\partial \ln g_{11}}{\partial \rho_{1}}\right)_{T,\underline{V},\{n_{j\neq1}\}}}{(1+(\Delta_{2}-\Delta_{N})\rho_{o})^{2}}$$

Eq. E-8 can be inserted yielding

$$\left(\frac{\partial \left(\Delta c^{(o)}/(N_A \underline{V})\right)}{\partial \rho_1}\right)_{T,\underline{V},\{n_{j\neq 1}\},\rho_o,\sigma_A} = x_1(1-X^A)\rho\left(\frac{\partial \ln g_{11}}{\partial \rho_1}\right)_{T,\underline{V},\{n_{j\neq 1}\}}$$
Eq. G-6

$$\ln \hat{\varphi}_{1}^{assoc} = \ln \frac{\rho_{o}}{\rho_{1}} - x_{1}(1 - X^{A})\rho \left(\frac{\partial \ln g_{11}}{\partial \rho_{1}}\right)_{T, \underline{V}, \{n_{j\neq 1}\}}$$
Eq. G-7

By inspection

$$\ln \hat{\varphi}_2^{assoc} = -x_1 (1 - X^A) \rho \left(\frac{\partial \ln g_{11}}{\partial \rho_2}\right)_{T, \underline{V}\{n_{j \neq 2}\}}$$
Eq. G-8

The compressibility factor contribution is

$$Z^{assoc} = \frac{1}{RT} \rho \left(\frac{\partial (A^{assoc})}{\partial \rho} \right)_{T, \{n_i\}}$$
Eq. G-9

The contribution to Z^{assoc} from the first four terms of $A^{assoc}/(RT)$ in Eq. D-7, is:

$$\rho \frac{\partial}{\partial \rho} \left(x_1 \ln \frac{\rho_o}{x_1 \rho} - \frac{2\sigma_{\Gamma-A}}{\rho} + \frac{\sigma_{\Gamma-A}^2}{\rho \rho_o} + x_1 \right)_{T,\{n_i\}}$$
Eq. G-10
$$= \rho \left(-x_1 \left(\frac{1}{\rho}\right) + \frac{2\sigma_{\Gamma-A}}{\rho^2} - \frac{\sigma_{\Gamma-A}^2}{\rho_o \rho^2} \right) = \left(-x_1 + \frac{2\sigma_{\Gamma-A}}{\rho} - \frac{\sigma_{\Gamma-A}}{\rho} \frac{\sigma_{\Gamma-A}}{\rho_o} \right)$$

where the values of $\sigma_{\Gamma-A}$ and ρ_0 are considered constant for the differentiation since it is evaluated at a stationary point. Inserting Eq. E-1 and the first equality of Eq. E-3

$$= -x_1 + 2x_1 X^A - \frac{\sigma_{\Gamma-A}}{\rho} \left(1 + \frac{\sigma_{\Gamma-A} \Delta_2}{1 + (\Delta_2 - \Delta_N)\rho_o} \right)$$
Eq. G-11

Recognizing Eq. E-8

$$= -x_{1} + 2x_{1}X^{A} - x_{1}X^{A} - \frac{1}{\rho} \left(\frac{\sigma_{\Gamma-A}^{2}\Delta_{N}}{1 + (\Delta_{2} - \Delta_{N})\rho_{o}} \right)$$

= $-x_{1}(1 - X^{A}) - x_{1}(1 - X^{A})(1 + (\Delta_{2} - \Delta_{N})\rho_{o})$
Eq. G-12

The derivative of the first four terms contributing to Z^{assoc} becomes

$$= -2x_1(1 - X^A) - x_1(1 - X^A)(\Delta_2 - \Delta_N)\rho_o$$
 Eq. G-13

The derivative we need for the last term is

$$\rho \left(\frac{\partial \left(\Delta c^{(o)} / N_A \underline{V} \rho \right)}{\partial \rho} \right)_{T,\{n_i\}} = \rho \left(-\frac{\sigma_{\Gamma-A}^2 \Delta_2}{\rho^2 (1 + (\Delta_2 - \Delta_N) \rho_o)} + \frac{\sigma_{\Gamma-A}^2 \Delta_2}{\rho (1 + (\Delta_2 - \Delta_N) \rho_o)} \left(\frac{\partial \ln g_{11}}{\partial \rho} \right)_{T,\{n_i\}} - \frac{\sigma_{\Gamma-A}^2 \Delta_2 (\Delta_2 - \Delta_N) \rho_o}{\rho (1 + (\Delta_2 - \Delta_N) \rho_o)^2} \left(\frac{\partial \ln g_{11}}{\partial \rho} \right)_{T,\{n_i\}} \right) \qquad \text{Eq. G-14}$$

Recognizing Eq. E-8

$$= -\left(x_{1}(1 - X^{A})(1 + (\Delta_{2} - \Delta_{N})\rho_{o}) - x_{1}(1 - X^{A})\rho\left(\frac{\partial \ln g_{11}}{\partial \rho}\right)_{T,\{n_{i}\}}\right)$$
 Eq. G-15

$$= -x_1(1 - X^A) \left(1 + (\Delta_2 - \Delta_N)\rho_o - \left(\frac{\partial \ln g_{11}}{\partial \ln \rho}\right)_{T,\{n_i\}} \right)$$
 Eq. G-16

Thus, the last contribution to Z^{assoc} is

$$-\rho \left(\frac{\partial \left(\Delta c^{(o)}/N_{A}\underline{V}\rho\right)}{\partial \rho}\right)_{T,\{n_{i}\}} = x_{1}(1-X^{A})\left(1+(\Delta_{2}-\Delta_{N})\rho_{o}-\left(\frac{\partial \ln g_{11}}{\partial \ln \rho}\right)_{T,\{n_{i}\}}\right)$$
Eq. G-17

Combining Eq. G-13 and Eq. G-17, we find

$$Z^{assoc} = -x_1(1 - X^A) \left(1 + \left(\frac{\partial \ln g_{11}}{\partial \ln \rho}\right)_{T, \{n_i\}} \right)$$
 Eq. G-18

And thus, because the standard state is at the same pressure as the mixture, the mixture pressure is used expressed using the mixture Z^{assoc} ,

$$-\frac{P^{\text{assoc}}}{RT}V_k = -Z^{\text{assoc}}\frac{V_k}{V} = x_1(1-X^A)\frac{V_k}{V}\left(1+\left(\frac{\partial\ln g_{11}}{\partial\ln\rho}\right)_{T,\{n_i\}}\right)$$
Eq. G-19

The activity coefficient for the associating component is obtained by inserting Eq. F-3 evaluated at purity, Eq. G-7, Eq. G-19.

$$\ln \gamma_1^{assoc} = \ln \frac{\rho_o}{x_1 \rho} + x_1 (1 - X^A) \left(\frac{V_1}{V} \left(1 + \left(\frac{\partial \ln g_{11}}{\partial \ln \rho}\right)_{T, \{n_i\}} \right) - \rho \left(\frac{\partial \ln g_{11}}{\partial \rho_1}\right)_{T, \underline{V}, n_2} \right) \quad \text{Eq. G-20}$$
$$- \ln \frac{\rho_{o, pure \, 1}}{\rho_{pure \, 1}} - (1 - X^A_{pure \, 1})$$

For the non associating component, the fugacity coefficient is given by Eq. G-8, where the third and fourth terms of Eq. G-19 drop out, and the expression is

$$\ln \gamma_2^{assoc} = x_1 (1 - X^A) \left(\frac{V_2}{V} \left(1 + \left(\frac{\partial \ln g_{11}}{\partial \ln \rho} \right)_{T, \{n_i\}} \right) - \rho \left(\frac{\partial \ln g_{11}}{\partial \rho_2} \right)_{T, \underline{V}, n_1} \right)$$
Eq. G-21



APPENDIX H: Regression Flow Diagram



APPENDIX I: Individual Isotherm Regression (Stage-1)

Figure I-1: Stage 1 regression of methanol in cyclohexane (left) and n-hexane (right).

Table I-1: Constants resulting from RTPT *Stage-1* regression where Δ_2 , Δ_N and ϵ_{BL} are adjusted for each isotherm for methanol in cyclohexane (left) and n-hexane (right). Goodness of fit (\mathbb{R}^2) is presented for each temperature.

methanol in cyclohexane						methanol in n-hexane			
	Units	T1	T2	T3		Units	T1	T2	T3
Т	[K]	283.15	298.25	313.25	Т	[K]	283.35	298.25	313.25
Δ_2	$[\mathrm{cm}^3]$	1946	289.9	50.00	Δ_2	[cm3]	1175	942.8	270.2
Δ_N	[cm ³]	26605	16930	9095	Δ_N	[cm3]	22801	14408	8175
$\epsilon_{\scriptscriptstyle BL}$	[dm ³ / mol-cm ²]	1804.9	1901.7	1608.8	ϵ_{BL}	[dm ³ / mol-cm ²]	1489.2	1528.7	1431.5
R ²		0.9917	0.9594	0.9527	R ²		0.9252	0.9308	0.9626



Figure I-2: Stage 1 regression of ethanol in cyclohexane (left) and n-hexane (right).

Table I-2: Constants resulting from RTPT <i>Stage-1</i> regression where Δ_2 , Δ_N and ϵ_{BL} are
adjusted for each isotherm for ethanol in cyclohexane (left) and n-hexane (right). Goodness of
fit (\mathbf{R}^2) is presented for each temperature.

ethanol in cyclohexane						ethanol in n-hexane				
	Units	T1	T2	T3		Units	T1	T2	T3	
Т	[K]	283.15	298.15	313.15	Т	[K]	283.35	298.15	313.15	
Δ_2	$[cm^3]$	329.8	938.1	326.8	Δ_2	[cm3]	1188	1095	454.5	
Δ_N	$[\mathrm{cm}^3]$	25772	15332	8257	Δ_N	[cm3]	25814	16238	10069	
ϵ_{BL}	[dm ³ / mol-cm ²]	1471.5	1426.3	1478.9	ϵ_{BL}	[dm ³ / mol-cm ²]	1498.6	1389.5	1430.3	
R ²		0.9164	0.9928	0.9941	\mathbf{R}^2		0.9781	0.9907	0.9890	



Figure I-3: Stage 1 regression of 1-propanol in n-hexane (left) and 2-propanol in n-hexane (right).

Table I-3: Constants resulting from RTPT *Stage-1* regression where Δ_2 , Δ_N and ϵ_{BL} are adjusted for each isotherm for 1-propanol in n-hexane (left) and 2-propanol in n-hexane (right). Goodness of fit (R²) is presented for each temperature.

1-propanol in n-hexane						2-propanol in n-hexane			
	Units	T1	T2	Т3		Units	T1	T2	Т3
Т	[K]	283.25	298.05	313.15	Т	[K]	283.35	298.15	313.25
Δ_2	[cm ³]	1498	699.7	369.5	Δ ₂	[cm3]	1645	970.1	558.7
Δ_N	$[cm^3]$	22451	12603	7156	Δ_N	[cm3]	22832	11972	6236
ϵ_{BL}	[dm ³ /mol- cm ²]	1308.1	1288.9	1306.1	ϵ_{BL}	[dm ³ /mol- cm ²]	1225.4	1127.8	1062.0
R ²		0.9957	0.9853	0.9960	R ²		0.9838	0.9986	0.9988

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Figure I-4: Stage 1 regression of 1-butanol in cyclohexane (left) and n-hexane (right).

Table I-4: Constants resulting from RTPT <i>Stage-1</i> regression where Δ_2 , Δ_N and ϵ_{BL} are
adjusted for each isotherm for 1-butanol in cyclohexane (left) and n-hexane (right). Goodness
of fit (\mathbf{R}^2) is presented for each temperature.

1-butanol in cyclohexane						1-butanol in n-hexane			
	Units	T1	T2	T3		Units	T1	T2	T3
Т	[K]	283.25	298.15	313.25	Т	[K]	283.45	298.15	313.25
Δ_2	[cm ³]	1674	539.6	362.7	Δ_2	[cm3]	1415.5	181.6	463.6
Δ_N	[cm ³]	23471	12271	8026	Δ_N	[cm3]	24139	11841	8408
ϵ_{BL}	[dm ³ /mol- cm ²]	1515.3	1564.1	1479.6	ϵ_{BL}	[dm ³ /mol- cm ²]	1474.8	1295.6	1376.7
R ²		0.9922	0.9975	0.9978	R ²		0.9818	0.8260	0.9961



Figure I-5: Stage 1 regression of 1-pentanol in n-hexane (left) and phenol in n-hexane (right).

Table I-5: Constants resulting from RTPT *Stage-1* regression where Δ_2 , Δ_N and ϵ_{BL} are adjusted for each isotherm for 1-pentanol in n-hexane (left) and phenol in n-hexane (right). Goodness of fit (R²) is presented for each temperature.

1-pentanol in n-hexane						phenol in n-hexane			
	UnitsT1T2T3Units					Units	T1	T2	T3
Т	[K]	283.25	298.25	313.15	Т	[K]	283.25	298.15	313.25
Δ_2	[cm ³]	900.6	3268	955.0	Δ_2	[cm3]	2353	1334	878.8
Δ_N	[cm ³]	22165	19703	9612	Δ_N	[cm3]	19409	10924	7356
ϵ_{BL}	[dm ³ /mol- cm ²]	1296.3	1597.6	1434.0	ϵ_{BL}	[dm ³ /mol- cm ²]	4021.0	3763.9	3793.1
R ²		0.9841	0.9824	0.9843	R ²		0.9981	0.9990	0.9962



Figure I-6: Stage 1 regression of 1-hexanol in cyclohexane (left) and n-hexane (right).

Table I-6: Constants resulting from RTPT <i>Stage-1</i> regression where Δ_2 , Δ_N and ϵ_{BL} are
adjusted for each isotherm for 1-hexanol in cyclohexane (left) and n-hexane (right). Goodness
of fit (\mathbf{R}^2) is presented for each temperature.

1-hexanol in cyclohexane						1-hexanol in n-hexane			
	Units	T1	T2	T3		Units	T1	T2	T3
Т	[K]	283.25	298.25	313.35	Т	[K]	283.35	298.25	313.35
Δ_2	[cm ³]	850.6	875.3	745.1	Δ_2	[cm3]	1094	1048	553.6
Δ_N	[cm ³]	20555	14275	8813	Δ_N	[cm3]	25632	15065	9129
ϵ_{BL}	[dm ³ /mol- cm ²]	1341.2	1477.0	1444.7	ϵ_{BL}	[dm ³ /mol- cm ²]	1477.7	1410.5	1416.7
R ²		0.9959	0.9976	0.9978	R ²		0.9921	0.9951	0.9974

APPENDIX J: Scaling Parameters for Ethanol and 1-Butanol

The following table provides parameters for the scaling function described in APPENDIX A: Detailed Summary of Attenuation Coefficient Function. Note that the values for 1-butanol are unchanged from the previous work.¹²²

parameter	units	ethanol	1-butanol	
m_1^f	cm·dm ² /mol	111.82007	121.51223	
m_2^f	cm·dm ² /mol	-125.11856	-130.83618	
m_3^f	cm·dm ² /mol	0	0	
b_1	dm ² /mol	-407576.02	-443631.92	
b_2	dm²/mol	471668.30	477672.97	
b_3	dm ² /mol	29583.780	29639.512	
${ ilde u}^f_R$	cm ⁻¹	3408.48207	3424.3849	
${\widetilde u}_B^f$	cm ⁻¹	3644.92767	3650.9240	
ϵ^f_R	dm ² /mol	29583.77998	29639.512	
$\epsilon^f_{\scriptscriptstyle B}$	dm ² /mol	0.04596044	5.140849E-3	
ϵ_{3645}	dm ² /mol	489.22132	819.56086	
Δ^f	cm ⁻¹	8.2589	8.3506	

Table J-1: Scaling constant parameters for ethanol and 1-butanol.

APPENDIX K: Parity Plots



Figure K-1: Parity plot for solutions of 1-butanol + cyclohexane at 30°C, 40 °C, 50 °C, and 60 °C.



Figure K-2: Parity plot for solutions of ethanol + cyclohexane at 30°C, 40 °C, 50 °C, and 60 °C.

APPENDIX L: Hydroxyl Populations

This section provides the hydrogen bond populations at 40 °C and 60 °C as evaluated using area of the fitted peaks and the fitted attenuation coefficient.



Figure L-1: Hydroxyl populations for binary solutions of ethanol + cyclohexane at 40 $^{\circ}$ C (left) and 60 $^{\circ}$ C (right).



Figure L-2: Hydroxyl populations for binary solutions of 1-butanol + cyclohexane at 40 $^{\circ}$ C (left) and 60 $^{\circ}$ C (right).

APPENDIX M: Hydroxyl Fractions

This section provides supplemental plots at 40 °C and 60 °C for the fraction of alcohol in each hydrogen bond moiety compared to the RTPT model.



Figure M-1: Fraction of alcohol in specific hydroxyl configurations for binary solutions of ethanol + cyclohexane at 40 °C (left) and 60 °C (right) overlayed with the RTPT model prediction (--). Predicted monomer fraction is depicted in black.



Figure M-2: Fraction of alcohol in specific hydroxyl configurations for binary solutions of 1butanol + cyclohexane at 40 °C (left) and 60 °C (right) overlayed with the RTPT model prediction (--). Predicted monomer fraction is depicted in black.



APPENDIX N: Limiting Activity Coefficient Regressions

Figure N-1: Cyclohexane dilute in methanol (upper-left), ethanol (upper-right), 1-butanol (middle-left), 1-pentanol (middle-right). Experimental data is from Lazzaroni et al.¹³⁹



Figure N-2: Cyclohexane dilute in 1-hexanol. Experimental data is from Lazzaroni et al.¹³⁹



Figure N-3: 2-propanol dilute in cyclohexane (left) and cyclohexane dilute in 2-propanol (right). Experimental data is from Lazzaroni et al.¹³⁹



APPENDIX O: Mapping RTPT onto TPT-1

Figure O-1: Mapping of RTPT predictions onto TPT-1 for 1-propanol (upper left), 1-butanol (upper right), 1-pentanol (lower left), and 1-hexanol (lower right) in cyclohexane.



Figure O-2: Mapping of RTPT predictions onto TPT-1 for 2-propanol (upper left), 2-butanol (upper right), i-butanol (lower left), and t-butanol (lower right) in cyclohexane.



APPENDIX P: Phase Equilibria and Excess Enthalpy

Figure P-1: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{184}$ and H^E $(right)^{185}$ for ethanol in cyclohexane.



Figure P-2: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{186}$ and H^E (right)¹⁷⁴ for 1-pentanol in cyclohexane.


Figure P-3: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{137}$ and H^E (right)¹⁸⁷ for 1-hexanol in cyclohexane.



Figure P-4: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{188-190}$ and H^E (right)¹⁹¹ for 2-propanol in cyclohexane.



Figure P-5: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{192}$ and H^E (right)¹⁷⁸ for 2-butanol in cyclohexane.



Figure P-6: RTPT (-) and TPT-1 (--) modeling of experimental phase behavior $(left)^{193,194}$ and H^E (right)¹⁹⁵ for i-butanol in cyclohexane.



APPENDIX Q: Contributions to the Excess Enthalpy at 318.15 K

Figure Q-1: Contributions to H^E for methanol (upper left), ethanol (upper right), 1-propanol (lower left), and 2-butanol (lower right) in cyclohexane at 318.15 K.



Figure Q-2: Contributions to H^E for i-butanol (left) and t-butanol (right) in cyclohexane at 318.15 K.

APPENDIX R: Attenuation Function Parameters

Regression of the attenuation function resulted in the parameter values presented in Table R-1. The variables correspond to the equations provided in APPENDIX A: Detailed Summary of Attenuation Coefficient Function. Parameters are provided with many significant figures because the equations require mathematical differences in large numbers.

	$\tilde{\nu}_R^f$	ϵ^f_R	$\widetilde{\nu}^f_B$	ϵ^f_B	m_1^f	Δ^f
	[cm ⁻¹]	[dm ² /mol]	[cm ⁻¹]	[dm ² /mol]	[cm·dm ² /mol]	[cm ⁻¹]
methanol	3528.257	27288.09	3614.807	0.043244	25.88124	39.20276
ethanol	3451.392	29125.72	3617.187	0.046733	18.93279	45.65274
1-propanol	3483.178	27228.19	3631.943	0.043689	17.96059	40.53972
1-butanol	3457.282	29236.2	3620.377	0.046913	19.29024	52.26124
1-pentanol	3455.176	27149.68	3623.741	0.043562	17.81814	55.22821
1-hexanol	3445.965	28504.22	3619.338	0.045737	18.67722	55.48942
i-butanol	3415.853	31797.42	3613.372	0.050383	21.52852	61.2826
2-propanol	3386.512	29347.7	3615.519	0.047091	18.92334	50.1112
2-butanol	3384.383	28389.56	3609.366	0.045554	17.84182	60.24368
t-butanol	3376.146	27617.83	3600.002	0.044309	24.39824	50.73637

Table R-1: Molar attenuation coefficient parameters for measured alcohol systems.

APPENDIX S: Tabulated X^A Values

methanol		X	A		ethanol		X	K ^A	
X	30 °C	40 °C	50 °C	60 °C	X	30 °C	40 °C	50 °C	60 °C
2.50E-03		0.991	0.980	0.982	1.07E-03	1.000	1.000	1.000	1.000
4.97E-03	0.909				4.25E-03	0.967	0.979	0.976	0.990
1.00E-02	0.683	0.819	0.910	0.965	6.37E-03	0.915	0.977	0.993	0.988
2.00E-02	0.459	0.573	0.678	0.833	1.27E-02	0.754	0.875	0.916	0.950
3.00E-02	0.328	0.465	0.623	0.735	2.53E-02	0.542	0.655	0.778	0.849
4.02E-02	0.307	0.421	0.492	0.607	3.15E-02	0.474	0.580	0.682	0.773
4.96E-02	0.257	0.363	0.449	0.527	4.85E-02	0.342	0.439	0.527	0.622
6.02E-02	0.215	0.297		0.512	6.40E-02	0.284	0.369	0.442	0.532
7.06E-02	0.205	0.286	0.349	0.437	9.42E-02	0.208		0.348	0.413
7.97E-02	0.188	0.289	0.346	0.418	1.50E-01	0.155	0.197	0.255	
8.98E-02	0.173	0.188	0.299	0.365	2.02E-01	0.111	0.146	0.196	
9.99E-02	0.165	0.179	0.291	0.342	3.03E-01	0.083	0.128	0.164	

Table S-1: Tabulated X^A values for methanol (left) and ethanol (right).

1-propanol			X ^A		1-butanol		X	A	
Х	30 °C	40 °C	50 °C	60 °C	X	30 °C	40 °C	50 °C	
9.98E-04	1.000	1.000	1.000	0.992	9.48E-04	0.944	0.949	0.958	
2.46E-03	0.962	0.971	1.023	0.998	1.18E-03	0.982	0.962	0.967	
4.98E-03	0.950	0.968	1.052	0.997	5.08E-03	0.952	0.979	0.990	
9.95E-03	0.795	0.905	0.941	0.950	5.80E-03	0.916	0.960	0.983	
2.01E-02	0.565	0.688	0.777	0.860	5.92E-03	0.933	0.974	0.983	
3.01E-02	0.447	0.553	0.644		1.00E-02	0.788	0.889	0.942	
4.00E-02	0.400	0.508	0.602		1.12E-02	0.744	0.857	0.930	
4.99E-02	0.309	0.404	0.512		1.12E-02	0.755	0.851	0.923	
5.96E-02	0.280	0.372	0.465		2.18E-02	0.549	0.645	0.794	
7.01E-02	0.240	0.318	0.408		2.72E-02	0.467	0.601	0.714	
8.04E-02	0.212	0.289	0.366		5.04E-02				
9.00E-02	0.195	0.268	0.334		6.80E-02	0.251	0.326	0.413	
9.96E-02	0.184	0.244	0.313		8.18E-02	0.217	0.285	0.361	
1.52E-01	0.140	0.192	0.240		1.00E-01	0.188		0.324	
2.03E-01	0.112	0.153	0.198		1.50E-01	0.153	0.203	0.251	
2.53E-01	0.095	0.133	0.168		1.50E-01	0.149	0.196	0.251	
3.02E-01	0.082	0.119	0.152		2.00E-01	0.127	0.168	0.213	
					2.00E-01	0.125	0.164	0.212	

Table S-2: Tabulated X^A values for 1-propanol (left) and 1-butanol (right).

1-pentanol			X ^A		1-hexanol		X	A	
X	30 °C	40 °C	50 °C	60 °C	X	30 °C	40 °C	50 °C	60 °C
1.00E-03	1.000	1.000	1.000	1.000	0.001	1.000	1.000	1.000	0.999
2.50E-03	0.989	0.986	1.000	1.000	0.003	0.976	0.977	0.978	0.978
5.00E-03	0.929	0.972	1.013	0.980	0.005	0.938	0.967	0.971	0.971
1.00E-02	0.762	0.870	0.919	0.957	0.010	0.742	0.904	0.927	0.942
2.00E-02	0.527	0.648	0.766		0.020		0.643	0.752	0.832
3.00E-02	0.395	0.511	0.627		0.030	0.403	0.511	0.643	0.740
4.00E-02	0.325	0.422	0.557	0.671	0.040	0.331	0.438	0.542	0.636
5.00E-02	0.268	0.368	0.481	0.579	0.050	0.284	0.385	0.474	0.569
6.00E-02	0.259	0.322	0.411	0.531	0.060	0.250	0.330	0.421	0.505
7.00E-02	0.212	0.282	0.369	0.476	0.070	0.222	0.299	0.392	0.471
8.00E-02	0.194	0.249	0.337	0.430	0.080	0.205	0.277	0.358	0.425
9.00E-02	0.169	0.228	0.299	0.391	0.090	0.192	0.253	0.333	0.389
1.00E-01	0.153	0.212	0.279	0.356	0.099	0.183	0.240	0.313	0.372
1.50E-01	0.111	0.152	0.213	0.276	0.151	0.154	0.199	0.247	0.301
2.00E-01	0.085	0.119	0.168	0.220	0.201	0.126	0.165	0.207	0.252
2.50E-01	0.078	0.105	0.142	0.182	0.252				0.217
3.00E-01		0.088		0.166					

Table S-3: Tabulated X^A values for 1-pentanol (left) and 1-hexanol (right).

2-propanol	X ^A							
X	30 °C	40 °C	50 °C	60 °C				
9.98E-04	1.000	1.000	1.000	0.992				
2.46E-03	0.962	0.971	1.023	0.998				
4.98E-03	0.950	0.968	1.052	0.997				
9.95E-03	0.795	0.905	0.941	0.950				
2.01E-02	0.565	0.688	0.777	0.860				
3.01E-02	0.447	0.553	0.644					
4.00E-02	0.400	0.508	0.602					
4.99E-02	0.309	0.404	0.512					
5.96E-02	0.280	0.372	0.465					
7.01E-02	0.240	0.318	0.408					
8.04E-02	0.212	0.289	0.366					
9.00E-02	0.195	0.268	0.334					
9.96E-02	0.184	0.244	0.313					
1.52E-01	0.140	0.192	0.240					
2.03E-01	0.112	0.153	0.198					
2.53E-01	0.095	0.133	0.168					
3.02E-01	0.082	0.119	0.152					

Table S-4: Tabulated X^A values for 2-propanol (left) and 2-butanol (right).

2-butanol		Х	A	
X	30 °C	40 °C	50 °C	60 °C
1.00E-03	1.000	1.000	1.000	1.000
2.47E-03	0.989	0.978	0.983	0.983
5.00E-03		0.986	0.987	0.970
9.99E-03	0.915			
2.00E-02	0.639	0.755	0.839	0.875
2.99E-02	0.517	0.629	0.782	0.796
3.98E-02	0.434	0.561	0.653	0.744
5.02E-02	0.370	0.467	0.570	0.646
9.97E-02	0.227	0.299	0.372	0.458
1.50E-01	0.175	0.223	0.270	0.348
2.00E-01	0.144	0.157	0.189	0.244
2.49E-01	0.143	0.160	0.201	0.253

i-butanol		Х	A			t-butanol		
X	30 °C	40 °C	50 °C	60 °C	_	X	30 °C	40 °C
9.94E-04	1.000	1.000	1.000	1.000		4.90E-04	1.000	1.000
2.46E-03	0.980	0.973	0.976	0.986		1.02E-03	1.000	1.000
4.91E-03	0.954	0.971	0.966	0.994		2.49E-03	0.993	0.991
9.93E-03	1.577	0.841	0.898	1.004		5.00E-03	0.970	0.982
1.98E-02	0.580	0.643	0.795	0.928		1.00E-02	0.850	0.922
3.03E-02	0.448	0.549	0.665	0.761		2.00E-02	0.657	0.758
3.96E-02	0.380	0.468	0.577	0.669		3.01E-02	0.543	0.647
5.05E-02	0.329	0.404	0.502	0.611		3.99E-02	0.469	0.587
6.03E-02	0.284	0.351	0.444	0.555		4.98E-02	0.416	0.527
7.98E-02	0.235	0.295	0.390	0.473		5.98E-02	0.369	0.482
1.00E-01	0.206	0.254	0.341	0.415		6.99E-02	0.343	0.425
1.49E-01	0.157	0.200	0.261	0.319		7.99E-02	0.307	0.401
2.02E-01	0.141	0.164	0.225	0.254		8.99E-02	0.284	0.388
2.48E-01	0.128	0.147	0.193	0.239	_	9.99E-02	0.271	0.356
						1.50E-01	0.216	0.291

Table S-5: Tabulated X^A values for i-butanol (left) and t-butanol (right).

1.99E-01

2.49E-01

2.99E-01

0.187

0.155

0.132

0.245

0.206

0.195

XA

50 °C

1.000

1.000

0.994

0.991

0.963

0.862

0.768

0.687

0.619

0.587

0.538

0.496

0.465

0.436

0.360

0.308

0.268

0.244

60 °C

1.000

1.000

1.000

0.996

0.972

0.907

0.833

0.746

0.706

0.659

0.625

0.586

0.554

0.520

0.426

0.381

0.330

0.301

APPENDIX T: Excess Volume Comparison

Solute	methanol	methanol	1-propanol	1-hexanol
Solvent	cyclohexane	cyclohexane	n-hexane	n-hexane
T [K]	298.15	298.15	298.15	298.15
x ₁	0.96005	0.0286	0.4988	0.5053
V_1 [cm ³ /mol]	40.733	40.733	75.146	125.305
V ₂ [cm ³ /mol]	108.757	108.757	131.578	131.578
V _{mixture} [cm ³ /mol]	43.623	106.932	103.598	127.974
V _{ideal} [cm ³ /mol]	43.450	106.812	103.430	128.408
V ^E [cm ³ /mol]	0.173	0.121	0.169	-0.433
V ^E /V (in %)	0.398	0.113	0.163	-0.338

Table T-1: Excess molar volumes for selected binary systems at 298.15 K.

	cyclohexane-d ₁₂	toluene-d ₈	benzene-d ₆	tetrahydrofuran-d ₈	pydridine-d5	chloroform-d
T/[K]	$\alpha_P / [10^{-3} \text{ K}^{-1}]$					
278.15		1.0574		1.1864	1.0118	1.2350
283.15	1.1905	1.0618	1.2029	1.1981	1.0148	1.2371
288.15	1.2023	1.0628	1.2066	1.2133	1.0139	1.2481
293.15	1.2158	1.0618	1.2123	1.2263	1.0178	1.2638
298.15	1.2267	1.0838	1.2155	1.2491	1.0265	1.2904
303.15	1.2502	1.1110	1.2460	1.2821	1.0401	1.3165
308.15	1.2575	1.1034	1.2502	1.2842	1.0372	1.3187
313.15	1.2626	1.1018	1.2420	1.2860	1.0385	1.3226
318.15	1.2948	1.1208	1.2683	1.3173	1.0597	1.3522
323.15	1.3192	1.1530	1.2946	1.3391	1.0715	1.3820
328.15	1.3375	1.1602	1.3146	1.3591	1.0817	1.3905
333.15	1.3542	1.1596	1.3247	1.3772	1.0952	
338.15	1.3820	1.1726	1.3328		1.1066	
343.15	1.4081	1.1809	1.3464		1.1100	
348.15		1.2181	1.3690		1.1250	
353.15		1.2270			1.1356	
358.15		1.2238			1.1263	
363.15		1.2411			1.1498	
368.15					1.1828	

APPENDIX U: Calculated Thermal Expansivities of Perdeutero Compounds

Table U-1: Calculated thermal expansivities of perdeutero compounds using finite differences (Part I).

	aastana d	dichlaramathana di	ethanol-d5	aastanitrila d.	mothenal d.	dimethyl
	acetone-u6	ulcinoromethane-u2	ethanor-us	acetomitime-u3	methanoi-u4	sulfoxide-d ₆
T/[K]	$\alpha_P / [10^{-3} \text{ K}^{-1}]$					
278.15	1.3820	1.3380	1.0490	1.3313	1.1740	
283.15	1.3961	1.3456	1.0675	1.3464	1.1778	
288.15	1.4229	1.3576	1.0823	1.3662	1.1862	
293.15	1.4312	1.3818	1.0883	1.3812	1.1996	
298.15	1.4523	1.4214	1.1042	1.3940	1.2056	0.9215
303.15	1.4788	1.4223	1.1324	1.4199	1.2257	0.9402
308.15	1.4919	1.4254	1.1325	1.4297	1.2295	0.9301
313.15	1.5286	1.4582	1.1283	1.4376	1.2375	0.9168
318.15	1.5536		1.1617	1.4640	1.2694	0.9365
323.15	1.5829		1.2036	1.4968	1.2992	0.9501
328.15	1.6130		1.2284	1.5293	1.3198	0.9555
333.15			1.2409	1.5431	1.3386	0.9614
338.15			1.2730	1.5549	1.3642	0.9638
343.15			1.3033			0.9611
348.15			1.3401			0.9770
353.15			1.3716			0.9785
358.15						0.9671
363.15						0.9679
368.15						0.9711

Table U-2: Calculated thermal expansivities of perdeutero compounds using finite differences (Part II).



APPENDIX V: Effect of Method for Determining Isobaric Thermal Expansivity

Figure V-1: Comparison of isobaric thermal expansivity calculation by two different means for acetone-d6 (upper left), acetonitrile-d3 (upper right), benzene-d6 (lower left), and chloroform-d (lower right). Data points were calculated using the finite difference method and then fitted to a polynomial expression which is depicted as a solid line. The dashed line was calculated by differentiating the polynomial expression that was fit to the density values. Differences are most evident at the low and high temperature endpoints.



Figure V-2: Comparison of isobaric thermal expansivity calculation by two different means for cyclohexane-d12 (upper left), dichloromethane-d2 (upper right), dimethyl sulfoxide-d6 (lower left), and ethanol-d6 (lower right). Data points were calculated using the finite difference method and then fitted to a polynomial expression which is depicted as a solid line. The dashed line was calculated by differentiating the polynomial expression that was fit to the density values. Differences are most evident at the low and high temperature endpoints.



Figure V-3: Comparison of isobaric thermal expansivity calculation by two different means for methanol-d4 (upper left), pyridine-d5 (upper right), tetrahydrofuran-d8 (lower left), and toluene-d8 (lower right). Data points were calculated using the finite difference method and then fitted to a polynomial expression which is depicted as a solid line. The dashed line was calculated by differentiating the polynomial expression that was fit to the density values. Differences are most evident at the low and high temperature endpoints.

$\rho\left[\frac{\mathrm{mol}}{\mathrm{cm}^3}\right] = C_1 T^2 + C_2 T + C_3$								
	C_1	C_2	C_3					
	[mol/cm ³ K ²]	[mol/cm ³ K]	[mol/cm ³]	\mathbb{R}^2				
	/10-8	/10 ⁻⁵						
ethanol	-2.18 <u>1</u> 4	-0.549 <u>1</u> 2	0.0206 <u>2</u> 2	0.999 <u>0</u> 9				
chloroform	-1.29 <u>7</u> 2	-0.840 <u>9</u> 8	0.0160 <u>4</u> 9	0.995 <u>3</u> 3				
pyridine	-0.304 <u>4</u> 7	-1.08 <u>6</u> 2	0.0158 <u>7</u> 3	0.999 <u>4</u> 1				
toluene	-0.561 <u>7</u> 9	-0.669 <u>2</u> 1	0.0118 <u>5</u> 2	0.999 <u>5</u> 3				
dichloromethane	-3.21 <u>5</u> 3	-0.273 <u>9</u> 4	0.0191 <u>7</u> 3	0.994 <u>5</u> 8				
benzene	-0.649 <u>2</u> 1	-0.972 <u>8</u> 3	0.0146 <u>6</u> 1	0.999 <u>3</u> 9				
cyclohexane	-0.529 <u>5</u> 5	-0.804 <u>7</u> 8	0.0121 <u>0</u> 6	0.999 <u>6</u> 0				
acetone	-0.530 <u>2</u> 5	-1.69 <u>0</u> 7	0.0190 <u>2</u> 5	0.997 <u>3</u> 9				
methanol	-1.24 <u>9</u> 3	-2.19 <u>3</u> 7	0.0322 <u>0</u> 2	0.999 <u>1</u> 4				
acetonitrile	-1.61 <u>2</u> 5	-1.67 <u>3</u> 7	0.0253 <u>4</u> 3	0.999 <u>4</u> 8				
dimethyl	0.257 <u>7</u> 7	-1.44 <u>4</u> 2	0.0180 <u>9</u> 8	0.999 <u>2</u> 1				
sulfoxide								
tetrahydrofuran	-0.269 <u>1</u> 4	-1.35 <u>6</u> 8	0.0165 <u>1</u> 7	0.999 <u>1</u> 3				

APPENDIX W: Protiated Molar Density Regression Coefficients

Table W-1: Protiated molar density regression coefficients used in molar volume comparison. Regressed using NIST accepted density values.

*underbar indicates the last significant digit

APPENDIX X: Uncertainty Analysis Equations

Calculation of Standard Uncertainty in Densimeter A-value

$$A(\tau_{air}, \tau_{H20}, \rho_{air}, \rho_{H20})$$
 Eq. X-1

$$u^{2}(A) = \left(\frac{\partial A}{\partial \tau_{air}}\right)^{2} u(\tau_{air})^{2} + \left(\frac{\partial A}{\partial \tau_{H20}}\right)^{2} u(\tau_{H20})^{2} + \left(\frac{\partial A}{\partial \rho_{air}}\right)^{2} u(\rho_{air})^{2} + \left(\frac{\partial A}{\partial \rho_{H20}}\right)^{2} u(\rho_{H20})^{2}$$
Eq. X-2

The period of oscillation for the air and water calibrants are τ_{air} and τ_{H20} , respectively. The uncertainty in this value is the same for both calibrant fluids; 0.0001 s. The tabulated density values for air and water were assumed to be uncertain in the last decimal place; 1E-6 g/cm³ for air and 1E-5 g/cm³ for water. The partial derivatives were evaluated using the following expressions.

$$\left|\frac{\partial A}{\partial \tau_{air}}\right| = \left|-\frac{2\tau_{air}}{\rho_{H2O} - \rho_{air}}\right|$$
Eq. X-3

$$\left|\frac{\partial A}{\partial \tau_{H20}}\right| = \left|\frac{2\tau_{H20}}{\rho_{H20} - \rho_{air}}\right|$$
Eq. X-4

$$\left|\frac{\partial A}{\partial \rho_{air}}\right| = \left|\frac{\tau_{H20}^2 - \tau_{air}^2}{(\rho_{H20} - \rho_{air})^2}\right|$$
Eq. X-5

$$\left|\frac{\partial A}{\partial \rho_{H20}}\right| = \left|\frac{\tau_{air}^2 - \tau_{H20}^2}{(\rho_{H20} - \rho_{air})^2}\right|$$
Eq. X-6

Calculation of Standard Uncertainty in Densimeter B-value

$$B(\tau_{air}, \rho_{air}, A)$$
 Eq. X-7

$$u^{2}(B) = \left(\frac{\partial B}{\partial \tau_{air}}\right)^{2} u(\tau_{air})^{2} + \left(\frac{\partial B}{\partial A}\right)^{2} u(A)^{2} + \left(\frac{\partial B}{\partial \rho_{air}}\right)^{2} u(\rho_{air})^{2}$$
Eq. X-8

The uncertainty of *B* was then calculated analogously to *A* using equations which follow.

$$\left|\frac{\partial B}{\partial \tau_{air}}\right| = |2\tau_{air}|$$
 Eq. X-9

$$\left|\frac{\partial B}{\partial A}\right| = \left|-\rho_{air}\right|$$
 Eq. X-10

$$\left|\frac{\partial B}{\partial \rho_{air}}\right| = |-A|$$
 Eq. X-11

Calculation of Combined Uncertainty for Density Measurement.

$$\rho(T, \tau_s, A, B, Purity(x), Percent Deuteration(x_D))$$
 Eq. X-12

$$u^{2}(\rho) = \left(\frac{\partial\rho}{\partial T}\right)^{2} u^{2}(T) + \left(\frac{\partial\rho}{\partial\tau_{s}}\right)^{2} u^{2}(\tau) + \left(\frac{\partial\rho}{\partial A}\right)^{2} u^{2}(A) + \left(\frac{\partial\rho}{\partial B}\right)^{2} u^{2}(B) + \left(\frac{\partial\rho}{\partial x}\right)^{2} u^{2}(x) + \left(\frac{\partial\rho}{\partial x_{D}}\right)^{2} u^{2}(x_{D})$$
Eq. X-13

 M_D and ρ_D denote the molecular weight and mass density of the deuterated compound, and M_H denotes molecular weight of the protiated form. The period of oscillation for the sample is τ_s . For samples where the purity was unavailable, 99% was assumed. It was assumed that the molecular mass of the impurity was 12 g/mol less than the analyte. The effect of percent deuteration was estimated as one minus the ratio of the molecular mass of the completely protiated compound relative to the molecular mass of the completely deuterated compound. This difference was then multiplied by the measured density of the deuterated sample. A detailed comprehensive error analysis for each compound as well as the air and water calibrants can be found in the tables within APPENDIX Y: Uncertainty Analysis Data.

$$\left|\frac{\partial \rho}{\partial T}\right| = |\rho \alpha_P| \qquad \qquad \text{Eq. X-14}$$

$$\left|\frac{\partial\rho}{\partial\tau}\right| = \left|\frac{2\tau}{A}\right|$$
 Eq. X-15

$$\left|\frac{\partial\rho}{\partial A}\right| = \left|\frac{\tau^2 - B}{A^2}\right|$$
 Eq. X-16

$$\left|\frac{\partial\rho}{\partial B}\right| = \left|\frac{1}{A}\right|$$
 Eq. X-17

$$\left|\frac{\partial\rho}{\partial x}\right| = \left|\left(1 - \frac{M_{impurity}}{M_D}\right)\rho_D\right|$$
 Eq. X-18

$$\left|\frac{\partial\rho}{\partial x_D}\right| = \left|\left(1 - \frac{M_H}{M_D}\right)\rho_D\right|$$
 Eq. X-19

APPENDIX Y: Uncertainty Analysis Data

Temperature	Temperature	τ(Air)	τ(Water)	ρ(Air)	ρ(Water)	Α	В
[°C]	[K]	[s]	[s]	[g/cm ³]	[g/cm ³]	[s ² cm ³ /g]	[s ²]
5.00	278.15	5.9054	7.4642	0.001227	1.000183	20.86233	34.84814
10.00	283.15	5.9036	7.4615	0.001206	0.999785	20.85112	34.82735
15.00	288.15	5.9018	7.4585	0.001185	0.999123	20.84084	34.80667
20.00	293.15	5.9001	7.4551	0.001164	0.998208	20.82892	34.78693
25.00	298.15	5.8983	7.4514	0.001145	0.997052	20.81863	34.76611
30.00	303.15	5.8966	7.4474	0.001125	0.995667	20.80744	34.74649
35.00	308.15	5.8949	7.4433	0.001107	0.994064	20.79934	34.72683
40.00	313.15	5.8932	7.4386	0.001089	0.992256	20.78656	34.70717
45.00	318.15	5.8916	7.4338	0.001072	0.990255	20.77576	34.6881
50.00	323.15	5.8899	7.4288	0.001055	0.988071	20.76578	34.66901
55.00	328.15	5.8883	7.4237	0.001037	0.985716	20.75726	34.65055
60.00	333.15	5.8867	7.4183	0.001021	0.983203	20.74762	34.63205
65.00	338.15	5.8852	7.4128	0.001006	0.980544	20.73839	34.61471
70.00	343.15	5.8838	7.4071	0.000992	0.977749	20.7278	34.59855
75.00	348.15	5.8825	7.4013	0.000976	0.974831	20.7171	34.58358
80.00	353.15	5.8813	7.3955	0.000963	0.971801	20.70725	34.57009
85.00	358.15	5.8802	7.3895	0.00095	0.968671	20.69553	34.55709
90.00	363.15	5.8792	7.3833	0.000937	0.965454	20.6821	34.5455
95.00	368.15	5.8781	7.3770	0.000924	0.96216	20.6688	34.53343

Table Y-2: Error analysis for densimeter constants.

u(τ Air)	u(7H2O)	u(pAir)	u(pH2O)
0.0001	0.0001	0.000001	0.00001

Temperature	Temperature	$\partial A/\partial \tau$	$\partial A/\partial \tau$	∂Α/∂ρ	∂Α/∂ρ	(A)	$\partial \mathbf{B}/\partial \mathbf{\tau}$	∂B/∂A	$\partial B/\partial \rho$	(D)
[°C]	[K]	[Air]	[H2O]	[Air]	[H2O]	u (A)	[Air]		[Air]	- u(B)
5.00	278.15	-11.8232	14.94401	20.88414	-20.8841	0.001917	11.8108	-0.00123	-20.8623	0.001181
10.00	283.15	-11.824	14.94423	20.88078	-20.8808	0.001917	11.8072	-0.00121	-20.8511	0.001181
15.00	288.15	-11.828	14.94782	20.8839	-20.8839	0.001918	11.80362	-0.00118	-20.8408	0.001181
20.00	293.15	-11.8352	14.95442	20.8907	-20.8907	0.001919	11.8002	-0.00116	-20.8289	0.00118
25.00	298.15	-11.8451	14.96405	20.9042	-20.9042	0.00192	11.7966	-0.00114	-20.8186	0.00118
30.00	303.15	-11.8579	14.97654	20.92164	-20.9216	0.001922	11.7932	-0.00112	-20.8074	0.00118
35.00	308.15	-11.8734	14.99218	20.94685	-20.9469	0.001924	11.7898	-0.00111	-20.7993	0.001179
40.00	313.15	-11.8914	15.00977	20.97179	-20.9718	0.001927	11.7864	-0.00109	-20.7866	0.001179
45.00	318.15	-11.912	15.03018	21.00295	-21.0029	0.001929	11.7831	-0.00107	-20.7758	0.001178
50.00	323.15	-11.9348	15.05306	21.03896	-21.039	0.001933	11.7798	-0.00106	-20.7658	0.001178
55.00	328.15	-11.9598	15.07841	21.08022	-21.0802	0.001936	11.7766	-0.00104	-20.7573	0.001178
60.00	333.15	-11.987	15.10575	21.12401	-21.124	0.00194	11.7734	-0.00102	-20.7476	0.001178
65.00	338.15	-12.0163	15.13531	21.17161	-21.1716	0.001944	11.7704	-0.00101	-20.7384	0.001177
70.00	343.15	-12.0476	15.16672	21.22103	-21.221	0.001949	11.7676	-0.00099	-20.7278	0.001177
75.00	348.15	-12.0809	15.20001	21.2733	-21.2733	0.001953	11.765	-0.00098	-20.7171	0.001177
80.00	353.15	-12.116	15.2353	21.32926	-21.3293	0.001958	11.76266	-0.00096	-20.7073	0.001176
85.00	358.15	-12.1527	15.27189	21.38584	-21.3858	0.001964	11.7604	-0.00095	-20.6955	0.001176
90.00	363.15	-12.191	15.30984	21.44296	-21.443	0.001969	11.75838	-0.00094	-20.6821	0.001176
95.00	368.15	-12.2304	15.34899	21.50232	-21.5023	0.001974	11.75628	-0.00092	-20.6688	0.001176

acetone-d ₆ purity	64.1161 0.99^{1}	[g/mol]									
xD	0.9996										
$M_{ m H}$	58.0791	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	52.1161	[g/mol]		0.05	0.0001			0.01	0.0001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	∂ρ/∂τ	∂ρ/∂Α	∂ρ/∂Β	∂ρ/∂x	∂ρ/∂xD	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.3277	0.903401	1.3820E-03	0.001249	0.702482	0.043303	0.047933	0.169081	0.085062	0.001696419	0.003325
283.15	7.3167	0.897158	1.3961E-03	0.001253	0.701804	0.043027	0.047959	0.167913	0.084474	0.001684753	0.003302
288.15	7.3057	0.890875	1.4229E-03	0.001268	0.701095	0.042747	0.047983	0.166737	0.083882	0.001673033	0.003279
293.15	7.2945	0.884482	1.4312E-03	0.001266	0.70042	0.042464	0.04801	0.16554	0.08328	0.001661078	0.003256
298.15	7.2835	0.878216	1.4523E-03	0.001275	0.69971	0.042184	0.048034	0.164367	0.08269	0.001649384	0.003233
303.15	7.2722	0.871727	1.4788E-03	0.001289	0.699	0.041895	0.04806	0.163153	0.082079	0.001637281	0.003209
308.15	7.2612	0.865325	1.4919E-03	0.001291	0.698214	0.041603	0.048078	0.161955	0.081477	0.001625319	0.003186
313.15	7.24976	0.858817	1.5286E-03	0.001313	0.697543	0.041316	0.048108	0.160737	0.080864	0.0016132	0.003162
318.15	7.23831	0.852197	1.5536E-03	0.001324	0.696804	0.041019	0.048133	0.159498	0.080241	0.001600853	0.003138
323.15	7.2269	0.845577	1.5829E-03	0.001338	0.696039	0.04072	0.048156	0.158259	0.079617	0.001588515	0.003113
328.15	7.2154	0.838812	1.6130E-03	0.001353	0.695217	0.040411	0.048176	0.156993	0.07898	0.001575906	0.003089

Table Y-3: Error analysis for acetone-d₆ (purity of 99% was assumed).

¹estimate

acetonitrile-d ₃	44.0704	[g/mol]									
purity	0.99 ¹										
xD	0.995										
$M_{ m H}$	41.0519	[g/mol]		u(T)	u (τ)			u(x)	u(xD)		k
mass (im)	32.0704	[g/mol]		0.05	0.0001			0.01	0.001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂p/∂B	∂ρ/∂x	∂ρ/∂xD	u(ρ)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.2612	0.856898	1.3313E-03	0.001141	0.696106	0.041074	0.047933	0.233326	0.058691	0.002337746	0.004582
283.15	7.25091	0.851194	1.3464E-03	0.001146	0.695494	0.040822	0.047959	0.231773	0.058301	0.002322224	0.004552
288.15	7.2406	0.845437	1.3662E-03	0.001155	0.694847	0.040566	0.047983	0.230205	0.057906	0.002306563	0.004521
293.15	7.2302	0.839643	1.3812E-03	0.00116	0.694246	0.040311	0.04801	0.228628	0.057509	0.002290797	0.00449
298.15	7.2198	0.83384	1.3940E-03	0.001162	0.69359	0.040053	0.048034	0.227048	0.057112	0.002275002	0.004459
303.15	7.2094	0.828019	1.4199E-03	0.001176	0.692964	0.039794	0.04806	0.225463	0.056713	0.002259176	0.004428
308.15	7.199	0.822082	1.4297E-03	0.001175	0.692233	0.039524	0.048078	0.223846	0.056307	0.002243016	0.004396
313.15	7.1885	0.816266	1.4376E-03	0.001173	0.691649	0.039269	0.048108	0.222262	0.055908	0.002227184	0.004365
318.15	7.178	0.810348	1.4640E-03	0.001186	0.690998	0.039004	0.048133	0.220651	0.055503	0.002211094	0.004334
323.15	7.1675	0.804402	1.4968E-03	0.001204	0.690318	0.038737	0.048156	0.219032	0.055096	0.002194938	0.004302
328.15	7.1569	0.798307	1.5293E-03	0.001221	0.68958	0.038459	0.048176	0.217372	0.054678	0.002178372	0.00427
333.15	7.1462	0.792193	1.5431E-03	0.001222	0.688869	0.038182	0.048198	0.215708	0.054259	0.002161738	0.004237
338.15	7.1356	0.786082	1.5549E-03	0.001222	0.688154	0.037905	0.04822	0.214044	0.053841	0.002145108	0.004204

Table Y-4: Error analysis for acetonitrile-d₃ (purity of 99% was assumed).

¹estimate

Table Y-5: Error analysis for benzene-d₆.

benzene-d ₆	84.1488	[g/mol]									
purity	1										
xD	0.9995										
$M_{ m H}$	78.1118	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	72.1488	[g/mol]		0.05	0.0001			0.0001	0.0001		1.96
Temperature	Period	Density	ITE	∂ρ/∂T	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂ρ/∂Β	∂ρ/∂x	∂ρ/∂xD	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
283.15	7.4069	0.960851	1.2029E-03	0.001156	0.710456	0.046082	0.047959	0.137022	0.068933	0.000140124	0.000275
288.15	7.3967	0.955072	1.2066E-03	0.001152	0.709827	0.045827	0.047983	0.136198	0.068519	0.000139724	0.000274
293.15	7.3865	0.949327	1.2123E-03	0.001151	0.709254	0.045577	0.04801	0.135378	0.068107	0.000139387	0.000273
298.15	7.3763	0.943563	1.2155E-03	0.001147	0.708625	0.045323	0.048034	0.134556	0.067693	0.000139001	0.000272
303.15	7.3662	0.937857	1.2460E-03	0.001169	0.708035	0.045073	0.04806	0.133743	0.067284	0.000139168	0.000273
308.15	7.3559	0.931877	1.2502E-03	0.001165	0.70732	0.044803	0.048078	0.13289	0.066855	0.000138788	0.000272
313.15	7.345735	0.926207	1.2420E-03	0.00115	0.706777	0.044558	0.048108	0.132081	0.066448	0.000138228	0.000271
318.15	7.3355	0.920374	1.2683E-03	0.001167	0.70616	0.0443	0.048133	0.131249	0.066029	0.00013832	0.000271
323.15	7.3253	0.914534	1.2946E-03	0.001184	0.705516	0.04404	0.048156	0.130417	0.06561	0.000138414	0.000271
328.15	7.315	0.908534	1.3146E-03	0.001194	0.704814	0.043769	0.048176	0.129561	0.06518	0.000138369	0.000271
333.15	7.3047	0.90259	1.3247E-03	0.001196	0.704148	0.043503	0.048198	0.128713	0.064754	0.000138145	0.000271
338.15	7.2944	0.896577	1.3328E-03	0.001195	0.703468	0.043233	0.04822	0.127856	0.064322	0.000137879	0.00027
343.15	7.2842	0.890641	1.3464E-03	0.001199	0.702844	0.042968	0.048244	0.127009	0.063896	0.000137738	0.00027
348.15	7.2739	0.884585	1.3690E-03	0.001211	0.702212	0.042698	0.048269	0.126146	0.063462	0.000137765	0.00027

Table Y-6: Error analysis for chloroform-d.

chloroform-d	120.3840	[g/mol]									
purity	1										
xD	0.9982										
$M_{ m H}$	119.378	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	108.384	[g/mol]		0.05	0.0001			0.0001	0.0001		1.96
Temperature	Period	Density	ITE	$\partial \rho / \partial T$	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂ρ/∂Β	∂ρ/∂x	∂ρ/∂xD	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	8.1702	1.531084	1.2350E-03	0.001891	0.783249	0.073303	0.047933	0.15262	0.012795	0.000195606	0.000383
283.15	8.1559	1.521629	1.2371E-03	0.001882	0.782299	0.072892	0.047959	0.151678	0.012716	0.000194798	0.000382
288.15	8.1416	1.512259	1.2481E-03	0.001887	0.781312	0.072475	0.047983	0.150744	0.012637	0.000194331	0.000381
293.15	8.1272	1.502753	1.2638E-03	0.001899	0.780376	0.072064	0.04801	0.149796	0.012558	0.000194063	0.00038
298.15	8.1128	1.493265	1.2904E-03	0.001927	0.779379	0.071644	0.048034	0.14885	0.012479	0.000194199	0.000381
303.15	8.09829	1.483483	1.3165E-03	0.001953	0.778403	0.071223	0.04806	0.147875	0.012397	0.000194327	0.000381
308.15	8.08338	1.473734	1.3187E-03	0.001943	0.777273	0.070766	0.048078	0.146903	0.012315	0.000193527	0.000379
313.15	8.068755	1.464048	1.3226E-03	0.001936	0.776343	0.070352	0.048108	0.145938	0.012234	0.000192874	0.000378
318.15	8.0542	1.45437	1.3522E-03	0.001967	0.775346	0.069925	0.048133	0.144973	0.012154	0.000193162	0.000379
323.15	8.0394	1.444381	1.3820E-03	0.001996	0.774293	0.069484	0.048156	0.143977	0.01207	0.000193436	0.000379
328.15	8.0245	1.434408	1.3905E-03	0.001995	0.773175	0.069029	0.048176	0.142983	0.011987	0.000192905	0.000378

Table Y-7: Error analysis for cyclohexane- d_{12} .

cyclohexane-d ₁₂	96.2334	[g/mol]									
purity	0.99										
xD	0.996										
M_{H}	84.1595	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	84.2334	[g/mol]		0.05	0.0001			0.01	0.001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂ρ/∂Β	$\partial \rho / \partial x$	∂ρ/∂xD	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
283.15	7.3253	0.903197	1.1905E-03	0.001075	0.702629	0.043316	0.047959	0.112626	0.113319	0.001139838	0.002234
288.15	7.3156	0.897821	1.2023E-03	0.001079	0.702045	0.04308	0.047983	0.111955	0.112645	0.001133122	0.002221
293.15	7.3058	0.892403	1.2158E-03	0.001085	0.701505	0.042844	0.04801	0.11128	0.111965	0.00112636	0.002208
298.15	7.296	0.88697	1.2267E-03	0.001088	0.700911	0.042605	0.048034	0.110602	0.111284	0.001119575	0.002194
303.15	7.2862	0.881522	1.2502E-03	0.001102	0.700345	0.042366	0.04806	0.109923	0.1106	0.0011128	0.002181
308.15	7.2764	0.875949	1.2575E-03	0.001102	0.699676	0.042114	0.048078	0.109228	0.109901	0.001105832	0.002167
313.15	7.2665	0.870507	1.2626E-03	0.001099	0.699154	0.041878	0.048108	0.108549	0.109218	0.001099027	0.002154
318.15	7.2566	0.864958	1.2948E-03	0.00112	0.698564	0.041633	0.048133	0.107857	0.108522	0.001092147	0.002141
323.15	7.2466	0.859308	1.3192E-03	0.001134	0.697937	0.041381	0.048156	0.107153	0.107813	0.001085126	0.002127
328.15	7.23667	0.853621	1.3375E-03	0.001142	0.697266	0.041124	0.048176	0.106444	0.107099	0.001078045	0.002113
333.15	7.2266	0.84789	1.3542E-03	0.001148	0.69662	0.040867	0.048198	0.105729	0.10638	0.001070906	0.002099
338.15	7.2166	0.842139	1.3820E-03	0.001164	0.695965	0.040608	0.04822	0.105012	0.105659	0.001063768	0.002085
343.15	7.2064	0.836251	1.4081E-03	0.001178	0.695337	0.040344	0.048244	0.104278	0.10492	0.001056457	0.002071

Table Y-8: Error analysis for dichloromethane-d₂.

dichloromethane- d_2	86.945	[g/mol]									
purity	1										
xD	0.99965										
$M_{ m H}$	84.933	[g/mol]		u(T)	u (τ)			u(x)	u(xD)		k
mass (im)	74.945	[g/mol]		0.05	0.0001			0.0001	0.00001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	∂ρ/∂τ	∂ρ/∂Α	∂ρ/∂Β	∂ρ/∂x	∂p/∂xD	u(ρ)	U(p)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.98399	1.38682	1.3380E-03	0.001856	0.765398	0.066391	0.047933	0.191407	0.032092	0.000185035	0.000363
283.15	7.96968	1.377542	1.3456E-03	0.001854	0.764437	0.065985	0.047959	0.190126	0.031878	0.000184406	0.000361
288.15	7.9553	1.368283	1.3576E-03	0.001858	0.763434	0.065571	0.047983	0.188848	0.031664	0.000183934	0.000361
293.15	7.9409	1.358965	1.3818E-03	0.001878	0.762488	0.065164	0.04801	0.187562	0.031448	0.000183911	0.00036
298.15	7.9263	1.349505	1.4214E-03	0.001918	0.761462	0.064742	0.048034	0.186256	0.031229	0.000184411	0.000361
303.15	7.9116	1.339782	1.4223E-03	0.001906	0.760459	0.064319	0.04806	0.184914	0.031004	0.000183563	0.00036
308.15	7.897	1.330448	1.4254E-03	0.001896	0.759351	0.063881	0.048078	0.183626	0.030788	0.000182797	0.000358
313.15	7.8822	1.320817	1.4582E-03	0.001926	0.758394	0.063465	0.048108	0.182297	0.030565	0.000183092	0.000359

dimethyl sulfoxide-d ₆	84.170	[g/mol]									
purity	0.9996										
xD	0.9993										
$M_{ m H}$	78.133	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	72.17	[g/mol]		0.05	0.0001			0.0001	0.0001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂ρ/∂Β	$\partial \rho / \partial x$	$\partial \rho / \partial x D$	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
298.15	7.7078	1.183751	9.2150E-04	0.001091	0.740471	0.05686	0.048034	0.168766	0.084903	0.000154741	0.000303
303.15	7.6983	1.178296	9.4020E-04	0.001108	0.739956	0.056629	0.04806	0.167988	0.084512	0.000154771	0.000303
308.15	7.6888	1.172672	9.3010E-04	0.001091	0.739331	0.05638	0.048078	0.167186	0.084109	0.00015418	0.000302
313.15	7.6794	1.167389	9.1680E-04	0.00107	0.738881	0.056161	0.048108	0.166433	0.08373	0.000153598	0.000301
318.15	7.67	1.16197	9.3650E-04	0.001088	0.738361	0.055929	0.048133	0.16566	0.083341	0.000153682	0.000301
323.15	7.6606	1.156507	9.5010E-04	0.001099	0.73781	0.055693	0.048156	0.164882	0.082949	0.000153645	0.000301
328.15	7.65126	1.150982	9.5550E-04	0.0011	0.737213	0.05545	0.048176	0.164094	0.082553	0.000153435	0.000301
333.15	7.6419	1.145509	9.6140E-04	0.001101	0.736653	0.055212	0.048198	0.163314	0.08216	0.000153255	0.0003
338.15	7.63255	1.139969	9.6380E-04	0.001099	0.736079	0.054969	0.04822	0.162524	0.081763	0.000153006	0.0003
343.15	7.6233	1.134522	9.6110E-04	0.00109	0.735563	0.054734	0.048244	0.161747	0.081372	0.000152679	0.000299
348.15	7.6141	1.129064	9.7700E-04	0.001103	0.735055	0.054499	0.048269	0.160969	0.080981	0.000152737	0.000299
353.15	7.6049	1.123491	9.7850E-04	0.001099	0.734516	0.054256	0.048292	0.160175	0.080581	0.000152496	0.000299
358.15	7.5958	1.118071	9.6710E-04	0.001081	0.734052	0.054025	0.04832	0.159402	0.080192	0.000152028	0.000298
363.15	7.5867	1.112678	9.6790E-04	0.001077	0.733649	0.053799	0.048351	0.158633	0.079806	0.000151824	0.000298
368.15	7.5776	1.107301	9.7110E-04	0.001075	0.73324	0.053574	0.048382	0.157866	0.07942	0.000151673	0.000297

Table Y-9: Error analysis for dimethyl sulfoxide-d₆.

Table Y-10: Error analysis for ethanol-d₆.

ethanol-d ₆	52.1054	[g/mol]									
purity	0.99										
xD	0.997										
$M_{ m H}$	46.0684	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	40.1054	[g/mol]		0.05	0.0001			0.01	0.001		1.96
Temperature	Period	Density	ITE	$\partial \rho / \partial T$	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂ρ/∂Β	∂p/∂x	∂ρ/∂xD	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.3371	0.910008	1.0490E-03	0.000955	0.703383	0.04362	0.047933	0.209577	0.105435	0.00210257	0.004121
283.15	7.3282	0.905235	1.0675E-03	0.000966	0.702907	0.043414	0.047959	0.208478	0.104882	0.002091581	0.004099
288.15	7.319195	0.900345	1.0823E-03	0.000974	0.70239	0.043201	0.047983	0.207352	0.104315	0.00208032	0.004077
293.15	7.3102	0.89549	1.0883E-03	0.000975	0.701928	0.042993	0.04801	0.206234	0.103753	0.002069133	0.004055
298.15	7.301175	0.890599	1.1042E-03	0.000983	0.701408	0.042779	0.048034	0.205107	0.103186	0.002057871	0.004033
303.15	7.2921	0.885656	1.1324E-03	0.001003	0.700913	0.042564	0.04806	0.203969	0.102613	0.002046506	0.004011
308.15	7.283	0.880569	1.1325E-03	0.000997	0.700311	0.042336	0.048078	0.202797	0.102024	0.002034777	0.003988
313.15	7.2739	0.875684	1.1283E-03	0.000988	0.699866	0.042127	0.048108	0.201672	0.101458	0.002023511	0.003966
318.15	7.2648	0.870689	1.1617E-03	0.001011	0.699354	0.041909	0.048133	0.200522	0.100879	0.002012034	0.003944
323.15	7.255565	0.865569	1.2036E-03	0.001042	0.6988	0.041682	0.048156	0.199343	0.100286	0.002000277	0.003921
328.15	7.2462	0.860271	1.2284E-03	0.001057	0.698185	0.041444	0.048176	0.198122	0.099672	0.001988092	0.003897
333.15	7.2368	0.855001	1.2409E-03	0.001061	0.697603	0.04121	0.048198	0.196909	0.099061	0.001975958	0.003873
338.15	7.2274	0.849661	1.2730E-03	0.001082	0.697007	0.04097	0.04822	0.195679	0.098443	0.001963687	0.003849
343.15	7.2178	0.844185	1.3033E-03	0.0011	0.696437	0.040727	0.048244	0.194418	0.097808	0.0019511	0.003824
348.15	7.2082	0.838658	1.3401E-03	0.001124	0.69587	0.040481	0.048269	0.193145	0.097168	0.001938407	0.003799
353.15	7.19848	0.832946	1.3716E-03	0.001142	0.695262	0.040225	0.048292	0.191829	0.096506	0.001925279	0.003774

Table Y-11: Error analysis for methanol-d₄.

methanol-d4	36.0665	[g/mol]									
purity	0.999										
xD	0.99981										
$M_{ m H}$	32.0419	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	24.0665	[g/mol]		0.05	0.0001			0.001	0.00001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	$\partial \rho / \partial \tau$	∂ρ/∂Α	∂ρ/∂Β	$\partial \rho / \partial x$	$\partial \rho / \partial x D$	u(ρ)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.3354	0.908813	1.1740E-03	0.001067	0.70322	0.043562	0.047933	0.302379	0.101413	0.000330765	0.000648
283.15	7.3257	0.903478	1.1778E-03	0.001064	0.702667	0.04333	0.047959	0.300604	0.100818	0.000328999	0.000645
288.15	7.3161	0.898172	1.1862E-03	0.001065	0.702093	0.043097	0.047983	0.298839	0.100225	0.000327279	0.000641
293.15	7.3064	0.892824	1.1996E-03	0.001071	0.701563	0.042865	0.04801	0.297059	0.099629	0.00032559	0.000638
298.15	7.2967	0.887461	1.2056E-03	0.00107	0.700978	0.042628	0.048034	0.295275	0.09903	0.000323843	0.000635
303.15	7.28706	0.882124	1.2257E-03	0.001081	0.700428	0.042395	0.04806	0.293499	0.098435	0.000322215	0.000632
308.15	7.2774	0.876649	1.2295E-03	0.001078	0.699772	0.042148	0.048078	0.291678	0.097824	0.000320418	0.000628
313.15	7.2677	0.871346	1.2375E-03	0.001078	0.699269	0.041919	0.048108	0.289913	0.097232	0.000318724	0.000625
318.15	7.2579	0.865866	1.2694E-03	0.001099	0.698689	0.041677	0.048133	0.28809	0.096621	0.000317147	0.000622
323.15	7.2481	0.860355	1.2992E-03	0.001118	0.698081	0.041431	0.048156	0.286256	0.096006	0.000315548	0.000618
328.15	7.2382	0.854688	1.3198E-03	0.001128	0.697414	0.041175	0.048176	0.284371	0.095373	0.000313828	0.000615
333.15	7.2283	0.849075	1.3386E-03	0.001137	0.696784	0.040924	0.048198	0.282503	0.094747	0.000312119	0.000612
338.15	7.2183	0.843322	1.3642E-03	0.00115	0.696129	0.040665	0.04822	0.280589	0.094105	0.000310417	0.000608

pyridine-d5	84.1307	[g/mol]									
purity	0.99^{1}										
xD	0.99										
$M_{ m H}$	79.0999	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	72.1307	[g/mol]		0.05	0.0001			0.01	0.01		1.96
Temperature	Period	Density	ITE	$\partial \rho / \partial T$	∂ρ/∂τ	∂ρ/∂Α	∂ρ/∂Β	∂ρ/∂x	∂ρ/∂xD	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.5522	1.063524	1.0118E-03	0.001076	0.724004	0.050978	0.047933	0.151696	0.063596	0.001651213	0.003236
283.15	7.5426	1.058143	1.0148E-03	0.001074	0.723472	0.050748	0.047959	0.150928	0.063274	0.001642891	0.00322
288.15	7.5331	1.052785	1.0139E-03	0.001067	0.722917	0.050515	0.047983	0.150164	0.062954	0.0016346	0.003204
293.15	7.5236	1.047468	1.0178E-03	0.001066	0.722418	0.050289	0.04801	0.149406	0.062636	0.001626381	0.003188
298.15	7.5141	1.042124	1.0265E-03	0.00107	0.721863	0.050057	0.048034	0.148644	0.062316	0.00161813	0.003172
303.15	7.5046	1.03677	1.0401E-03	0.001078	0.721338	0.049827	0.04806	0.14788	0.061996	0.001609874	0.003155
308.15	7.4952	1.03134	1.0372E-03	0.00107	0.720715	0.049585	0.048078	0.147105	0.061671	0.00160147	0.003139
313.15	7.4857	1.026073	1.0385E-03	0.001066	0.720244	0.049362	0.048108	0.146354	0.061357	0.001593331	0.003123
318.15	7.4762	1.020683	1.0597E-03	0.001082	0.719704	0.049129	0.048133	0.145585	0.061034	0.001585035	0.003107
323.15	7.4667	1.015257	1.0715E-03	0.001088	0.719135	0.048891	0.048156	0.144811	0.06071	0.001576666	0.00309
328.15	7.4573	1.009804	1.0817E-03	0.001092	0.718525	0.048648	0.048176	0.144034	0.060384	0.001568256	0.003074
333.15	7.44779	1.004334	1.0952E-03	0.0011	0.717942	0.048407	0.048198	0.143253	0.060057	0.001559824	0.003057
338.15	7.4383	0.998805	1.1066E-03	0.001105	0.717346	0.048162	0.04822	0.142465	0.059726	0.001551299	0.003041
343.15	7.4288	0.993281	1.1100E-03	0.001103	0.716796	0.04792	0.048244	0.141677	0.059396	0.001542769	0.003024
348.15	7.4194	0.987779	1.1250E-03	0.001111	0.716259	0.047679	0.048269	0.140892	0.059067	0.001534295	0.003007
353.15	7.41	0.982168	1.1356E-03	0.001115	0.715691	0.047431	0.048292	0.140092	0.058731	0.001525645	0.00299
358.15	7.4006	0.976626	1.1263E-03	0.0011	0.715188	0.04719	0.04832	0.139301	0.0584	0.001517066	0.002973
363.15	7.3913	0.971169	1.1498E-03	0.001117	0.714753	0.046957	0.048351	0.138523	0.058073	0.001508681	0.002957
368.15	7.38162	0.965459	1.1828E-03	0.001142	0.714276	0.046711	0.048382	0.137708	0.057732	0.001499921	0.00294

Table Y-12: Error analysis for pyridine-d₅ (purity of 99% was assumed).

MEAN 0.003089

¹estimate

tetrahydrofuran-d ₈	80.155	[g/mol]									
purity	0.99^{1}										
xD	0.9982										
M_{H}	72.1057	[g/mol]		u(T)	u(τ)			u(x)	u(xD)		k
mass (im)	68.155	[g/mol]		0.05	0.0001			0.01	0.0001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	∂ρ/∂τ	∂ρ/∂Α	∂ρ/∂Β	∂ρ/∂x	∂ρ/∂xD	u(ρ)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.4778	1.011463	1.1864E-03	0.0012	0.716871	0.048409	0.047933	0.151426	0.101573	0.001521068	0.002981
283.15	7.4673	1.005425	1.1981E-03	0.001205	0.716249	0.048148	0.047959	0.150522	0.100966	0.001512044	0.002964
288.15	7.4567	0.999353	1.2133E-03	0.001213	0.715585	0.047879	0.047983	0.149613	0.100357	0.001502978	0.002946
293.15	7.4461	0.993259	1.2263E-03	0.001218	0.714977	0.047615	0.04801	0.148701	0.099745	0.001493877	0.002928
298.15	7.435465	0.98713	1.2491E-03	0.001233	0.714309	0.047345	0.048034	0.147783	0.099129	0.001484744	0.00291
303.15	7.4248	0.98084	1.2821E-03	0.001258	0.713668	0.047075	0.04806	0.146841	0.098498	0.001475393	0.002892
308.15	7.4141	0.97475	1.2842E-03	0.001252	0.712917	0.04679	0.048078	0.14593	0.097886	0.001466276	0.002874
313.15	7.4033	0.968473	1.2860E-03	0.001245	0.712316	0.046523	0.048108	0.14499	0.097256	0.001456882	0.002855
318.15	7.392555	0.962201	1.3173E-03	0.001268	0.711652	0.046247	0.048133	0.144051	0.096626	0.001447558	0.002837
323.15	7.3817	0.955759	1.3391E-03	0.00128	0.710948	0.045964	0.048156	0.143087	0.095979	0.001437961	0.002818
328.15	7.37083	0.949366	1.3591E-03	0.00129	0.710193	0.045672	0.048176	0.14213	0.095337	0.001428432	0.0028
333.15	7.3599	0.942861	1.3772E-03	0.001299	0.709469	0.045384	0.048198	0.141156	0.094684	0.001418733	0.002781

Table Y-13: Error analysis for tetrahydrofuran-d $_8$ (purity of 99% was assumed).

¹estimate

Table Y-14: Error analysis for toluene-d₈.

toluene-d ₈	100.1877	[g/mol]									
purity	1										
xD	0.9980										
$M_{ m H}$	92.1384	[g/mol]		u (T)	u (τ)			u(x)	u(xD)		k
mass (im)	88.1877	[g/mol]		0.05	0.0001			0.0001	0.0001		1.96
Temperature	Period	Density	ITE	∂ρ/∂Τ	$\partial \rho / \partial \tau$	∂ρ/∂Α	$\partial \rho / \partial B$	∂p/∂x	$\partial \rho / \partial x D$	u(p)	U(ρ)
[K]	[τ]	[g/cm ³]	[K ⁻¹]		[sample]					[combined]	
278.15	7.40808	0.960176	1.0574E-03	0.001015	0.710187	0.046024	0.047933	0.115005	0.077143	0.000137125	0.000269
283.15	7.3988	0.955099	1.0618E-03	0.001014	0.709679	0.045806	0.047959	0.114397	0.076735	0.000136808	0.000268
288.15	7.3896	0.950035	1.0628E-03	0.00101	0.709146	0.045585	0.047983	0.113791	0.076328	0.00013644	0.000267
293.15	7.3804	0.945002	1.0618E-03	0.001003	0.708668	0.04537	0.04801	0.113188	0.075924	0.000136062	0.000267
298.15	7.37127	0.940000	1.0838E-03	0.001019	0.708142	0.045152	0.048034	0.112589	0.075522	0.00013609	0.000267
303.15	7.3619	0.934814	1.1110E-03	0.001039	0.707622	0.044927	0.04806	0.111967	0.075105	0.000136212	0.000267
308.15	7.3527	0.929614	1.1034E-03	0.001026	0.707013	0.044694	0.048078	0.111345	0.074687	0.000135711	0.000266
313.15	7.3434	0.924557	1.1018E-03	0.001019	0.706553	0.044479	0.048108	0.110739	0.074281	0.000135362	0.000265
318.15	7.33416	0.919428	1.1208E-03	0.00103	0.706031	0.044255	0.048133	0.110125	0.073869	0.000135365	0.000265
323.15	7.3249	0.914252	1.1530E-03	0.001054	0.705478	0.044027	0.048156	0.109505	0.073453	0.000135601	0.000266
328.15	7.3155	0.908886	1.1602E-03	0.001054	0.704862	0.043786	0.048176	0.108862	0.073022	0.000135378	0.000265
333.15	7.306285	0.903706	1.1596E-03	0.001048	0.704301	0.043557	0.048198	0.108242	0.072606	0.000135046	0.000265
338.15	7.297	0.898406	1.1726E-03	0.001053	0.703719	0.043321	0.04822	0.107607	0.07218	0.000134947	0.000264
343.15	7.2878	0.893171	1.1809E-03	0.001055	0.703191	0.043091	0.048244	0.10698	0.071759	0.000134784	0.000264
348.15	7.27856	0.887859	1.2181E-03	0.001082	0.702662	0.042856	0.048269	0.106343	0.071333	0.000135127	0.000265
353.15	7.2692	0.882356	1.2270E-03	0.001083	0.702092	0.042611	0.048292	0.105684	0.07089	0.000134954	0.000265
358.15	7.26001	0.877032	1.2238E-03	0.001073	0.701602	0.042378	0.04832	0.105047	0.070463	0.000134597	0.000264
363.15	7.25069	0.871623	1.2411E-03	0.001082	0.701156	0.042144	0.048351	0.104399	0.070028	0.000134604	0.000264
										MEAN	0.000266