Relation of Wertheim Association Constants to Concentration-based Equilibrium Constants for Mixtures with Chain-forming Components

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Abstract

Several association modeling approaches have been developed to accurately describe the properties of polar solutions. Chemical theory and Wertheim's perturbation theory are among the most popular of these and they have been shown to yield similar functional forms for the contributions of association to Helmholtz energy and activity coefficients. In this paper, we study Flory polymerization theory through the work of Campbell and elucidate its correlation to Wertheim's theory. A simple key relationship between the concentration-based equilibrium constant and Wertheim's association constant is developed for systems in which all associating components have one acceptor and one donor site. Algebraic and numerical proofs are given for the equivalence of Flory's polymerization theory and Wertheim's perturbation theory for pure fluids and mixtures. Additionally, a new generalized activity expression is developed for Wertheim's theory.

Keywords

Association, Chemical theory, Perturbation theory, Wertheim theory

1. Introduction

1.1. Motivation

As global demand for renewable chemicals and fuels increases, new pathways for their manufacture are being proposed. These projects include upgrading of natural oils, and fermentation of pyrolysis products to chemicals and fuels. The ubiquitous presence of polar components in biobased process streams complicates the design of industrial separation units. Traditional thermodynamic models, such as NRTL and UNIQUAC, are incapable of accurately representing liquid-liquid equilibria (LLE) and vapor-liquid-liquid equilibria (VLLE) in these systems without utilizing more parameters than can be determined with confidence of physical relevance [1].

The limitations of traditional models for polar systems are largely due to their crude representation of important molecular interactions; specifically, hydrogen bonding. Polar molecules hydrogen bond (or associate) with each other, forming clusters of chains and/or rings and causing large deviations from ideal behavior. These interactions are responsible for higher boiling points and enthalpies of vaporization of polar compounds compared to nonpolar molecules of comparable size. The extent and nature of association varies under different conditions including composition, temperature and pressure. Therefore, it is necessary for thermodynamic models to incorporate hydrogen bonding explicitly rather than lumping the contributions with nonpolar interactions.

1.2. Historical Perspective

Association models can be classified into three categories: chemical theories, lattice models and perturbation theories. Apelblat[2,3] presents a historical summary of the advancements made in association modeling from 1884 to 1984. Among the most noteworthy contributions is Dolezalek's[4] theory of representing a hydrogen bond as an equilibrium reaction governed by an equilibrium constant. The original theory, often called 'simple' or 'ideal' chemical theory, considers the true species formed through hydrogen bonding to otherwise behave ideally. In other words, physical interactions between the complexes in solution are ignored; a simplification that is difficult to justify and has proved erroneous for many systems especially in

modeling liquid-liquid immiscibility. The Dolezalek body of work was therefore enhanced by adding a ‘physical’ contribution such as NRTL[5] or UNIQUAC[6].

With chemical theory, several decisions must be made a priori regarding the species that exist in solution and the equilibrium constants for various hydrogen bonds. The continuous association model, also known as the Mecke-Kempton model, makes the simplification that the value of the equilibrium constant does not depend on the chain or ring size formed. While there has been some discussion on the contradiction of this assumption with spectroscopic evidence[7], it is often adopted as a first-order representation of the complexation in solution.

Lattice models represent the system as a lattice of empty and occupied sites and investigate the extent of association by quantifying bonds between adjacent occupied sites. Perhaps the most prominent lattice model is the one presented by Guggenheim[8] which accounts for nonrandomness in the solution. Hydrogen bonding has since been integrated into several lattice models[9–12].

Perturbation theories add the association to a nonassociating reference fluid. Gubbins[13] recently presented a review of work done in this area. Several perturbation theories[14–16] have been developed but the simplest and most popular is Wertheim’s theory[17–20], which is the basis of a number of equation of state (EOS) models including Elliott-Suresh-Donohue (ESD)[21,22], cubic plus association (CPA)[23,24] and the statistical associating fluid theory (SAFT) family of equations[25–30].

Numerous independent researchers [31–33] have compared association models. Economou and Donohue[31] found that for many systems, both chemical theory (using activity-based K_a) and Wertheim’s theory yield essentially the same functional form for the association contribution, despite differences in their origins and derivations. Wolbach and Sandler derived relations between K_a and Wertheim’s association constant and used quantum calculations to determine values of the Wertheim association constant for molecules with multiple sites[32,34]. Chapman *et al.*[25] noticed the similarity in polymer distributions using Wertheim’s theory in the SAFT model compared to Flory’s polymerization theory (using concentration-based K_C). Campbell rearranged the Flory polymerization theory and was able to find a similar algebraic form but the terms were not identical [35]. Thus, the analytical equivalence of the Wertheim theory and Flory’s polymerization theory has not yet been proven. In this work, we compare the two

approaches for systems of chain-forming species in which the associating components each have an acceptor site and a donor site to contribute to association. Examples of these systems include pure alcohols, alcohol + inerts and alcohol + alcohol mixtures. We also provide algebraic and numerical proofs of the equivalence of Flory’s theory and Wertheim’s theory when the packing factor is universal and the excess volume is zero.

2. Theory and Analysis

A nonideal system’s behavior is described using either deviations from ideal gas mixtures using fugacity coefficients, or deviations from ideal solutions using activity coefficients as discussed by Prausnitz and Tavares[36]. Fugacity coefficients are readily calculated with an equation of state through the compressibility factor, Z . It is common practice to separate contributions to Z according to the nature of the nonideality causing the deviations:

$$Z - Z^{ig} = Z - 1 = Z^{rep} + Z^{att} + Z^{assoc} \quad 1$$

where Z^{rep} and Z^{att} represent effects of the repulsive and attractive forces and Z^{assoc} accounts for hydrogen bonding between molecules. Contributions to the Helmholtz energy departure at fixed T and V are correspondingly:

$$(A - A^{ig})_{T,V} = A^{rep} + A^{att} + A^{assoc} \quad 2$$

In a model such as the SAFT EOS, a *bond* term is added to both $Z - Z^{ig}$ and $(A - A^{ig})_{T,V}$. An alternative approach is to consider the excess Gibbs energy (G^E), related directly to the activity coefficient, γ , of each component and separate perturbations according to their sources. Deviations caused by differences in the size and shapes of molecules are accounted for by an entropic combinatorial contribution which ignores all attractive interactions and is the only term remaining at infinitely high temperatures. The association contribution represents nonidealities due to hydrogen bonding and the residual term accounts for other interactions that are not as well-understood and typically includes adjustable parameters. Combining all the contributions yields the activity coefficient:

$$\ln \gamma = \ln \gamma^{comb} + \ln \gamma^{res} + \ln \gamma^{assoc} \quad 3$$

The focus of this work is the γ^{assoc} term. We begin by introducing the nomenclature used to describe the apparent and true concentrations in associating solutions. Here, the term ‘apparent’

is used to denote ‘stoichiometric’ or ‘superficial’ species in a mixture. The speciation that occurs in solution results in ‘true’ species, which are model-dependent. For example, in a pure alcohol, the apparent mole fraction of alcohol is unity, but the solution can also be described in terms of concentrations of true monomers, dimers, trimers and so on. Notations vary in literature, and the distinction between apparent and true mole is not always clear. In this work, a subscript T is used to denote the true quantities. Every solution will contain some ‘free’ or ‘unassociated’ molecular species which is described as monomer and denoted with the subscript M, which is understood to be a ‘true’ quantity.

2.1. Association term – Wertheim’s Theory

Wertheim’s perturbation theory calculates the probabilities of various site interactions that result in the formation of a complex. Each molecule type in solution may have any number of acceptor (A) and/or donor (D) sites and bonding between each pair is governed by an association strength parameter, $\Delta^{A_i D_j}$. Notation for the acceptor and donor sites subscripts differs in literature, thus comparisons must be done carefully. In early literature, the i and j denote the host component. However, as noted by Michelsen[37], the summations are greatly simplified by indexing the sites rather than the site hosts because site hosts can have more than one type of each site. We write summations over sites in this work. The acceptor and donor terminology allows the model to lend itself to any type of complexation, including covalent bonding. Depending on the number and types of sites attributed to a molecule of a component, different association schemes can be used as reviewed by Kontogeorgis and Folas[38]. Alcohols, for example, are commonly modeled using the 2B association scheme which corresponds to having one acceptor and one donor site per molecule (Figure 1). We follow this convention in the present work. A detailed explanation of the assumptions and implications of Wertheim’s theory is given by Chapman[25].

Figure 1: Hydrogen bonded oligomers with two bonding sites per molecule. The acceptor and donor sites are labeled on the leftmost molecule.

The Helmholtz energy departure at fixed temperature and volume due to association derived from Wertheim's theory is implemented in SAFT, ESD and CPA as:

$$\frac{(\underline{A} - \underline{A}^{ig})_{T,V}^{assoc}}{RT} = \sum_{\substack{\text{all site} \\ \text{types } B_i}} n_{0,B_i \text{ host}} N_{B_i} \left(\ln X^{B_i} - \frac{X^{B_i}}{2} + \frac{1}{2} \right) \quad 4$$

where B_i is generic notation for an acceptor, donor, or bivalent (acceptor/donor) site, $n_{0,B_i \text{ host}}$ is the apparent number of moles of the component hosting site B_i , N_{B_i} is the number of identical sites of type B on the host. The term $X^{B_i} = n^{B_i,free} / n^{B_i,total}$ is the fraction of sites of type B that

$$X^{B_i} = \left(1 + \sum_{\substack{\text{mating} \\ \text{sites } E_j}} x_{E_j \text{ host}} N_{E_j} X^{E_j} \rho \Delta^{B_i E_j} \right)^{-1} \quad 5$$

remain nonbonded at equilibrium, calculated through the balance on the probability of binding:

where E_j is generic notation for a site which mates with site B_i , $x_{E_j \text{ host}}$ denotes the component apparent mole fraction of the site E_j host and $\Delta^{B_i E_j}$ is an association strength parameter between site i of type B and site j of type E . In this work ρ is molar density and thus $\Delta^{B_i E_j}$ has units of molar volume.

With chain-forming components, when each hydrogen bond formed, one acceptor (A) and one donor (D) site are consumed. Thus, in a pure fluid with the 2B association scheme, the fraction of molecules nonbonded at each acceptor site is the same as those free at the donor sites.

$$X^{A_i} = X^{D_i} \quad 6$$

Therefore, numbering acceptor and donor sites on the same host using the same subscripts,

For mixtures of associating species with the 2B model, Eq. (6) is contingent on $\Delta^{A_i D_j} = \Delta^{D_j A_i}$, which is true when certain cross-coefficients equations are used. The reader should recognize that site indexes i and j match the host indexes for the 2B model indexing discussed here. The

combining rules we use to calculate cross-coefficients are consistent with Eq. (6) and are discussed in Section 2.6.

To derive a formula for γ_i^{assoc} using Wertheim's theory, we consider the work of Michelsen and Hendriks[39] in deriving a generalized function which reduces to Eq. (4) when maximized and results in the association contribution to chemical potential. This approach is extended to calculate the fugacity coefficient of each component in the mixture in Elliott and Lira[40] (Important corrections are made in the errata[41]). Calculating the activity coefficient from the fugacity coefficient for a given component (Appendix A) for the case of conventional mixing

$$\ln \gamma_k^{assoc} = \sum_{\substack{\text{sites } B_i \\ \text{on } k}} N_{B_i} \left[\ln \left(\frac{X^{B_i}}{X^{B_i,0}} \right) - \frac{1}{2} (1 - X^{B_i,0}) \right] + \frac{1}{2} \frac{\rho}{\rho_k} \sum_{\substack{\text{all} \\ \text{sites } B_i}} x_{B_i \text{ host}} N_{B_i} (1 - X^{B_i}) \quad 7$$

rules, van der Waals Z^{rep} , a universal packing factor, and no excess volume yields:

where X^{B_i} is given by Eq. (5), and $X^{B_i,0}$ represents the fraction of sites free when the host for the site is pure. These constraints are identical to those used in Flory's polymerization theory. This activity coefficient equation is easier to apply than the equation of Fu and Sandler [42] because derivatives of X^{B_i} are not needed. A more general expression is derived by substituting Eq. (A10) of Appendix A into Eq. (A14).

2.2. Flory's Concentration-based Equilibrium Constant

In chemical theory, the energetic effects associated with hydrogen bonding are embedded within an equilibrium constant, K . This parameter could be based on the concentrations (K_C), mole fractions (K_x) or activities (K_a) of the products and reactants. Flory's well-known work on oligomer modeling used a concentration-based equilibrium constant and provides a discussion on the inconsistency of K_x with statistical mechanics[43]. Flory's original form of K_C and variations of it have since been applied in several publications. Chemical kinetics are commonly described in practice using concentrations, and for reversible reactions are consistent with K_C , which is frequently assumed to be independent of composition. This simplification is valid only when noncombinatorial effects are invariant with composition. For pure alcohols or alcohol-inert systems, some of the variations of K_C for the formation of a chain of size $i+1$ from a complex of size i and a monomer are shown in Table 1.

Table 1: Variations of the concentration based equilibrium constant used in literature. The subscript numeral on K_C differentiates between models.

K_C	References	Eqn
$K_{C1} = \frac{C_{T,i+1}}{C_{T,i}C_M} = \frac{x_{T,i+1}}{x_{T,i}x_M} \frac{1}{\rho_T}$	Flory[43], Renon and Prausnitz[44,45] (eqn. 2)	8
$K_{C2} = \frac{\Phi_{T,i+1}}{\Phi_{T,i}\Phi_M} \frac{i}{i+1} = \frac{x_{T,i+1}}{x_{T,i}x_M} \frac{\rho_A}{\rho_T} = K_{C1}\rho_A$	Flory[43], Nagata[46], Nath and Bender[47], Renon and Prausnitz[44,45] (eqn. 1)	9
$K_{C3} = \frac{\Phi_{T,i+1}}{\Phi_{T,i}\Phi_M} = \frac{x_{T,i+1}}{x_{T,i}x_M} \frac{\rho_A}{\rho_T} \frac{i+1}{i} = K_{C1}\rho_A \frac{i+1}{i}$	Nagata[48]	10
$K_{C4} = \frac{\Phi_{T,i+1}}{\Phi_{T,i}\Phi_M} \frac{ir_A}{i+1} = \frac{x_{T,i+1}}{x_{T,i}x_{T,M}} \frac{\rho^{ref}}{\rho_T} = K_{C1}\rho^{ref}$	Brandani[49,50], Campbell[35]	11

Here, ρ_A represents the pure alcohol molar density. Φ_i is the volume fraction. The variable $\rho_T = n_T/V$, is the true molar density which is smaller than the apparent molar density $\rho = n_0/V$, because bonding reduces the number of moles, $n_T \leq n_0$. In Eq. (11), r_A is a measure of the molecular size of the associating species relative to some reference ($r_A = \rho^{ref}/\rho_A$), chosen by Campbell to be the molar density of methanol at 303.15 K.

2.3. Relationship between K_a , K_C and Δ

To understand the relationship between K_a and K_C , we use equations for a pure component with one acceptor and one donor. These are later extended to mixtures using combining rules in section 2.6. We begin with the thermodynamic definition of the activity based equilibrium constant:

$$K_a = \frac{x_{T,i+1}}{x_{T,i}x_{T,M}} \frac{\hat{\phi}_{i+1}}{\hat{\phi}_i\hat{\phi}_M} \frac{P^\circ}{P} \quad 12$$

where P° is the standard state pressure, typically 1 bar. Inserting Eq. (8) into Eq. (12) yields:

$$K_a = K_{C1}\rho_T \frac{\hat{\phi}_{i+1}}{\hat{\phi}_i\hat{\phi}_M} \frac{P^\circ}{P} \quad 13$$

Economou and Donohue[31] discuss different conventions used for equilibrium constants. By comparing the monomer fraction derived from various models, they conclude that Δ must be

proportional to K_a at the same T . Wolbach and Sandler[32] explore the relationship further and

$$\Delta^{\text{ig}} = f K_a \frac{RT}{P^\circ} \quad 14$$

show that in the case where the vapor phase is ideal:

where f is a constant that depends on the association scheme used to model the component in solution. For liquid components modeled with 2B, Eq. (14) becomes:

$$\Delta = e^g K_a \frac{RT}{P^\circ} \quad 15$$

where g is a function that depends on the equation of state used to calculate the fugacity coefficient ratio. The value of this function depends on the mixing rules used for the true solution of monomers and oligomers. The most accepted and widely used combining rules for complexes, introduced by Heidemann and Prausnitz[51], are:

$$a_i = i^2 a_M \quad 16$$

$$b_i = i b_M \quad 17$$

where a_M and b_M are the interaction and size parameters for monomers respectively. Heidemann and Prausnitz[51] show that when Eqs. (16) and (17) and the Lorentz-Berthelot mixing rules

$$g = \int_0^\eta \frac{Z^{\text{rep}}}{\eta} d\eta \quad 18$$

($b = \sum_j x_j b_j$, $a = \sum_j \sum_k x_j x_k a_{jk}$) are followed, then g is given by Eq. (18)

From this equation, an important observation can be made. While K_a depends only on temperature, Wertheim's association strength Δ of Eq. (15) is also a function of the density of the solution due to the g function. Kontogeorgis and Folas[38] summarized the assumptions taken in various models in literature and the resulting forms of g . When the van der Waals repulsive term is used, Eq. (18) gives the radial distribution function at contact distance, $g(\sigma)$. Moreover, applying the combining rules (Eqs. (16) and (17)) to the van der Waals equation for the component fugacity coefficients provides a useful relationship between the fugacity coefficient and true compressibility factor as shown in Appendix B. Calculating the ratio of the fugacity

coefficients for the reaction of a complex of size i and a monomer to form a complex of size $i+1$ yields:

$$\ln \left(\frac{\hat{\phi}_i \hat{\phi}_M}{\hat{\phi}_{i+1}} \right) = g(\sigma) - \ln Z_T \quad 19$$

or

$$e^{g(\sigma)} = \frac{PV}{n_T RT} \frac{\hat{\phi}_i \hat{\phi}_M}{\hat{\phi}_{i+1}} \quad 20$$

Substituting Eq. (20) into Eq. (15), then converting to apparent density and inserting Eq. (13):

$$\Delta = \frac{PV}{P^\circ n_T} \frac{\hat{\phi}_i \hat{\phi}_M}{\hat{\phi}_{i+1}} K_a = \frac{PK_a}{P^\circ \rho_0} \frac{\hat{\phi}_i \hat{\phi}_M}{\hat{\phi}_{i+1}} \frac{n_0}{n_T} = \frac{K_{C1} \rho_T}{\rho_0} \frac{n_0}{n_T} \quad 21$$

Recognizing that $\rho_T/\rho_0 = (n_T/V)/(n_0/V) = n_T/n_0$ yields a remarkably simple Δ - K_C relationship for pure fluids:

$$\Delta = K_{C1} \quad 22$$

This result is intuitive considering the conclusions arrived at by several investigators[31,33,39] on the mathematical similarity of chemical and Wertheim's theories. However, it is powerful in that it allows one to use and compare both association models with ease.

2.4. Association term – Campbell's Chemical Theory Model

Pradhan *et al.*[52] developed a chemical theory model by integrating an equilibrium constant into the Flory-Huggins (FH) theory. Campbell[35] extended the expression to systems containing any number of alcohols. In this section, we clarify the relationship between this set of equations and other association models.

$$\ln \gamma_i^{chem} = \ln \left(\frac{C'_{M_i}}{x_i C'^0_{M_i}} \right) - r_i (\Psi - \Psi_i^0) \quad 23$$

Following Flory[43], Campbell writes:

where C'_{M_i} and $C'^0_{M_i}$ are the dimensionless true monomer concentration of component i in a mixture and at purity, respectively. All concentrations, C' , are made dimensionless by dividing

by the liquid density of methanol at 303.15. Ψ is the total molar concentration of the true

$$\Psi = \sum_i \Psi_i; \quad \Psi_i = \frac{C'_i}{1 + \sum_j K_{C4,ji} \Psi_j} \quad 24$$

complexes in solution which Campbell shows is given by:

where the summations are over apparent species and C'_i is the apparent dimensionless concentration of component i . As shown in Appendix C, Campbell's Ψ_i can be recognized as the total molar concentration of species with a free end group i .

The Flory concentration-based $K_{C4,ji} = C'_{T(j,n+1)} / (C'_{T(i,n)} C'_{T(j,1)})$ is the equilibrium constant for the association between a chain of length n with a nonbonded acceptor i forming a bond with monomer j donor, resulting in a chain of length $n + 1$ with a nonbonded j acceptor end. Campbell does not discuss acceptors or donors, but the nomenclature helps clarify how, when the alcohol monomer donor bonds to an end of a chain, it can still participate through its free acceptor. Note that the nomenclature for acceptors and donors could be flipped without changing the balances. Campbell provides mathematical derivations for Eqs. (23) and (24). The free end on a chain could be an acceptor or a donor. Considering the end to be an acceptor, Ψ_i represents the dimensionless molar concentration of nonbonded acceptors of type i . Recognizing that, because each alcohol molecule possesses one acceptor site, the dimensionless apparent molar concentration of all acceptors on component i in solution is equal to C'_i . Therefore, the fraction of

$$\frac{\Psi_i}{C'_i} = \frac{n^{A_i}}{n^{A_i,T}} = X^{A_i} \quad 25$$

unbonded acceptors is

or $\Psi_i = C'_i X^{A_i}$. Substituting the dimensionless concentration in terms of molar densities $C'_i =$

$$\Psi_i = x_i \rho X^{A_i} / \rho^{ref} \quad 26$$

$\Phi_i \rho_i / \rho^{ref} = x_i \rho / \rho^{ref}$, we find that:

Therefore, $\sum_j K_{Cji} \Psi_j$ can be written as $\sum_j x_j \rho K_{C4,ji} X^{Dj} / \rho^{ref}$. Simple manipulation will show that the right expression of Eq. (24) is the same as Eq. (5).

2.5. Algebraic Equivalence of Chemical and Wertheim's Theory

$$\begin{aligned} \ln \gamma_1^{assoc} &= 2 \ln \left(\frac{X^A}{X^{A,0}} \right) - (1 - X^{A,0}) + \frac{\rho}{\rho_1} x_1 (1 - X^A) \\ &= 2 \ln \frac{X^A}{X^{A,0}} + X^{A,0} - (1 - \Phi_1) - X^A \Phi_1 \end{aligned} \quad 27$$

$$\ln \gamma_2^{assoc} = \frac{\rho}{\rho_2} x_1 (1 - X^A) = \frac{\Phi_2}{x_2} x_1 (1 - X^A) \quad 28$$

For a binary alcohol (1) – inert (2) system, Wertheim's theory (Eq. (7)) gives:

For the same system, we begin the analysis of Campbell's model by calculating Ψ and Ψ_i^0 by combining Eqs. (24) and (26):

$$\Psi = \Psi_1 + \Psi_2 = \frac{x_1 \rho X^A}{\rho^{ref}} + \frac{x_2 \rho}{\rho^{ref}} \quad 29$$

$$\Psi_1^0 = \frac{\rho_1 X^{A,0}}{\rho^{ref}}; \quad \Psi_2^0 = \frac{\rho_2}{\rho^{ref}} \quad 30$$

Next, we calculate the values of C'_{T,M_i} and C'^0_{T,M_i} . Campbell provides the relationship between the concentration of monomers ending with group i and C'_i given as $C'_{T,M_i} = \Psi_i^2 / C'_i$. Substituting into this equation with the definition of C'_i and Eq. (28), we find for both components in the mixture and at purity:

$$C'_{T,M_1} = \frac{x_1 \rho}{\rho^{ref}} (X^A)^2; \quad C'_{T,M_2} = \frac{x_2 \rho}{\rho^{ref}} \quad 31$$

$$C'^0_{T,M_1} = \frac{\rho_1}{\rho^{ref}} (X^{A,0})^2; \quad C'^0_{T,M_2} = \frac{\rho_2}{\rho^{ref}} \quad 32$$

Therefore, by combining Eqs. (29-32), Eq. (23) for the alcohol becomes:

$$\ln \gamma_1^{chem} = 2 \ln \frac{X^A}{X^{A,0}} + \ln \left(\frac{\Phi_1}{x_1} \right) - X^A \Phi_1 - \frac{\Phi_1}{x_1} + \Phi_1 + X^{A,0} \quad 33$$

Adding and subtracting 1, and rearranging yields:

$$\begin{aligned}\ln \gamma_1^{chem} &= 2 \ln \frac{X^A}{X^{A,0}} + X^{A,0} - (1 - \Phi_1) - X^A \Phi_1 + \ln \left(\frac{\Phi_1}{x_1} \right) + 1 - \frac{\Phi_1}{x_1} \\ &= \ln \gamma_1^{assoc} + \ln \gamma_1^{Flory}\end{aligned}\quad 34$$

where Flory's equation[43] for the combinatorial contribution to activity coefficients is

$$\ln \gamma_i^{Flory} = \ln \left(\frac{\Phi_i}{x_i} \right) + 1 - \frac{\Phi_i}{x_i} \quad 35$$

Similarly, rearranging Eq. (23) and substituting Eqs. (29-32) for the inert solvent gives:

$$\ln \gamma_2^{chem} = \frac{x_1 \rho}{\rho_2} (1 - X^A) + \ln \left(\frac{\Phi_2}{x_2} \right) + 1 - \frac{\Phi_2}{x_2} = \ln \gamma_2^{assoc} + \ln \gamma_2^{Flory} \quad 36$$

Thus, this provides analytical proof that Campbell's chemical theory incorporates combinatorial effects through Flory's equation. Consequently, when Wertheim's theory is compared to Campbell's model, the Flory term must be added separately. When calculating activity

$$\ln \gamma_i^{chem} = \ln \gamma_i^{assoc} + \ln \gamma_i^{Flory} \quad 37$$

coefficients using Campbell's chemical theory, the combinatorial term is inherently included.

2.6. Calculating Association Parameters

To clarify the comparison further, we provide some numerical calculations. Early work done in determining K_C for binary alcohol-inert systems used data reduction of mixture data to fit association constants[44,45]. Commonly, the value of K_C is assumed to be independent of solvent species or concentration. Therefore, models based only on the properties of the pure associating compound were developed. Nath and Bender[47] based K_C on the temperature and enthalpy of vaporization at the normal boiling point of the alcohol. Lobien[53] calculated smaller K_C values than others using limiting activity coefficient data. Because these approaches differ considerably, there is significant scatter in the resulting K_C values for the same alcohol [47]. For CPA and SAFT, the $\Delta^{A_i D_j}$ values are typically determined by fitting density and vapor pressure[23,25,54].

In this work, to provide numerical calculations, we follow the approach outlined by Nagata[46] in applying the Brandani[49]'s work. The model essentially assumes that the only differences between the vapor pressure of an alcohol and that of a nonassociating compound with an

identical molecular weight and chemical formula, i.e. its homomorph, are the consequences of hydrogen bonding. Therefore, K_C is determined by matching the two vapor pressures through Eq. (38).

$$P_A^{vap} = \gamma_M^0 x_M^0 P_h^{vap} \exp \left(\frac{(P_A^{vap} - P_h^{vap})(V_A^L - B_A^{free})}{RT} \right) \quad 38$$

where B_A^{free} is the free contribution to the second virial coefficient evaluated using Hayden and O'Connell's calculations[55] and γ_{AM}^0 is the activity coefficient of the alcohol monomer in pure alcohol as given by Flory's equation.

The volume and mole fractions of monomer in pure alcohol are calculated as[46]:

$$\Phi_M^0 = \frac{1 + 2K_{C2} - \sqrt{1 + 4K_{C2}}}{2K_{C2}^2} \quad 39$$

$$x_M^0 = 1 - K_{C2} \Phi_M^0 \quad 40$$

Ethers were selected as homomorphs for alcohols and their vapor pressures were determined using Ambrose's[56] correlation with the same n^* (effective number of carbon atoms in the ether homomorph) values as Nagata. Our resulting values of K_{C2} are given in Table 2.

Table 2: Equilibrium constant for primary alcohols at 50 °C

Alcohol	K_{C2}	$K_{C1} = \Delta$
Methanol	111.0	4549
Ethanol	81.48	4803
1-Propanol	71.27	5381
1-Butanol	69.88	6458
1-Pentanol	57.09	6233

We have refitted the K_{C2} values to be consistent with all of our physical properties. We assume Nagata's[46] values for the enthalpy for the formation of a hydrogen bond.

To extend the analysis to alcohol mixtures, the cross-association parameters for dissimilar components are related through combining rules. Common combining rules that have been developed and tested[22,23,27,34,57–59] are variations of an arithmetic or geometric mean of the pure components' association energy and volume parameters. Kontogeorgis[38] outlines a number of these and provides a brief summary of work done in identifying the most accurate rules for various classes of mixtures. We find that Flory's polymerization theory and Wertheim's perturbation theory yield identical results for alcohols described with a 2B model, regardless of the combining rules used if Eq. (22) is maintained for the cross coefficients. Therefore, further

exploration of the effect of the combining rules lies beyond the scope and intentions of this work and for alcohol mixtures, we use Suresh and Elliott's[22] combining rule given by:

$$\Delta^{A_i B_j} = \Delta^{A_j B_i} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}} \quad 41$$

2.7. Numerical Equivalence of Chemical and Wertheim's Theory

We implement the abovementioned approaches to provide numerical evidence for the equivalence of chemical theory and Wertheim's theory. Within the constraints discussed, we find that the two approaches produce exactly the same results for systems in which the associating components can be described by the 2B association scheme. This is illustrated in Table 3 for two alcohol-inert systems at 30 and 80 mol% of alcohol and one alcohol-alcohol system at 30 mol% of methanol. Both theories yield the same monomer fractions and activity coefficients.

Table 3: Calculated parameters and intermediate values for Flory and Wertheim's theories for three systems. The reference density of methanol used for Campbell's theory calculations is 0.02440 mol/cm³. For methanol + ethanol, the cross coefficient is $\Delta^{A_1 D_2} = \Delta^{A_2 D_1} = 2559 \text{ cm}^3/\text{mol}$ or $K_{C4,ij} = 62.44$

System		Ethanol (1) + <i>n</i> -heptane (2)		1-Pentanol (1) + <i>n</i> -heptane (2)		Methanol (1) + Ethanol (2)	
x_1		0.3	0.8	0.3	0.8	0.3	
$T(K)$		344.9	344.7	368.4	383.1	347.0	
Component i		1	1	1	1	1	2
Campbell's Chemical Theory	K_{C4}	67.37	67.65	53.60	40.30	60.76	64.16
	Ψ	0.2680	0.1790	0.2427	0.1419	0.1025	
	Ψ_i^0	0.0944	0.0942	0.0749	0.0849	0.1203	0.0966
	$C'_{i,M}$	0.0101	0.0123	0.0119	0.0184	0.0043	0.0095
	$C'^0_{i,M}$	0.0128	0.0128	0.0149	0.0192	0.0145	0.0134
	$x_M \frac{n_0}{n_T}$	0.0301	0.0230	0.0396	0.0527	0.0056	0.0124
	$\ln \gamma_i^{chem}$	0.7195	0.06100	0.5280	0.03109	-0.002853	-0.0004456
Wertheim's Theory	$\Delta^{A_i D_i}$ (cm ³ /mol)	2761	2773	2197	1652	2490	2629
	$X^{A_i} = X^{D_i}$	0.3167	0.1696	0.3633	0.2566	0.1361	0.1330

$x_M \frac{n_0}{n_T}$	0.0301	0.0230	0.0396	0.0527	0.0056	0.0124
$\ln \gamma_i^{assoc}$	0.9281	0.09320	0.5513	0.03344	0.02999	0.004305
$\ln \gamma_i^{Flory}$	-0.2086	-0.03220	-0.02337	-0.002351	-0.03285	-0.004751
$\ln \gamma_i^{chem}$	0.7195	0.06100	0.5280	0.03109	-0.0028533	-0.0004455

These results prove that Campbell’s observation of the similarities between his association model and Wertheim’s perturbation theory are justified. Indeed, when combinatorial effects are added to the perturbation theory and the correct relationship between the association parameters of the two models is implemented, their mathematical forms become identical. Chapman’s recognition that Wertheim’s model gives the same distribution as Flory’s model is also consistent with this work. Future work in this area will look at extending the analysis to components with multiple acceptors and donors.

3. Conclusions

In this work, we outline derivations for Wertheim’s perturbation theory’s activity coefficient model and chemical theory and compare the two models. The focus is for the 2B scheme where each associating component has at one acceptor and one donor site per molecule such as alcohol-inert and alcohol-alcohol mixtures. In these cases, the association strength $\Delta^{A_i B_j}$ in Wertheim’s theory is found to be equal to the concentration based equilibrium constant K_{C1} used in Flory’s polymerization theory. This elucidates the relationship between the two association models. Furthermore, we consider Campbell’s implementation of chemical theory and show that the activity coefficient model is the sum of Flory’s combinatorial term, calculated on a superficial basis, and the association contribution calculated with Wertheim’s perturbation theory. The similarities drawn by Campbell between his theory and Wertheim’s theory are therefore consistent with this work. The correlation between the association models also supports Chapman’s understanding that the species distribution predicted by Flory’s and Wertheim’s models are identical. Finally, we provide in Eq. (7) an activity coefficient equation based on Wertheim’s theory useful for common situations when the packing factor is universal and excess volume is zero. In Eqs. (A10) and (A14) we provide a new generalized expression for activity coefficients.

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List of Symbols

a	interaction parameter of mixture
a_i	interaction parameter of species i
a_{ij}	interaction parameter between species i and j
A	Helmholtz energy
b	van der Waal size parameter of mixture
b_i	van der Waal size parameter of species i
B^{free}	free contribution to the second virial coefficient
C_i	concentration of component i (apparent unless accompanied by subscript T)
f	constant in Eq. (14)
g	function defined by Eq. (18)
G	Gibbs energy
h	function defined by Eq.(A1)
K	equilibrium constant
n	number of moles
$n^{B_i,free}$	number of nonbonded sites of type B_i
$n^{B_i,total}$	total number of sites of type B_i in solution
n^*	effective number of carbon atoms in an ether homomorph molecule
$N_{B,i}$	number of sites identical to site i of type B
P	pressure
P_i^{vap}	vapor pressure of component i
r_i	ratio of ρ of methanol at 303.15 K and ρ_i
R	universal gas constant
T	temperature
V_i	molar volume of pure component i
V	volume
x_i	liquid mole fraction of component i (apparent unless accompanied by subscript T)
X^{B_i}	fraction of sites identical to site i of type B that remain nonbonded at equilibrium
Z	compressibility factor

Greek Letters

$\alpha_{j,i}$	function defined by Eq. (C2)
γ	activity coefficient
Δ	Wertheim's association strength
η	packing fraction
ρ	molar density (apparent unless accompanied by subscript T)
σ	contact distance
φ_i	fugacity coefficient of pure component i
Φ_i	volume fraction of component or species i (apparent unless accompanied by subscript T)
Ψ	total true dimensionless concentration of complexes (Campbell's work)
Ψ_i	true dimensionless concentration of all chains that end in i (Campbell's work)

Subscripts

O	pertaining to apparent species
a	activity based
A	pertaining to the alcohol
C	concentration based
D	dimer
h	hypothetical fluid in Brandani's work
$host$	pertaining to component hosting the site
M	monomer
T	pertaining to true species
x	mole fraction based

Superscripts

$'$	Dimensionless (used for Campbell's concentration)
$^\circ$	standard state property
O	at purity
$assoc$	association (Wertheim's) contribution
$attr$	attractive contribution
$B_i E_j$	interaction between site i of type B and site j of type E

<i>chem</i>	chemical theory
<i>comb</i>	combinatorial contribution
<i>E</i>	excess property
<i>Flory</i>	Flory's theory
<i>ig</i>	ideal gas
<i>L</i>	pertaining to a liquid
<i>ref</i>	pertaining to a reference state
<i>rep</i>	repulsive contribution
<i>res</i>	residual contribution

Special notation

<u> </u> as in $\underline{A}$	extensive property
$\overline{\quad}$ as in $\overline{V}$	partial molar property
$\hat{\quad}$ as in $\hat{\phi}$	property of component in a mixture

Appendix A

Following Michelsen and Hendricks[39] and to abbreviate notation, we define, at equilibrium,

$$h = \sum_{\substack{\text{all site} \\ \text{types } B_i}} x_{B_i \text{ host}} N_{B_i} (1 - X^{B_i}) \quad \text{A1}$$

Elliott and Lira[40] show that:

$$Z^{assoc} = -0.5 \left(1 + \left(\frac{\partial \ln g}{\partial \ln \eta_P} \right)_{T,n} \right) h \quad \text{A2}$$

$$\ln \hat{\phi}_k^{assoc} = \sum_{\substack{\text{sites } B_i \\ \text{only on } k}} N_{B_i} \ln X^{B_i} - 0.5 n_0 \left(\frac{\partial \ln g}{\partial n_k} \right)_{T, \underline{V}, n_{j \neq k}} h \quad \text{A3}$$

We will use these equations to calculate and simplify the equation for γ^{assoc} . By definition, Helmholtz energy is a natural function of temperature and volume:

$$\underline{A}(\underline{V}, \{n\}, T) \quad \text{A4}$$

For an activity coefficient, we need a derivative of Helmholtz energy at constant T and P [42]. At constant T ,

$$d\underline{A} = \left(\frac{\partial \underline{A}}{\partial \underline{V}} \right)_{T,n} d\underline{V} + \sum_k \left(\frac{\partial \underline{A}}{\partial n_k} \right)_{T, \underline{V}, n_{j \neq k}} dn_k \quad \text{A5}$$

The expansion rule gives

$$\left(\frac{\partial \underline{A}}{\partial n_k} \right)_{T,P, n_{j \neq k}} = \left(\frac{\partial \underline{A}}{\partial \underline{V}} \right)_{T,n} \left(\frac{\partial \underline{V}}{\partial n_k} \right)_{T,P, n_{j \neq k}} + \left(\frac{\partial \underline{A}}{\partial n_k} \right)_{T, \underline{V}, n_{j \neq k}} \quad \text{A6}$$

Recalling that

$$\frac{1}{RT} \left(\frac{\partial \underline{A}^{assoc}}{\partial n_k} \right)_{T, \underline{V}, n_{j \neq k}} = \ln \hat{\phi}_k^{assoc} \quad \text{A7}$$

and

$$\left(\frac{\partial \underline{A}^{assoc}}{\partial \underline{V}} \right)_{T,n} = -P^{assoc} \quad \text{A8}$$

And making the appropriate substitutions into Eq. (A6):

$$\frac{1}{RT} \left(\frac{\partial A^{assoc}}{\partial n_k} \right)_{T,P,n_{j \neq k}} = -\frac{Z^{assoc}}{V} \bar{V}_k + \ln \hat{\phi}_k^{assoc} \quad A9$$

Substituting Eqs. (A2 and A3) yields the universal equation:

$$\begin{aligned} \frac{1}{RT} \left(\frac{\partial A^{assoc}}{\partial n_k} \right)_{T,P,n_{j \neq k}} &= \sum_{\substack{\text{sites } B_i \\ \text{only on } k}} N_{B_i} \ln X^{B_i} \\ &+ \frac{1}{2} h \left[\frac{\bar{V}_k}{V} \left(1 + \left(\frac{\partial \ln g}{\partial \ln \eta_P} \right)_{T,n} \right) - n_0 \left(\frac{\partial \ln g}{\partial n_k} \right)_{T,\underline{V},n_{j \neq k}} \right] \end{aligned} \quad A10$$

To simplify this further, we assume that Z^{rep} is given by the van der Waals equation. Applying Eq. (18) results in $g = 1/(1 - b\rho) = (1/(1 - \eta_P))$.

$$\begin{aligned} \left(\frac{\partial \ln g}{\partial \ln \eta_P} \right)_{T,n} &= \eta_P / (1 - \eta_P) \\ n_0 \left(\frac{\partial \ln g}{\partial n_k} \right)_{T,\underline{V},n_{j \neq k}} &= \frac{b_k \rho_k}{1 - \eta_P} \left(\frac{V_k}{V} \right) \end{aligned} \quad A11$$

Eq. (A10) becomes:

$$\frac{1}{RT} \left(\frac{\partial A^{assoc}}{\partial n_k} \right)_{T,P,n_{j \neq k}} = \sum_{\substack{\text{sites } B_i \\ \text{only on } k}} N_{B_i} \ln X^{B_i} + \frac{1}{2} h \left[\frac{\bar{V}_k}{V} \left(\frac{1}{1 - \eta_P} \right) - \frac{V_k}{V} \left(\frac{b_k \rho_k}{1 - \eta_P} \right) \right] \quad A12$$

If excess volume is zero and the packing factor is universal,

$$\frac{1}{RT} \left(\frac{\partial A^{assoc}}{\partial n_k} \right)_{T,P,n_{j \neq k}} = \sum_{\substack{\text{sites } B_i \\ \text{only on } k}} N_{B_i} \ln X^{B_i} + \frac{1}{2} \left(\frac{\rho}{\rho_k} \right) \sum_{\substack{\text{all site} \\ \text{types } B_i}} x_{B_i \text{ host}} N_{B_i} (1 - X^{B_i}) \quad A13$$

Using this equation, γ^{assoc} can be calculated as:

$$\gamma_k^{assoc} = \frac{1}{RT} \left(\frac{\partial A^{assoc}}{\partial n_k} \right)_{T,P,n_{j \neq k}} \Big|_{\text{mix}} - \frac{1}{RT} \left(\frac{\partial A^{assoc}}{\partial n_k} \right)_{T,P,n_{j \neq k}} \Big|_{\text{pure } k} \quad A14$$

This results in Eq. (7) in the text. Note that $x_i \rho / \rho_k = \Phi_i$ when excess volume is zero.

Appendix B

Beginning with the fugacity coefficient relation, we substitute van der Waals equation of state:

$$Z_T = \frac{PV}{n_T RT} = 1 + \frac{b\rho_T}{1 - b\rho_T} - \frac{a\rho_T}{RT} \quad \text{B1}$$

and its implementation into the Helmholtz departure equation:

$$\frac{(\underline{A} - \underline{A}^{ig})_{T,V}}{n_T RT} = -\ln(1 - b\rho_T) - \frac{a\rho_T}{RT} \quad \text{B2}$$

For a true associated species in a pure fluid:

$$\ln \hat{\phi}_i = -\ln(1 - b\rho_T) + \frac{b_i\rho_T}{1 - b\rho_T} - \frac{2\rho_T \sum_j x_{T,j} a_{ij}}{RT} - \ln Z_T \quad \text{B3}$$

Applying Eq. (16) and (17), calculating Eq. (B3) for a monomer and a dimer gives:

$$\ln \frac{\hat{\phi}_M^2}{\hat{\phi}_D} = -\ln(1 - b\rho_T) - \ln Z_T \quad \text{B4}$$

or

$$\frac{\hat{\phi}_D}{\hat{\phi}_M^2} = Z_T(1 - b\rho_T) = \frac{PV(1 - b\rho_T)}{n_T RT} = \frac{\hat{\phi}_{i+1}}{\hat{\phi}_i \hat{\phi}_M} \quad \text{B5}$$

Appendix C

Here, we provide proof that Ψ_i is the true concentration of all chains ending with i . Beginning with the definition of Ψ_i in Campbell's[35] paper:

$$\Psi_i = C'_{i,1} + \sum_j \alpha_{j,i}(C'_{j,1} + \sum_k \alpha_{k,j}(C'_{k,1} + \sum_l \alpha_{l,k}(C'_{l,1} + \dots \quad \text{C1}$$

where

$$\alpha_{j,i} = K_{C4,ji} C'_{i,1} \quad \text{C2}$$

Multiplying through Eq. (C1),

$$\Psi_i = C'_{i,1} + \sum_j \alpha_{j,i} C'_{j,1} + \sum_j \alpha_{j,i} \sum_k \alpha_{k,j} C'_{k,1} + \sum_j \alpha_{j,i} \sum_j \alpha_{k,j} \sum_l \alpha_{l,k} C'_{l,1} + \dots \quad \text{C3}$$

In Campbell's appendix C, the concentration of all chains of length n ending in i is given by:

$$C_{i,n} = \sum_j \alpha_{j,i} C_{j,n-1} \quad \text{C4}$$

This equation provides a recursion for simplification. Recognizing equation C4 in the second, third, and fourth term on the right hand side of Eq. (C3) can be expressed as:

$$C'_{i,2} = \sum_j \alpha_{j,i} C'_{j,1} \quad \text{and} \quad C'_{j,2} = \sum_k \alpha_{k,j} C'_{k,1} \quad \text{and} \quad C'_{k,2} = \sum_l \alpha_{l,k} C'_{l,1} \quad \text{C5}$$

Then

$$\Psi_i = C'_{i,1} + C'_{i,2} + \sum_j \alpha_{j,i} C'_{j,2} + \sum_j \alpha_{j,i} \sum_j \alpha_{k,j} C'_{k,2} + \dots \quad \text{C6}$$

Simplifying the third and fourth term on the right with Eq. (C4) again,

$$\Psi_i = C'_{i,1} + C'_{i,2} + C'_{i,3} + \sum_j \alpha_{j,i} C'_{j,3} + \dots \quad \text{C7}$$

This procedure applied continuously to all sums in Eq. (C3) yields the result that Ψ_i is also the true concentration of all chains that end in i .

$$\Psi_i = C'_{i,1} + C'_{i,2} + C'_{i,3} + C'_{i,4} + \dots = \sum_j C'_{i,j} \quad \text{C8}$$

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