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Modeling of Dielectric Properties of Complex Fluids with an Equation of State

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ABSTRACT: The static permittivity is a key property for describing solutions containing polar and hydrogen bonding compounds. However, the precise relationship between the molecular and dielectric properties is not well-established. Here we show that the relative permittivity at zero frequency (static permittivity) can be modeled simultaneously with thermodynamic properties. The static permittivity is calculated from an extension of the framework developed by Onsager, Kirkwood, and Fröhlich to associating mixtures. The thermodynamic properties are calculated from the cubic-plus-association (CPA) equation of state that includes the Wertheim association model as formulated in the statistical associating fluid theory (SAFT) to account for hydrogen bonding molecules. We show that, by using a simple description of the geometry of the association, we may calculate the Kirkwood $g$-factor as a function of the probability of hydrogen bond formation. The results show that it is possible to predict the static permittivity of complex mixtures over wide temperature and pressure ranges from simple extensions of well-established theories simultaneously with the calculation of thermodynamic properties.

INTRODUCTION

Dielectric spectroscopy is widely used to gain insight into molecular properties of fluids.1−4 The dielectric properties of fluids are characterized from the complex permittivity $\varepsilon^* = \varepsilon' + i\varepsilon''$, which can be measured from the response of the fluid to an external electrical field.1−4 The electrical response ultimately depends on many factors, including transport and thermodynamic properties (density, viscosity, etc.), molecular properties (dipole moment, molecular polarizability, etc.), and also the fluid structure (e.g., due to hydrogen bonding).1−9 The zero-frequency limit of the relative permittivity of a material, also known as the static relative permittivity, or the dielectric constant, is a measure of the ratio of the capacitance of a medium relative to the capacitance of a vacuum.12,9 The static permittivity is required as input to models for the Coulombic interactions between ions in a polar medium,10 such as the Debye–Hückel11 theory and the Born12 model of the solvation free energy.

The static permittivity has also been used to correlate solubility and speciation of neutral compounds and pharmaceuticals13 and to predict the scaling propensity of produced water containing gas hydrate inhibitors.14 Online measurements of the permittivity are used for nondestructive sensing of moisture content of soils and food.4,15 It also serves as a valuable resource for assessment of water saturation in geological formations and determination of the hydrocarbon content in the presence of fresh formation water or water with unknown salinity.16

The theoretical background for predicting the static permittivity ($\varepsilon_r$) of polar compounds from molecular properties relies on the famous papers by Onsager5 and Kirkwood.6 Fröhlich7 introduced the Kirkwood $g$-factor accounting for the local structure in Onsager's relations, and Hasted4 extended the formulation to mixtures, as shown in eq 1.

$$\frac{(2\varepsilon_r + \varepsilon_\infty)(\varepsilon_r - \varepsilon_\infty)}{\varepsilon_r(\varepsilon_\infty + 2)^2} = \frac{N_A}{9\varepsilon_0 k_b T v} \sum_i x_i \mu_{i,0}^2$$

(1)

In eq 1, $\varepsilon_r$ is the static permittivity, $\varepsilon_\infty$ is the permittivity at infinite frequency, $\varepsilon_0$ is the vacuum permittivity, $N_A$ is Avogadro’s constant, $T$ is the temperature, $k_b$ is the Boltzmann constant, $x_i$ is the mole fraction of component $i$, $v$ is the molar volume, and $\mu_{i,0}$ is the vacuum dipole moment of component $i$.

Equation 1 can be derived using the procedure by Buckingham17 and by assuming the same infinite frequency permittivity $\varepsilon_\infty$ for all spherical enclosures (see the full derivation in the Supporting Information). $\varepsilon_\infty$ is calculated from the Clausius–Mossotti18 equation for mixtures shown in eq 2:

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} = \frac{1}{3\varepsilon_0} \frac{N_A}{v} \sum_i x_i \mu_{i,0}^2$$

(2)
In eq 2, \( \alpha_{ij} \) is the molecular polarizability of molecule \( i \). Oster and Kirkwood\(^8\) derived a model for the pure component \( g \)-factor for water and alcohols using eq 3:

\[
g = 1 + z (\cos \gamma) \tag{3}
\]

in which \( z \) is the coordination number (four in the case of water) and \( \langle \cos \gamma \rangle \) is a statistical mechanical average projected angle for the dipole moment of the surrounding molecules. Haggis et al.\(^5\) used the “broken-down-ice” structure of water, to accurately predict the static permittivity of water over wider temperature ranges by accounting for a reduction in the degree of hydrogen bonding. Suresh and Naik\(^18,19\) presented a model for predicting the dielectric constant of binary mixtures of methanol, water, and acetone by calculating \( \langle \cos \gamma \rangle \) from molecular geometry and the probability of association determined by a chemical model for hydrogen bonding. Suresh improved the model for mixtures\(^20\) and used the model to analyze two proposed schemes for the cross-association between water and dimethyl sulfoxide.

This article presents a novel method for predicting the static permittivity of hydrogen-bonding mixtures over wide ranges of temperature and pressure using eq 1 through a geometrical model for calculation of Kirkwood’s \( g \)-factor coupled with Wertheim’s association theory within the cubic-plus-association (CPA) equation of state.\(^21–23\)

**Theoretical Basis.** The following section summarizes the development of a new model for the static permittivity of mixtures containing hydrogen-bonding compounds. It extends the model for mixtures shown in eq 1, in which the \( g \)-factor can be calculated from eq 4 (see derivation in the Supporting Information):

\[
g_i = 1 + \frac{1}{\mu_{ij}} \left( \sum_{j \neq i} \mu_{0i} \mu_{0j} \right) \tag{4}
\]

In eq 4, \( \mu_{0j} \) denotes the dipole moment of molecules surrounding the central dipole. We will approximate eq 4 from the projected dipole moments of all molecules that are hydrogen bonded to a fixed central molecule \( C \). A sketch of the innermost neighbor is shown in Figure 1.

![Figure 1](image1.png)

**Figure 1.** Sketch of bonding angles and dipole moments with the innermost neighbor.

We may calculate the angle between the two dipole moments \( \gamma \) from the projection of the dipole moment of a decentral molecule \( \mu_D \) onto the central molecule \( \mu_C \) using eq 5:

\[
\langle \cos \gamma \rangle = \frac{\langle \mu_C \cdot \mu_D \rangle}{\mu_C \mu_D} \tag{5}
\]

If we assume free rotation around the hydrogen bond, we may write eq 5 in terms of the dipole moment in the direction of the hydrogen bond \( \mu_H \) toward the other molecule:

\[
\langle \cos \gamma \rangle = \frac{\mu_H \mu_D}{\mu_C \mu_D} \tag{6}
\]

Using simple trigonometric relationships to evaluate eq 6, we may obtain eq 7 for tetrahedral and eq 8 for planar networks (we refer to the derivation shown in the Supporting Information):

\[
\langle \cos \gamma \rangle = -\frac{\mu_{OH} + \mu_{OR} \cos \varphi (\mu_{OH} \cos \theta + \mu_{OR})}{\mu_C \mu_D} \left( \cos \theta \cos \varphi - \frac{1}{2} \sin \theta \sin \varphi \right) \tag{7}
\]

\[
\langle \cos \gamma \rangle = -\frac{\mu_{OH} + \mu_{OR} \cos \varphi (\mu_{OH} \cos \theta + \mu_{OR})}{\mu_C \mu_D} \left( \cos \theta \cos \varphi - \sin \theta \sin \varphi \right) \tag{8}
\]

In eqs 7 and 8, \( \mu_{OH} \) and \( \mu_{OR} \) are the constituents to the dipole moment in the O–H and O–R directions, respectively. Equations 7 and 8 may be used for pure components and mixtures to determine angles between proton donors and proton acceptors and vice versa. For predictions, we use \( \theta = 109.47^\circ \) for the tetrahedral network and \( \theta = 120^\circ \) for the planar network.

Assuming that the central molecule can form up to \( z \) hydrogen bonds, we may calculate the contribution to the scalar product of the dipole moments of the first \( z \) neighbors using eq 9:

\[
\langle \mu_C \cdot \mu_D \rangle_1 = z \mu_C \mu_D \langle \cos \gamma \rangle \tag{9}
\]

In order to determine the projected dipole moment from all neighbors to the central molecule, we construct a simplified picture of the hydrogen bonding network, as shown in Figure 2, that includes hydrogen-bonded molecules from the first, second, and \( n \)th shell.

![Figure 2](image2.png)

**Figure 2.** Sketch of color-coded important dipole moments and angles in a hydrogen-bonding system.

If the molecules can form more than two hydrogen bonds, each shell will contain more molecules than the first. As shown by Suresh and Naik,\(^18\) the geometrical configurations in the tetrahedrally coordinated shells result in the dipole moments of all but \( z \) molecules being canceled out. We will therefore assume that there are only \( z \) molecules in each shell that give a net contribution to the central dipole moment. The projected dipole moment from the \( k \)th shell onto the first shell may then
be calculated from the rotation angle \( \theta \) which is multiplied onto the projected dipole moment of the first shell using eq 10:

\[
\langle \mathbf{m}_c \cdot \mathbf{m}_d \rangle^{(k)} = \langle \mathbf{m}_c \cdot \mathbf{m}_d \rangle^{(1)} \cos^{-1}(\pi - \theta), \quad k = 2, \ldots \infty
\]  

(10)

We will then approximate the statistical mechanical average in eq 4 for mixtures of associating compounds by a summation over the surrounding shells for all molecules given by eq 11:

\[
\langle \sum_{j \neq i} \mathbf{m}_{0,i} \cdot \mathbf{m}_{0,j} \rangle = \langle \sum_k \sum_j \langle \mathbf{m}_{0,i} \cdot \mathbf{m}_{0,j} \rangle \rangle
\]  

(11)

The statistical mechanical average \( \langle \mathbf{m}_{0,i} \cdot \mathbf{m}_{0,j} \rangle \) depends on the probability of molecules \( i \) and \( j \) being associated \( (P_j) \) and on the projection of the dipole moment onto the central molecule.

Using eq 9, we may calculate the statistical mechanical average of the projection of the dipole moments from the first hydration shell onto the central molecule using eq 12, in which we have dropped the bracket notation \( \langle \rangle \) for the statistical mechanical average:

\[
\sum_j \langle \mathbf{m}_{0,i} \cdot \mathbf{m}_{0,j} \rangle = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij}
\]  

(12)

In eq 12, \( z_j \) is the coordination number of molecule \( j \) around a central molecule \( i \) and the angle \( \cos \gamma_{ij} \) corresponds to the angle between the two dipole moment, as shown in Figure 1. The contributions from the second, third, and the \( k \)th shells are calculated using eq 10. The probability of the \( k \)th shell to exist is equal to \( P_j \), where \( P_j = \sum_{S \in S} P_i \) is the probability of the molecule \( i \) to be bonded to any of the molecules in the set \( S \). The contribution from the \( k \)th shell to eq 11 is then given by eq 13:

\[
\sum_j \langle \mathbf{m}_{0,i} \cdot \mathbf{m}_{0,j} \rangle^{(k)} = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij} = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij} = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij}
\]  

(12)

We may then calculate the sum of the contributions over all shells, as shown in eq 14:

\[
\langle \sum_k \sum_j \langle \mathbf{m}_{0,i} \cdot \mathbf{m}_{0,j} \rangle \rangle = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij} = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij} = \mathbf{m}_{0,i} \sum_j P_j \mathbf{m}_{0,j} \cos \gamma_{ij}
\]  

(14)

By inserting eq 14 in eq 4, we obtain the explicit expression shown in eq 15 for the \( g \)-factor in mixtures of associating compounds:

\[
g_i = 1 + \sum_j \frac{z_j P_j \cos \gamma_{ij}}{P_i \cos \theta_{ij} + 1} \mathbf{m}_{0,j}
\]  

(15)

Note that eq 15 does not account for closed (e.g., ring-like) structures. Furthermore, the parameters for eq 15 cannot easily be deduced for components with multiple conformers and must be fitted to experimental data. Note also that if \( \cos \gamma_{ij} \) is negative (corresponding to the dipoles being aligned antiparallelly), eq 15 may result in \( g < 1 \).

**Examples.** By applying eq 7 in the case of water \( (\mu_0 = 1.855 \text{ D}, \varphi = 104.5^\circ, \theta = 109.5^\circ) \), we obtain \( \varphi = 69.4^\circ \). By assuming that the bond length of the O–H bond does not change significantly in water compared to alcohols and by using the value \( \mu_{\text{OH}} = 1.52 \text{ D} \), we calculate the angle \( \gamma \) for methanol \( (\mu_0 = 1.7 \text{ D}) \) yields the angle \( \gamma = 57.8^\circ \) with a planar configuration.

The nature of the problem changes in the case of multifunctional molecules and molecules with internal degrees of freedom, as these conformational changes may affect the overall magnitude and direction of the dipole moment. In such situations, the total mixture may contain different conformers of the molecules and essentially requires us to perform a calculation of the distribution of conformers and then perform calculations for each geometrical configuration. In general, we have to fit the parameters \( \cos \gamma \) and \( \cos \theta \) to experimental data for such cases, but if the geometrical configuration and coordination number are known, we may fit the data using \( \cos \theta \) and eq 7 or eq 8.

**Selection of Hydrogen Bonding Network.** Before any calculations of the static permittivity can be performed, it is necessary to determine the hydrogen bonding network. Using experimental data for the static permittivity, we may determine the Kirkwood \( g \)-factor by rearranging eq 1 to form eq 16:

\[
g_i = 1 \left( \frac{2e_i + e_\infty}{e_i - e_\infty} \right) \frac{9\varepsilon_0 \varepsilon_\infty}{N_i}
\]  

(16)

The \( g \)-factor calculated near the freezing point temperature (i.e., at a high degree of association) serves as a good indicator for the choice of the hydrogen bonding network. It may be compared to the maximum \( g \)-factor that is calculated from the model by inserting \( P_i = 1 \) into eq 15 for a pure component:

\[
g_{\text{max}} = 1 + \frac{z_j \cos \gamma_{ij}}{\cos \theta_{ij} + 1}
\]  

(17)

To illustrate how the choice of hydrogen network affects the calculated \( g \)-factors, we calculate the experimental \( g \)-factor for methanol in the range 3.25–3.5 at 163–183 K. If methanol was in a tetrahedral configuration \( (\theta = 104.7^\circ) \) with a maximum of three hydrogen bonds (from the two lone pairs on oxygen and the one hydrogen bond), the maximum \( g \)-factor calculated using eqs 17 and 7 is 2.76, and thus, this hydrogen bonding configuration cannot reproduce the experimental data. If we instead use a planar configuration \( (\theta = 120^\circ) \) with two hydrogen bonds, the maximum \( g \)-factor calculated using eqs 17 and 8 is 3.67, which is in much better accordance with the observed values.

**Thermodynamic Model.** The CPA\(^{21–23}\) equation of state (EoS) consists of the Soave–Redlich–Kwong (SRK)\(^{24}\) cubic EoS with the Wertheim association theory,\(^{25}\) as formulated by the statistically associated fluid theory (SAPT)\(^{26}\) to account for association of hydrogen bonding components. The model has been used to calculate phase equilibrium and liquid densities for many complex mixtures, especially in relation to the phase equilibrium of water, oil, natural gas, and chemicals. The pressure equation of CPA is calculated from eq 18:\(^{21–23}\)

\[
P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) - \frac{1}{2}RT} \left(1 + \rho \frac{dg}{d\rho}\right)
\]  

\[
\sum_i \sum_j (1 - X_{ij}^A)
\]  

(18)

In eq 18, \( P \) is the pressure, \( R \) is the ideal gas constant, \( T \) is the temperature, \( b \) is the covolume parameter of the mixture, \( x_i \) is the mole fraction of molecule \( i \), \( v \) is the molar volume, \( \rho \) is the molar density, \( X_{ij} \) is the fraction of molecules of component \( i \) not bonded at site \( j \), and the radial distribution function in CPA is calculated from \( g(r) = (1 - 1.9\rho)_+ \), where the packing
factor \( \eta \) is given by \( b/4v \). For mixtures, CPA uses the vdW1f mixing rules for the SRK \( a(T) \) and \( b \) parameters, as shown in eqs 19 and 20:

\[
a(T) = \sum_i \sum_j x_i x_j \sqrt{a(T) a_i(T)} (1 - k_{ij})
\]

(19)

\[
b = \sum_i x_i b_i
\]

(20)

In which \( a_i(T) \) is given by eq 21:

\[
a_i(T) = a_{0i}(1 + c_i(1 - \sqrt{T/T_{ci}}))^2
\]

(21)

In eq 21, \( a_0 \) and \( c_i \) are pure component parameters and \( T_{ci} \) is the critical temperature of component \( i \). Given a pressure and a temperature, eq 18 is solved for the volume root \( v \) of the desired phase. Phase equilibrium is determined from the fugacity coefficients calculated using the equation of state:

\[
\frac{1}{X_{A}} = 1 + \frac{1}{v} \sum_{j} x_j \sum_{B} X_{B} \Delta_{A,B}
\]

(22)

In eq 22, \( X_{A} \) is the fraction of site \( A \) on molecule \( i \) that is not bonded to any other component and \( \Delta_{A,B} \) is the association strength (equilibrium constant), which in CPA is calculated from eq 23:

\[
\Delta_{A,B} = g(\rho) \nu_{A,B} \left[ \exp \left( \frac{\varepsilon_{A,B}}{k_B T} \right) - 1 \right]
\]

(23)

In eq 23, \( \nu_{A,B} \) is the association volume and \( \varepsilon_{A,B} \) the association energy. The probability of two sites to be hydrogen bonded is calculated from eq 24, where \( X_A \) denotes the fraction of sites of type \( A \) on molecule \( i \) that are not associated to other sites:

\[
P_{A,B} = \rho X_{A} \Delta_{A,B} X_{A} X_{B}
\]

(24)

For a pure component, the probability of two molecules to be bonded may be obtained using eq 25:

\[
\text{Table 1. CPA Parameters, Association Volumes, and Reduced Energy for Selected Components}^{21-23}
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>( T_c ) (K)</th>
<th>( b ) (cm(^3)/mol)</th>
<th>( \Gamma = (a_0/Rb_b) ) (K)</th>
<th>( c_i )</th>
<th>( \varepsilon_{A,B} ) (cm(^3)/mol)</th>
<th>( \varepsilon_{A,B}/k_B ) (K)</th>
<th>Association scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>647.13</td>
<td>14.52</td>
<td>1017.3</td>
<td>0.6736</td>
<td>1.004</td>
<td>2003.25</td>
<td>4C</td>
</tr>
<tr>
<td>Methanol</td>
<td>512.64</td>
<td>30.98</td>
<td>1573.7</td>
<td>0.4310</td>
<td>0.499</td>
<td>2957.78</td>
<td>2B</td>
</tr>
<tr>
<td>Ethanol</td>
<td>513.92</td>
<td>49.11</td>
<td>2123.8</td>
<td>0.7369</td>
<td>0.393</td>
<td>2589.85</td>
<td>2B</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>536.78</td>
<td>64.11</td>
<td>2234.5</td>
<td>0.9171</td>
<td>0.519</td>
<td>2525.86</td>
<td>2B</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>563.05</td>
<td>79.70</td>
<td>2368.6</td>
<td>0.9784</td>
<td>0.654</td>
<td>2525.86</td>
<td>2B</td>
</tr>
<tr>
<td>Octan-1-ol</td>
<td>652.5</td>
<td>148.5</td>
<td>3368.0</td>
<td>1.1486</td>
<td>0.0208</td>
<td>3218.55</td>
<td>2B</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>719.7</td>
<td>51.40</td>
<td>2531.7</td>
<td>0.6744</td>
<td>0.725</td>
<td>2375.75</td>
<td>4C</td>
</tr>
<tr>
<td>Diethylether</td>
<td>466.7</td>
<td>92.36</td>
<td>2302.7</td>
<td>0.5946</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>373.53</td>
<td>28.5</td>
<td>1878.2</td>
<td>0.6027</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>507.6</td>
<td>107.9</td>
<td>2640.0</td>
<td>0.8313</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decane</td>
<td>617.7</td>
<td>178.7</td>
<td>3190.5</td>
<td>1.1324</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{Table 2. Pure Component Properties for Calculating the Static Permittivity Using Densities from DIPPR Correlations and the Deviation from Experimental Data}
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>( \alpha_0 \times 10^{26} ) [(C(^2) m(^2))/J]</th>
<th>( \mu_0 ) (D)</th>
<th>( \nu ) (deg)</th>
<th>( \gamma ) (deg)</th>
<th>( \psi ) (deg)</th>
<th>( \theta ) (deg)</th>
<th>( z ) (deg)</th>
<th>AAD</th>
<th>RAD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.613</td>
<td>1.855</td>
<td>78.8</td>
<td>80.1</td>
<td>69.5</td>
<td>104.5</td>
<td>108.9*</td>
<td>0.80</td>
<td>3.04</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.661</td>
<td>1.70</td>
<td>34.0</td>
<td>33.0</td>
<td>52.7</td>
<td>109.47</td>
<td>118.7*</td>
<td>2</td>
<td>1.9</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6.019</td>
<td>1.69</td>
<td>25.2</td>
<td>25.3</td>
<td>52.3</td>
<td>109.47</td>
<td>120.1*</td>
<td>2</td>
<td>1.0</td>
</tr>
<tr>
<td>Propanol</td>
<td>7.499</td>
<td>1.68</td>
<td>20.8</td>
<td>20.8</td>
<td>51.8</td>
<td>109.47</td>
<td>124.5*</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>9.880</td>
<td>1.66</td>
<td>18.5</td>
<td>17.8</td>
<td>50.8</td>
<td>109.47</td>
<td>126.8*</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>11.80</td>
<td>1.70</td>
<td>15.4</td>
<td>15.1</td>
<td>52.7</td>
<td>109.47</td>
<td>127.8*</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>1-Hexanol</td>
<td>13.84</td>
<td>1.65</td>
<td>12.8</td>
<td>13.0</td>
<td>50.3</td>
<td>109.47</td>
<td>127.9*</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>17.92</td>
<td>1.76</td>
<td>10.6</td>
<td>10.3</td>
<td>55.4</td>
<td>109.47</td>
<td>126.7*</td>
<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>6.342</td>
<td>2.36</td>
<td>43.4</td>
<td>41.4</td>
<td>72.4</td>
<td>109.47</td>
<td>115.6*</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>Diethylether</td>
<td>11.35</td>
<td>1.3</td>
<td>4.39</td>
<td>4.27</td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>4.395</td>
<td>0.978</td>
<td>5.17</td>
<td>5.93</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td>0.3</td>
</tr>
</tbody>
</table>

In connection with prediction of the static permittivity, CPA is used to calculate the volume and the probability of association, which is already calculated by solving eq 22 within the equation of state:

\[
\frac{1}{X_{A}} = 1 + \frac{1}{v} \sum_{j} x_j \sum_{B} X_{B} \Delta_{A,B}
\]

(22)

In eq 22, \( X_{A} \) is the fraction of site \( A \) on molecule \( i \) that is not bonded to any other component and \( \Delta_{A,B} \) is the association strength (equilibrium constant), which in CPA is calculated from eq 23:

\[
\Delta_{A,B} = g(\rho) \nu_{A,B} \left[ \exp \left( \frac{\varepsilon_{A,B}}{k_B T} \right) - 1 \right]
\]

(23)

In eq 23, \( \nu_{A,B} \) is the association volume and \( \varepsilon_{A,B} \) the association energy. The probability of two sites to be hydrogen bonded is calculated from eq 24, where \( X_A \) denotes the fraction of sites of type \( A \) on molecule \( i \) that are not associated to other sites:

\[
P_{A,B} = \rho X_{A} \Delta_{A,B} X_{A} X_{B}
\]

(24)
We use eq 24 to determine the Kirkwood g-factor from eq 15.

RESULTS AND DISCUSSION
The static permittivity has been calculated for pure compounds using the densities calculated from correlations available in the DIPPR database and the probability of association calculated from solving eq 22 using the parameters from Table 1. The results are summarized in Table 2. While it is possible to obtain a good correspondence with experimental data (within 5% RAD for most fluids) by only fitting the parameter \( \theta \) to \( \varepsilon_r \) at 20 °C, the parameters shown in Table 2 were fine-tuned against all available data.

DIPPR database and the probability of association calculated from solving eq 22 using the parameters from Table 1. The results are summarized in Table 2. While it is possible to obtain a good correspondence with experimental data (within 5% RAD for most fluids) by only fitting the parameter \( \theta \) to \( \varepsilon_r \) at 20 °C, the parameters shown in Table 2 were fine-tuned against all available data.
Table 2 generally shows excellent agreement with the experimental data for static permittivity of the pure compounds that are hydrogen bonding. The biggest deviation is observed for hydrogen sulfide, which is not calculated as an associating component, and thus eq 1 reduces to the Onsager equation. For hexane and n-decane, the static permittivity \( \varepsilon_r \) becomes equal to the infinite frequency permittivity \( \varepsilon_\infty \). However, one of the difficulties arising for accurate calculation of the dielectric constant is the scatter in the experimental data reported in the literature for the vacuum dipole moment (see Figure 3 for the case of 1-alcohols as a function of chain length). In general, we use the dipole moment recommended by the DIPPR database, but in cases where this does not match the data well, we may have to fit the dipole moment along with \( \cos \theta \).

The results indicate that the model is suitable for calculation of the static permittivity of pure components; however, in general, we are interested in the prediction of static permittivity
for multicomponent systems over wide ranges of temperature and pressure. To enable calculation for multicomponent systems, we couple the model with the CPA EoS using the calculation procedure shown below:

- Specification of temperature, pressure, and composition
  - Solve numerically for liquid volume (eq 18)
  - Solve association equations numerically (eq 22)
  - Calculate static permittivity (eqs 1 and 15)

While the CPA parameters are fitted to vapor pressure and liquid density, the CPA EoS does not always yield perfect agreement with DIPPR densities. This affects the calculation of the static permittivity in accordance with eq 1, and it is therefore necessary to adjust the parameters slightly to match the experimental data. Table 3 shows the results and parameters when densities are calculated using CPA.

In the case of water, the unsatisfactory representation of the liquid density (see Figure 4) made it necessary to fit both angles ($\theta$ and $\gamma$) to obtain a satisfactory fit with RAD < 5%. For the other compounds, it was only necessary to adjust $\theta$.

A comparison of the static permittivity of pure water calculated from DIPPR and CPA densities is shown in Figure 5. A comparison of the present model with experimental data for methanol and ethylene glycol is presented in Figures 6 and 7, showing good correspondence with the experimental data.

Mixtures. In the case of mixtures, we need to determine bonding angles, coordination numbers, and the type of hydrogen bonding network. While we may fit the parameters to experimental data, in this work, we predict the binary bonding angles from eq 7 assuming tetrahedral ($\theta = 109.47^\circ$) hydrogen bonding networks in the mixtures. We assume that methanol coordinates three molecules in its tetrahedral configuration, and that ethylene glycol and water will coordinate up to four molecules. The binary parameters are summarized in Table 4.

We use the near-Elliott combining rule shown in eqs 26 and 27 to determine cross-association energies and volumes between positive and negative sites on the molecules:

$$\nu_{AB} = \sqrt{\nu_{A,B} \cdot \nu_{A,B}}$$  \hspace{2cm} (26)

$$\varepsilon_{AB} = \frac{\varepsilon_{A,B} + \varepsilon_{A,B}}{2}$$  \hspace{2cm} (27)

Since no parameters are fitted to the experimental data, the results shown in this section are predictions from the pure component parameters.

Figure 8 compares the predicted static permittivity of mixtures of water and methanol with the experimental data as a function of temperature and composition. Figure 8 reveals good agreement with the experimental data, except for the sudden jump in static permittivity at low methanol mole fractions observed in the data from Travers and Douzou, which is attributed to experimental error.

Figure 9 shows results for the temperature dependence of the static permittivity in the binary water–ethylene glycol system. Note that the data from Akerlöf are consistently underestimating the static permittivity of ethylene glycol rich mixtures. This deviation is attributed to experimental error, as the data for pure component ethylene glycol from Akerlöf shown in Figure 7 is significantly lower than data from other sources.

Figure 10 shows the static permittivity of water–ethylene glycol mixtures at 25 °C as a function of pressure and composition. Figure 10 shows that the new model captures the pressure dependence up to high pressures (2500 bar).

Figure 11 shows the predicted static permittivity with the experimental data of the ternary mixture containing water, methanol, and ethylene glycol as a function of temperature. Ethylene glycol is assumed to coordinate four water and methanol in a tetrahedral configuration.

As seen by Figures 8–11, the static permittivity of binary and ternary mixtures of associating compounds is well predicted by the present model. No new parameters were fitted to the binary or ternary systems; instead, the model parameters were calculated directly from eq 7, and thus the presented results arise from true predictions of the model.

■ CONCLUSION

This work has extended the framework for calculating the static permittivity to associating compounds using an equation of state based on the Wertheim association theory. A model for the geometrical arrangements in hydrogen-bonding systems has been derived, and it was shown how this model allows for prediction of the static permittivity of pure compounds and mixtures over wide ranges of temperature and pressure when used within an equation of state using the association term by Wertheim. The model does not account for ring-type structures, or multiple conformers, but it is our experience that the model parameters can be tuned to match experimental data. Fitting one parameter to the static permittivity at 20 °C is sufficient for most compounds, provided that the density is accurately reproduced by the equation of state. The static permittivity of mixtures may be predicted solely from parameters calculated by a model of the geometrical configuration of the hydrogen-bonding structure involving the binary compounds.

■ ASSOCIATED CONTENT

§ Supporting Information

Derivation of eqs 1, 7, and 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure 11. Static permittivity of mixtures of different volume fractions (prepared at 20 °C) of water–ethylene glycol–methanol, as a function of temperature. Data from Travers et al. 60
Notes
The authors declare no competing financial interest.

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# LIST OF SYMBOLS

- $b$: SRK covolume
- $g$: Kirkwood g-factor for molecule $i$
- $g(\rho)$: radial distribution function
- $k_B$: Boltzmann constant ($1.3806503 \times 10^{-23}$ J/K)
- $N_A$: Avogadro number
- $P$: pressure
- $P_{A,B}$: probability of association between site $A$ on molecule $i$ and site $B$ on molecule $j$
- $P_i$: probability of molecule $i$ and $j$ to be hydrogen bonded
- $R_i$: ideal gas constant ($8.3144621 \ldots$ J/mol/K)
- $T$: temperature
- $T_{ci}$: critical temperature of component $i$
- $v$: molar volume
- $x_i$: mole fraction of molecule $i$
- $X_i$: fraction of site $A$ on molecule $i$ that is not bonded to any other components
- $z_i$: coordination number of molecule $i$
- $\bar{a}_{ii}$: polarizability of molecule $i$
- $\cos \gamma_{ij}$: angle between the dipole moment of central molecule $i$ and surrounding molecule $j$
- $\Gamma_i$: CPA $\Gamma$ parameter for component $i$, related to $\bar{a}_{ii}$ and $b_{0i}$ through $\Gamma_i = (\bar{a}_{ii}/b_{0i})$
- $\Delta_{A,B}$: association strength (equilibrium constant) between site $A$ on molecule $i$ and site $B$ on molecule $j$
- $\varepsilon$: static permittivity relative to vacuum
- $\varepsilon_0$: infinite frequency permittivity relative to vacuum
- $\varepsilon_i$: vacuum permittivity ($8.854189 \ldots \times 10^{-12}$ F/m)
- $\varepsilon_{A,B}$: association energy between site $A$ on molecule $i$ and site $B$ on molecule $j$
- $\cos \theta_{ij}$: hydrogen bond angle between molecule $j$ in the shell around molecule $i$ and the second shell neighbor
- $\eta$: packing factor $\eta = b/4\pi$
- $\mu_{A,i}$: dipole moment in vacuum of molecule $i$
- $\mu_{B,i}$: dipole moment vector of central molecule
- $\mu_{A,B}$: dipole moment vector of surrounding molecules
- $\nu_{A,B}$: association volume between site $A$ on molecule $i$ and site $B$ on molecule $j$
- $\phi_{ij}$: internal R–OH bonding angle of molecule $i$
- $\rho$: molar density of fluid
- AAD: absolute average deviation
- RAD: relative average deviation

# REFERENCES


