

Association based equation of state for substances forming monomers, dimers and trimers

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Abstract

An exact expression is reported for an association based equation of state that allows the formation of monomers, dimers and trimers. To demonstrate the utility of this exact solution, the phase equilibrium results of acetic acid are obtained from this exact expression and are compared with a numerical approach as well as a fitted functional form. The exact form is preferred over the numerical as well as the fitted function form based on issues that arise from the computational time (the former) and accuracy of derivative properties (the latter).

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1. Introduction

It is well known that hydrogen-bonding interactions have profound effects on both the microscopic as well as the macroscopic properties of associating substances. When cubic equations of state such as Peng–Robinson (PREOS) [1] are applied for substances that show strong association interactions, they fail to correlate and predict the experimental data accurately [2]. This is mainly because the association interactions are not specifically included in these types of equations of state. Many thermodynamic modeling approaches for strongly associating systems focus on the proper capturing of the association interactions within the system [3–7]. Hence, the selection of an association scheme that is descriptive of the system of interest is quite important.

Incorporating association into cubic equations of state has been in practice for several decades now [8]. In this approach, it is necessary to know the types of oligomer species that are present in the system. The formation of these oligomers is described as a series of chemical reactions with appropriate equilibrium constants [9]. A cubic equation of state is then included to describe the physical interactions between the associated species. This approach provides the freedom to specify the existence of spe-

cific oligomers beforehand, if such information is available. However, if the oligomer distribution chosen is one that does not result in an exact closed-form equation of state, other approximate means are required to extract the requisite thermodynamic information from the model. These approximate techniques, as we demonstrate in this work, are problematic from both a computational efficiency and accuracy standpoint.

Currently, exact closed-form expressions have been reported for only two association schemes: the monomer–dimer model [6,9] and the model that allows for the formation of an infinite number of oligomers [5,6,9]. In this work, we report an exact closed-form expression for an association model that allows the formation of monomers, dimers and trimers. This type of association is seen in systems such as acetic acid [10–15] propanoic acid [12,15], methanol [16,17], etc. As a demonstration to the importance of using closed-form expressions, we use this monomer–dimer–trimer model to correlate the phase equilibria of acetic acid and compare these results to approximate techniques that one would employ when an exact closed-form expression is not available. Note the latter situation occurs when higher-order oligomers are used in an association scheme [4,18–20].

2. Formulation of the model

The association interactions are specified using Anderko's association + equation state (AEOS) approach, [19] which is best

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described in terms of the compressibility factor (Z). Similar to the decomposition of second virial coefficients, [21] the compressibility factor here is divided into two parts, a chemical part (Z^{ch}) and a physical part (Z^{ph}), and accordingly it can be written as

$$Z = Z^{\text{ph}} + Z^{\text{ch}} - 1 \quad (1)$$

The Z^{ch} describes the association interactions including the formation of clusters through appropriate association schemes (here the monomer, dimer and trimer was allowed to be formed), while the Z^{ph} describes the non-specific interactions between these clusters, including the monomers, using a cubic equation of state (here, Peng–Robinson was used) [3].

The chemical contribution to the compressibility factor is defined as the ratio of the total number of moles of all species in an associated mixture (n_T) to the number of moles of all species that would exist without association (n_0) [9].

$$Z^{\text{ch}} = \frac{n_T}{n_0} \quad (2)$$

In the AEOS formulation, the equilibrium constants of the i -merization reactions (K_i),

$$iA_1 \rightleftharpoons A_i \quad (3)$$

are described as a function of the dimerization constant (K) and are given by,

$$K_i \rightleftharpoons K^{i-1} \quad (4)$$

Once an association scheme is prescribed, the Z^{ch} term can then be calculated if the K_i equilibrium constants are known. For an associating component where the association scheme features monomers, dimers, trimers, etc., up to n -mers (not necessarily consecutive), the chemical part becomes

$$Z^{\text{ch}} = \frac{\sum_{i=1}^n K_i (Z^{\text{ch}} z_{A1} RT/v)^i}{\sum_{i=1}^n i K_i (Z^{\text{ch}} z_{A1} RT/v)^i} \quad (5)$$

where, z_{A1} is the monomer mole fraction of the associating component, R is the universal gas constant, T is the absolute temperature and v is the specific volume. Based on a mass balance, it can be shown that the denominator of Eq. (5) is equal to RT/v [9], so the value of Z^{ch} at a given state can be obtained by solving for $Z^{\text{ch}} z_{A1} RT/v$ and then substituting it back in the equation to find Z^{ch} [3].

In the AEOS approach, based on the association scheme adopted, Z^{ch} can be obtained in three different ways: (i) using the exact closed-form (if available) expression obtained by solving the material balance equation, (ii) by solving the material balance equations numerically using an iterative procedure and (iii) by using a fitted functional form that mimics the behavior of the numerical Z^{ch} [19]. Since Z^{ch} is described as a ratio of polynomials with the order of the polynomials directly related to the association scheme adopted (Eq. (5)), obtaining the exact closed-form expression for Z^{ch} is not possible for most association schemes.

As we will show, when one calculates Z^{ch} numerically, it is difficult to achieve the required level of accuracy relative to

the exact closed-form solution without compromising on computational time. Also, when a fitted functional form is used to describe Z^{ch} , the accuracy of some of the thermodynamic properties predicted using this functional form suffers, especially when calculating derivative properties.

3. Exact closed-form expression for 1-2-3 association scheme

Similar to the procedure that was described earlier, an exact closed-form expression for an association scheme that allows the formation of monomer, dimer and trimer (1-2-3) was obtained and is shown in Eq. (6). Note that this can be used to correlate and predict phase coexistence properties of any substance that allows the formation of monomers, dimers and trimers.

$$Z_{1-2-3}^{\text{ch}} = \frac{1 + M + M^2}{1 + 2M + 3M^2} \quad (6)$$

where,

$$M = \frac{X^2 - 4X - 20}{18X} \quad (7)$$

and X is given by,

$$X = \left(152 + 972q + 36\sqrt{3}\sqrt{(8 + 76q + 243q^2)} \right)^{1/3} \quad (8)$$

and $q = RTK/v$ is the reduced density. The temperature-dependent dimerization constant K is expressed as

$$\ln K = \frac{-\Delta H^\circ + \Delta C_p^\circ T^\circ}{RT} + \frac{1}{R}(\Delta S^\circ - \Delta C_p^\circ(1 + \ln T)) + \frac{\Delta C_p^\circ \ln T}{R} \quad (9)$$

here the superscript ‘ $^\circ$ ’ corresponds to the reference state 273.15 K.

The dimerization constant consists of three descriptive parameters, ΔH° , ΔS° and ΔC_p° , the standard enthalpy, entropy, and heat capacity of dimerization, respectively. The Z^{ph} is described by four parameters: the apparent critical temperature T'_C , critical pressure P'_C and acentric factor ω' , as in the original form of the PREOS [1] and a volume parameter, b . Overall, there are seven parameters that need to be optimized for minimum deviation from the experimental values. These parameters can be used to predict other pure component as well as mixture properties.

The fugacity coefficient (ϕ) expression [3] for this association model is given as,

$$\ln \phi = \lambda^{\text{ch}} + \lambda^{\text{ph}} - \ln(Z) + Z - 1 \quad (10)$$

where λ^{ph} and λ^{ch} are the physical and chemical parts of the natural logarithm of the fugacity coefficient, respectively, obtained through the relationship [3],

$$\lambda = \int_0^q \frac{Z - 1}{q} dq \quad (11)$$

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