Modified van der Waals and Redlich-Kwong Equations of State for Associating Fluids


[1,3]. Universidade Estadual de Campinas (UNICAMP), BRAZIL
[2]. PETROBRAS, BRAZIL
[4]. University of Illinois at Chicago, USA

ABSTRACT

Accurate prediction of thermodynamic properties and phase equilibria of systems containing associating fluids such as water and/or alcohols is of fundamental importance for many industrial processes. Modifications that allow the van der Waals and the Redlich-Kwong-Soave cubic equations of state to describe these systems with good accuracy are obtained by the proper incorporation of the self-association phenomenon.

The new equations: the Associating van der Waals (AVDW) and Associating Redlich-Kwong-Soave (ARSK) equations of state have several adjustable parameters that can be obtained through regression of pure component PVT data. The volumetric and phase equilibrium results obtained for water, ammonia and light-weight alkanols were found to be in excellent agreement with the experimental data.

NOTATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>attractive parameter of the equations of state</td>
</tr>
<tr>
<td>( A )</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>( b )</td>
<td>repulsive parameter of the equations of state</td>
</tr>
<tr>
<td>( c )</td>
<td>parameter of new model</td>
</tr>
<tr>
<td>( F )</td>
<td>distribution function</td>
</tr>
<tr>
<td>( m )</td>
<td>component</td>
</tr>
<tr>
<td>( n )</td>
<td>number of moles</td>
</tr>
<tr>
<td>( P )</td>
<td>pressure</td>
</tr>
<tr>
<td>( r )</td>
<td>reduced</td>
</tr>
<tr>
<td>( R )</td>
<td>ideal gas constant</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>( V )</td>
<td>molar volume</td>
</tr>
<tr>
<td>( x )</td>
<td>mole fraction</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Soave’s correction of temperature</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>gamma function</td>
</tr>
<tr>
<td>( \eta )</td>
<td>parameter of gamma function</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>parameter of gamma function</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>standard deviation</td>
</tr>
<tr>
<td>( 0 )</td>
<td>ideal gas</td>
</tr>
</tbody>
</table>

Superscripts

\[ \text{Superscripts} \]

\[ 0 \] ideal gas

[1]. Corresponding author

Present address: Chemical Engineering Department, Engineering School, University of Sao Paulo, Brazil, pedro.pessoa@poli.usp.br.

[2]. Present address: Laboratory of Petroleum Engineering and Exploration, Universidade Estadual do Norte Fluminense-UNEF, Macae’-RJ, Brazil, adolfo.puime@gmail.com

[3]. mohamed@feq.unicamp.br

[4]. Address: (M/C 063) Chicago, IL 60607-7052, mansoori@uic.edu
1.0 INTRODUCTION

Cubic equations of state have been widely used in the chemical and petroleum industry for thermodynamic property calculation. In the case of polar substances that self-associate, such as water or alcohol, these equations are of very limited use in the correlation and prediction of thermodynamic properties and phase behavior. In associating fluids, both physical and chemical interactions simultaneously exist and interrelate. These fluids form dimers, trimers, and other species through hydrogen bonding and charge transfer between molecules. Phase and thermodynamic property behavior in systems containing associating species show large deviation from ideality. The development of a viable theory for associating fluids that accounts for both types of interactions and provides accurate prediction of thermodynamic properties and phase equilibria of systems containing water and/or alcohols is of fundamental importance for many industrial processes and is an active field of research in thermodynamics.

Contributions to the development of a theory for associating fluids began with Heidemman and Praunstiz (1976). Ikonominu and Donohue (1986) showed the compressibility factor can be separated in a physical term and a chemical one. Anderko (1989a,b) refined and applied this concept to cubic equations of state. Shinta and Firoozabadi (1995) applied this theory using the Peng-Robinson equation of state. Al-Mutawa et al. (1993) used the polydisperse thermodynamic theory to describe the associating fluid.

2.0 DEVELOPMENT OF NEW MODELS

The development of this model is similar to that of Al-Mutawa et al. (1993) as it assumes the associating fluid to be a polydisperse mixture of aggregates of different sizes and shapes that can be described by one of the many convenient distribution functions. Choosing the gamma function to represent the mole fraction distribution, together with the conformal solution theory, that assumes the existence of a pure hypothetical fluid with the same properties of the mixture at the same density and temperature, we obtain new expressions to describe the volumetric behavior of an associating fluid. The new van der Waals equation is different from that of Al-Mutawa et al. (1993) as it includes new concepts and simplifications that make it more consistent and representative of the physical situation being modeled.

A continuous distribution function can be used to describe the composition by attributing a portion of the integral of the distribution function to each mole fraction:

\[ x_i = \int F(i) \, di \]  \hspace{1cm} (2)

The distribution function must satisfy:

\[ \int_{i_0}^{\infty} F(i) \, di = 1 \]  \hspace{1cm} (3)

In a self-associating compound, the number of moles is related to the number of monomers by the equation:

\[ \tilde{n} = n \sum_i x_i \]  \hspace{1cm} (4)

With the substitution of the distribution function in equation (4), we have:

\[ \tilde{n} = n \int_{i_0}^{\infty} i F(i) \, di \]  \hspace{1cm} (5)

The integral in equation (5) defined by \( q = \int_{i_0}^{\infty} i F(i) \, di \) is a measure of the extent of association.

2.1 Associating van der Waals (AVDW)

The configurational Helmholtz free energy departure function for a van der Waals fluid is:
using the expressions suggested by Heidemman and Prausnitz (1976), we have:

\[ a(i) = a_i i^2 \]  
\[ b(i) = b_i \]  

one can calculate the value of the attractive and repulsive parameter for the self-associating fluid as a function of the monomer parameters and the extent of association parameter, \( q \):

\[ a = a_i q^2 \]  
\[ b = b_i q \]  

Volumetric data experimentally obtained indicate apparent molar volumes as they assume that the fluid is present in the form of monomers only and do not account for the self-association occurring in the fluid. We can then define the apparent volume as:

\[ \bar{V} = V \frac{q}{q} \]  

and substitute the \( a, b \) and \( \bar{V} \) expressions into the Helmholtz free energy departure function and we obtain the expression:

\[ A(V, T) - A^o(V^o, T) = RT \ln \left( \frac{V^o}{V - b} \right) - a_i q \bar{V} \]  

The pressure equation can be obtained through the following thermodynamic equation:

\[ \dot{P} = -\left( \frac{\partial A}{\partial V} \right)_T \]  

Since the molecular Helmholtz free energy is independent of volume, the pressure equation can be obtained with from the partial derivative of the configurational contribution of the Helmholtz energy with respect to the volume at constant temperature. Using the chain rule, because the differentiation must be done with respect to the actual volume, not to the apparent one and after some mathematical rearrangement we get the following expression for the van der Waals equation for self-associating fluids (AVDW):

\[ P = \left[ 1 - b_i \left( \frac{\partial q}{\partial \bar{V}} \right)_T \right] \frac{RT}{q(\bar{V} - b_i)} - \left( \frac{\partial q}{\partial V} \right)_T - \frac{a_i q}{\bar{V}^2} \]  

2.2 Associating Redlich-Kwong-Soave (ARSK)

Starting with the Helmholtz free energy for the Redlich-Kwong-Soave equation and following similar steps to those used to obtain the AVDW, we obtain the expression:

\[ P = \left[ 1 - b_i \left( \frac{\partial q}{\partial \bar{V}} \right)_T \right] \frac{RT}{q(\bar{V} - b_i)} - \left( \frac{\partial q}{\partial V} \right)_T \ln \left( \frac{\bar{V}}{\bar{V} + b_i} \right) - b \frac{q}{\bar{V}^2} \left( \frac{\partial q}{\partial V} \right)_T \]  

which represents the Soave-Redlich-Kwong equation for self-associating fluids (ASRK).

In order to be able to apply the equations (14) and (15) to describe the volumetric behavior of self-associating fluids, we need to obtain an expression for the \( q \) parameter. Following Al-Mutawa et al (1993), and using the gamma distribution function for the compositional distribution,

\[ F(I) = \left( \frac{i}{i_o} \right)^{i-1} e^{-\frac{\eta}{\eta_i \Gamma(\kappa)}} \]  

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Allowing the parameters $\eta$ and $\kappa$ to depend on temperature and apparent volume and
using the expressions given by Al Mutawa et al (1993):

$$\eta = \eta_c \frac{T^{-c_1}}{1 - \frac{c_2 T}{V}}$$

$$\kappa = 1 + \frac{c_3}{T}$$

with $c_1$, $c_2$, $c_3$ all greater than zero.

The $q$ function obtained from its definition and considering that monomers are always
present is:

$$q = 1 + \kappa \eta$$

The parameters can all be obtained by minimizing the mean absolute deviation in the
calculated saturation pressure and liquid volumes.

3. RESULTS AND DISCUSSION

The equations (14) and (15) were used to correlate reliable experimental PVT data
available in the literature. The mean deviations between experimental and calculated data for
the six associating fluids: water, ammonia, methanol, ethanol, 1-propanol and 2-propanol are
presented in Tables 1 and 2, for the saturated pressure and liquid molar volume, respectively.
The mean deviations are compared with those obtained with the Redlich-Kwong-Soave
equation of state. The results clearly show the large improvement obtained with the use of the
associated model expressions in comparison with the original van der Waals and Redlich-
Kwong-Soave model. This improvement is more pronounced in the case of the liquid molar
volume where the results of the associating models are within the normal experimental errors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>VDW</th>
<th>RKS</th>
<th>AVDW</th>
<th>ASRK</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>2134.6</td>
<td>7.53</td>
<td>13.82</td>
<td>3.88</td>
<td>Vargaftik (1975)</td>
</tr>
<tr>
<td>ammonia</td>
<td>509.1</td>
<td>3.25</td>
<td>9.08</td>
<td>0.98</td>
<td>Vargaftik (1975)</td>
</tr>
<tr>
<td>methanol</td>
<td>14641.1</td>
<td>16.20</td>
<td>22.58</td>
<td>7.19</td>
<td>Smith e Srivastava (1986)</td>
</tr>
<tr>
<td>ethanol</td>
<td>5790.4</td>
<td>18.34</td>
<td>20.13</td>
<td>5.49</td>
<td>Smith e Srivastava (1986)</td>
</tr>
<tr>
<td>1-propanol</td>
<td>2449.5</td>
<td>7.21</td>
<td>12.34</td>
<td>1.20</td>
<td>Smith e Srivastava (1986)</td>
</tr>
</tbody>
</table>

Mean Deviation = \(\frac{1}{n} \sum |\text{calculated-experimental}|/\text{experimental}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>VDW</th>
<th>RKS</th>
<th>AVDW</th>
<th>ASRK</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>105.4</td>
<td>39.88</td>
<td>7.74</td>
<td>1.97</td>
<td>Vargaftik (1975)</td>
</tr>
<tr>
<td>ammonia</td>
<td>88.1</td>
<td>31.11</td>
<td>8.60</td>
<td>1.84</td>
<td>Vargaftik (1975)</td>
</tr>
<tr>
<td>methanol</td>
<td>108.6</td>
<td>38.04</td>
<td>8.64</td>
<td>1.73</td>
<td>Smith e Srivastava (1986)</td>
</tr>
<tr>
<td>ethanol</td>
<td>90.6</td>
<td>24.59</td>
<td>8.66</td>
<td>1.12</td>
<td>Smith e Srivastava (1986)</td>
</tr>
<tr>
<td>1-propanol</td>
<td>79.7</td>
<td>21.87</td>
<td>8.78</td>
<td>2.48</td>
<td>Smith e Srivastava (1986)</td>
</tr>
<tr>
<td>2-propanol</td>
<td>86.1</td>
<td>23.28</td>
<td>8.69</td>
<td>2.09</td>
<td>Smith e Srivastava (1986)</td>
</tr>
</tbody>
</table>

Liquid molar volumes and saturation pressure for ethanol and ammonia are presented in
Figures 1 to 4 with similar behavior obtained for the other four systems.
Figures 1 and 3, may erroneously imply that the model merely introduces a volume translation. The results show, however, that we also obtain better saturation pressure values, a result that could not have been obtained by a mere volume displacement. Figures 1 through 4, show that the proposed new models tend to overshoot the experimentally observed critical point temperature and pressure. In fact, the largest deviations between experimental and calculated values occur at the critical point where association effects are less important.

The ASRK equation was also used to calculate the molar liquid volume at pressures higher than the saturation pressure (a situation where association effects are expected to be more pronounced). Figures 5 and 6 show the excellent agreement with experimental data except for extremely high pressures. The predicted liquid molar volumes for all the isotherms presented for ammonia are in average within 1% of the data of Ichihara and Uematsu (1994), and within 2% of the data presented by Takigushi and Uematsu (1996) for the case of ethanol.
CONCLUSIONS

The incorporation of polydisperse distribution to account for self-association in pure fluids into the van der Waals and the Redlich-Kwong-Soave cubic equations resulted in the formulations of the AVDW and ASRK equations of state. The new models were able to correlate and predict PVT data for water, ammonia, methanol, ethanol, 1-propanol and 2-propanol with excellent accuracy except at the critical point where the models showed the largest deviation from experimental data.

REFERENCES

Anderko, A., 1989b, Extension of the AEOS equation of state to systems containing any number of associating and inert compounds, Fluid Phase Equilibria, Vol. 50, pp 21-52.
PROCEEDINGS
INTERNATIONAL CONFERENCE ON
Fluid and Thermal Energy Conversion
FTEC 1997
Yogyakarta, INDONESIA

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