Fluid Phase Equilibria 306 (2011) 97–111

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Extending the GC-SAFT-VR approach to associating functional groups: Alcohols, aldehydes, amines and carboxylic acids

M. Carolina dos Ramos [a], Jessica D. Haley [a], Joel R. Westwood [a], Clare McCabe [a,b,*]

[a] Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, United States
[b] Department of Chemistry, Vanderbilt University, Nashville, TN 37235, United States

ARTICLE INFO

Article history:
Received 22 November 2010
Received in revised form 25 March 2011
Accepted 29 March 2011
Available online 20 April 2011

Keywords:
Equation of state
GC-SAFT-VR
Group contribution
Association
Vapor–liquid equilibria
Alcohols
Aldehydes
Amines
Carboxylic acids

ABSTRACT

The statistical associating fluid theory is a widely used molecular-based equation of state that has been successfully applied to study a broad range of fluid systems. It provides a framework in which the effects of molecular shape and interactions on the thermodynamics and phase behavior of fluids can be separated and quantified. In the original approach, molecules were modeled as chains composed of identical segments; the heterogeneity of molecules in terms of structure and functional groups was described implicitly through effective parameters. To overcome this limitation, in recent works [Peng et al. Fluid Phase Equilib. 227(2), 131 (2009); Ind. Eng. Chem. Res. 49(3), 1378 (2010)] the GC-SAFT-VR approach has been developed to extend the theory to model chains composed of segments of different size and/or energy of interaction and enable the development of a group-contribution approach within the SAFT-VR framework in which molecular heterogeneity and connectivity is explicitly accounted for. The parameters for several key functional groups (CH_3, CH_2, CH, $CH_2{=}CH$, C=O, C_6H_5, esters, ethers, *cis*-alkenes and *trans*-alkenes groups) were determined by fitting to experimental vapor pressure and saturated liquid density data for a number of small molecules containing the functional groups of interest and transferability of the parameters tested by comparing the theoretical predictions with experimental data for pure fluids not included in the fitting process and binary mixtures of both *simple* fluids and the VLE and LLE of small molecules in polymer systems. In this work, we further extend the applicability of the GC-SAFT-VR approach through the study of the vapor–liquid phase behavior of associating systems, such as linear and branched alcohols, primary and secondary amines, aldehydes, and carboxylic acids, and their mixtures. In the study of these new molecules several new functional groups (OH (linear and branched), HC=O, NH_2, NH and C=OOH) are defined and their molecular parameters characterized. The transferability of the parameters is again tested by comparing the theoretical predictions with experimental data for pure fluids and binary mixtures not included in the fitting process. The GC-SAFT-VR approach is found to predict the phase behavior of the systems studied in most cases in good agreement with experimental data and accurately captures the effects of changes in structure and molecular composition on phase behavior.

1. Introduction

Associating fluids and their mixtures can exhibit very interesting non-ideal phase behavior because of the strong and highly directional nature of their attractive hydrogen bonding interactions. There are many examples in the literature of the impact of association interactions on phase behavior. For example, in pure fluids, the vapor pressure curves and critical points of associating fluids are shifted to higher temperatures [1] relative to those of non-associating systems. In mixed systems the impact of association interactions is more diverse, perhaps the most familiar being the existence of closed-loop liquid-liquid immiscibility behavior (i.e. the existence of an upper critical end point (UCEP) and a lower critical end point (LCEP)) in the phase diagrams of aqueous mixtures with aliphatics, aromatic alcohols, and amines, in which association interactions play an important role [2–6]. Hence, the importance of incorporating these strong, anisotropic molecular interactions explicitly into theoretical models in order to accurately describe the thermodynamic properties and phase equilibria of associating systems is now widely recognized.

Statistical mechanics based theories, such as the statistical associating fluid theory (SAFT) [1,7], which in turn is based

---

* Corresponding author at: Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, TN 37235, United States. Tel.: +1 865 974 0227; fax: +1 865 974 4910.
E-mail address: c.mccabe@vanderbilt.edu (C. McCabe).

0378-3812/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2011.03.026

Nomenclature

A	Helmholtz free energy
EOS	equation of state
f	Mayer f-function
g	radial distribution function
GC	group contribution
HS	hard sphere
K	Boltzmann's constant
K^{HB}	bonding volume between association sites
LCEP	lower critical end point
LLE	liquid–liquid equilibria
m_i	functional group chain length
m_{ki}	overall contribution to the chain length of the molecule
N	number of molecules
n	number of components
n_{ia}	number of association sites of type a on group of type i
$n_k{}'$	number of types of functional groups in component k
ns'	total number of site types on a given functional group
P	pressure
r	distance between two spherical segments
r_{d}	distance between center of association site and segment
r_{c}	range of association interaction
SAFT	statistical associating fluid theory
SW	square well
T	temperature
TPT1	Wertheim's first-order perturbation theory
u	pair potential
UCEP	upper critical end point
u^{HB}	association interaction potential
V	volume
VLE	vapor–liquid equilibria
VR	variable range
X	fraction of association sites not bonded
x_k	mole fraction
y	background correlation function
%AAD P	percentage of absolute average deviation for the pressure
%AAD ρ_{liq}	percentage of absolute average deviation for the saturated liquid density
%AAD y	percentage of absolute average deviation for the vapor composition
%AAD T	percentage of absolute average deviation for the temperature

Greek letters

β	inverse temperature
Δ	association strength
$\varepsilon_{ki,lj}$	square-well potential depth
ε^{HB}	energy between association sites
$\lambda_{ki,lj}$	square-well potential range
μ_k	chemical potential
ρ	number density
$\sigma_{ki,lj}$	diameter of the interactions
υ_{ki}	number of each type of functional group

Subscripts

a,b	index for association sites
i,j	index for functional group parameters
k,l	index for molecular parameters

Superscripts

assoc	association contribution
chain	chain contribution
exp	experimental data
HB	hydrogen bonding
ideal	ideal contribution
mono	monomer–monomer contribution
theo	theoretical calculations

on Wertheim's first-order perturbation theory (TPT1) [8–11], have shown particular success in describing the thermodynamics and phase behavior of associating fluids. In the SAFT approach, molecules are described by chains of tangentially bonded homonuclear (i.e., identical) monomer segments that interact via common dispersion and, when appropriate, association interactions. The free energy of the fluid is obtained by summing the different contributions that account for the monomer–monomer interactions, chain formation, and intermolecular association, e.g., hydrogen bonding interactions. Because the different microscopic effects can be explicitly defined and accounted for, the SAFT approach has been shown to be a reliable equation of state (EOS). Since the introduction of the original SAFT expressions, there have been many versions and applications of SAFT-based approaches in the literature; the reader is directed to the reviews of Müller and Gubbins [12], Economou [13], Tan et al. [14], and McCabe and Galindo [15] for a comprehensive overview. In this work we focus on the SAFT-VR approach [16,17], in which the monomer segments interact through a potential of variable attractive range, typically a square-well potential. The SAFT-VR approach has been successfully used to describe the phase behavior of a wide variety of industrially important systems such as short alkanes through to simple polymers of high molecular weight and their binary mixtures [18–34], as well as fluorinated molecules [35–40], hydrogen bonding fluids such as water [41–44] and refrigerants [45–48], and electrolyte solutions [49–53].

In an effort to expand SAFT into a more powerful and predictive equation of state with which to determine the thermodynamic properties and phase equilibria of a wide range of complex fluids and their mixtures, several research groups have recently combined various versions of the SAFT equation with group contribution (GC) type schemes. In such approaches a system is characterized by the different functional groups that represent the molecule, with the assumption that the thermodynamic behavior of the molecule can be obtained from the sets of parameters that describe each functional group. In the first such approach by Lora et al. [54], parameters for low-molecular-weight propanoates with the original homonuclear version of SAFT due to Huang and Radosz [55,56] were used to calculate the size and energy parameters of polyacrylates [57]. Subsequently, Tobaly and co-workers [58–64] presented the GC-SAFT equation in which functional group parameters were fitted to experimental vapor pressure and saturated liquid density data for different chemical families in successive steps according to the structure and composition of the molecule; however, we note that in this approach the molecules are described using a homonuclear model, and as such, molecular heterogeneity is not explicitly taken into account within the theory. More recently, the implementation of a heteronuclear model in which the monomer segments are not identical and have different interaction parameters, and so enables the differentiation of functional groups at the molecular level, has been proposed in both the SAFT-γ [65,66] and GC-SAFT-VR [67,68] equations. In both approaches, the functional group parameters are determined by fitting the theory to experimental vapor pressure and saturated liquid density data for the smaller