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Modeling derivative properties and binary mixtures with CO_2 using the CPA and the quadrupolar CPA equations of state

Martin G. Bjørner*, Georgios M. Kontogeorgis

Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, DK-2800 Kgs. Lyngby, Denmark

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ABSTRACT

The cubic plus association (CPA) equation of state (EoS) is extended to include quadrupolar interactions. The quadrupolar term is based on a modification of the perturbation terms by Larsen et al. (1977) [5] for a hard sphere fluid with a symmetric point quadrupole moment. The new quadrupolar CPA (qCPA) can be used without introducing any additional pure compound parameters. Alternatively a single additional adjustable parameter can be employed.

To evaluate qCPA several pure compound properties are predicted. The model is furthermore evaluated for its ability to predict and correlate binary vapor–liquid equilibria (VLE) and liquid–liquid equilibria (LLE) of mixtures containing CO_2 and hydrocarbons, water, alcohols, or selected quadrupolar compounds.

The results indicate that most pure compound property predictions are satisfactory but similar to other CPA approaches. When binary mixtures are considered, qCPA appear to offer a systematic improvement as compared to the cases where quadrupolar interactions are ignored. This improvement is particularly pronounced when mixtures of CO_2 and hydrocarbons are considered, where the model is almost fully predictive. Using the same modeling approach qCPA can accurately correlate both the phase behaviour of CO_2 + hydrocarbon mixtures as well as mixtures of CO_2 + a self-associating compound.

1. Introduction

In recent years CO_2 has received a significant amount of negative attention due to its status as a greenhouse gas and the fact that the amount of CO_2 in the atmosphere continues to rise. This is believed to be largely due to the combustion of fossil fuels. Technologies are thus needed, which can limit the emission of CO_2 to the atmosphere. One such potential technology is carbon capture and storage. During this process, transport of CO_2 rich mixtures is an important step which requires accurate knowledge of the phase behaviour, as well as other thermodynamic properties, of mixtures containing hydrocarbons, water and other fluids such as alcohols [1].

Accurate equilibrium predictions of CO_2 containing mixtures, however, are challenging with traditional equations of state. The reason for this may be that CO_2 has a large quadrupole moment. The large quadrupole moment of CO_2, as well as size asymmetry, are for instance believed to be the reasons for the liquid-liquid equilibrium (LLE) between CO_2 and heavy hydrocarbons, and the reason for the low temperature azeotrope formed between mixtures of CO_2 and lighter hydrocarbons. Cubic equations of state such as the Soave–Redlich–Kwong (SRK) equation of state (EoS), however, treat CO_2 as an inert compound. Even in a modern EoS such as the Statistical Association Fluid Theory (SAFT) only dispersive forces are usually considered for CO_2. The continued use of these models may be attributed to the fact that several mixtures, such as CO_2 + hydrocarbons, are described quite well, when a single binary interaction parameter (k_{ij}), is used.

To deal with polar and quadrupolar interactions a number of multipolar terms have been suggested in the literature. These terms are mainly based on a third order perturbation theory developed from statistical mechanics by Stell and co-workers [2–5]. The perturbation theory was originally developed for pure fluids using the Stockmayer potential or the conceptually simpler hard sphere model with a central point dipole or quadrupole. Using the former potential, Gubbins and Twu [6,7] developed directly applicable expressions for polar and quadrupolar fluid mixtures.

During the last decade a number of quadrupolar terms have been included in the SAFT framework. Inspired by Stell and co-

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* Corresponding author.
E-mail address: mgabj@kt.dtu.dk (M.G. Bjørner).

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Nomenclature

$A^r(T;V;\mathbf{n})$	Residual Helmholtz energy
A_2^r	second order term in the perturbation expansion for quadrupolar interactions
A_3^r	third order term in the perturbation expansion for quadrupolar interactions
A_i	bonding sites on molecule i
B	second virial coefficient or expression for co-volume mixing term
C_P^{res}	the residual isobaric heat capacity
C_V^{res}	the residual isochoric heat capacity
D	mixing rule for the energetic part of SRK
I_{TQ}	three-body correlation integral
I_n	two-body correlation integral
N_A	Avogadro's constant
P_C	critical pressure
P	pressure
Q	quadrupole moment
R	the gas constant
S	constant in expression for the second virial coefficient of the association term
T_C	critical temperature
T_r	reduced temperature $T_r = T/T_c$
T	temperature in Kelvin
V	volume
X_{A_i}	fraction of sites A on molecule i which do *not* form bonds with other sites (site monomer fraction)
Z	compressibility factor
$\Delta^{A_iB_j}$	association strength between site A on molecule i and site B on molecule j
$\beta^{A_iB_j}$	cross-association volume
η	reduced density
$\mathbf{n}$	vector of molar composition
μ_{JT}	the Joule–Thomson coefficiient
ρ	density
σ	hard-sphere diameter
$\varepsilon^{A_iB_j}$	cross-association energy
a_0	pure compound energetic parameter in the SRK term
a_{ij}	cross energetic parameter in the SRK term
b_0^Q	co-volume parameter in the quadrupolar term
b_0	pure compound co-volume
b_{ii}	pure compound co-volume for component i
b_{ij}	cross-covolume
c_1	pure compound parameter in the SRK term
g	radial distribution function
k_b	Boltzmann's constant
k_{ij}	binary interaction parameter
n	total composition
s^{exp}	standard deviation
u	the speed of sound

workers [2–5] Gross [8] developed a new quadrupolar expression using the two center Lennard–Jones pair potential as the reference fluid. The resulting quadrupolar contribution was added to the Perturbed-Chain SAFT (PC-SAFT) to give the Perturbed-Chain Polar SAFT (PCP-SAFT). This EoS can be used without any additional adjustable parameters.

Karakatsani et al. [9,10] and Karakatsani and Economou [11] introduced two quadrupolar terms to the PC-SAFT framework. Both terms are based on the perturbation terms from by Larsen et al. [5], which use the pure hard sphere fluid as the reference fluid. The authors suggest two quadrupolar terms; an expression which employs the full correlation integrals from Larsen et al. [5], this term does not use any additional adjustable parameters, and a simpler version where the correlation integrals are truncated at the zeroth order term.

Later, NguyenHuynh et al. [12] extended a group contribution SAFT EoS to quadrupolar (and polar) fluid mixtures. The quadrupolar term used by the authors is based on the theory of Gubbins and Twu [6,7]. The term is extended to chain molecules using a procedure suggested by Jog et al. [13] and Jog and Chapman [14].

It seems that improved predictions and correlations (smaller k_{ij}) are typically obtained for binary vapor liquid equilibrium (VLE) when a quadrupolar term is coupled to SAFT or PC-SAFT. The quadrupolar models, however, have some limitations; The models are only applicable to molecules with a highly symmetric quadrupole moment, so that the quadrupole moment reduces to a single scalar value. It has furthermore been shown that false liquid–liquid splits may be predicted by the models [15]. Mixtures of several quadrupolar molecules are challenging, and the results are often better if only one component is assumed to have a quadrupole moment [8].

Another more pragmatic approach to account for the quadrupole moment of CO_2 is to consider CO_2 to be a self-associating compound. Such procedures often work well resulting in improved predictions and correlations with small interaction parameters [16–19]. Unfortunately the improvement is obtained at the cost of additional pure component parameters and, in some cases, an extra adjustable parameter for the binary mixtures.

In this work, inspired by the recent advances within the SAFT-family, and in an effort to obtain a physically more correct and predictive model, a quadrupolar term is proposed and combined with the well-known cubic plus association (CPA) EoS (Kontogeorgis et al. [20]). The term is based on the explicit expressions developed by Larsen et al. [5] for a hard sphere fluid with a point quadrupole. To simplify the expressions we truncate the correlation integrals at the zeroth order term, similar to the approach used in the truncated Perturbed-Chain Polar SAFT (tPC-PSAFT) [10,11].

To evaluate the new quadrupolar CPA (qCPA) the pure fluid properties of CO_2 are predicted both in the critical region and in the compressed liquid region. The model is furthermore applied for the prediction and correlation of binary mixtures with CO_2 and n-alkanes, water, alcohols and a few quadrupolar compounds. The model is compared with two other CPA approaches namely non-associating (n.a.) CPA, where CO_2 is assumed to be an inert compound, and the case when CO_2 is assumed to be self-associating following the 4C association scheme (notation from Huang and Radosz [21]). Tsivintzelis et al. [18] have published similar results with the two CPA approaches for most of the binary mixtures investigated in this work.

2. Models

The CPA EoS (Kontogeorgis et al. [20]) is an engineering EoS which has been extensively studied in the literature (e.g. [22–24]). It combines the SRK EoS with the association term from Wertheim's theory, which is also employed in SAFT [25–27]. The SRK term accounts for the physical interactions between molecules, while the association term takes hydrogen bonding interactions into