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Prediction of volumetric properties of carbon dioxide-expanded organic solvents using the Predictive Soave–Redlich–Kwong (PSRK) equation of state

Chie-Shaan Su*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei, Taiwan

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ABSTRACT

In this study, the Predictive Soave–Redlich–Kwong (PSRK) EOS is adopted for predicting the volumetric properties of carbon dioxide (CO_2)-expanded organic solvents including the volume expansions, molar volume fractions and partial molar volumes of the solvent. The solvent systems considered in this study include hydrocarbons, alcohols, esters, ketones and other organic solvents. In addition to acceptable prediction of the volumetric properties, the PSRK EOS also provides the ability to predict solubilities of a solid solute in a CO_2-expanded organic solvent. This study demonstrates that the PSRK EOS is a simple model with sufficient accuracy and predictive ability for evaluation of the volumetric properties and solubilities of solid solutes in CO_2-expanded organic solvents. In addition, analysis of predicted results by molecular parameters and improvement of volumetric property calculations using a translated-volume are also discussed.

1. Introduction

In recent years, CO_2-expanded organic solvents can be used as an alternate green solvent for various applications such as chemical reactions, crystallization and purification by fine-tuning its thermodynamic and transport properties [1–4]. For example, CO_2-expanded organic solvents have been adopted for recrystallization, micronization and production of composite particles of pharmaceutical compounds as the batch supercritical antisolvent (SAS) process [5–7]. In addition, CO_2-expanded organic solvents have also been employed as a promising alternate media for performing chemical reactions such as homogeneous catalytic oxidation, hydroformylation and solid–acid catalyzed reactions [8–11]. To optimize the CO_2-expanded media for industrial use, the knowledge of the volumetric properties of CO_2-expanded organic solvents is essential. For example, the behavior of volume expansion and molar volume fraction can be used as the guidelines to select appropriate solvents and operating conditions in the batch SAS process [12,13]. The partial molar volume of the solvent can be applied for evaluating the solubilities of solid solutes in CO_2-expanded organic solvents [14,15]. Thus, experimental measurement and thermodynamic simulation of phase behavior and volumetric properties of CO_2-expanded organic solvents have been widely studied [16–19]. However, the prediction of volumetric properties of CO_2-expanded organic solvents such as volume expansions, molar volume fractions and partial molar volumes of the solvent has not been found in literature.

Regarding the calculation of volumetric properties of CO_2 expanded organic solvent, the consideration of equations of state is the most commonly used. In this method, the volumetric properties of CO_2-expanded organic solvents can be obtained by computing the thermodynamic properties of binary vapor–liquid equilibria (VLE) of CO_2 and organic solvent. The conventional approach to calculating the binary VLE of CO_2 and organic solvent uses a correlative equation of state (EOS) such as the Peng–Robinson EOS with the two-parameter van der Waals mixing rule. This EOS provides excellent correlation ability but the adjustable parameters in the mixing rule must be optimized specifically for each mixture using experimental data. In order to totally predict the volumetric properties of CO_2-expanded organic solvents, a group-contribution EOS, the Predictive Soave–Redlich–Kwong (PSRK) EOS is considered [20,21]. Regarding the PSRK EOS, it contains 149 function groups and has been applied for predicting phase equilibria, excess properties, critical lines and Henry coefficients [22–24]. More than 900 interaction parameter sets are available in literature. Moreover, the required pure component properties including critical properties and Mathias–Copeman constants are also available in literature for about 1000 components [22].

In this study, the PSRK EOS is adopted for predicting the volumetric properties of CO_2-expanded organic solvents for hydrocarbons, alcohols, esters, ketones and other organic solvents. The calculated results are compared with those from two commonly used equations of state and the predicted deviations are discussed by molecular parameters. In addition, a translated-volume is

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* Tel.: +886 2 27712171.
E-mail address: cssu@ntut.edu.tw

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also adopted for evaluating the improvement of volumetric property calculations. For further applying the volumetric properties predicted in this study, the solubilities of a solid solute in a CO_2-expanded organic solvent are finally predicted.

Nomenclature

AADD	average deviation of the liquid-phase density
AADV	average deviation of the volume expansion
AADX	average deviation of the liquid-phase composition of CO_2
a, b	parameters in EOSs
a_i, b_i	parameters in EOSs for the pure component
a_m, b_m	parameters in EOSs for the fluid mixture
a_{nm}, b_{nm}, c_{nm}	group interaction parameters in the UNIFAC model
c_1, c_2, c_3	Mathias–Copeman parameters in the PSRK EOS
g_0^E	excess Gibbs energy
k_{ij}, l_{ij}	adjustable parameters in the two-parameter van der Waals mixing rule
P	pressure
$P_{c,i}$	critical pressure for the pure component
R	gas constant
T	temperature
$T_{c,i}$	critical temperature for the pure component
T_r	reduced temperature
V	total volume
v	molar volume in the binary (CO_2–solvent) system
$\bar{v}$	partial molar volume in the binary (CO_2–solvent) system
x	mole fraction of compound in the ternary (CO_2–solvent–solute) system
X	liquid-phase mole fraction in the binary (CO_2–solvent) system
α_i	temperature dependence function in the PSRK EOS for the pure component
ω	acentric factor
ρ	density
ψ_{nm}	parameter in the UNIFAC model

Subscripts

1	carbon dioxide
2	organic solvent
3	solid solute
0	reference state
L	liquid phase

Superscripts

cal	calculated value
exp	experimental value

2. Mathematical model

2.1. The PSRK EOS

In this study, the PSRK EOS proposed by Holderbaum and Gmehling [21] is employed for predicting the volumetric properties of CO_2-expanded organic solvents by modeling the binary VLE of CO_2 and organic solvent. The PSRK EOS is expressed as:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \tag{1}$$

The pure component parameters a_i and b_i can be calculated from the critical properties $T_{c,i}$ and $P_{c,i}$:

$$a_i(T) = 0.42748\frac{R^2T_{c,i}^2}{P_{c,i}}\alpha_i(T) \tag{2}$$

$$b_i = 0.08664\frac{RT_{c,i}}{P_{c,i}} \tag{3}$$

The temperature dependence function (α_i) of the pure component parameter a_i in original SRK EOS was:

$$\alpha_i(T) = [1 + (0.48 + 1.574\omega_i - 0.176\omega_i^2)(1 - T_r^{0.5})]^2 \tag{4}$$

where ω_i is the acentric factor. In order to correctly reproduce the vapor pressures of pure component, the Mathias–Copeman parameters were adopted in the PSRK EOS for describing the temperature dependence function (α_i) as:

$$\alpha_i(T) = [1 + c_{1,i}(1 - T_r^{0.5}) + c_{2,i}(1 - T_r^{0.5})^2 + c_{3,i}(1 - T_r^{0.5})^3]^2 \quad \text{for} \quad T_r < 1 \tag{5}$$

$$\alpha_i(T) = [1 + c_{1,i}(1 - T_r^{0.5})]^2 \quad \text{for} \quad T_r > 1 \tag{6}$$

The pure fluid parameters $c_{1,i}$, $c_{2,i}$, and $c_{3,i}$ are taken from the literature [22]. For applying the PSRK EOS to fluid mixture, the parameters a_m and b_m can be calculated using the PSRK mixing rule:

$$a_m = b_m\left[\frac{g_0^E}{A_1} + \sum x_i\frac{a_i}{b_i} + \frac{RT}{A_1}\sum x_i\ \ln\left(\frac{b_m}{b_i}\right)\right] \tag{7}$$

$$b_m = \sum x_i b_i \tag{8}$$

The value of A_1 for the PSRK mixing rule is -0.64663. g_0^E in Eq. (7) is the excess Gibbs energy at a reference state, which can be calculated by the UNIFAC model [23]. While the original UNIFAC parameters are temperature independent, an alternate temperature dependent function for the parameter ψ_{nm} in the UNIFAC model was adopted in the PSRK EOS:

$$\psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T}\right) \tag{9}$$

The temperature-dependent group interaction parameters (a_{nm}, b_{nm} and c_{nm}) for the parameter Ψ_{nm} in the UNIFAC model are also taken from the literature [22]. In this study, all parameters required in the UNIFAC model are given as supplementary material.

In order to compare the calculated results from the PSRK EOS, the original Soave–Redlich–Kwong (SRK) EOS is employed in this study. The original SRK EOS is expressed as Eqs. (1)–(4). The parameters a_m and b_m of fluid mixture can be calculated by applying the two-parameter van der Waals mixing rule:

$$a_m = \sum_i\sum_j x_i x_j a_{ij} \tag{10}$$

$$a_{ij} = \sqrt{(a_i a_j)}(1 - k_{ij}) \tag{11}$$

$$b_m = \sum_i\sum_j x_i x_j b_{ij} \tag{12}$$

$$b_{ij} = \left(\frac{b_i + b_j}{2}\right)(1 - l_{ij}) \tag{13}$$