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Preliminary Evaluation of the SPUNG Equation of State for Modelling the Thermodynamic Properties of CO_2 – Water Mixtures

Mohamed Ibrahim[a], Geir Skaugen[b], Ivar S. Ertesvåg[a]

[a] *NTNU, Kolbjørn Hejes veg 1A, N-7465Trondheim, Norway*
[b] *Sintef Energy Research, Kolbjørn Hejes veg 1A, N-7465Trondheim, Norway*

Abstract

The accuracy of the extended corresponding state equation SPUNG is preliminary evaluated for the density, and Vapor Liquid Equilibrium (VLE) calculations of the CO_2 -water mixtures. The evaluation is done by comparing the behavior of SPUNG to experimental data whenever possible, and three other state-of-the-art equations of state (EoS) of different classes. The three EoS are; the cubic equation Soave-Redlich-Kwong (SRK) with the van der Waals mixing rules, SRK with Huron Vidal mixing rules (SRK-HV), and the multi-parameter approach GERG-2004. The latter is used as a reference in the single phase region. The single phase studies for both liquid and vapor state are conducted at a mixture of 98% CO_2 and 2% H_2O. Recommendation for future work is highlighted.

Keywords: corresponding state , extended corresponding state, CCS, VLE

Nomenclature

Symbols

A	Helmholtz energy [J]
A^0	Reduced Helmholtz energy [K mol]
a,b	Gas parameters in SRK [J m^3 mol^{-2}], [m^3 mol^{-1}]

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C	Arbitrary variable [-]
f	Function of [-]
fug	Fugacity [N m^{-2}]
G_{∞}^{E}	Excess Gibbs energy at infinite pressure [J mol^{-1}]
k	Binary interaction parameter
N	Total number of points
n	Amount of substance [mol]
NC	Number of components in a mixture
P	Pressure [Pa]
R	Universal gas constant [J K^{-1} mol^{-1}]
T	Temperature [K]
V	Volume [m^3]
x	Mole fraction [-]
Z	Compressibility factor [-]
θ	Shape factor [-]
φ	Shape factor [-]
ω	Acentric factor [-]
Subscripts/Superscripts	
c	Critical state
exp	Experimental
i, j	Component i, j
M	Mixture
R	Reduced variable
Ref	Reference fluid co-ordinate
s	Simulation

1. Introduction

One important aspect for the CCS processes analysis and detailed simulations is the modeling of the thermodynamic properties for pure CO_2 and CO_2 mixtures. Indeed, the choice of models may have a great impact on the decisions about issues such as; process design, energy efficiency, economy and safety.

While the accuracy of a model is of higher importance to its computational efficiency for the process analysis, the computational efficiency plays a significant effect on the cost and feasibility of a CFD simulation. Three other dimensions of the challenge of developing or selecting a model are the generality with respect to different fluids and mixtures, consistency, and numerical stability when using it in conjunction with CFD simulations.

A consistent approach that shows a good compromise in accuracy and efficiency for hydrocarbons [1], and CO_2 with some binary and ternary impurities [2] is the SPUNG EoS. Since generality is a critical aspect when selecting a model to be used in CFD, this work aims to preliminary study the behavior of SPUNG EoS for the polar mixture of CO_2 – water. The study of the SPUNG generality with respect to CO_2 – water mixtures is of particular importance as it occurs often in CCS industry.

Here, an evaluation is done by comparing the behavior of SPUNG to three other state-of-the-art equations of state (EoS) of different classes. The three EoS are the cubic equation Soave-Redlich-Kwong (SRK) with the van der Waals mixing rule [4], SRK with Huron Vidal mixing rules (SRK-HV) [5], and the multi-parameter approach GERG-2004. The four approaches have different level of sophistication which usually has a direct proportionality to accuracy and computational complexity.

While SRK-HV is used because it shows a very good results for the investigated mixture as reported by Austegard et al. [3], the classical SRK is chosen because it’s a simple model and commonly used in industry. The EoS GERG04 is used here as a reference for the comparison in the single phase region.

2. Equations of State

An EoS is a model that calculates for both the liquid and gas phase using the same expression, which enhances the continuity near the critical point. An EoS for an N component mixture is an expression for pressure as a function of the mole fraction x, the temperature T, and the volume V;

$$P = P(x, T, V) \tag{1}$$

Given this expression, it can be manipulated to calculate the fugacity of each component fug_i. In the following subsection, a brief description of the EoS used in the work will be given together with references for further reading.

2.1. The standard SRK

The classical SRK model with Van der Waals mixing rules [4] is a cubic EoS that is written for a mixture as:

$$P = \frac{RTn}{V - bn} - \frac{an^2}{V^2 + bn\,V} \tag{2}$$

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i\, a_j}\left(1 - k_{ij}\right), \qquad b = \sum_i x_i b_i \tag{3}$$

$$a_i = \alpha_i \frac{0.42748\, R^2 {T_{c,i}}^2}{P_{c,i}}, \qquad b_i = \frac{0.08664\, RT_{c,i}}{P_{c,i}} \tag{4}$$

Here, $T_{c,i}$, $P_{c,i}$ are the critical temperature and pressure of component i. In order to close the system, an expression for α_i should be provided and a lot of varieties already exist.

2.2. The SRK Model with Huron Vidal mixing rules

This model suggested by Huron and Vidal [5], is an improvement from the classical SRK, as it drives a definition for the mixing rules from the excess Gibbs energy at infinite pressure (G_{∞}^{E}). A detailed description of that model has been made by Solbraa [6].

2.3. The corresponding state principle

The principle of corresponding state assumes that all substances exhibit the same behavior at a reduced state. A corresponding state EoS typically has one or more reference components described very accurately by a reference EoS. Therefore, the compressibility of the investigated fluids or mixtures can be evaluated as:

$$Z = f\left(V_{Ref}, T_{Ref}, \omega, \dots.\right)_{Ref} \quad (5)$$

In corresponding state approach the reference fluid V_{Ref} , and T_{Ref} are the reduced volume and temperature V_R, and T_R of the fluid or the mixture investigated.

2.4. The extended corresponding state principle

In the extended corresponding state concept, the mapping between the investigated fluid or mixture T, and V the reference fluid V_{Ref}, T_{Ref} is done via the shape factors φ, θ. Those shape factors take into account how the fluids or the mixture in consideration differs from the reference fluid.

$$T_{Ref} = \frac{T}{\theta} \quad (6)$$

$$V_{Ref} = \frac{V}{\varphi} \quad (7)$$

The shape factors φ, and θ can be computed analytically, using exact EoS, or using simpler forms of EoS.

2.5. The SPUNG with SRK

The SPUNG EoS investigated here, is an extended corresponding state approach that uses SRK cubic EoS to calculate the shape factors, and propane as a reference fluid. The SPUNG EoS uses the accurate modified Benedict-Webb-Rubin (MBWR) [7] EoS for the reference fluid. The SPUNG was introduced in the PhD thesis by Jørstad in 1993 [1] for low temperature hydrocarbon mixtures. Propane was chosen as the reference fluid to ensure that the reduced temperature of the considered mixtures would be above the reduced triple point of the reference fluid in order to avoid extrapolation of the reference equation. For CO_2 mixtures the choice of a difference reference fluid and equation should be considered, but in this initial work the original SPUNG EoS formulation has been used. The quality of the result will also depend on the quality of the reference equation itself as shown by [11] where choosing a more accurate reference equation for Methane improved the extended corresponding predictions considerably in the near-critical region.

2.6. The GERG

The state- of- the-art GERG EoS presented by Kunz et al. [8] is a multi-parameter approximation:

$$\frac{A_M(T,V,x)}{RT} = A_M^0(T,V,x) + \sum_{j=1}^{NC} x_j\, A^0{}_{j,R}(T_R,V_R) + \Delta A^0{}_{M,R}(T_R,V_R,x) \qquad (8)$$

Here, A denotes the Helmholtz energy and subscript M denotes a mixture. $\Delta A_{M,R}$ is the departure function which accounts for non-idealities of the mixture. The challenge with such formulations in addition to the high computational cost is that a reference EoS for each of the involved components should exist and be valid over an appropriate range of conditions.

3. Methodology

3.1. Numerical Tools

The NTNU-SINTEF in-house thermodynamic library is mainly used for the study presented. The library is a tool for predicting the thermodynamic properties using various approaches that ranges in level of sophistication and founding theory. The implementation of the NIST thermodynamics library REFPROP [9] is used for the calculations via GERG-2004.

3.2. Setup

3.2.1. Vapor Liquid Equilibrium (VLE) simulations

The set of experimental data by Bamberger et al. [10] is used for validation of the solubility of CO_2 and H_2O in each other at VLE conditions. The comparison is done at a temperature of 323.2 K and a pressure that varies between 4 and 14 MPa. The two-phase solubility at a specific pressure and temperature does not depend on the feed composition, but the vapor fraction does. Therefore, in order to numerically get a feed composition that gets the mixture into VLE at the specified pressure and temperature, the investigators start the simulation at every tested pressure from Pure CO_2, incrementing the H_2O mole fraction until VLE is reached.

3.2.2. Single phase simulations

For both liquid and vapor single phase simulations the author uses a mixture of 98% CO_2 and 2% H_2O in this preliminary study. This choice represents a common situation in CO_2 transport where CO_2 is dominant containing low H_2O impurities. The choice of temperatures and pressures was done by going parallel to the saturation line evaluated numerically using SRK-HV. The shift is done by subtracting and adding a five degree to the saturation temperature at a given pressure. A subsequent check of phase matching at this list of pressure and temperature pairs is performed. The GERG EoS is used as a reference for the density validation at in both liquid and gas phase comparisons. The author argument for using GERG as a reference for this mixture is that it exhibited very low error for the same mixture during the work reported by Kunz. et al. [8].

3.3. Error definition

The error of an EoS is measured here by the Average of Absolute Deviation (AAD) defined for an arbitrary variable C as:

$$AAD(C,\%) = \frac{100}{N}\sum_{r=1}^{N}\frac{(C_s - C_{exp,s})}{C_{exp,s}} \qquad (9)$$

4. Results

4.1. Vapor phase results

The density is computed for the 98% CO_2 and 2% H_2O mixture in the gas phase as explained in the setup section. The AADs of SPUNG, SRK, and SRK-HV with respect to GERG are 0.05, 0.44, and 0.72 % respectively. Figure 1 shows the comparison between the different models.

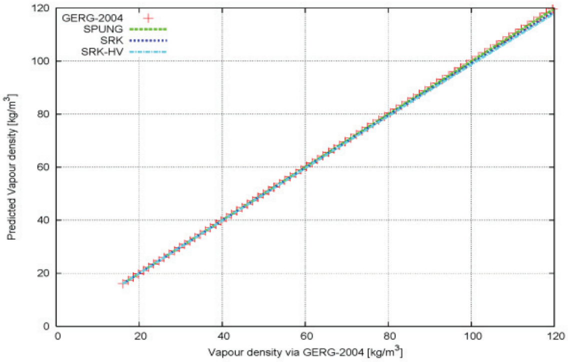

Figure 1 Comparison between the predicted densities for vapour phase

4.2. Liquid phase results

In the liquid region, the AADs of SPUNG, SRK, and SRK-HV with respect to GERG are 1.97, 9.75, and 10.6 respectively. Figure 2 shows the comparison between the different models behaviour for density calculations.

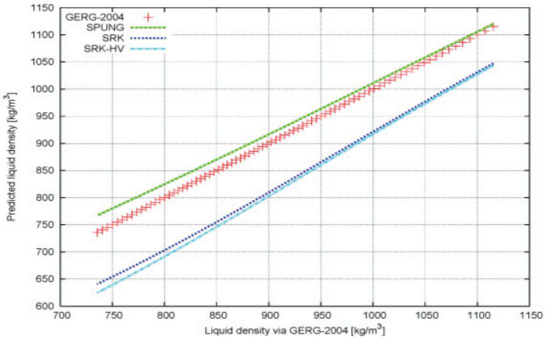

Figure 2 Comparison between the computed GERG densities as a reference to the predicted densities for liquid phase

4.3. VLE results

The predicted solubilities of CO_2 in water and water in CO_2 in comparison to experimental data are shown in Figures 3. The AADs of each EoS computing both components solubility is listed in Table 1.

Table 1 The AAD of each EoS for computing the mutual solubility of CO_2 and H_2O

	AAD (Solubility of H_2O) %	AAD (Solubility of CO_2) %
SRK-HV	4.23	2.09
SRK	18.22	91.83
SPUNG	24.88	91.70

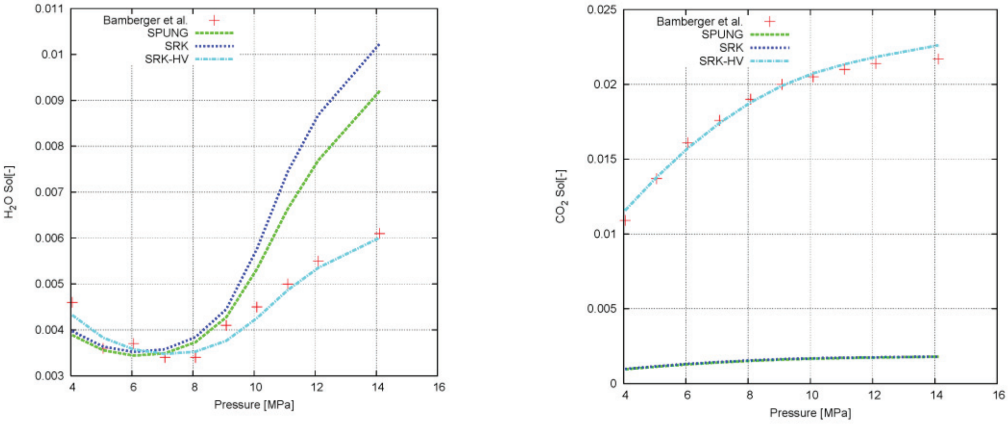

Figure 3 Solubility of H_2O and CO_2 in each other at temperature of 323.2 K

5. Discussion

The regions of superiority or failure of each model tested in this work is marked with +, or – in table 2. All models behave the same with a very good match in the gas phase since the max AAD is negligible. In the CO_2 rich liquid phase, the results of both cubic EoS get much worth as it goes up to 9.75 and 10.6 % for SRK and SRK-HV respectively. The SPUNG EoS shows a superior predictability in this region with a maximum AAD of 1.97%. In VLE calculations, the advantage of using Huron Vidal mixing rules appears clearly for computing both components solubilities as shown in Figures 3 and 4. This result is very consistent to the work done by Austegard et al. [3]. The standard SRK and SPUNG behave well for H_2O solubility up to 10 MPa (100 bars) which is a large interval of industrial interest, and beyond that value the error grows aggressively as shown in Figure 3. The two methods error for CO_2 solubility is intolerable over the whole range of the simulated pressure values. The observation that SPUNG and SRK have the same behavior at VLE conditions, suggests that the SPUNG problems at these conditions might have been inherited from SRK unpredictability reported by Austegard et al. [3].

Table 2 the domain of success of each tested method

	SPUNG	SRK	SRK-HV
CO_2 Liquid phase	+	-	-
Gas phase	+	+	+
Bamberger et al.: H_2O solubility(40-100 bars)	+	+	+
Bamberger et al.: H_2O solubility (100-140 bars)	-	-	+
Bamberger et al.: CO_2 Solubility	-	-	+

6. Conclusion and outlook

The standard SRK and its modification with Huron Vidal mixing rules are behaving almost the same in the in the single phase for this polar mixture, what shows no advantage of using SRK-HV instead of the standard formulation for both liquid and gas phase calculations. The SPUNG error in the liquid phase is one-fifth of the cubic equation models and very close to the GERG results with less than 2% AAD, while it is much less expensive compare to the GERG complexity. Although SPUNG was developed for better prediction of hydrocarbon behavior, these results show a great potential in capturing CO_2 -water in the cases where VLE is not of interest, and motivates for further development of the approach to improve its VLE prediction capability. In order to generalize the SPUNG advantages or disadvantages highlighted here in dealing with CO_2 – water, a detailed study on more sets of experimental data, feed compositions and phases should be performed.

7. Acknowledgement

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