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Preliminary Evaluation of SPUNG with SRK for Modelling the Thermodynamic Properties of CO₂ – Water Mixtures

By

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Outline

- Motivation
- Models
- Reference for Validation
- Numerics
- Results
- Summery
- Conclusions
- Outlook



Motivation

- SPUNG is a consistent approach, that showed a very good results for:
 - I. Hydrocarbons as reported by Jørstad in his thesis "Equations of State for Hydrocarbon Mixtures, Phd-thesis, *NTH*, 1993"
 - II. CO₂ with some binary and ternary impurities, in the work by Willhelmsen et. al. "Willhelmsen, Ø., Skaugen, G., Jørstad, O. and Li, H.L. "Evaluation of SPUNG and other Equations of State for use in Carbon Capture and Storage modelling" (Presented at TCCS-6)

Therefore;

- It can be considered as an approach with high generality potential, and to generalize the results to CO₂ - polar mixtures, a detailed evaluation is required



Models

- ***Soave-Redlich-Kwong (SRK)***, which is a cubic equation of state (EoS) first introduced on 1972;
(Soave G, Equilibrium constants from a modified Redlich-Kwong equation of state, Chemical Engineering Science, Volume 27, Issue 6, June 1972, Pages 1197-1203)
- ***The SRK Model with Huron Vidal mixing rules (SRK-HV)***, This model suggested by Huron and Vidal on 1979;
(Huron M.J, Vidal J. New mixing rules in simple equations of state for representing vapour-liquid equilibrium of strongly non-ideal mixtures. *Fluid Phase Equilibria*. 1979; **3**:255-271)
- **The SPUNG approach** which is the scope of this work, and was first introduced by O. Jørstad in his PhD thesis;
(Equations of State for Hydrocarbon Mixtures, Phd-thesis, *NTH*, 1993)
- ***GERG2004*** first introduced by O. Kunz, et. al.;
(The GERG-2004 Wide-Range Equation of State for Natural Gases and other mixtures. Düsseldorf: VDI Verlag; 2007)



Reference for Validation

➤ Single phase

- For Liquid and gas phase simulations GERG2004 was used as a reference, our argument is that it has showed a maximum AAD of 0.75% at a similar conditions of these that are tested here

➤ VLE

- The experimental work done by A. Bamberger was used for VLE data validation;

(A. Bamberger, G. Sieder, G. Maurer, High-pressure (vapor+liquid) equilibrium in binary mixtures of (carbon dioxide+water or acetic acid) at temperatures from 313 to 353 K, The Journal of Supercritical Fluids, Volume 17, Issue 2, 10 April 2000, Pages 97-110)



Numerics

➤ Numerical tools

- For SPUNG, SRK, SRK-HV an in-house thermodynamics library is used,
- For computation using GERG; the NIST implementation REFPROP is used.

➤ Error definition

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

Where C can be any quantity

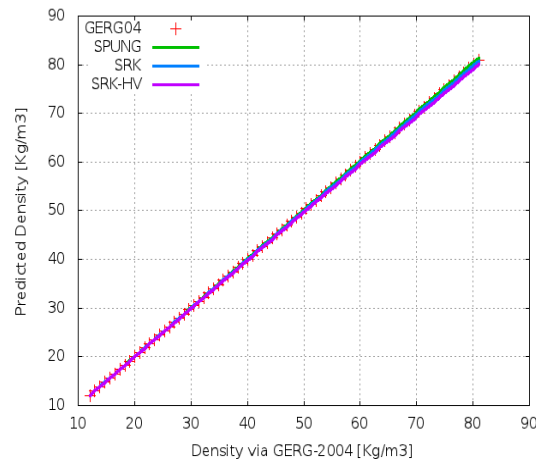


Results (1)

➤ Gas Phase

- A mixture of 98% CO₂ and 2% H₂O is used in this preliminary study. This choice represents a CO₂ dominant but still H₂O profound mixture
- The choice of temperatures and pressures was done by going parallel to the dew line and then adding 5 degrees to the dew temperature

	AAD %
SRK-HV	0.72
SRK	0.44
SPUNG with SRK	0.05



predicted density for liquid phase VS. GERG as a reference



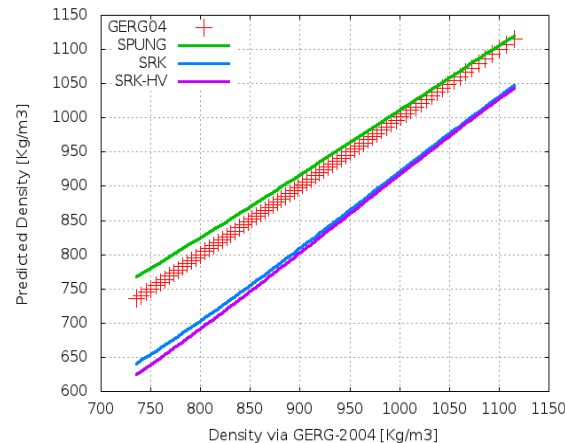
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Results (2)

➤ Liquid Phase

- Again a mixture of 98% CO₂ and 2% H₂O is used in this preliminary study
- The choice of temperatures and pressures was done by going parallel to the bubble line and then subtracting 5 degrees from the bubble temperature

	AAD %
SRK-HV	10.6
SRK	9.75
SPUNG with SRK	1.97



predicted density for liquid phase VS. GERG as a reference

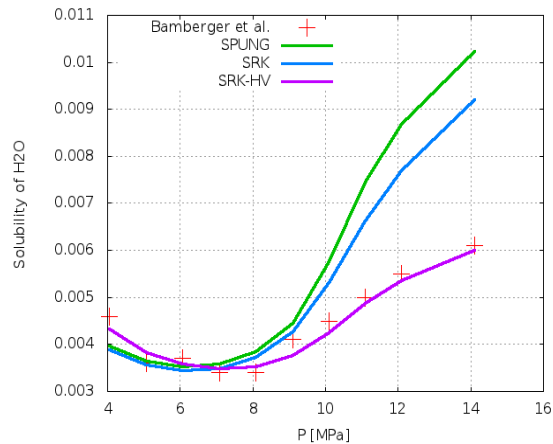


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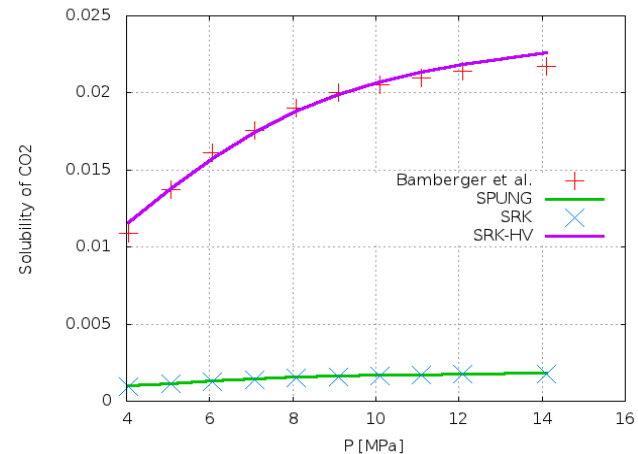
Results (3)

➤ VLE

	AAD (Solubility of H ₂ O) %	AAD (Solubility of CO ₂) %
SRK-HV	4.23	2.09
SRK	18.22	91.83
SPUNG with SRK	24.88	91.70



Solubility of H₂O in CO₂ at temperature of 323.2 K



Solubility of CO₂ in H₂O at temperature of 323.2 K

Summery

	SPUNG	SRK	SRK-HV
CO ₂ rich liquid phase	+	-	-
Gas phase	+	+	+
LLE (Not yet reported)	+	-	-
Bamberger et al.: H ₂ O solubility(40-100 bars)	+	+	+
Bamberger et al.: H ₂ O solubility (100-140 bars)	-	-	+
Bamberger et al.: CO ₂ Solubility	-	-	+

Conclusions

- In gas phase all The Three EoS matches very well with a negligible error,
- in liquid phase SRK standing alone and SRK-HV are behaving the same with an AAD of $\approx 10\%$. Therefore, for a single phase simulation its no advantage of using Huron Vidal mixing rules,
- SPUNG EoS behaves much better in the liquid region with an AAD of $\approx 2\%$,
- SRK with Huron-Vidal behaves very accurate in the VLE region in consistency to the work done by Austegard et al.
- SPUNG and SRK do well for the solubility of H₂O in CO₂ up to 100 bars, beyond that the error grows aggressively
- The predictability of SPUNG and SRK is intolerable for the CO₂ solubility in H₂O.



Outlook

- Testing a range of feed concentrations for the single phase simulations,
- using experimental data for the single phase validation,
- testing over a larger set of conditions in the VLE region,
- regression of the interaction parameters over a rich set of experimental data,
- Modifying SPUNG to solve the VLE solubility problem, and

Thank you for your attention

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