AN IMPROVED GROUP CONTRIBUTION VOLUME TRANSLATED PENG-ROBINSON EQUATION OF STATE - VGTPR

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Introduction

- The Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) cubic equations of state (CEOS) are two of the major 'work-horses' in common day chemical engineering applications - especially process simulation.
- A number of advancements have been made on the traditional van der Waals type mixing rules, which have increased the range of applicability of these CEOS to non-ideal systems.
- One advancement has been the development of the excess Gibbs energy (g^E) mixing rules, which use the g^E calculated from a model to calculate the CEOS mixture attractive parameter, a_m [1].
- The more recent development of group-contribution g^E models (eg. UNIFAC [2] and mod UNIFAC (Do) [3]) has meant that a CEOS using a g^E mixing rule may be fully predictive - only group-contribution parameters are required (i.e. no binary interaction parameters are needed). These models are commonly known as Group-Contribution Equations of State (GCEOS).
- Predictive Soave-Redlich-Kwong (PSRK) [4] is at present one of the most widely used GCEOS models in process simulations.
- However, PSRK is laden with a number of problems in special cases.
- Volume Translated Peng-Robinson (VTPR) [5] was developed to correct these problems and provide an improved model over PSRK.
- Despite VTPR being a better GCEOS than PSRK, a severe lack of parameters available for use in VTPR means that PSRK will continue to be the model of choice for some time to come.

Problems with g^E Mixing Rules

- In order to derive the g^E mixing rules, the following assumption is made:

$$g^E_{\mathrm{EOS}} = g^E_{\mathrm{g^E\text{-}model}}$$

- However, when using the g^E mixing rules the following inequality is found regarding activity coefficient (γ) calculations:

$$\gamma_{i,\mathrm{EOS}} \neq \gamma_{i,\mathrm{g^E\text{-}model}}$$

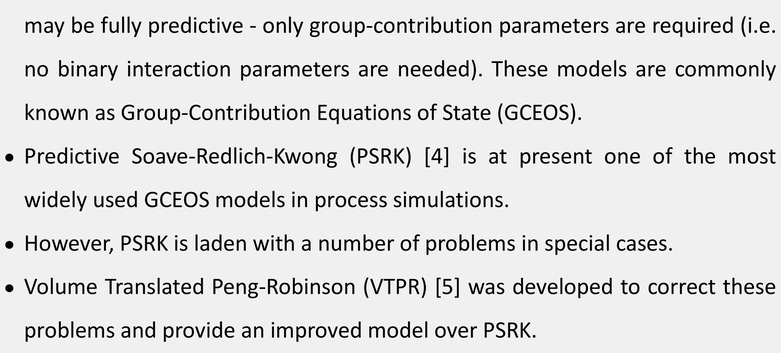

Fig. 1. γ vs x_1 for the system Propane (1) + Benzene (2) at 310K (— g^E model (mod UNIFAC (VTPR)), - - - EOS (VTPR))

- Temperature dependent g^E model parameters (such as those from mod UNIFAC (Do)) lead to poor results when used in a g^E mixing rule - these parameters need to be refitted specifically for use in the mixing rule.

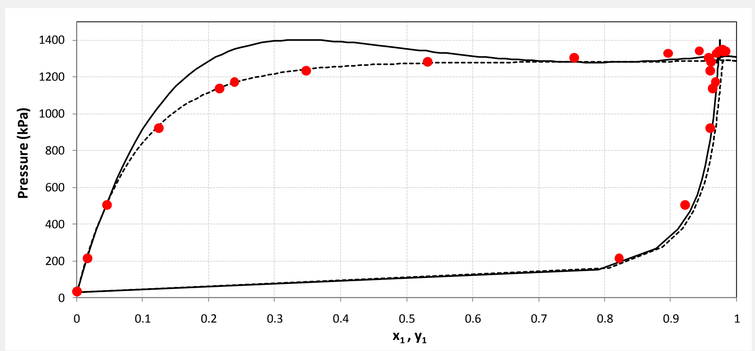

Fig. 2. P-x-y diagram for the system Propane (1) + Methanol (2) at 310.7K showing the poor prediction that results from temperature dependent g^E model parameters (● experimental data taken from the DDB [6], — VTPR using mod UNIFAC (Do) parameters, - - - mod UNIFAC (Do))

The Solution - An Exact g^E Mixing Rule

- Introduce a correction term into the EOS to force the calculation of each γ_i to exactly match that provided by the g^E model [7].

Advantages of an Exact g^E Mixing Rule

- Exact match of γ's from the EOS and the g^E model allows interchange of the 2 approaches in a simulation without discrepancies in results.
- Therefore, a process simulation does not need to be restricted to one approach - the EOS approach and the g^E model approach may be used simultaneously while only requiring the parameters from the g^E model.
- This then allows the use of all existing mod UNIFAC (Do) parameters in the VTPR model, making available with immediate effect the advantages it contains in many more applications (see Fig. 3).

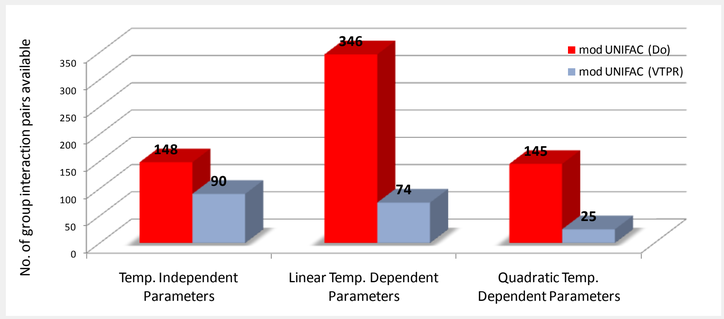

Fig. 3. Comparison of parameters available for use in mod UNIFAC (Do) and the VTPR model (taken from DDBSP 2009)

The VGTPR Model

- **VGTPR** = Volume and Gibbs Translated Peng - Robinson [7]
- VTPR is theoretically the best GCEOS to date, therefore the idea of an exact g^E mixing rule is applied to this model.
- Limited parameter availability is no longer a problem.
- A translation (correction) term is introduced into the a_m mixing rule from VTPR in order to force each γ_i calculated from the EOS to exactly match the g^E model values:

$$a_m = b_m\left(\sum_{i=1}^{nc} z_i \frac{a_i}{b_i} - \frac{g^E_{res} + g^E_{trans}}{0.53087}\right)$$

- The translation g^E term may be defined using γ-translation terms as follows:

$$g^E_{trans} = R \cdot T \cdot \sum_{i=1}^{nc} z_i \cdot \ln \gamma_{i,trans}$$

- Each $\gamma_{i,\mathrm{trans}}$ is found by an iterative procedure as follows:

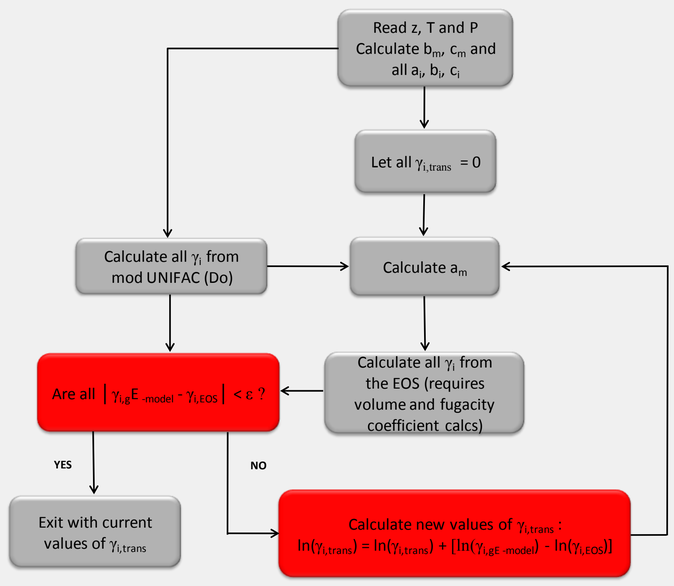

Fig. 4. Flow sheet showing how the $\gamma_{i,\mathrm{trans}}$ values are iteratively calculated in the VGTPR model

- As a result of the above procedure (Fig. 4), the following is obtained for the same system represented in Fig. 1:

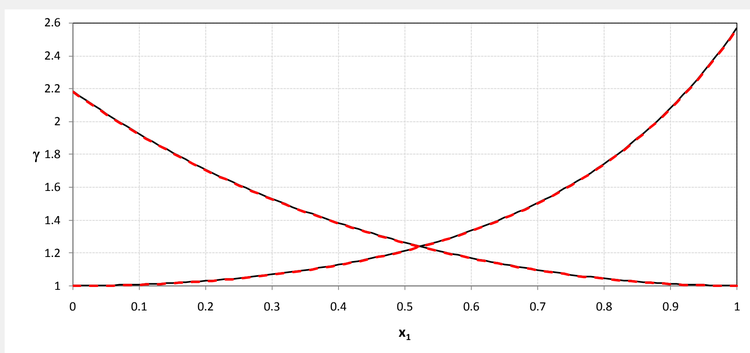

Fig. 5. γ vs x_1 for the system Propane (1) + Benzene (2) at 310K (— g^E model (mod UNIFAC (Do)), - - - EOS (VGTPR))

- The result of a Bubble-P calculation using VGTPR is displayed in Fig. 6 below. The results obtained are compared to those of PSRK, VTPR and mod UNIFAC (Do):

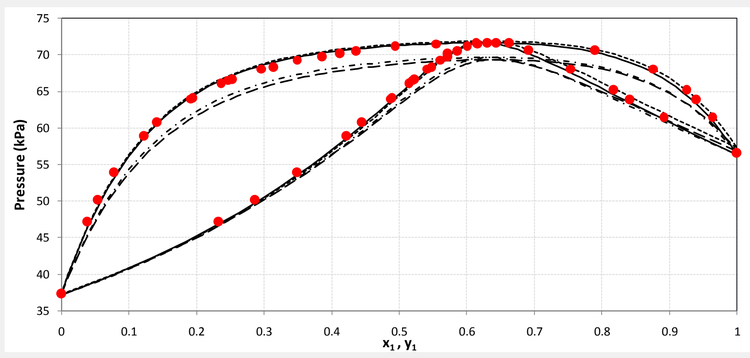

Fig. 6. P-x-y diagram for the system Acetone (1) + Hexane (2) at 313.15K (● experimental data taken from the DDB [8], — VGTPR, - - - mod UNIFAC (Do), — — — PSRK, - · - VTPR)

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Fixed Reference Volume Idea

- **PROBLEM**: calculating $\gamma_{i,\mathrm{EOS}}$ as T_r approaches and exceeds 1
- Because this calculation is not possible, the VGTPR model as described in Fig. 4 fails at these elevated temperatures.
- The idea of [7] then was to calculate the $\gamma_{i,\mathrm{EOS}}$ at a fixed (dense) reference volume (v*) and use these values to determine the $\gamma_{i,\mathrm{trans}}$ for use in the calculations at the actual system conditions. (i.e. the procedure of Fig. 4 is identical except $\gamma_{i,\mathrm{EOS}}$ is calculated using v* instead of the saturated liquid volume).
- v* was defined as follows (v* and b are pure component or mixture values):

$$v^* = 1.22489 \cdot b$$

- It was assumed that the γ's at subcritical conditions have a very weak pressure or density dependence [7], therefore the $\gamma_{i,\mathrm{EOS}}$ could be calculated at v* and assumed equal to that at the saturated liquid density. This allows calculation of $\gamma_{i,\mathrm{EOS}}$ under supercritical conditions and greatly simplifies subcritical calculations.
- This assumption though has been found to not hold true. Investigations of subcritical systems (see Fig. 7) have shown that $\gamma_{i,\mathrm{trans}}$ (and therefore $\gamma_{i,\mathrm{EOS}}$) differs greatly between the reference state and the saturated state.
- The fixed reference volume also forces $\gamma_{i,\mathrm{trans}}$ to become a temperature independent parameter (Fig. 7).

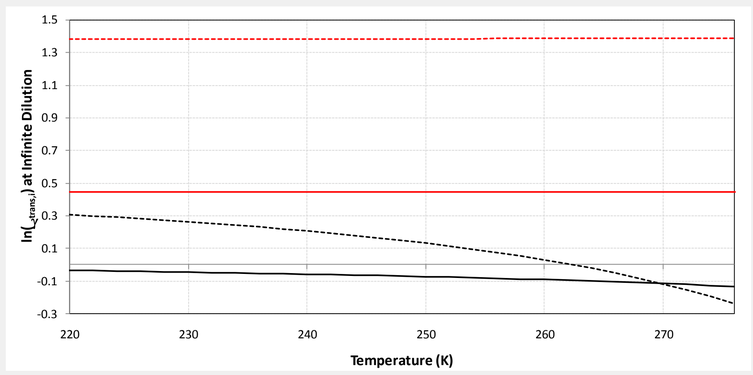

Fig. 7. $\ln(\gamma_{i,\mathrm{trans}})$ at infinite dilution vs Temperature for the system Ethane (1) + Heptane (2) (— Ethane at infinite dilution calculated using the saturated liquid volume, - - - Heptane at infinite dilution calculated using the saturated liquid volume, — Ethane at infinite dilution calculated using the fixed reference volume, - - - Heptane at infinite dilution calculated using the fixed reference volume)

- **Consequence**: Incorrect $\gamma_{i,\mathrm{trans}}$ values are calculated using v* which leads to incorrect $\gamma_{i,\mathrm{EOS}}$ values when calculated for the actual system conditions.
- $\gamma_{i,\mathrm{EOS}}$ is no longer forced to equal $\gamma_{i,g^E\text{-model}}$ (see Fig. 8).

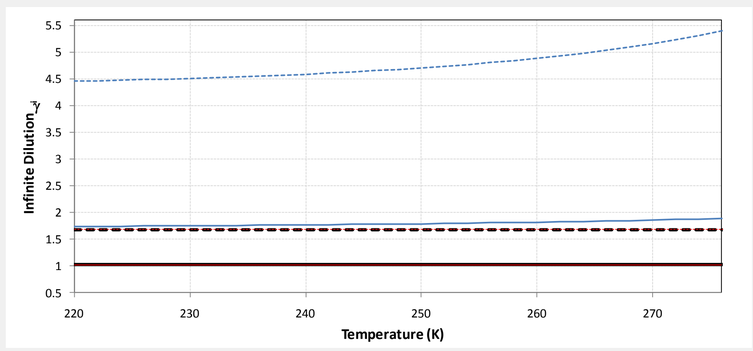

Fig. 8. Infinite dilution γ vs Temperature for the system Ethane (1) + Heptane (2) (— Ethane at infinite dilution from mod UNIFAC (Do), - - - Heptane at infinite dilution from mod UNIFAC (Do), — Ethane at infinite dilution from VGTPR with no ref. volume, - - - Heptane at infinite dilution from VGTPR with no ref. volume, — Ethane at infinite dilution from VGTPR using ref. volume, - - - Heptane at infinite dilution from VGTPR using ref. volume)

Conclusions and Future Work

- The idea is sound and provides promising results for subcritical calculations.
- The fixed reference volume idea of [7] for calculations at elevated temperatures appears to be flawed even for subcritical calculations.
- More work needs to be done to extend VGTPR to supercritical calculations, which will require the calculation of $\gamma_{i,\mathrm{EOS}}$ at some reference state from which the $\gamma_{i,\mathrm{trans}}$ may be determined and related to the actual state of the system.

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