Measurement and prediction of multi-property data of CO$_2$-N$_2$-O$_2$-CH$_4$ mixtures with the "Peng-Robinson + residual Helmholtz energy-based" model

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A B S T R A C T

The so-called "Peng-Robinson + residual Helmholtz energy-based mixing rules" equation of state is a promising thermodynamic model that enables the accurate representation of VLE properties of highly non−ideal binary mixtures including the Type-III phase behaviour, according to the classification of van Konynenburg and Scott.

So far, the accuracy of this model has been assessed only considering data over which it has been optimized. This publication aims at presenting a multi-property validation of this model over vapour-liquid equilibrium data of the ternaries CO$_2$-N$_2$-O$_2$ and CO$_2$-CH$_4$-N$_2$ and experimental values of enthalpy changes due to mixing of binary mixtures CO$_2$-N$_2$ and CO$_2$-CH$_4$ found in the literature. To integrate the scarce amount of available multicomponent data, this paper also presents new experimental isothermal VLE data for the mixture CO$_2$-N$_2$-O$_2$ at 273 and 233 K, also used along the model validation process.

Finally, modelling results obtained from the model "Peng-Robinson + residual Helmholtz energy-based mixing rules" are compared with calculations performed with the widely applied standard Peng-Robinson equation of state.

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1. Introduction

One of the current unsolved issues that affects the field of applied thermodynamics is related to the modelling of vapour-liquid equilibria of mixtures composed by species characterized by very different volatilities and consequently by significant deviations to ideality.

Previous papers by the same authors [1—3] highlight that the combination of the Peng-Robinson (PR) Equation of State (EoS) with the residual part of the Wilson excess Helmholtz energy model ($a_{res}^{E,Wilson}$) enables to define mixing rules for the energy parameter of cubic equations of state. Such a "PR + EoS/$a_{res}^{E,Wilson}$" model has resulted to be highly accurate in the representation of thermodynamic vapour-liquid equilibrium properties of highly non-ideal binary mixtures of Type III, according to the classification of van Konynenburg and Scott [4,5], typically encountered in modelling fluids treated by CO$_2$ Capture and Storage (CCS) and Enhanced Oil Recovery (EOR) applications.

Whilst these previous papers have been focussed on the optimization of this model over VLE data of typical binary mixtures, the present work aims to validate such an optimized model over multicomponent and multiproperty data. Thus, after a brief introduction (section 2) of the PR + EoS/$a_{res}^{E,Wilson}$ model, as well as of the standard Peng-Robinson equation of state with which it will be compared, this work: (i) introduces new vapour-liquid experimental measurements for the ternary system CO$_2$-N$_2$-O$_2$ (section 3); (ii) validates the PR + EoS/$a_{res}^{E,Wilson}$ model and compares it with the standard Peng-Robinson equation of state, over VLE ternary measurements here presented and over other available VLE ternary measurements and mixing enthalpy data of binary mixtures (section 4).

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2. The model

The model that this work aims to validate, presented and optimized in Refs. [1,2,6], is based on the Peng-Robinson (PR) Equation of State (EoS):

$$P(T, v, \mathbf{z}) = \frac{RT}{v - b_m} - \frac{a_m}{v^2 + 2b_m \cdot v - b_m^2} \tag{1}$$

Mixing rules for a_m and b_m in the standard PR EoS are:

$$\begin{cases} a_m = \sum_i^{NC} \sum_j^{NC} z_i z_j \sqrt{a_i a_j}\, (1 - k_{ij}) \\ b_m = \sum_i^{NC} z_i b_i \end{cases} \tag{2}$$

The model that we aim to compare with the standard PR equation of state differs from the original PR formulation in the applied class of mixing rules (MR), which in this new case is the "Residual Excess Helmholtz energy — based" MR, namely EoS/a_{res}^E MR (see Ref. [1] for their derivation), with the particular selection of the quadratic mixing rule and Lorentz [7] combining rule for the covolume:

$$\begin{cases} b_m = \sum_{i=1}^{NC} \sum_{j=1}^{NC} z_i z_j \left(\frac{b_i^{1/s} + b_j^{1/s}}{2} \right)^s \\ \frac{a_m}{b_m} = \sum_{i=1}^{NC} z_i \frac{a_i}{b_i} + \frac{a_{res}^{E,\gamma}}{\Lambda_{EoS}} \end{cases} \tag{3}$$

Pure component energy and covolume parameters, a_i and b_i, are calculated as in the original PR model:

$$\begin{cases} a_i(T) = a_{c,i} \cdot \alpha_i(T) \\ \alpha_i(T) = \left[1 + m_i \left(1 - \sqrt{T/T_{c,i}} \right) \right]^2 \\ m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \\ a_{c,i} = \Omega_a \cdot \frac{R^2 T_{c,i}^2}{P_{c,i}} \\ b_i = \Omega_b \cdot \frac{RT_{c,i}}{P_{c,i}} \\ X = \frac{-1 + \left(6\sqrt{2} + 8 \right)^{1/3} - \left(6\sqrt{2} - 8 \right)^{1/3}}{3} \\ \Omega_a = \frac{8 + 40X}{49 - 37X} \sim 0.45724 \\ \Omega_b = \frac{X}{X + 3} \sim 0.07780 \end{cases} \tag{4}$$

Pure component properties (critical temperature, T_c, pressure, P_c, and acentric factor, ω) considered in this work are reported in Ref. [2].

It is worth highlighting that the Soave α-function used in the original PR equation of state is retained in this formulation, to model pure component energy parameters, since it holds the thermodynamically consistent [8,9] *positive - monotonically decreasing - convex* temperature dependency within the temperature domains that characterize most of the systems of engineering applications.

Moreover, considering the formulations of the applied mixing rules (equ. (3)):

- parameter s has been set to *2*, as proposed by Voutsas et al. when they developed the UMR-PR (Universal Mixing Rule−Peng-Robinson) model [10].
- parameter Λ, present in the mixing rule for a_m, has been considered equal to -0.52398, that is the value found by Michelsen along the derivation of the MHV1 [11] mixing rule, as justified in Ref. [1].
- the Wilson's activity coefficient model has been applied to derive the expression for the residual part of the excess Helmholtz energy model, $a_{res}^{E,Wilson}$:

$$a_{res}^{E,Wilson}(T, \mathbf{z}) = a^{E,Wilson} - a_{comb}^{E,Wilson}$$

$$= \underbrace{-\sum_{i=1}^{NC} z_i ln \left(\sum_{j=1}^{NC} z_j \Lambda_{ij}(T) \right)}_{a^{E,Wilson}} - \underbrace{\sum_{i=1}^{NC} z_i ln \left(\frac{\Phi_i}{z_i} \right)}_{a_{comb}^{E,Wilson}} \tag{5}$$

where:

- $\Phi_i = z_i v_i / \sum_{j=1}^{NC} z_j v_j$ is the volume fraction of the *i-th* molecule

- $\Lambda_{ij}(T) = \frac{v_j}{v_i} \exp\left(-\frac{A_{ij}}{T} \right)$ is the local composition parameter, expressed as an exponential function of two adjustable parameters, A_{ij}, proportional to molecular interaction energies, $\varepsilon_{ji} - \varepsilon_{ii}$: $A_{ij} = N_A(\varepsilon_{ji} - \varepsilon_{ii})$.

The application of these mixing rules requires the knowledge of parameters A_{ij} that, for many of the CO_2-Capture and Storage systems treated in this series of papers, have been optimized over the available vapour-liquid equilibrium data of binary systems, as explained and justified in Refs. [1–3]. Although the Wilson model is derived by assuming parameters A_{ij} as being independent of temperature, it has been shown that these parameters are actually temperature dependent, despite the original assumption.

The validation of this model is performed over multiparameter and multicomponent data, partially presented in the next section 3 and measured by Lasala during her doctorate [6].

3. Experimental activity

This section presents new isothermal VLE measurements for ternary mixtures CO_2-N_2-O_2 measured at 273 K and 233 K, in the pressure ranges 40—150 bar.

3.1. Experimental VLE apparatus

The main features of the experimental apparatus used to perform the measurements here presented have already been detailed in Refs. [1,12]. For this reason, we ask the reader to refer to these published works for more information about the operation of the apparatus and the procedures for the calibration of temperature, pressure and compositional measurements. In the following section 3.2, we report some differences in performing this experimental campaign over ternary systems, with respect to the one previously [1] carried out when measuring binary VLE data.

3.2. Experimental procedure

Binary phase diagrams have been obtained in Ref. [1] by first introducing into the equilibrium cell the less volatile component (in that campaign CO_2) and then by progressively increasing the pressure with the introduction of a second component (either O_2 or N_2 or Ar). For each pressure level, the compositions of vapour and liquid phases were measured and an isothermal phase diagram was obtained by increasing the pressure from the saturation pressure of