Abstract

Multi-fluid mixture models for highly accurate multiparameter equations of state have been applied very successfully in the past years in order to accurately model thermophysical properties of mixtures. However, this work shows that the predictive capability of this type of mixture model is rather limited. Therefore, a new model is proposed, which is a combination of the multi-fluid model with excess Gibbs energy models. This new approach results in a theoretically based formulation for the departure function of the multi-fluid model. It is shown that the new model yields very good results for the description of binary mixtures of the components ethanol, ethane, carbon dioxide, propene, and benzene. While the state-of-the-art multi-fluid model with either predictive linear mixing rules or Lorentz-Berthelot combining rules for the parameters of the reducing functions does not represent the phase equilibria for the investigated binary mixtures well, and in case of the azeotropes predicts quantitatively wrong mixture behavior, the new model is capable of accurately representing the phase equilibria of all binary mixtures investigated.

1 Introduction

Phase equilibria of fluid mixtures have been an important and frequently studied topic in science. They also play an important role in many industrial applications such as rectification or distillation processes. As a consequence, various models for calculating phase equilibria of fluid mixtures have been proposed, some of them based on one-fluid mixture models, e.g., the cubic equations of state Soave-Redlich-Kwong [1, 2], Peng-Robinson [3], and various modifications, see, e.g., [4–6] and others based on multi-fluid approximations, e.g., [7–9]. All of these models contain adjustable parameters, which need to be fitted to experimental data of typically binary mixtures, such as vapor-liquid equilibria (VLE), densities, isobaric heat capacities, etc. In the case of simple cubic equations of state, usually quadratic mixing rules for the energy parameter $a$ and either linear or quadratic mixing rules for the covolume parameter $b$ are used, for which either one or two adjustable binary interaction parameters can be fitted to experimental data. For this approach, however, experimental data are needed for each binary mixture of interest in order to fit the interaction parameters. Predicting VLE or liquid-liquid equilibria (LLE) for mixtures on the basis of already adjusted binary interaction parameters for other mixtures is rather difficult [10]. Therefore, another more predictive approach was developed: For almost 40 years now [11, 12], cubic equations of state (one-fluid models), have been combined with models explicit in the excess Gibbs energy ($g^E$-models), such as UNIQUAC [13], UNIFAC [14], or NRTL [15]. With these methods, phase equilibria of various systems can be described very accurately (see, e.g., [11, 16–19]). While the combination of cubic equations of state with UNIQUAC or NRTL also requires adjusting binary interaction parameters, the combination of equations of state with UNIFAC allows for a more predictive way of modeling mixtures. The UNIFAC group interaction model describes interactions of structural groups of molecules. Therefore, the idea behind this approach is that group interaction parameters can be adjusted for mixtures for which data exist and subsequently these group interaction parameters can be used in order to describe mixtures for which no data exist. While this concept is well established for the combination of cubic equations of state with $g^E$-models, as far as the authors know, no attempts have been made to combine multi-fluid based mixture models for highly accurate multiparameter equations of state with $g^E$-models. In this work, a combination of the multi-fluid model with $g^E$-models is proposed. The performance of the new model is evaluated for all binary mixtures of the polar component ethanol (C$_2$H$_5$OH) and the nonpolar components ethane (C$_2$H$_6$), carbon dioxide (CO$_2$), propene (C$_3$H$_6$), and benzene (C$_6$H$_6$). The experimental data that were used to compare the models to and to fit the new model parameters are the following: ethane+CO$_2$ [20–25], ethane+propene [26, 27], ethane+benzene [28], ethane+ethanol [29], CO$_2$+propene [21, 26], CO$_2$+benzene [30–33], CO$_2$+ethanol [34–46], propene+benzene [47, 48], propene+ethanol [49], benzene+ethanol [50–53].

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2 Multi-fluid Mixture Models - State of the Art

The most commonly used mixture model for multiparameter Helmholtz equations of state was developed by Lemmon and Tillner-Roth [54]. In later years, Kunz and Wagner [7, 8] improved the model. The model of Kunz and Wagner covers 21 substances, comprising the main natural gas components as well as typical minor components in natural gas mixtures. The structure of the mixture model was also used by Gernert and Span [9], who established a model for the most relevant components in captured CO2 which can be used to assess capture and transport processes for Carbon Capture and Storage (CCS) applications. The general structure of all of these mixtures models reads:

\[ \alpha (\delta, \tau, \bar{x}) = \alpha^0 (\rho, T, \bar{x}) + \alpha^r (\delta, \tau, \bar{x}), \]

where \( \alpha^0 \) is the ideal part of the reduced Helmholtz energy of the mixture, and \( \alpha^r \) is the residual part of the reduced Helmholtz energy of the mixture. For the ideal part, the following mixing rule is applied:

\[ \alpha^0 (\rho, T, \bar{x}) = \sum_{i=1}^{N} x_i \left[ \alpha^0_{oi} (\rho, T) + \ln (x_i) \right], \]

where \( N \) stands for the number of components in the mixture, \( x_i \) stands for the mole fraction of component \( i \) in the mixture and \( \alpha^0_{oi} \) is the ideal part of the reduced Helmholtz energy of pure component \( i \). It is important to note that the ideal part of Eq. 1 may not be confused with the ideal mixture of ideal gases. The ideal part of the mixture model is equal to the ideal mixture of ideal gases in the limit of zero density, if the residual part goes to zero. However, throughout this article, the term "ideal part" refers to the ideal part of the mixture model according to Eq. 2. The common mixing rule for the residual part reads

\[ \alpha^r (\delta, \tau, \bar{x}) = \sum_{i=1}^{N} x_i \alpha^r_{oi} (\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha^r_{ij} (\delta, \tau), \]

where \( \alpha^r_{ij} \) is the residual part of the reduced Helmholtz energy of pure component \( i \) and the last term on the right hand side of Eq. 3 is the sum over the so called binary departure functions \( \alpha^r_{ij} (\delta, \tau) \). \( \delta \) and \( \tau \) are the reduced density and the inverse reduced temperature, respectively, it is

\[ \delta = \frac{\rho}{\rho_t (\bar{x})} \quad \text{and} \quad \tau = \frac{T_t (\bar{x})}{T}, \]

where \( T_t (\bar{x}) \) is the reducing function for the temperature, \( T \) is the temperature, \( \rho_t (\bar{x}) \) is the reducing function for the density, and \( \rho \) is the density of the mixture. Both reducing functions depend on the composition of the mixture and different functional forms have been tried for the reducing functions, see, e.g., Tillner-Roth and Lemmon [54] and Kunz and Wagner [7, 8]. The reducing functions of Kunz and Wagner [7, 8] have been successfully applied to typical natural gas mixtures [7, 8] and CCS-relevant mixtures [9] and read:

\[ T_t (\bar{x}) = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} \cdot T_{c,j})^{0.5}, \]

\[ \frac{1}{\rho_t (\bar{x})} = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8} \left( \frac{1}{\rho_{c,i}} + \frac{1}{\rho_{c,j}} \right)^3, \]

with \( T_{c,i} \) denoting the critical temperature of component \( i \) and \( \rho_{c,i} \) denoting the critical density of component \( i \). The reducing functions contain four adjustable parameters per binary mixture, namely \( \beta_{T,ij} \), \( \gamma_{T,ij} \), \( \beta_{v,ij} \), and \( \gamma_{v,ij} \). These parameters are usually fitted to experimental data of binary mixtures. However, when no data are available for a certain binary mixture, the mixing rules can also be used in a predictive way by either setting all reducing parameters to 1, i.e.,

\[ \beta_{T,ij} = \gamma_{T,ij} = \beta_{v,ij} = \gamma_{v,ij} = 1, \]

in which case simple quadratic mixing rules with Lorentz-Berthelot combining rules for the critical parameters are used. Furthermore, if the reducing parameters of the reduced density are set to

\[ \beta_{v,ij} = 1 \quad \text{and} \quad \gamma_{v,ij} = 4 \left( \frac{1}{\rho_{c,i}} + \frac{1}{\rho_{c,j}} \right)^3, \]
the mixing rules yield linear mixing of the critical volumes

\[ \frac{1}{\rho_r} = v_r = \sum_{i=1}^{N} x_i v_{c,i}. \]  \tag{9} 

For the reducing parameters of the reduced temperature, the same applies. By setting

\[ \beta_{T,ij} = 1 \text{ and } \gamma_{T,ij} = 0.5 \frac{T_{c,i} + T_{c,j}}{(T_{c,i} \cdot T_{c,j})^{0.5}} \]  \tag{10} 

the reducing function becomes a linear function of the critical temperatures of the pure fluids

\[ T_r = \sum_{i=1}^{N} x_i T_{c,i}. \]  \tag{11} 

Hence, when using the multi-fluid mixture model predictively, either linear mixing rules or Lorentz-Berthelot combining rules can be used, but in both cases no departure function can be utilized because its structure is not known a priori and usually developed during the fitting procedure. Comparisons of experimental VLE data and calculated phase equilibria for all binary mixtures of the components ethane (multiparameter equation of state (EOS) by [55] for the pure substance used), carbon dioxide (EOS: [56]), propene (EOS: [57]), benzene (EOS: [58]), and ethanol (EOS: [59]) using either Lorentz-Berthelot combining rules according to Eq. 7 or linear mixing rules according to Eqs. 8-11 are given in Fig. 1 and Fig. 2.
Figure 1: Comparison of experimental VLE data (symbols) and calculated VLE data (lines) using the multi-fluid mixture model according to Eqs. 1-6 and linear mixing rules according to Eqs. 8-11.
Figure 2: Comparison of experimental VLE data (symbols) and calculated VLE data (lines) using the multi-fluid mixture model according to Eqs. 1-6 and Lorentz-Berthelot combining rules according to Eq. 7.

As can be seen in Fig. 1 and Fig. 2, the standard mixing rules according to Eqs. 7-11 yield quite good results for the binary systems of ethane+propene, propene+benzene, and ethanol+propene, reasonable results for the binary systems of CO$_2$+benzene, CO$_2$+propene, and ethane+benzene, and basically fail to predict the binary systems of ethane+CO$_2$, CO$_2$+ethanol, ethanol+benzene, and ethane+ethanol. The reader should be aware that for some mixtures metastable VLE is shown and, in these cases, LLE would be the stable phase equilibrium. This is the case, when the bubble line exhibits minima and maxima, as can be seen for example for ethanol+propene with Lorentz-Berthelot combining rules. Overall, the linear mixing rules yield a slightly better representation of phase equilibria for the chosen binary systems than the Lorentz-Berthelot combining rules. Furthermore, we note that the azeotropic mixtures of ethane+CO$_2$ and ethanol+benzene cannot be described qualitatively correctly with linear mixing rules or Lorentz-Berthelot combining rules. Also, for CO$_2$+ethanol and ethane+ethanol linear mixing rules as well as Lorentz-Berthelot combining rules predict...
LLE, which contradicts the available experimental data. The same is true for the binary mixture of ethane+benzene in the case of Lorentz-Berthelot combining rules.

In order to represent the most accurate data available for a mixture or to describe more complicated mixing behavior, usually the reducing parameters are fitted to experimental data and additionally, the binary departure functions $\alpha_{ij}(\delta, \tau)$ need to be taken into account. Fitting a departure function is a very demanding task, as not only the coefficients but also the terms of the departure functions are not known a priori. Therefore, we propose to adapt the successful concept of combining equations of state with $g^E$-models. This concept allows for the use of highly accurate multiparameter Helmholtz equations of state for the pure components in a predictive mixture model.

### 3 Combining Multiparameter Helmholtz EOS with $g^E$ Models

The basic idea of combining any equation of state with $g^E$ models (GE), such as UNIQUAC [13], UNIFAC [14], or NRTL [15] is equating the molar excess Gibbs energy or molar excess Helmholtz energy at some specified reference pressure $p_0$

\[
g_{\text{EOS}}(p_0) = g_{\text{GE}}(p_0), \tag{12}\]

\[
a_{\text{EOS}}(p_0) = a_{\text{GE}}(p_0). \tag{13}\]

For cubic EOS, such as van-der Waals [60], Soave-Redlich-Kwong [1, 2], and Peng-Robinson [3], expressions for the calculation of $a^E$ and $g^E$ from these models can be derived and are for example given by Kontogeorgis and Coutsikos [12].

The molar excess Helmholtz energy $a^E$ calculated from multi-fluid mixture models using multiparameter Helmholtz equations of state for the pure fluid contributions can be derived by starting from the general definition for the molar excess Helmholtz energy

\[
a^E(T, p, \bar{x}) = a(T, p, \bar{x}) - RT \sum_{i=1}^{N} x_i \ln (x_i) - \sum_{i=1}^{N} x_i a_{oi}(T, p) \tag{14}\]

where $a^E$ denotes the molar excess Helmholtz energy of the mixture, $a$ the overall molar Helmholtz energy of the mixture, $R$ the universal gas constant, $T$ the temperature, $p$ the pressure, $\bar{x}$ the molar composition of the mixture, and $a_{oi}$ the molar Helmholtz energy of pure component $i$.

The overall molar Helmholtz energy can be obtained from the mixture model, which is formulated in the reduced Helmholtz energy $\alpha$ (see Eq. 1), according to

\[
a(T, p, \bar{x}) = RT(\alpha^0(p, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x})). \tag{15}\]

The density of the mixture needs to be calculated at given pressure which is done by an iterative density solver [7, 61]. Thus, for the density of the overall mixture it is

\[
\rho = \rho(T, p, \bar{x}) \tag{16}\]

and for the reduced density $\delta$ and the inverse reduced temperature $\tau$ Eq. 4 applies. Finally, with Eqs. 2 and 3 and under consideration of Eq. 16, the overall molar Helmholtz energy from the mixture model divided by $RT$ reads

\[
a(T, p, \bar{x}) = \sum_{i=1}^{N} x_i \alpha_{oi}^0(p, T) + \sum_{i=1}^{N} x_i \ln (x_i) + \sum_{i=1}^{N} x_i \alpha_{oi}^r(\delta, \tau) + \alpha^{\text{Dep}}(T, p, \bar{x}), \tag{17}\]

where the term of Eq. 3 containing the departure function was replaced by a term $\alpha^{\text{Dep}}(T, p, \bar{x})$ which does not have a fixed structure yet and which is a function of temperature, pressure, and composition of the mixture.

The molar Helmholtz energy of pure fluid $i$ from multiparameter equations of state can be calculated according to

\[
a_{oi}(T, p) = \alpha_{oi}^0(\rho_i, T) + \alpha_{oi}^r(\delta_i, \tau_i). \tag{18}\]

Again, it is important to note that all Helmholtz energies have to be evaluated at the same pressure and thus it is

\[
\rho_i = \rho_i(T, p) \tag{19}\]

with

\[
\delta_i = \rho_i / \rho_{ci} \tag{20}\]

and

\[
\tau_i = T_{ci} / T. \tag{21}\]

In general, the densities of the mixture and the respective pure fluids are different at the same temperature and pressure.
Finally, after combination of Eqs. 14, 17, and 18, the molar excess Helmholtz energy divided by the product of $RT$ calculated from multiparameter Helmholtz models becomes

$$
\frac{a^E(T, p, \tilde{x})}{RT} = \sum_{i=1}^{N} x_i \alpha_{oi}^0 (\rho_i, T) + \sum_{i=1}^{N} x_i \ln (x_i) + \sum_{i=1}^{N} x_i \alpha_{oi}^f (\delta, \tau) + \alpha^{Dep}(T, p, \tilde{x})
$$

\[
- \sum_{i=1}^{N} x_i \ln (x_i) - \sum_{i=1}^{N} x_i \alpha_{oi}^0 (\rho_i, T) - \sum_{i=1}^{N} x_i \alpha_{oi}^f (\delta_i, \tau_i).
\] (22)

The term $\sum_{i=1}^{N} x_i \ln (x_i)$ cancels out and after some rearrangements Eq. 22 reads

$$
\frac{a^E(T, p, \tilde{x})}{RT} = \sum_{i=1}^{N} \left[ x_i \alpha_{oi}^0 (\rho_i, T) - x_i \alpha_{oi}^0 (\rho_i, T) \right] + \sum_{i=1}^{N} \left[ x_i \alpha_{oi}^f (\delta, \tau) - x_i \alpha_{oi}^f (\delta_i, \tau_i) \right] + \alpha^{Dep}(T, p, \tilde{x}).
$$ (23)

The ideal gas parts $\alpha_{oi}^0$ of pure fluids $i$ under mixture conditions and under pure fluid conditions in Eq. 23 are evaluated at the same temperature but different densities. These ideal gas parts can be split into a temperature-dependent part and a density-dependent part according to

$$
\alpha_{oi}^0 (\rho_i, T) = f_i(T) + \ln \left( \frac{\rho_i}{\rho_{c,i}} \right)
$$ (24)

and

$$
\alpha_{oi}^0 (\rho_i, T) = f_i(T) + \ln \left( \frac{\rho_i}{\rho_{c,i}} \right)
$$ (25)

with $f_i(T)$ denoting the temperature-dependent part (see [7] and [62], respectively). Since all Helmholtz energies are evaluated at the same temperature, the temperature-dependent part cancels and the molar excess Helmholtz energy divided by $RT$ calculated from multiparameter Helmholtz equations of state can be written according to

$$
\frac{a^E(T, p, \tilde{x})}{RT} = \sum_{i=1}^{N} x_i \ln \left( \frac{\rho_i}{\rho_{c,i}} \right) + \sum_{i=1}^{N} x_i [\alpha_{oi}^f (\delta, \tau) - \alpha_{oi}^f (\delta_i, \tau_i)] + \alpha^{Dep}(T, p, \tilde{x}).
$$ (26)

For the combination of the multiparameter Helmholtz equations of state with an appropriate $g^E$ or $a^E$ model, a reference pressure has to be specified. For the established combination of cubic equations of state with excess models, different definitions of the reference pressure exist.

For example, the Huron-Vidal mixing rule [11] and the mixing rule by Wong and Sandler [16] use an infinite pressure as reference pressure. At infinite pressure, often the assumption is made that the molar volume of the mixture $v$ equals the covolume of the mixture $b$ and that the molar volumes of the pure substances $v_i$ equal the covolumes of the pure substances $b_i$, respectively. Furthermore, the excess volume $v^E$ is often assumed to be zero and hence $g^E = a^E$. However, while Huron and Vidal [11] equated the molar excess Gibbs energy of the SRK with the molar excess Gibbs energy of the $g^E$ model, Wong and Sandler [16] equated the excess Helmholtz energy $a^E$ of the cubic equation of state with the $g^E$ model. Furthermore, Wong and Sandler [16] note that "Further, if one examines the derivation of $g^E$ models, it is evident that it is really a model for $\bar{A}^E$ which has been derived". This can for example be seen in the derivation of the UNIQUAC model by Abrams and Prausnitz [13], where the model is originally a model for $\bar{a}^E$ and the assumption is made that $\bar{g}^E \approx \bar{a}^E$.

It shall be noted here, that the infinite reference pressure cannot be straightforwardly applied to multiparameter Helmholtz models. While cubic equations have a "built-in" physical limit - the covolume $b$ - multiparameter equations of state do not exhibit a limit in volume when the pressure approaches infinity. Thus, a different choice for the reference pressure is needed.

Other choices for the reference pressure in literature are mainly based on the exact zero pressure mixing rule by Michelsen [63,64]. This mixing rule ensures full reproduction of the $g^E$ model and relatively few assumptions are needed (see [12]). However, the major shortcoming of this reference state definition is that a liquid volume root of the used equation of state at zero pressure is needed. For temperatures well below the critical temperature, molar volumes of the liquid phase at zero pressure exist. But unfortunately, the liquid volume solution disappears as the temperature approaches the critical temperature. This problem was overcome by Dahl and Michelsen [65] by doing a linear approximation (MHV1 mixing rules) or quadratic approximation (MHV2 mixing rules) which shall not be discussed here in detail. The interested reader will find more detailed information in the original publications or the comprehensive review by Kontogeorgis and Coutsis [12]. However, later it was shown by Fischer and Gmehling [66] that the derivation of the MHV1 mixing rules
can be alternatively done by assuming a constant reciprocal packing fraction \( u \) in the liquid phase for the mixture as well as for the pure fluids according to

\[
u = \frac{v}{b} = \frac{v_i}{b_i},
\]

where \( u \) is the reciprocal packing fraction of the mixture, \( b \) is the covolume of the mixture according to the cubic equation of state used, \( u_i \) is the reciprocal packing fraction of pure fluid \( i \) and \( b_i \) is the covolume of pure fluid \( i \).

Fischer and Gmehling [66] investigated the reciprocal packing fractions \( u_i \) for about 80 substances at atmospheric pressure. They calculated the normal boiling temperatures with the Antoine equation with parameters from Dortmund Data Bank (DDB) [67], the volume of the saturated liquid was calculated using the DIPPR equation [68], and the covolume of the SRK equation was used. Following this procedure, they confirmed that the average reciprocal packing fraction at atmospheric pressure can be assumed to be about 1.1, which was also found before by Holderbaum and Gmehling [4] by fitting \( u \) to experimental VLE data.

Following this method, in this work also standard atmospheric pressure was selected as reference pressure (i.e., \( p_0 = 101325 \) Pa) at which the molar excess Helmholtz energy of the multiparameter model is equated with the excess model. In Figure 3, the calculated reciprocal packing fractions at the normal boiling point of 121 fluids for which multiparameter Helmholtz equations are available are displayed.

![Figure 3: Reciprocal packing fractions \( u_i \) calculated with multiparameter Helmholtz equations of state.](image)

In general, the results confirm the assumption of a constant reciprocal packing fraction of around 1.1 - 1.2 at the normal boiling point, when the covolume of the SRK is used for \( b \). However, some outliers are apparent. Substances with a comparably low critical temperature have higher reciprocal packing fractions at atmospheric pressure. These substances are neon (\( u_\text{neon} = 1.397 \)), deuterium (\( u_\text{deuterium} = 1.507 \)), hydrogen (\( u_\text{hydrogen} = 1.545 \)), orthohydrogen (\( u_\text{orthohydrogen} = 1.557 \)), parahydrogen (\( u_\text{parahydrogen} = 1.542 \)), and helium (\( u_\text{helium} = 1.948 \)). Some examples of substances with significantly lower reciprocal packing fractions are water (\( u_\text{water} = 0.890 \)), heavy water (\( u_\text{heavy water} = 0.881 \)), and acetic acid (\( u_\text{acetic acid} = 0.876 \)).

Furthermore, it shall be noted that for three of the substances displayed in Fig. 3 the atmospheric pressure is below the triple-point pressure. For these substances, namely carbon dioxide, sulfur hexafluoride, and cyclopropane, the saturated liquid volumes have been evaluated at a pressure slightly above the triple-point pressure of the substances.

Assuming a constant reciprocal packing fraction \( u \), the liquid density of the mixture at reference pressure can be written according to

\[
\rho_{\text{ref}} = \frac{1}{u \cdot b}.
\]

For pure fluids, it is

\[
\rho_{i,\text{ref}} = \frac{1}{u_i \cdot b_i}.
\]

Finally, the departure function for the combination of multiparameter models with excess models can be obtained according to

\[
\alpha_{\text{Dep}}(T, \bar{x}) = \frac{\alpha_{\text{GE}}(T, \bar{x})}{RT} = \sum_{i=1}^{N} x_i \ln \left( \frac{b_i}{b} \right) - \sum_{i=1}^{N} x_i \left[ \alpha_{\text{GE}}^r(\delta_{\text{ref}}, \tau_i) - \alpha_{\text{GE}}^r(\delta_{i,\text{ref}}, \tau_i) \right]
\]

(30)
with
\[ \delta_{\text{ref}} = \frac{1}{u \cdot b \cdot \rho_r(x)} \] (31)
and
\[ \delta_{i,\text{ref}} = \frac{1}{u \cdot b_i \cdot \rho_{r,T}}. \] (32)
Note that the excess-based departure function as given in Eq. 30 is not a function of density and thus not a function of pressure any more. However, in order to assure proper behavior of the mixture model in the gas phase, the residual Helmholtz energy and thus also the departure function should go to zero as \( \delta \) goes to zero. It is obvious that this is not the case for the new excess-based departure function proposed in Eq. 30. Hence, another inspiration is drawn from the combination of cubic equations of state with \( g^{R_k} \) models. The Helmholtz translation of the PSRK can be written according to [4, 69]
\[ \alpha_{\text{PSRK}} = -\ln(1 - \beta p) + \frac{\ln(1 + \beta p)}{\ln(1 + \frac{1}{u})} \left( \frac{g^E}{RT} - \frac{1}{RT} \ln \left( 1 + \frac{1}{u} \right) \right) \sum_{i=1}^{N} x_i \frac{a_i}{b_i} - \sum_{i=1}^{N} x_i \ln \left( \frac{b_i}{b} \right). \] (33)
For the PSRK, a reciprocal packing fraction of \( u = 1.1 \) is used, which results in \( \ln \left( 1 + \frac{1}{u} \right) \approx 0.64663 \). Note that this is the negative value of the constant \( A_1 = -\ln \left( 1 + \frac{1}{1.1} \right) \) used in the PSRK, see [4]. Comparing Eq. 33 with Eq. 30, there is a density-dependent part in the PSRK which ensures that the residual reduced Helmholtz energy goes to zero when the density goes to zero. We propose to apply this term also to the new excess-based departure function, which upon combination finally reads:
\[ \alpha^{\text{Dep}}(T, \rho, x) = \frac{\ln(1 + \beta p)}{\ln(1 + \frac{1}{u})} \left[ \frac{g^E_{\text{GB}}(T, x)}{RT} - \sum_{i=1}^{N} x_i \ln \left( \frac{b_i}{b} \right) - \sum_{i=1}^{N} x_i \left[ \alpha_{\text{ref}, \delta}(\delta_{\text{ref}}, \tau) - \alpha_{\text{ref}, \delta}(\delta_{i,\text{ref}}, \tau_i) \right] \right]. \] (34)

4 Calculation of thermodynamic properties
Thermodynamic properties can be calculated from multiparameter models by combining derivatives of the reduced Helmholtz energy with respect to \( \delta, \tau, \) and \( x_i \). For example, the pressure \( p \) is obtained from the relation
\[ p = \rho RT \left( 1 + \delta \left( \frac{\partial \alpha^{\text{Dep}}}{\partial \delta} \right)_{\tau, x} \right) \] (35)
and the fugacity of component \( i \) in the mixture can be calculated from the relation
\[ f_i = x_i \rho RT \left( \frac{\partial \alpha^{\text{Dep}}}{\partial \nu_i} \right)_{T,V,n_j}. \] (36)

Relations for the most important thermodynamic properties to the reduced Helmholtz energy and its derivatives can for example be taken from Span [62], Kunz et al. [7], and Gernert et al. [61]. Multiparameter equations of state and their derivatives are implemented in thermophysical property libraries such as NIST REFPROP [70], CoolProp [71], and TREND [72]. In order to implement the proposed departure function from excess models into these property softwares, derivatives of the departure function with respect to \( \delta, \tau, \) and \( x_i \) are needed. For the calculation of the most common properties as well as for the algorithms for flash calculations, i.e., calculation of VLE and LLE, the following derivatives of the excess-based departure function according to Eq. 34 are needed:
\[ \frac{\partial \alpha^{\text{Dep}}}{\partial \delta}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial \delta^2}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial \delta \partial \tau}, \frac{\partial \alpha^{\text{Dep}}}{\partial \tau}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial \tau^2}, \frac{\partial \alpha^{\text{Dep}}}{\partial x_i}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial x_i \partial \tau}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial x_i \partial x_j}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial x_i \partial \delta}, \frac{\partial^2 \alpha^{\text{Dep}}}{\partial x_i \partial \tau}. \] (37)
The variables held constant for the partial derivatives in Eq. 37 have been omitted for the sake of compactness. Note that always when doing a partial derivative to an independent variable of the reduced Helmholtz energy \( \alpha \) all other independent variables are constant. The second derivative of the excess-based departure function with respect to \( \tau \) and \( \delta \) can for example be written according to
\[ \frac{\partial^2 \alpha^{\text{Dep}}}{\partial \delta \partial \tau} = \left( \frac{\partial}{\partial \tau} \left( \frac{\partial \alpha^{\text{Dep}}}{\partial \delta} \right)_{\tau, x} \right)_{\delta, x}. \] (38)
All required derivatives have been used analytically and are given in the supplementary material add link later to this article. The new model and all of its derivatives have been implemented in the thermophysical property software TREND 3.0 [72] and will be made available in one of the upcoming versions.
5 Validation and Results

The final implementation of the excess-based departure function was done using the following assumptions and conventions:

- The average reciprocal packing fraction according to Fig. 3 was found to be around \( u = 1.17 \) for the fluids taken into account. Thus, \( u = 1.17 \) was used in this work.

- The covolume needed in Eq. 34 was taken from the SRK for all fluids, i.e., \( b_i = 0.08664 \frac{RT}{c_i} \) with \( R = 8.3144598 \text{ J mol}^{-1} \text{ K}^{-1} \). For the covolume of the mixture, a linear mixing rule is used, i.e., \( b = \sum_{i=1}^{N} x_i b_i \).

- In order for the model to have predictive capabilities, a mixing rule for the reducing parameters has to be chosen and maintained for all binary mixtures. As for the investigated binary mixtures linear mixing rules give slightly better results than Lorentz-Berthelot combining rules (see Figs. 1 and 2), linear mixing rules according to Eqs. 8-11 have been chosen in this work. However, more results also with Lorentz-Berthelot combining rules are supplied in the supplementary material to this article.

- The UNIFAC model used for the excess-based departure function is the same as the model used for PSRK [4] and VTPR [17]. More details are given in the supplementary material to this article.

- Following the argumentation of Wong and Sandler [16], we assumed that UNIFAC gives the excess Helmholtz energy directly. No further conversion was done, which is equivalent to assuming \( g^E = a^E \).

Like for the VTPR [17] and in accordance with the literature (see, e.g., [12, 73]), the combinatorial part of the UNIFAC excess model is assumed to cancel with the term \( \sum_{i=1}^{N} x_i \ln \left( \frac{R_i}{b_i} \right) \). Eq. 34 then becomes

\[
\alpha^{\text{Dep}}(T, \rho, \bar{x}) = \frac{\ln(1 + bp)}{\ln(1 + \frac{p}{RT})} - \sum_{i=1}^{N} x_i \left[ a^E_i(\delta_{\text{ref}}, \tau_i) - a^E_i'(\delta_{\text{ref}}, \tau_i) \right]
\]

with

\[
g_{\text{GI}}^{E,R} = RT \sum_{i=1}^{N} x_i \ln \left( \gamma_{i}^{R} \right).
\]

In Table 1, the critical densities \( \rho_{c,i} \) and the critical temperatures \( T_{c,i} \) used for the fluids in this work are given.

### Table 1: Critical temperatures and critical densities used for the pure fluids in this work. The values are given as they are used in TREND [72] and NIST REFPROP [70].

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( T_{c,i} / \text{K} )</th>
<th>( \rho_{c,i} / (\text{mol m}^{-3}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>304.1282</td>
<td>10624.9063</td>
</tr>
<tr>
<td>ethane</td>
<td>305.322</td>
<td>6856.886685</td>
</tr>
<tr>
<td>propene</td>
<td>364.211</td>
<td>5457.0</td>
</tr>
<tr>
<td>benzene</td>
<td>562.02</td>
<td>3901.0</td>
</tr>
<tr>
<td>ethanol</td>
<td>514.71</td>
<td>5930.0</td>
</tr>
</tbody>
</table>

The fragmentation rules (i.e., the definition of structural groups) for the fluids considered in this work have been adopted from the PSRK EOS and are also the same in the VTPR EOS. The subgroups and main groups for each of the considered fluids are given in Table 2.

### Table 2: Subgroups and main groups for the pure fluids considered in this work.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Main group</th>
<th>No.</th>
<th>Subgroup</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>1 \times \text{CO}_2</td>
<td>56</td>
<td>1 \times \text{CO}_2</td>
<td>117</td>
</tr>
<tr>
<td>ethane</td>
<td>2 \times \text{CH}_2</td>
<td>1</td>
<td>2 \times \text{CH}_3</td>
<td>1</td>
</tr>
<tr>
<td>propene</td>
<td>1 \times \text{CH}_2</td>
<td>1</td>
<td>1 \times \text{CH}_3</td>
<td>1</td>
</tr>
<tr>
<td>benzene</td>
<td>1 \times \text{C} = \text{C}</td>
<td>2</td>
<td>1 \times \text{CH}_2 = \text{CH}</td>
<td>5</td>
</tr>
<tr>
<td>benzene</td>
<td>6 \times \text{ACH}</td>
<td>3</td>
<td>6 \times \text{ACH}</td>
<td>9</td>
</tr>
<tr>
<td>ethanol</td>
<td>1 \times \text{CH}_2</td>
<td>1</td>
<td>1 \times \text{CH}_3</td>
<td>1</td>
</tr>
<tr>
<td>ethanol</td>
<td>1 \times \text{OH}</td>
<td>5</td>
<td>1 \times \text{OH}</td>
<td>14</td>
</tr>
</tbody>
</table>

The fragmentation rules (i.e., the definition of structural groups) for the fluids considered in this work have been adopted from the PSRK EOS and are also the same in the VTPR EOS. The subgroups and main groups for each of the considered fluids are given in Table 2.
For example, ethane consists of two structural subgroups CH\(_3\) which belong to the main group CH\(_2\) and ethanol consists of one subgroup CH\(_3\), which belongs to main group CH\(_2\), one subgroup CH\(_2\), which also belongs to main group CH\(_2\), and one subgroup OH (primary alcohol), which belongs to the main group OH. According to UNIFAC, each subgroup is assigned an individual subgroup surface area \(Q_k\), which can be fitted to experimental data. Furthermore, for main group interactions between a main group \(n\) and a main group \(m\), the parameters of the temperature-dependent group interaction term

\[
\Psi_{nm} = \exp \left( -\frac{a_{nm} + b_{nm}T + c_{nm}T^2}{T} \right)
\]  

(41)

can be adjusted to experimental data. As a first test, the VTPR parameters of [17, 19] have been directly used in the excess-based departure function according to Eq. 34. These parameters are summarized in Table 3 and Table 4.

Table 3: Group surface area parameters \(Q_k\) of UNIFAC as used in the VTPR EOS, see [17].

<table>
<thead>
<tr>
<th>Subgroup no.</th>
<th>(Q_k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2958</td>
</tr>
<tr>
<td>2</td>
<td>0.9471</td>
</tr>
<tr>
<td>5</td>
<td>1.1507</td>
</tr>
<tr>
<td>9</td>
<td>0.4972</td>
</tr>
<tr>
<td>14</td>
<td>1.0189</td>
</tr>
<tr>
<td>117</td>
<td>0.982</td>
</tr>
</tbody>
</table>

Table 4: Interaction parameters \(a_{nm}, b_{nm}, c_{nm}, a_{mn}, b_{mn}, c_{mn}\) for UNIFAC as used in the VTPR EOS.

<table>
<thead>
<tr>
<th>(n)</th>
<th>(m)</th>
<th>(a_{nm})</th>
<th>(b_{nm})</th>
<th>(c_{nm})</th>
<th>(a_{mn})</th>
<th>(b_{mn})</th>
<th>(c_{mn})</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>171.47</td>
<td>0.0432</td>
<td>0.0</td>
<td>-87.609</td>
<td>-0.0544</td>
<td>0.0</td>
<td>[17]</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>54.259</td>
<td>0.2882</td>
<td>0.0</td>
<td>35.483</td>
<td>-0.3693</td>
<td>0.0</td>
<td>[17]</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>1809.5</td>
<td>-0.4856</td>
<td>-2.3211 × 10(^{-3})</td>
<td>725.66</td>
<td>-0.905</td>
<td>3.1538 × 10(^{-3})</td>
<td>[17]</td>
</tr>
<tr>
<td>1</td>
<td>56</td>
<td>403.11</td>
<td>-0.1999</td>
<td>-6.68 × 10(^{-5})</td>
<td>204.83</td>
<td>-1.3096</td>
<td>1.1967 × 10(^{-3})</td>
<td>[17]</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>69.495</td>
<td>-1.1411</td>
<td>1.3205 × 10(^{-3})</td>
<td>101.92</td>
<td>0.5243</td>
<td>3.4756 × 10(^{-4})</td>
<td>[17]</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>756.09</td>
<td>1.4097</td>
<td>-1.9269 × 10(^{-3})</td>
<td>2049.9</td>
<td>6.3523</td>
<td>-1.3347 × 10(^{-3})</td>
<td>[17]</td>
</tr>
<tr>
<td>2</td>
<td>56</td>
<td>7.9448</td>
<td>0.0</td>
<td>0.0</td>
<td>218.62</td>
<td>0.0</td>
<td>0.0</td>
<td>[17]</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>1065.5</td>
<td>0.2236</td>
<td>-1.7246 × 10(^{-3})</td>
<td>1234.6</td>
<td>1.3853</td>
<td>1.5753 × 10(^{-4})</td>
<td>[17]</td>
</tr>
<tr>
<td>3</td>
<td>56</td>
<td>161.38</td>
<td>0.0</td>
<td>0.0</td>
<td>37.2</td>
<td>0.0</td>
<td>0.0</td>
<td>[17]</td>
</tr>
<tr>
<td>5</td>
<td>56</td>
<td>440.88</td>
<td>0.0</td>
<td>0.0</td>
<td>578.82</td>
<td>0.0</td>
<td>0.0</td>
<td>[19]</td>
</tr>
</tbody>
</table>

The results of the new excess-based multi-fluid mixture model with VTPR parameters for UNIFAC and linear mixing rules for the reducing functions are given in Fig. 4. Additional results for the new model in combination with the VTPR parameters for UNIFAC but Lorentz-Berthelot combining rules for the reducing functions and for the new model in combination with PSRK parameters for UNIFAC with linear and Lorentz-Berthelot combining rules are supplied in the supplementary material to this article add link later.
We note that especially the description of the azeotropic mixtures, i.e., ethane+CO$_2$ and ethanol+benzene is much better with the excess-based departure function than with the standard mixing rules, see Figs. 1 and 2. In case of the binary mixtures of ethane+CO$_2$ and CO$_2$+propene, the higher temperature VLE could not be entirely calculated because the vapor density solution tends to vanish at higher pressures. This means that the leftmost maximum in pressure of the isotherm (when looking at pressure as a function of density at constant composition) is very close to the dew point pressure. This causes numerical instabilities when trying to calculate the VLE. Nevertheless, the parts of the VLE which could be calculated seem reasonable. A more detailed discussion of this problem is given in section 5.1. In order to demonstrate that an even more accurate description of phase equilibria is possible with the new model, some binary group interaction parameters have been refitted, which will be discussed in the next section.
5.1 Fitting of Binary Group Interaction Parameters

In order to improve the description of experimental VLE for the ten chosen binary systems with the new excess-based multi-fluid model, a Levenberg-Marquardt [74–76] based fitting algorithm with analytical derivatives of the new excess-based multi-fluid model with respect to the adjustable model parameters was implemented in the thermophysical property software TREND [72]. The data that have been used for fitting are experimental bubble-point pressures (BP) at given temperature and liquid-phase composition as well as vapor-liquid equilibria (VLE). Usually, BP and VLE are the most commonly available experimental phase equilibrium data and therefore these data have been chosen for fitting in this work. However, other data such as dew points or Henry’s constants could be implemented into the fitting procedure in a similar fashion. The sum of squares for fitting was defined to be

\[ \chi^2 = \frac{N_{\text{exp}}}{\sigma_p^2} \left( \frac{p_{\text{exp},i} - p_{\text{calc},i}(T_{\text{exp},i}, \tilde{x}_j^L)}{\sigma_p} \right)^2 + \sum_{j=1}^{N_{\text{VLE}}} \left[ \frac{f_{1,j}^L(T_{\text{exp},j}, p_{\text{exp},j}, \tilde{x}_j^L) - f_{1,j}^L(T_{\text{exp},j}, p_{\text{exp},j}, \tilde{x}_j^L)}{1 + f_{1,j}^L(T_{\text{exp},j}, p_{\text{exp},j}, \tilde{x}_j^L)} \right]^2 \cdot w_j. \quad (42) \]

In Eq. 42, \( N_{\text{BP}} \) denotes the number of experimental bubble-points, \( N_{\text{VLE}} \) the number of experimental VLE data, \( p_{\text{exp},i} \) is the experimentally measured bubble-point pressure of data point \( i \), \( p_{\text{calc},i} \) is the bubble-point pressure calculated from the model at experimental temperature \( T_{\text{exp},i} \) and experimental liquid composition \( \tilde{x}_j^L \), \( \sigma_p \) is the experimental uncertainty of the bubble-point pressure measurement, \( w_i \) and \( w_j \) are individual weighting factors for data points, \( f_{1,j}^L \) and \( f_{1,j}^V \) are the fugacities of component 1 of the \( j \)th data point in the liquid and vapor phase, respectively, and \( f_{2,j}^L \) and \( f_{2,j}^V \) are the fugacities of component 2 of the \( j \)th data point in the liquid and vapor phase, respectively. The fugacities are calculated from the model at experimental temperatures \( T_{\text{exp},j} \), pressures \( p_{\text{exp},j} \), and compositions of the vapor \( \tilde{x}_j^V \) and liquid phase \( \tilde{x}_j^L \). Usually, all experimental data points would need to be critically evaluated in order to get a reasonable estimate for the combined experimental uncertainty of the bubble-point pressures \( \sigma_p \). However, for the purpose of demonstrating that the proposed new model works, all data points have been used for fitting and for all bubble-points the value \( \sigma_p = 0.01 \cdot p_{\text{exp},i} \) was chosen. In order to bring the contributions of BP data and VLE data to about the same order of magnitude, the weights have been chosen to be \( w_1 = 1 \) and \( w_j = 10 \).

The required analytical derivatives of the new model with respect to the UNIFAC parameters \( Q_k, a_{am}, b_{am}, c_{am}, a_{mn}, b_{mn}, c_{mn} \) are given in the supplementary material to this article [add link later]. The purpose of fitting these parameters is to demonstrate that the representation of the experimental data can be improved by fitting the UNIFAC parameters. We did not try to find the optimal set of parameters for all binary mixtures investigated but rather tried to keep group interaction parameters that already yield good results and only refit the parameters for systems for which the data are not represented well. Furthermore, group surface areas \( Q_k \) have also not been refitted but kept the same as given in Table 3. The finally obtained group interaction parameters are provided in Table 5 and comparisons of the new excess-based multi-fluid model to experimental VLE data are given in Fig. 5.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( m )</th>
<th>( a_{am} )</th>
<th>( b_{am} )</th>
<th>( c_{am} )</th>
<th>( a_{mn} )</th>
<th>( b_{mn} )</th>
<th>( c_{mn} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>171.47</td>
<td>−0.0432</td>
<td>0.0</td>
<td>−87.609</td>
<td>−0.0544</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>3.83945 \times 10^1</td>
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<td>0.0</td>
<td>1.24794 \times 10^1</td>
<td>−3.74927 \times 10^{-1}</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>6.50353 \times 10^2</td>
<td>−6.36859 \times 10^{-1}</td>
<td>−2.40991 \times 10^{-3}</td>
<td>5.96522 \times 10^2</td>
<td>−8.95155 \times 10^{-1}</td>
<td>3.13271 \times 10^{-3}</td>
</tr>
<tr>
<td>1</td>
<td>56</td>
<td>4.34634 \times 10^2</td>
<td>−2.91289 \times 10^{-1}</td>
<td>−1.11135 \times 10^{-4}</td>
<td>2.59363 \times 10^2</td>
<td>−1.52293 \times 10^0</td>
<td>1.09420 \times 10^3</td>
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<td>2</td>
<td>3</td>
<td>69.495</td>
<td>−1.1411</td>
<td>1.3205 \times 10^{-3}</td>
<td>101.92</td>
<td>0.5243</td>
<td>3.4756 \times 10^{-4}</td>
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<td>2</td>
<td>5</td>
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<td>−1.9269 \times 10^{-3}</td>
<td>2049.9</td>
<td>6.3523</td>
<td>−1.3347 \times 10^{-3}</td>
</tr>
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<td>56</td>
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</tr>
<tr>
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</tr>
<tr>
<td>3</td>
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<td>1.97175 \times 10^{-3}</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>5</td>
<td>56</td>
<td>5.18058 \times 10^2</td>
<td>2.00954 \times 10^{-1}</td>
<td>0.0</td>
<td>5.63105 \times 10^0</td>
<td>−1.22094 \times 10^{-2}</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Table 5: Interaction parameters \( a_{am}, b_{am}, c_{am}, a_{mn}, b_{mn}, c_{mn} \) for UNIFAC used in combination with the new model. The fitted parameters are highlighted in bold font.
As can be seen, all models for the binary mixtures of the investigated fluids have been improved compared to the results of the other models shown in Figs. 1, 2, and 4. However, the results could be further improved, as can for example be seen for the binary mixtures of ethane+ethanol and CO$_2$+ethanol. As already noted, the primary objective of this work was not to provide the best set of parameters for the studied fluids but to prove that the method works in general. It shall further be noted that the binary group interaction parameters for main group 1 with main group 2, main group 2 with main group 3, main group 2 with main group 5, and main group 3 with main group 5 have not been adjusted at all. For interactions of main group 1 and main group 3, four parameters have been adjusted by fitting to experimental data of the binary system propene+benzene. For the interaction of main group 1 with main group 5, the group interaction parameters have been fitted to experimental data for the binary system of ethane+ethanol. The
representation of the experimental data for this binary mixture by the new model was significantly improved compared to the version of the new model with VTPR parameters. However, the model still predicts LLE, whereas the data seem to suggest VLE. Nevertheless, the representation of experimental data for the binary mixture of ethanol+propene (which also contains interactions of main group 1 with main group 5) with the new model was significantly improved without directly fitting any of the model parameters for this binary mixture. Furthermore, the representation of the VLE data for the binary mixture of ethanol+benezene was also improved without any direct fitting for this system. For binary mixtures with CO$_2$, in a first step the binary group interaction parameters for main group 1 with main group 56 have been fitted to experimental data for the binary system ethane+CO$_2$. Subsequently, the interaction parameters for main group 2 with main group 56 have been fitted in order to improve the representation of the binary system CO$_2$+propene, which also contains the previously fitted group interactions of main group 1 with main group 56. As can be seen, the binary CO$_2$+propene system is now represented well and the convergence problems at the highest isotherms disappeared. For the binary system of CO$_2$+benzene, the interaction parameters of main groups 3 and 56 have been refitted. The experimental data are also represented well for this mixture. Finally, for CO$_2$+ethanol the main group interactions of groups 5 and 56 have been refitted. Concerning the binary system of CO$_2$+ethanol, we emphasize that this system is in general difficult to model, because most models tend to predict LLE for this system, which according to the experimental data does not exist, see, e.g. [77].

For ethane+CO$_2$, the convergence problem when tracing the highest isotherm was slightly reduced by fitting, however, it still exists. In order to investigate this problem, the main group interaction parameter $c_{1,56}$ has been slightly changed manually to $c_{1,56} = -6 \times 10^{-4}$, while all other main group interaction parameters have been kept constant (see Table 5). The parameter has been changed manually, in order to lower the calculated bubble-point pressures and find out if by doing so, the convergence problems could be minimized or avoided. The results can be seen displayed as solid line in Fig. 6.

![Graph](image)

Figure 6: Comparison of the results of the new model (lines) and experimental data (symbols) for the binary mixture of ethane+CO$_2$ with manually adjusted main group interaction parameter $c_{1,56}$. The other parameters have been kept constant and can be found in Table 5. The solid lines correspond to the mixture model using the reference equations for ethane [55] and CO$_2$ [56] and the dashed lines to the same mixture model but using short equations of state for CO$_2$ [78] and ethane [79].

As can be seen, the highest isotherms could still not be entirely traced. The reason for this is, as briefly mentioned in section 5, that the vapor solution of the isotherm vanishes, as can be seen in Fig. 7.
In order to investigate the influence of the pure fluid equations on these problems, the reference equations for ethane [55] and CO$_2$ [56] have been replaced with short multiparameter equations of state for CO$_2$ [78] and ethane [79]. The results when replacing the equations of state for the pure fluids are shown as dashed lines in Fig. 6 and Fig. 7.

It can be seen that only by replacing the pure fluid equations of state, the higher temperature isotherms can be calculated, because the first maximum at low densities of the isotherms is at higher pressures when using the short equations of state compared to when using the reference equations of state. It is beyond the scope of this work to investigate in detail what is causing these problems. However, it should be emphasized that the new mixture model is in principle also capable of correctly predicting the high pressure isotherms for the binary mixture of CO$_2$+ethane.

5.2 Predictive mode

In order to demonstrate the predictive capabilities of the new mixture model with the fitted parameters but also in order to discuss the current limitations of the model, phase equilibria for the binary mixture of CO$_2$+propane have been calculated and compared to experimental data. In order to avoid convergence problems at higher temperature, as discussed in the preceding section, the short equation for CO$_2$ [78] was used. For propane, the reference equation of state [80] was applied. This binary mixture was not considered in the fitting procedure and the relevant main group interaction parameters of main groups 1 and 56 have been fitted to experimental data of the binary system ethane+CO$_2$ only. The results for four isotherms (244.26 K, 266.46 K, 294.26 K, 344.26 K) can be seen in Fig. 8.
Figure 8: Comparison of the results of the new model (lines) and experimental data [81, 82] (symbols) for the binary mixture of CO$_2$+propane.

As can be seen, most of the experimental VLE data for CO$_2$+propane are represented well by the new model. However, as expected, the representation of the VLE of this system (especially at higher temperatures) could be improved by also including the VLE data for this system into the fitting procedure of main group interaction parameters.

6 Conclusions

The predictive capabilities of the state-of-the-art formulation of multi-fluid mixture models with either linear mixing rules or Lorentz-Berthelot combining rules for the reducing function parameters are rather limited. This fact is demonstrated in this work for phase equilibria of the binary mixtures of the components ethanol, ethane, carbon dioxide, propene, and benzene. For example, neither linear mixing rules nor Lorentz-Berthelot combining rules are capable of qualitatively correctly predicting the azeotropic behavior of CO$_2$+ethane or ethanol+benzene mixtures. In order to overcome these limitations, a new approach for combining multi-fluid mixture models with g$_E$-models is proposed in this work. The model formulation results in a theoretically based departure function which depends on the chosen g$_E$-model. It is demonstrated that the new model can be combined with existing UNIFAC parameters, for example from the VTPR model [17, 19] and that, without any fitting of parameters, the new model with the excess-based departure function is capable of predicting VLE relatively well for the binary mixtures studied in this work. While linear mixing rules and Lorentz-Berthelot combining rules for the standard model are not able to qualitatively correctly describe the azeotropic mixtures of, for example, CO$_2$+ethane and ethanol+benzene, the new model with the excess-based departure function correctly predicts azeotropes for these mixtures, when using VTPR parameters.

In order to demonstrate the capabilities of the new model to accurately represent VLE data, some UNIFAC parameters have been refitted to the data while the others have been kept constant. The representation of the available VLE data was improved for all fitted binary mixtures. In some cases, the representation of VLE for binary mixtures was not improved by direct fitting but indirectly by fitting another binary mixture which contains the same main groups.

Thus, we demonstrated that phase equilibria of binary mixtures can be described significantly better with the new model than with the state-of-the-art multi-fluid model using either linear mixing rules or Lorentz-Berthelot combining rules for the parameters of the reducing functions. Furthermore, the new model can be used in a very flexible way as any g$_E$-model could be used in the excess-based departure function and, as also demonstrated, any equation of state could be used in the multi-fluid model, for example also cubic equations of state [69].

Future work should focus on refitting the UNIFAC parameters to all available data for binary mixtures for which multiparameter equations of state are available. Furthermore, even more predictive g$_E$-models could be tried, for example the latest versions of COSMO-SAC, see, e.g, [83].
References


[67] Dortmund Data Bank.


7 Supplemental Data

- Document with analytical derivatives of the new model for the calculation of all common thermophysical properties and with analytical derivatives with respect to the adjustable parameters of UNIFAC.
- Additional results with different model parametrizations.

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