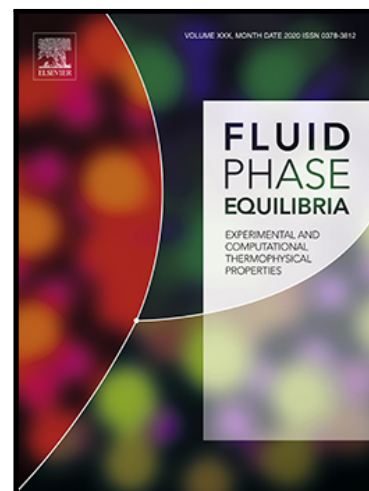


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A comparative Study Between Helmholtz and Entropy Scaling Approaches for Viscosity of Natural Gas Mixtures Based on the GERG-2008 Equation of State

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Abstract

This study scaling approach, the residual entropy scaling approach, and the modified entropy scaling approach proposed by Bell for predicting the viscosities of pure n-alkanes, as well as other light compounds, and natural gas mixtures at different pressure and temperature conditions. The modified entropy scaling approach showed the lowest global average absolute deviation (AAD) for pure components, with a value of 2.37%. In comparison, the Helmholtz scaling approach had a slightly higher value of 2.70%, while the entropy scaling approach produced the highest value at 4.02%. The predictive performance of different mixing rules was evaluated for a strongly asymmetric binary system (methane + n-decane), across a broad range of compositions, pressures, and temperatures. For all-natural gas mixtures, excellent results were achieved with similar AAD values obtained for entropy and Helmholtz scaling approaches, at 2.73% and 2.72%, respectively. The modified entropy scaling approach presented an AAD value of 3.12%. The results obtained with each of the binary and multicomponent mixtures allowed us to confirm the accuracy of the Helmholtz scaling, entropy scaling, and modified entropy scaling approach using GERG 2008 in the prediction of natural gas viscosities when appropriate mixing rules were selected for each approach.

Keywords: *Viscosity, Natural gas, Helmholtz scaling, Entropy scaling, Modified Entropy scaling, GERG 2008*

1. Introduction

In the study of natural gas properties and processes, precise knowledge of their thermodynamic properties is very important, as well as an accurate approximation of their transport properties such as viscosity, across a broad range of pressure and temperature conditions. Viscosity, in particular, plays a critical role in the design and equipment simulation of natural gas production, processing, and transportation. Therefore, obtaining a thorough understanding of viscosity is essential for ensuring the efficient and safe operation of these systems.

Moreover, as new technologies such as supersonic gas separation [1] are developed for conditioning natural gas by removing condensable fractions [2], accurate viscosity data is becoming increasingly important. This technology demands precise viscosity information to optimize the separation process and achieve high levels of efficiency. Therefore, obtaining reliable viscosity data is necessary for the successful development and implementation of innovative technologies in the natural gas industry.

Although natural gas viscosity is crucial, for some applications such as process simulation at reservoir conditions, the available data are limited particularly for multicomponent systems. Additionally, experimental determination of natural gas viscosity at reservoir conditions, while necessary, is a costly and time-consuming process, especially when considering the wide range of components present in the fluid. Therefore, it is necessary to utilize predictive models to obtain reliable approximations of natural gas viscosity.

In recent decades, various approaches have been proposed to correlate fluid viscosities with properties obtained from an equation of state. Baled et al.[3] presented a comparison of seven viscosity models that represent different correlative and predictive approaches. This study considered viscosity data up to extremely high pressure and temperature conditions.

The review by Baled discusses theories and methods for calculating viscosities of both dilute and dense natural gas fluids. One of the most widely used theoretical models for calculating the gas viscosity is the Chapman-Enskog theory [4], when coupled with a correction factor proposed by Chung et al [5], this model accurately predicts viscosity at low pressures. For dense fluids, one semi-theoretical approach is the entropy scaling method, which was first proposed by Rosenfeld [6]. He established a linear relationship between the reduced viscosity and the residual entropy. This approach is a hypothesis based on the analysis of hard spheres in the liquid phase and has been investigated with isomorph theory [7–11].

However, for more complex molecules, a mono-variable relationship between dimensionless viscosity η^* and residual entropy s^{res} is still valid, but the relation is no longer linear and substance-specific parameters are required to establish a relationship between η^* and s^{res} [12].

Rosenfeld and others pointed out that for gases [13–15], Rosenfeld's definition of dimensionless viscosity leads to a collapse onto a single curve, but there is a steep increase in the low-density regime. This makes it difficult to calculate transport properties in the low-density limit, and a complex ansatz function is required to alleviate the problem. Different approaches have been proposed to obtain a dimensionless form of transport properties. Some authors suggest using generalized Rosenfeld transport coefficients, which apply the second Virial coefficient [15]. Others use the dilute gas Chapman-Enskog formulation in two different ways: either by calculating a residual viscosity [14,16] or by dividing the actual viscosity by the Chapman-Enskog value [14,15,17–19].

Entropy scaling has been demonstrated to be an effective approach for predicting viscosity of pure compounds and mixtures under high pressures [3]. Novak [14,18,20–22] employed residual entropy scaling with various thermodynamic models for s^{res} to determine the viscosity and self-diffusion coefficients of numerous systems of non-hydrogen-bond-forming molecules and also presented result for natural gas mixtures. In this scaling approach, the actual viscosity was divided by dilute-gas viscosity, and then expressed as a function of the residual entropy. In the same way, Lötgering-Lin and Gross [23] proposed a simple model for viscosities based on entropy scaling for pure compounds and mixtures. The residual entropy is calculated with the PCP-SAFT equation of state. A total of 140 parameters were estimated for pure compounds and 566 mixtures, with an average relative deviation from the experimental data of about 5%. The work of Lötgering-

Lin et al. [23] demonstrated that the binary interaction parameter k_{ij} , typically adjusted with vapor-liquid equilibrium data, can enhance viscosity prediction of mixtures in entropy scaling. Kai Kang et al. [24] proposed a modified theory of Quantitative Structure-Property Relationship (QSPR) to provide reasonably estimated values of k_{ij} with an additional dispersion term.

One of the unfavorable aspects of macroscopic scaling is the divergence of the scaled viscosity as the density approaches zero caused by term $1/\rho_N^{2/3}$. The Novak scaling approach, while proposing a solution to the divergence problem, introduces a new issue by dividing the viscosity by the dilute-gas viscosity rather than $1/\rho_N^{2/3}\sqrt{mk_B T}$. In order to apply isomorph theory, it is necessary to nondimensionalize viscosity using the appropriate dimensional scales. The use of $\sigma^2\sqrt{mk_B T}$, the resulting viscosity scaling parameter, instead of $1/\rho_N^{2/3}\sqrt{mk_B T}$, results in the destruction of the monovariate scaling in the liquid phase for small molecules such as argon. However, for larger molecules, replacing omega with the microscopic length scale σ in place of $1/\rho_N^{-1/3}$ has a relatively modest impact, and it is possible to develop accurate transport models [25].

Bell [25–29] presents a new approach to residual entropy, the modified entropy scaling approach, which applies an entropy – dependent scaling. The new approach is based on the combination of various recent insights related to the use of residual entropy scale, especially a new way to scale viscosity to be consistent with the dilute gas limit. The objective of modified entropy scaling approach is to fix the divergence at zero density, use the correct length scale, and retain the nearly monovariate scaling in the liquid phase. The author obtained excellent results using this approach for propane [25] and n-alkanes series [27]. Later Yang et al., extended the use of this new approach to pure refrigerants, including natural refrigerants, hydrofluoroolefins, hydrochlorofluoroolefins, perfluorocarbons, hydrofluorocarbons, chlorofluorocarbons, and hydrochlorofluorocarbons and their mixtures [30].

It has been defined that scaling the viscosity using the Chapman-Enskog dilute gas value is not a suitable option because it uses a scaled length scale that is only appropriate for the gas phase, but inappropriate for the liquid phase, which would cause deviations from the single-variable relationship between the residual entropy and the scaled viscosity for small molecules in the liquid phase [26,28]. However, Mairhofer [12] presents a model for viscosity based on residual entropy scaling, using as a thermodynamic model to calculate the residual entropy the GERG 2008 equation of state [31] and Chapman-Enskog dilute gas to nondimensionalize viscosity. In the work of Mairhofer, the dimensionless viscosity of a pure component as a function of the residual entropy is correlated by a third-order polynomial. For pure compounds, an overall average deviation of 3.21% was obtained. In addition, excellent results were obtained for natural gas mixtures, with an average deviation of 3.09% [12]. No increased deviations for small molecules such as argon, helium, or methane are reported by Mairhofer.

Goncalves et al. [32] proposed an alternative Helmholtz energy scaling approach for the calculation of viscosity, which applies the Chapman-Enskog relation, an Ansatz function, and the PCP-SAFT equation of state to predict viscosity. This approach was applied to different groups of substances including n-alkanes, alcohols, aromatics, ethers,

chlorofluorocarbons, carbon dioxide, and nitrogen. For pure compounds, five parameters are fitted to correlate the viscosity of experimental data. The viscosities of 33 binary mixtures were evaluated under different conditions. For pure compounds, the minimum and maximum average absolute deviations (AAD) were 1.51 and 6.53%, respectively. For the mixtures, the corresponding minimum and maximum values were 0.70 and 23.95%. The Helmholtz scaling was compared to the entropy scaling approach, resulting in lower AAD for most of the pure compounds and mixtures with the Helmholtz approach. Although Gonçalves et al. have implemented Helmholtz scaling using the PCP-SAFT as the equation of state, this new approach has in principle the potential for coupling to other EoS [32]. The GERG 2008 equation of state developed by Kunz and Wagner has been adopted as a standard international reference equation of state for natural gases and similar mixtures.

The objective of our work is to predict the viscosities of natural gas. Furthermore, to compare Helmholtz scaling method to the residual entropy approach and modified entropy scaling. In this study, it is assumed that any deviations observed originate from the approach used to calculate viscosity, rather than the equation of state. This assumption is based on the adoption of GERG 2008 as an ISO standard, which provides highly accurate results for calculating thermodynamic properties of natural gas and its mixtures [33]. While cases of binary systems, such as (CH₄ + C₄H₁₀), have been identified where the capability of the GERG-EoS to describe rich natural gases at low temperatures is limited and requires reparameterization with new available data, as demonstrated by Darren et al. [34], in general, the original GERG 2008 version has provided accurate results for natural gas mixtures beyond these particular cases. Consequently, these approaches can be compared on a more objective basis compared to most studies that employ engineering equations of state, which often introduce a certain level of error in thermodynamic properties, particularly under varying pressure and temperature conditions. Another analysis included in this work is the study of mixing rules in binary mixtures and natural gas, as applied to these viscosity prediction approaches.

The GERG 2008 EoS calculations were made with the Python package "PyForFluids" which contains EoS implementations in Fortran that can be accessed from a Python interface using the software f2py [35] The package is public to use and modify under the MIT license and can be accessed at [36].

2. Models and mixing rules

In this section, we describe the essentials of the approaches, reference viscosity model and mixing rules considered in this study. This includes the main equations and citing the fundamental references.

2.1. Hard sphere viscosity model

As summarized by Mairhofer [12], several studies have shown that the hard sphere model proposed by Chapman-Enskog is the best choice to represent the reference viscosity used in residual entropy approaches for scaling viscosity. For a pure compound the Chapman-Enskog viscosity [37] is obtained as

$$\eta^{CE} = \frac{5}{16} \frac{\sqrt{Mk_B T / (N_A \pi)}}{\sigma^2 \Omega^{(2,2)*}} \quad (1)$$

Where η^{CE} is the reference viscosity of a system composed of hard spheres, M is the molecular mass of the compound, k_B is Boltzmann's constant, N_A is Avogadro's number, σ is the Lennard-Jones segment diameter. The collision integral $\Omega^{(2,2)*}$ is calculated using the empirical expression of Neufeld et al. [38] which is a function of temperature and Lennard-Jones energy parameter ε .

$$\Omega^{(2,2)*} = \frac{1.16145}{T^{*0.14874}} + \frac{0.52487}{\exp(0.7732T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \times 10^{-4} T^{*0.14874} \sin(18.0323T^{*-0.7683} - 7.27371) \quad (2)$$

Where T^* is defined as $T^* = \frac{k_B T}{\varepsilon}$.

The Chapman Enskog viscosity for mixtures is calculated with Wilke's [39] approximation.

$$\eta_{mix}^{CE} = \sum_{i=1}^N \frac{x_i \eta_i^{CE}}{\sum_{j=1}^N x_j \phi_{ij}} \quad (3)$$

Where η_i^{CE} is the viscosity of the pure component calculated with (eq 1) x_i is the mole fraction of component i and ϕ_{ij} is given by (eq 4).

$$\phi_{ij} = \frac{\left(1 + \left(\eta_i^{CE}/\eta_j^{CE}\right)^{1/2} (M_j/M_i)^{1/4}\right)^2}{\left(8(1+M_i/M_j)\right)^{1/2}} \quad (4)$$

2.2. Residual Entropy Scaling

Rosenfeld [6] demonstrated that for a liquid fluid described by spherical, monoatomic molecules, transport properties such as viscosity can be described as a function of the residual entropy. Rosenfeld presented a linear relationship between a dimensionless viscosity and the residual entropy. For more complex molecules substance-specific parameters are required to establish a relationship between η^* and s^{res} . The molar residual entropy used for these approaches is the difference between the actual entropy of the fluid and the entropy of an ideal gas at the same temperature and molar density,

$$s^{res}(T, \rho) = s(T, \rho) - s_{ig}(T, \rho) \quad (5)$$

GERG 2008 equation of state was used to obtain the values of residual entropy s^{res} . Based on Novak study [21], Lötgering-Lin et al [23] [40] shows that the relation of the logarithm of the dimensionless viscosity $\ln \eta^*$ with the residual entropy s^{res} can be accurately represented with a third-order polynomial ansatz function (eq 6) for different real molecules. In this approach, the dimensionless viscosity is defined as the relation between the viscosity of the component and the reference viscosity $\eta^* = \eta/\eta^{CE}$.

$$\ln \eta_i^* = a_i + b_i(s_i^{res}/R) + c_i(s_i^{res}/R)^2 + d_i(s_i^{res}/R)^3 \quad (6)$$

2.3. Modified Entropy Scaling

The Modified Entropy Scaling, like the Entropy Approach applied by Gross, relates viscosity to thermodynamic properties obtained through an equation of state, but with appropriate dimensionless units for viscosity. The value of the dimensionless molar residual entropy s^{res} is expressed by Bell as follows:

$$s_i^+ = -s_i^{res}/R \quad (7)$$

As Bell defined [25,27], the plus scaled reduced residual viscosity η_{res}^+ is defined as,

$$\eta_{res,i} = \eta_i - \eta_{i,\rho \rightarrow 0}(T) \quad (8)$$

$$\eta_{res,i}^+ = \frac{\eta_{res,i}}{\rho_N^{2/3} \sqrt{mk_B T}} \times (s_i^+)^{2/3} \quad (9)$$

Here, η_{res} is the residual viscosity, defined as the difference between the viscosity of the dense fluid η and the viscosity of the dilute gas $\eta_{\rho \rightarrow 0}(T)$ at the same temperature. The number density (ρ_N) is expressed in units of m^{-3} . The mass of a single molecule is represented as ' m ' and is measured in units of kg. The Boltzmann constant $k_B = 1.380649 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$ is also used. The dilute gas viscosity was calculated with Chapman Enskog as show above.

For mixtures, the effective mass of a particle ' m ' must be replaced by the mole fraction weighted average of the components m_{mix}

$$m_{mix} = \sum_i x_i * m_i \quad (10)$$

In this work, we implemented the empirical function proposed by Yang [30] to relate η_{res}^+ with s^+ ,

$$\ln(\eta_{res,i}^+ + 1) = a_i s_i^+ + b_i (s_i^+)^{1.5} + c_i (s_i^+)^2 + d_i (s_i^+)^{2.5} \quad (11)$$

2.4. Helmholtz energy scaling

Based on the theoretical fundament of residual entropy scaling, Goncalves et al. [32] proposed a semi-theoretical model inspired on the idea that the dimensionless viscosity of a system (scaled with the viscosity of a well-known and described reference system) can be described as an Ansatz function of the Helmholtz molar energy of the system, subtracted by the Helmholtz Energy of the reference system, i.e. $\ln(\eta/\eta^{CE}) = f(\bar{A}^*/(RT))$. The original work used the Chapman-Enskog hard spheres model as the reference viscosity. The Helmholtz scaling method is derived from Eyring's absolute rate theory [41]. Goncalves derived a method for the Helmholtz free energy as:

$$\left(\frac{\bar{A}^*}{RT}\right) = \left(\frac{\bar{A}}{RT}\right) - \left(\frac{\bar{A}_{hs}}{RT}\right) \quad (12)$$

For the \bar{A}_{hs} term Goncalves et al. already consider the ideal contribution, and the residual part is calculated as proposed by Gross and Sadowski [42].

$$\frac{\bar{A}_{hs}}{RT} = \frac{\bar{A}_{id}}{RT} + \bar{m} \frac{1}{\zeta_0} \left[\frac{3\zeta_1\zeta_2}{(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} + \left(\frac{\zeta_2^3}{\zeta_3^2} - \zeta_0\right) \ln(1 - \zeta_3) \right] \quad (13)$$

Where,

$$\zeta_n = \frac{\pi}{6} \rho \sum_i^{nc} x_i m_i d_i^n \quad n \in \{0,1,2,3\} \quad (14)$$

d_i is the temperature-dependent segment diameter defined in [42] while \bar{m} is the average number of the segments, calculated from (Eq 15).

$$\bar{m} = \sum x_i m_i \quad (15)$$

However, a direct relationship between (\bar{A}^*/RT) and $\ln(\eta/\eta_{hs})$ is difficult to obtain, so the authors introduced a scaling factor Ψ to facilitate this correlation.

$$\left(\frac{\Psi \bar{A}^*}{RT}\right) = \Psi \left[\left(\frac{\bar{A}}{RT}\right) - \left(\frac{\bar{A}_{hs}}{RT}\right)\right] \quad (16)$$

Ψ is defined as a reduced temperature function with a substance-dependent parameter θ and T^* is calculated as shown in the hard-sphere model (the same as for Eq. 2).

$$\Psi = (T^*)^\theta \quad (17)$$

For pure compounds, the author then defines a relation between the dimensionless viscosity and an Ansatz function with a third-degree polynomial as follows.

$$\ln(\eta_i^*) = a_i + b_i \left(\frac{\Psi_i \bar{A}_i^*}{RT}\right) + c_i \left(\frac{\Psi_i \bar{A}_i^*}{RT}\right)^2 + d_i \left(\frac{\Psi_i \bar{A}_i^*}{RT}\right)^3 \quad (18)$$

To illustrate how the Helmholtz scaling approach works, figure 1 shows different data points of $\ln(\eta^*)$ from the NIST database [43] correlations for heptane taken vs temperature, corresponding to isochoric lines between 10MPa and 100 MPa and temperature range between 200K and 600K.

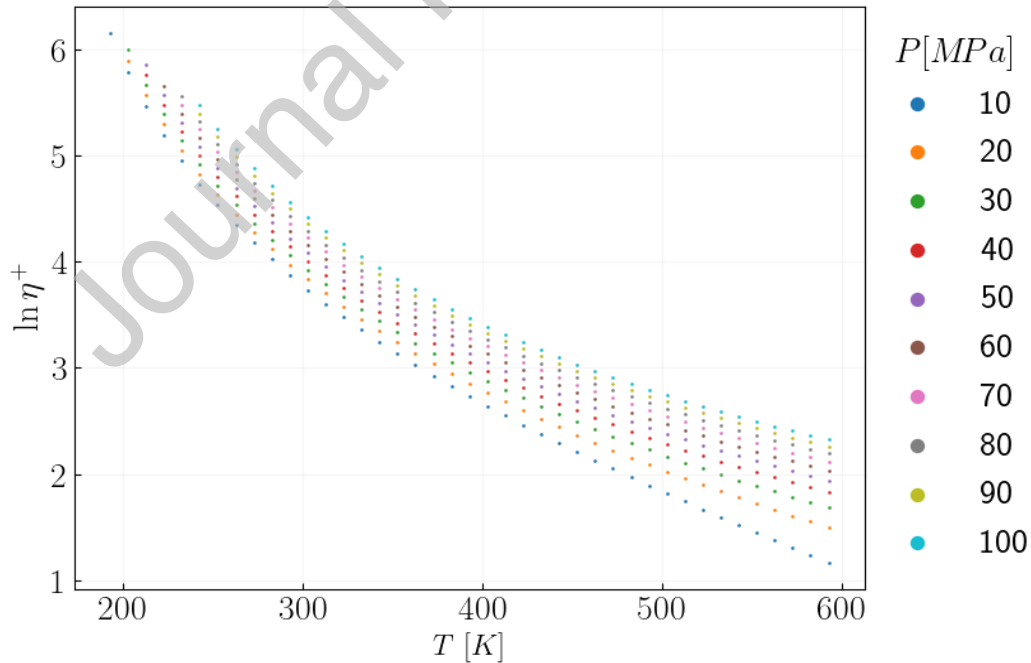


Figure 1. Values of $\ln(\eta^*)$ vs temperature for heptane data points from correlations of NIST data base [43].

After applying the Helmholtz scaling approach, we can fit all corresponding points in figure 1 to a single polynomial function of order three as shown in figure 2.

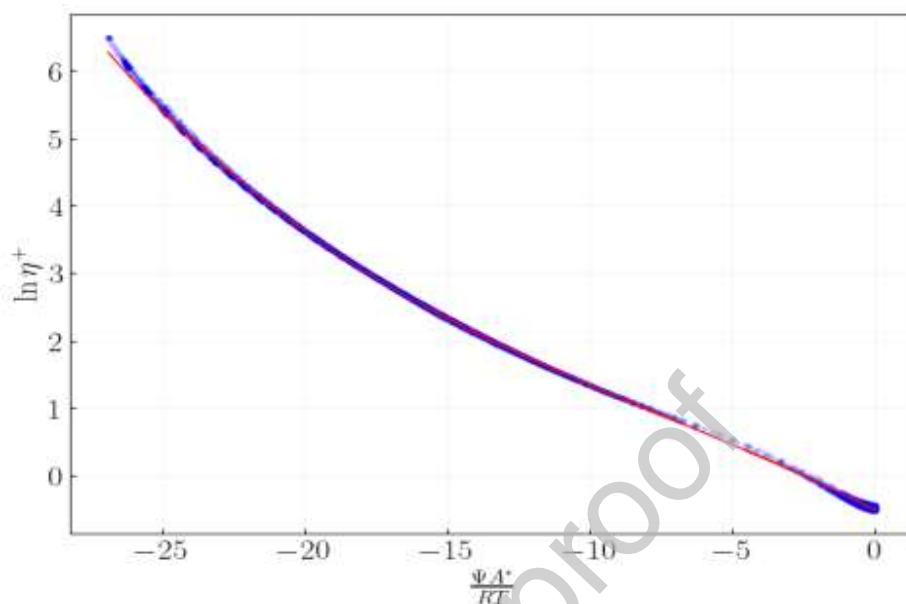


Figure 2. Helmholtz scaling approach applied to data point of heptane obtained from NIST[43], red line represent the function fitted by the correlation.

2.5. Coupling the Helmholtz scaling approach with the GERG 2008 EoS

We couple the Helmholtz energy scaling approach with the GERG 2008 equation of state to compute the residual Helmholtz energy. The reference viscosity was calculated using, the Chapman Enskog hard sphere model (Eq. 1) in this study. Due to using a different equation of state than the PCP-SAFT or any other SAFT model, we propose two ways to obtain the Helmholtz free energy difference \bar{A}^* in (Eq 12), and reference viscosity η_{ref} . The difference between them is in the method for calculating the hard-sphere contribution \bar{A}_{hs} of (Eq.13) and Chapman Enskog reference viscosity (Eq.1), depending on whether Chung et al. correlations or PC-SAFT are the source for the used parameters, as indicated in Table 1.

We identify the two alternatives by the subscripts *Chung* and *SAFT* respectively.

Table 1. Definition of the two alternatives to compute the hard-sphere Helmholtz free energy (eq13) and reference viscosity (eq.1).

Parameter	Chung Method	SAFT Method
σ	Chung et al. correlations	PC-SAFT parameter
ε/k_B	Chung et al. correlations	PC-SAFT parameter
m	1	PC-SAFT parameter

Parameter m takes a value of one for the Chung method, as the molecule is considered as a sphere (Chung correlations), unlike the SAFT method, which considers segments.

Eq 1 requires the parameters σ and ε/k_B for the calculation of the reference viscosity. In the case of the Chung method, the molecule is assumed to be a hard sphere, and these parameters are directly obtained from the correlations of Chung et al. On the other hand, for the SAFT method, the volume of a spheric segment is calculated using the parameter σ - PCSAFT, which is then multiplied by the number of segments, m , to obtain the total volume of the molecule as a chain. Then, the equivalent diameter sigma for a hard sphere is calculated based on the total volume obtained in the previous step.

2.6. Mixing rule selection

The summary of the generic parameter mixing rules applicable to different parameters studied in this work are listed below, where φ_i represents the pure substance parameter.

$$\varphi_{mix1} = \sum_i x_i \varphi_i \quad (19)$$

$$\varphi_{mix2} = \sum_i \frac{x_i m_i^\chi \varphi_i}{\sum_j x_j m_j^\chi} \quad (20)$$

$$\varphi_{mix3} = \sum_i \frac{x_i \varphi_i}{MW_i^\chi \sum_j \frac{x_j}{MW_j^\chi}} \quad (21)$$

$$\varphi_{mix4} = \ln(\sum_i x_i \exp(\varphi_i)) \quad (22)$$

Mairhofer used for each parameter a linear mixing rule such as the one presented in the eq 19.

$$\varphi_{mix} = \sum_{i=1}^N x_i \varphi_i \quad \varphi_i \in \{a, b, c, d\} \quad (23)$$

Lötgering-Lin et al. [23] proposed the mixing rule φ_{mix2} with a value of $\chi = 1$, for parameter b, c, d and a linear rule φ_{mix1} for parameter a , which results in the following equation:

$$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} \frac{x_i m_i}{\bar{m}} b_i (S^{res}/R) + \sum_i^{nc} \frac{x_i m_i}{\bar{m}} c_i (S^{res}/R)^2 + \sum_i^{nc} \frac{x_i m_i}{\bar{m}} d_i (S^{res}/R)^3 \quad (24)$$

Goncalves et al. [32] performed an analogous procedure to that of Lötgering-Lin et al., adapted for use with the Helmholtz approach.

$$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i \left(\Psi_i \frac{m_i \bar{A}^*}{\bar{m} RT} \right) + \sum_i^{nc} x_i c_i \left(\Psi_i \frac{m_i \bar{A}^*}{\bar{m} RT} \right)^2 + \sum_i^{nc} x_i d_i \left(\Psi_i \frac{m_i \bar{A}^*}{\bar{m} RT} \right)^3 \quad (25)$$

In this work, we extended Cisneros' [18] weighted fraction exponential rule for z_i to mixing parameters, leading to the expression shown in (eq 21). For the mixing rule φ_{mix3} we found a value of $\chi = -1/3$ to be suitable. φ_{mix4} is the mixing rule used to calculate the dilute gas limit mixture contribution [44]. Various combinations of these mixing rules

presented in equations (eq 19, eq 20) are considered for viscosity calculation, as outlined in Table 2 and Table 3, and evaluated for different approaches.

In previous works, already cited here, binary interaction parameters have not been considered in the mixing rules for viscosity. In this work, they were not considered either, because we aim for a fully predictive approach to mixtures. Although more parameters could be added, requiring the reformulation of each mixing rule, this would diminish the predictive utility of the model.

Table 2. The Ansatz function scaled to mixtures for Helmholtz scaling approach, based on mixing rules given by Eqs. 19-22.

Mixing Rule (MR)	Equation	Comments
H-MR1	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right) + \sum_i^{nc} x_i c_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)^2 + \sum_i^{nc} x_i d_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)^3$	φ_{mixl} applied to all terms of polynomial.
H-MR2	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right) + \sum_i^{nc} x_i c_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right)^2 + \sum_i^{nc} x_i d_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right)^3$	Parameter Ψ_{mix} obtained with φ_{mixl} previously, then apply mixing rule Y_{mixl} to all polynomial terms regardless of PC SAFT parameters m_i .

H-MR3	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right) + \sum_i^{nc} x_i c_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right)^2 + \sum_i^{nc} x_i d_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right)^3$	<p>Parameter Ψ_{mix} obtained with φ_{mix4} previously, then apply mixing rule Y_{mix1} to all polynomial terms regardless of PC SAFT parameters m_i.</p>
H-MR4	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right) + \sum_i^{nc} x_i c_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right)^2 + \sum_i^{nc} x_i d_i \left(\Psi_{mix} \frac{\bar{A}^*}{RT} \right)^3$	<p>Parameter Ψ_{mix} obtained with φ_{mix3} and $\chi = -1/3$ previously, then apply mixing rule φ_{mix1} to all polynomial terms regardless of PC SAFT parameters m_i.</p>

H-MR5	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i m_i^{0.5} a_i}{\sum_j x_j m_j^{0.5}} + \sum_i^{nc} \frac{x_i m_i^{0.5} b_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)}{\sum_j x_j m_j^{0.5}}$ $+ \sum_i^{nc} \frac{x_i m_i^{0.5} c_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^2}{\sum_j x_j m_j^{0.5}} + \sum_i^{nc} \frac{x_i m_i^{0.5} d_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^3}{\sum_j x_j m_j^{0.5}}$	φ_{mix2} apply to all polynomial terms and $\chi = 1/2$.
H-MR6	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i m_i a_i}{\sum_j x_j m_j} + \sum_i^{nc} \frac{x_i m_i b_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)}{\sum_j x_j m_j}$ $+ \sum_i^{nc} \frac{x_i m_i c_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^2}{\sum_j x_j m_j} + \sum_i^{nc} \frac{x_i m_i d_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^3}{\sum_j x_j m_j}$	φ_{mix2} apply to all polynomial terms and $\chi = 1$.
H-MR7	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i a_i}{m_i \sum_j \frac{x_j}{m_j}} + \sum_i^{nc} \frac{x_i b_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)}{m_i \sum_j \frac{x_j}{m_j}}$ $+ \sum_i^{nc} \frac{x_i c_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^2}{m_i \sum_j \frac{x_j}{m_j}} + \sum_i^{nc} \frac{x_i d_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^3}{m_i \sum_j \frac{x_j}{m_j}}$	φ_{mix2} apply to all polynomial terms and $\chi = -1$.
H-MR8	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i a_i}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}} + \sum_i^{nc} \frac{x_i b_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}}$ $+ \sum_i^{nc} \frac{x_i c_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^2}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}} + \sum_i^{nc} \frac{x_i d_i \left(\Psi_i \frac{\bar{A}^*}{RT}\right)^3}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}}$	φ_{mix3} apply to all polynomial terms and $\chi = -1/3$.

H-MR9	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i a_i}{MW_i^{0.7} \sum_j \frac{x_j}{MW_j^{0.7}}} + \sum_i^{nc} \frac{x_i b_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)}{MW_i^{0.7} \sum_j \frac{x_j}{MW_j^{0.7}}}$ $+ \sum_i^{nc} \frac{x_i c_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)^2}{MW_i^{0.7} \sum_j \frac{x_j}{MW_j^{0.7}}} + \sum_i^{nc} \frac{x_i d_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)^3}{MW_i^{0.7} \sum_j \frac{x_j}{MW_j^{0.7}}}$	φ_{mix3} apply to all polynomial terms and $\chi = 0.7$
H-MR10	$\ln(\eta_{mix}^*) = \ln \left(\sum_i x_i \exp(a_i) \right) + \ln \left(\sum_i x_i \exp \left(b_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right) \right) \right)$ $+ \ln \left(\sum_i x_i \exp \left(c_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)^2 \right) \right) + \ln \left(\sum_i x_i \exp \left(d_i \left(\Psi_i \frac{\bar{A}^*}{RT} \right)^3 \right) \right)$	φ_{mix4} apply to all polynomial terms
H-MR11	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i \left(\Psi_i \frac{m_i \bar{A}^*}{\bar{m} RT} \right)$ $+ \sum_i^{nc} x_i c_i \left(\Psi_i \frac{m_i \bar{A}^*}{\bar{m} RT} \right)^2 + \sum_i^{nc} x_i d_i \left(\Psi_i \frac{m_i \bar{A}^*}{\bar{m} RT} \right)^3$	Mixing rule used by Goncalves

Table 3. The Ansatz function scaled to mixtures for Entropy scaling approach, based on mixing rules given by Eqs. 19-22.

Mixing Rule (MR)	Equation	Comments
S-MR1	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i b_i (S^{res}/R)$ $+ \sum_i^{nc} x_i c_i (S^{res}/R)^2 + \sum_i^{nc} x_i d_i (S^{res}/R)^3$	Linear mixing rule φ_{mix1} applied to all parameters
S-MR2	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i m_i^{0.5} a_i}{\sum_j x_j m_j^{0.5}} + \sum_i^{nc} \frac{x_i m_i^{0.5} b_i (S^{res}/R)}{\sum_j x_j m_j^{0.5}}$ $+ \sum_i^{nc} \frac{x_i m_i^{0.5} c_i (S^{res}/R)^2}{\sum_j x_j m_j^{0.5}} + \sum_i^{nc} \frac{x_i m_i^{0.5} d_i (S^{res}/R)^3}{\sum_j x_j m_j^{0.5}}$	φ_{mix2} apply to parameter a_i, b_i, c_i, d_i with $\chi = 0.5$

S-MR3	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i \frac{m_i}{\bar{m}} a_i + \sum_i^{nc} x_i \frac{m_i}{\bar{m}} b_i (S^{res}/R)$ $+ \sum_i^{nc} x_i \frac{m_i}{\bar{m}} c_i (S^{res}/R)^2 + \sum_i^{nc} x_i \frac{m_i}{\bar{m}} d_i (S^{res}/R)^3$	Φ_{mix2} apply to parameter a_i, b_i, c_i, d_i with $\chi = 1$.
S-MR4	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i a_i}{m_i \sum_j \frac{x_j}{m_j}} + \sum_i^{nc} \frac{x_i b_i (S^{res}/R)}{m_i \sum_j \frac{x_j}{m_j}}$ $+ \sum_i^{nc} \frac{x_i c_i (S^{res}/R)^2}{m_i \sum_j \frac{x_j}{m_j}} + \sum_i^{nc} \frac{x_i d_i (S^{res}/R)^3}{m_i \sum_j \frac{x_j}{m_j}}$	Φ_{mix2} apply to parameter a_i, b_i, c_i, d_i , with $\chi = -1$
S-MR5	$\ln(\eta_{mix}^*) = \sum_i^{nc} \frac{x_i a_i}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}} + \sum_i^{nc} \frac{x_i b_i (S^{res}/R)}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}}$ $+ \sum_i^{nc} \frac{x_i c_i (S^{res}/R)^2}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}} + \sum_i^{nc} \frac{x_i d_i (S^{res}/R)^3}{MW_i^{-\frac{1}{3}} \sum_j \frac{x_j}{MW_j^{-\frac{1}{3}}}}$	Φ_{mix3} applied to all parameters , with $\chi = -1/3$
S-MR6	$\ln(\eta_{mix}^*) = \ln(\sum_i x_i \exp(a_i)) + \ln(\sum_i x_i \exp(b_i (S^{res}/R)))$ $+ (\sum_i x_i \exp(c_i (S^{res}/R)^2)) + (\sum_i x_i \exp(d_i (S^{res}/R)^3))$	Φ_{mix4} applied to all parameters
S-MR7	$\ln(\eta_{mix}^*) = \sum_i^{nc} x_i a_i + \sum_i^{nc} x_i \frac{m_i}{\bar{m}} b_i (S^{res}/R)$ $+ \sum_i^{nc} x_i \frac{m_i}{\bar{m}} c_i (S^{res}/R)^2 + \sum_i^{nc} x_i \frac{m_i}{\bar{m}} d_i (S^{res}/R)^3$	Φ_{mix2} apply to parameter b_i, c_i, d_i , with $\chi = 1$ (mixing rule used by Lötgering- Lin et al.)

2.7. Data selection and parameter adjustment

The valid range of the GERG 2008 equation of state was considered. The normal range of validity of this equation of state includes temperatures from 90-450 K and pressures up to 35 MPa. The extended validity range goes from 60 -700 K and up to 70 MPa [31]. We used NIST correlations [43] as a smooth and practical representation of experimental data within

the temperature ranges suggested by GERG-2008. However, pressure values up to 100 MPa were included to evaluate reservoir conditions. We included data points from the entire fluid phase region (gas, liquid, and supercritical regions), including saturated states. The NIST database is considered standard reference data. As an illustration, parameter fitting was performed for propane using the modified entropy approach. In one case, available data for propane in Bell's work [25] were used, while in the other case, viscosity values at the same conditions were obtained using the NIST database. No significant deviations were found in the parameter fitting between both data sources, confirming the reliability of the NIST database as a representation of experimental data for pure components. The results obtained from this test are available in the figure S1 in [supplementary material](#). For binary and multicomponent mixtures, experimental data from referenced sources were used. To estimate the five parameters for each pure substance we used the Nelder-Mead [45] optimization method. The objective function is defined by,

$$F_{\text{obj}} = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} \frac{|\eta_i - \eta_i^{\text{exp}}|}{\eta_i^{\text{exp}}} \quad (26)$$

As viscosity data for pure compounds are available at certain pressure and temperature conditions, it is important to ensure a certain degree of extrapolation capability of the model for values of $-s^{res}$ or A^{res} (depending on the scaling approach) outside the range of the data used for parameter fitting of equations (eq 6, eq 11, eq 18).

For entropy scaling, the lowest values for $-s^{res}$, considering all-natural gas and sour gas data, were -2.76 and -1.54, respectively. For all the available data on pure compounds, the minimum value obtained for $-s^{res}$ was -3.65. Hence, the fitted parameters of pure compounds adequately cover the range of the studied mixtures. The maximum and minimum values of residual entropy for the studied mixtures in this work are presented in table S1 of the [supplementary material](#) file.

However, if the aim is to ensure a higher degree of extrapolation capability in all compounds, this means that the polynomial describing our model should not exhibit maxima for $\ln(\eta_{res}^+ + 1)$ at very low values of dimensionless reduced molar residual entropy (remember that our case study is the modified entropy approach). In this study, we have implemented a solution similar to those proposed by Mairhofer and Gross in previous works [12,17], we take the modified entropy scaling approach as an example. The coefficient of the cubic term of equation (eq 27) D_i is not individually adjusted; instead, a generalized correlation is proposed as follows,

$$D_i = n1 * T_{c,i} + n2 * MW_i + n3 T_{c,i} * MW_i \quad (27)$$

Where $T_{c,i}$ is the critical temperature and MW_i is the molecular mass of component i , we proposed a three-parameter model that is not specific to the component, namely $n1$, $n2$ and $n3$. These parameters are adjusted simultaneously with the component-specific parameters A_i , B_i and C_i . To calculate these parameters, only the series of n-alkanes was considered. Not adjusting the value of D_i individually resulted in a loss of correlation accuracy. The readjusted parameters and the extrapolated polynomials obtained are shown in the [supplementary material](#) for all components, only for the modified entropy approach. The same methodology is valid for the Helmholtz approach. Figure 3 demonstrates, using

Methane as an example, how this method shifts the position of the maximum to a significantly lower value of residual entropy. This enables the derivation of more reliable polynomials, which exhibit a reasonable trend of $\ln(\eta_{res}^+ + 1)$ with respect to s^+ , even when extrapolated to higher values of s^+ that are not available for parameter tuning.

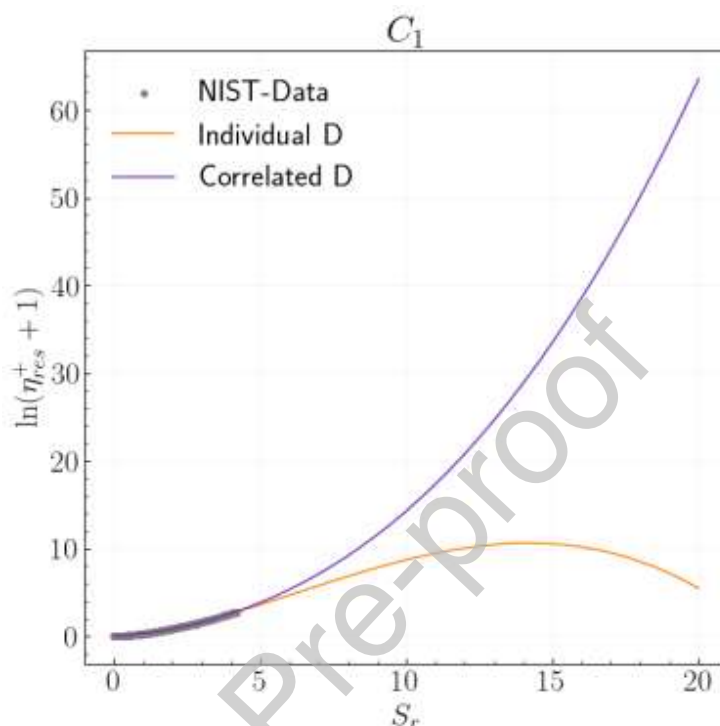


Figure 3. Result obtained of eq 11, and individual adjusted parameter (orange line) are compared to results where D parameter is obtained from eq 27 (purple line). Symbols represent data points obtained from NIST [43].

It is important to clarify that the analysis for the studied mixtures was performed with individual parameter adjustments for each component. This was possible due to the availability of ample data on pure components, which covered the entire range of conditions for the studied mixtures.

3. Results

For each scaling approach, we consider first pure substances, followed by the highly asymmetric binary system methane + n-decane systems, and finally multicomponent mixtures. The results are presented considering the alternatives that we identified as Chung and SAFT depending on the source of the parameters used in the estimation of the reference viscosity and of the hard sphere contribution term.

3.1. Pure components

Table 4 presents the parameters of pure compounds using the *Chung* correlations for the estimation of the reference viscosity and the hard sphere contribution term. This way was called Chung method. results are presented for both entropy and Helmholtz scaling

approaches. Table 5 corresponds to the parameters obtained for pure compounds, now using the SAFT alternative, which takes PC SAFT from [42] to estimate of the reference viscosity and the hard sphere contribution term. Table 6 corresponds to the parameters obtained for pure compounds, using the modified entropy scaling approach, which uses the Chung correlations. Figure 4 and Figure 5 show the correlation of Helmholtz and entropy scaling respectively using the Chung method. Figure 6 and Figure 7 show the correlation of Helmholtz and entropy scaling considering the SAFT method. Figure 8 shows the modified entropy scaling using Chung method, this approach shows a linear behavior in the liquid region. Based on the results presented in Table 7, for most pure compounds, %AADs are well below 5%. For Helmholtz scaling, better performance was achieved using the SAFT method. In the case of entropy scaling, similar performances were reported for both the Chung and SAFT methods. However, among the different approaches, the modified entropy scaling using the Chung method yielded slightly better results.

For Helmholtz scaling, a global AAD of 3.42% was obtained using the Chung method, while using the SAFT method yielded a lower at 2.70%. Regarding entropy scaling, a global AAD of 4.19% was obtained using the Chung method and 4.02% for SAFT method. The modified entropy scaling approach obtained a global AAD of 2.37%. For \bar{A}_{Chung}^* approach the minimum and maximum absolute average deviations (AADs) were 1.20 and 6.67% respectively. Whereas \bar{A}_{SAFT}^* the minimum and maximum were 1.08 and 4.37%. Using Entropy scaling with *Chung* method the values of absolute average deviations (AADs) obtained were 2.31% and 8.23%. the same values whit SAFT method for entropy were 2.22% and 7.38%. In the case of modified entropy scaling with *Chung* method the minimum and maximum values of absolute average deviations (%AADs) obtained were 1.25% and 8.56%. The low AAD values obtained for methane across all applied approaches (between 1.25 - 2.67%) are a promising result, considering that natural gas mixtures have a high methane content in their composition. It is important to clarify that the Helmholtz energy scaling approach, although defined as a third-degree polynomial, has five adjustable parameters, while the entropy and modified entropy scaling approaches have four adjustable parameters each.

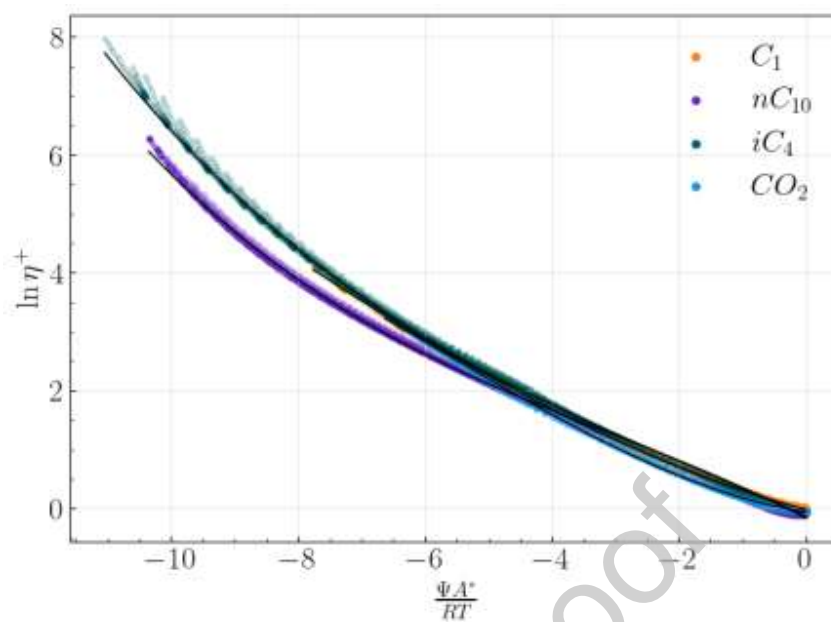


Figure 4. Scaling for methane, decane, iso-butane and carbon dioxide in this work. Symbols represent data point from NIST data base [43] and black solid lines represent the Helmholtz scaling for *hs* – *Chung* method correlation.

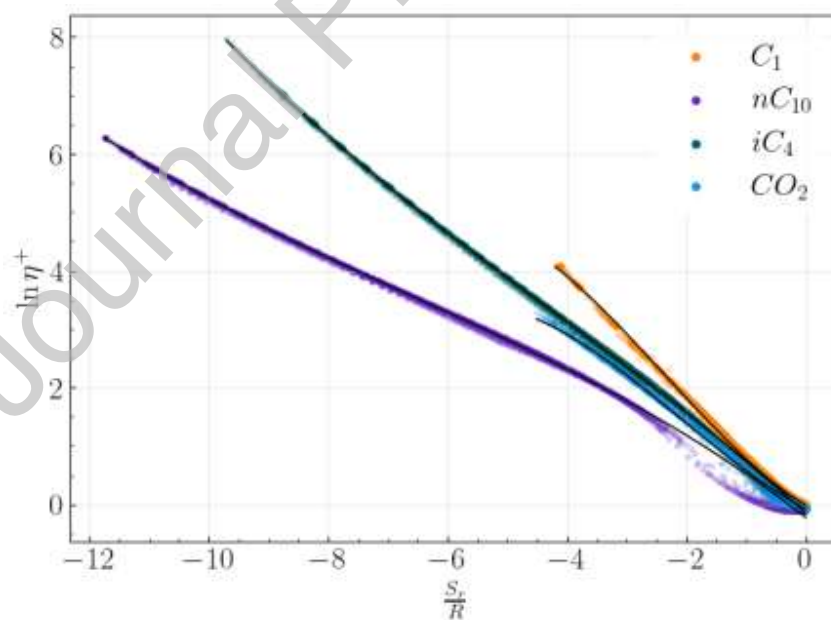


Figure 5. Scaling for Methane, Decane, Iso-butane and Carbon Dioxide in this work. Symbols represent data point from NIST data base [43] and black solid lines represent the entropy scaling for *hs* – *Chung* method correlation.

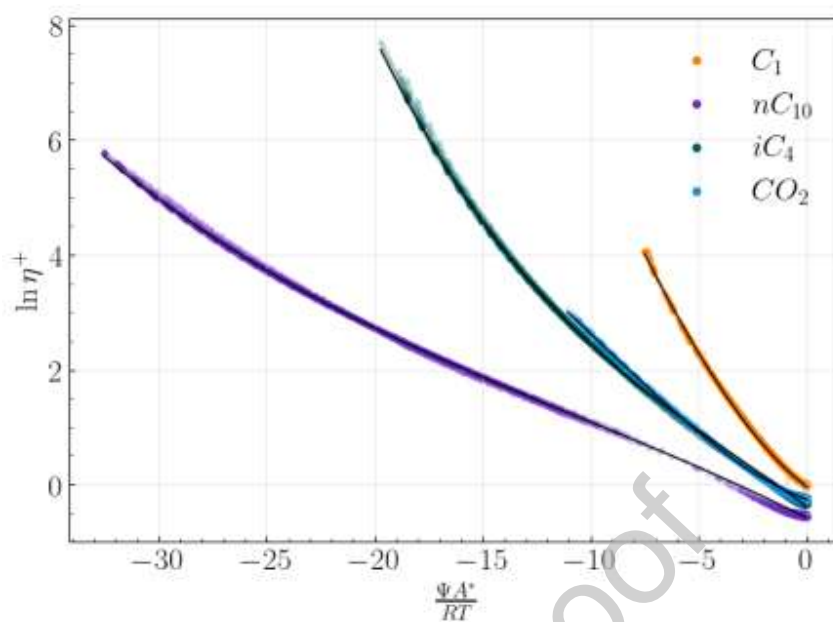


Figure 6. Scaling for Methane, Decane, Iso-butane and Carbon Dioxide in this work. Symbols represent data point from NIST data base [43] and black solid lines represent the Helmholtz scaling for *SAFT* method correlation.

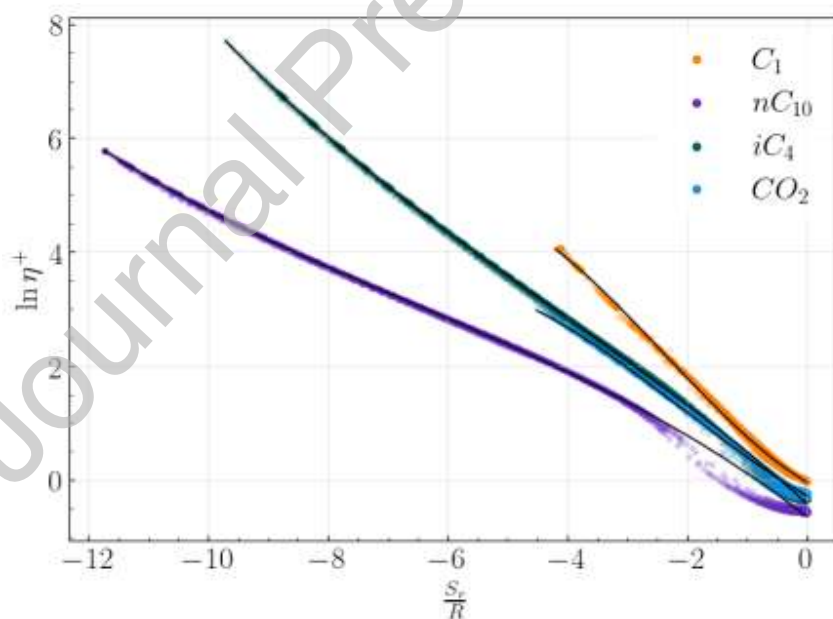


Figure 7. Scaling for Methane, Decane, Iso-butane and Carbon Dioxide in this work. Symbols represent data point from NIST data base [43] and black solid lines represent the entropy scaling for *SAFT* method correlation.

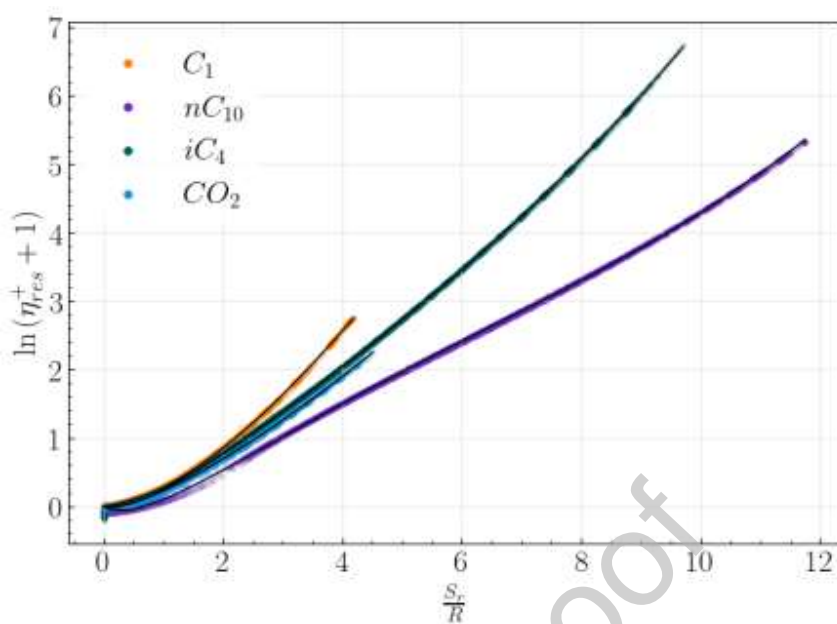


Figure 8. Scaling for Methane, Decane, Iso-butane and Carbon Dioxide in this work. Symbols represent data point from NIST data base [43] and black solid lines represent the entropy scaling for *SAFT* method correlation.

In Tables 4 and 5, we can observe a change in the sign (positive/negative) of the parameters c and d values for pure compounds. This change is related to the model's ability to extrapolate. As explained in the section "Data selection and parameter adjustment," it means that the polynomial describing our model should not have maxima (as they lack physical significance) for $\ln \eta^*$ at very high values of $\Psi \bar{A}^*/RT$ (Helmholtz scaling approach) or S^{res}/R (residual entropy approach). Similarly, for the modified Bell entropy scaling, our model should not exhibit a maximum for $\ln \eta^*$ at low values of the dimensionless $-S^{res}/R$.

Generally, we can observe in Tables 4 and 5 that compounds with low molecular weight and higher sphericity, such as methane, nitrogen, carbon dioxide, hydrogen, oxygen, carbon monoxide, hydrogen sulfide, and argon, mostly have positive values for the parameters c and d (negative values for modified entropy scaling in Table 6). For these compounds, the corresponding polynomials exhibit maxima at higher values of $\Psi \bar{A}^*/RT$ (for Helmholtz scaling) and S^{res}/R (for entropy scaling). On the contrary, other compounds that have negative values for the parameters c and d , without presenting maxima in the fitted ansatz functions in the range of interest, have a higher degree of non-sphericity. The supplementary material includes graphs illustrating the extrapolation capability of the models for pure components using the Bell approach.

Table 4. Helmholtz and Entropy Scaling parameters for *Chung* method and pure substances.

Substances	Helmholtz Approach					Entropy Scaling			
	a	b	c	d	θ	a	b	c	d

methane	-	-	0.0369	0.0009	0.6307	-	-	0.2079	0.0293
nitrogen	-	-	0.0714	0.0040	0.6684	-	-	0.3173	0.0471
carbon_dioxide	-	-	0.0804	0.0046	0.8918	-	-	0.1462	0.0233
ethane	-	-	0.0087	-	0.7490	-	-	-	-
propane	-	-	-	-	0.7593	-	-	-	-
butane	-	-	-	-	0.8639	-	-	-	-
isobutane	-	-	-	-	0.8011	-	-	-	-
pentane	-	-	-	-	0.7339	-	-	-	-
isopentane	-	-	-	-	0.8373	-	-	-	-
hexane	-	-	-	-	0.9357	-	-	-	-
heptane	-	-	-	-	0.9479	-	-	-	-
octane	-	-	-	-	0.9434	-	-	-	-
nonane	-	-	-	-	0.9647	-	-	-	-
decane	-	-	-	-	1.0277	-	-	-	-
hydrogen	-	-	-	-	0.3112	-	-	-	-
oxygen	-	-	-	-	0.7311	-	-	-	-
carbon_monoxide	-	-	-	-	0.6543	-	-	-	-
hydrogen_sulfide	-	-	-	-	0.7350	-	-	-	-
argon	-	-	-	-	0.6579	-	-	-	-

Table 5. Helmholtz and Entropy Scaling parameters for *SAFT method* and pure substances.

Compound	Helmholtz Approach					Entropy Scaling			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	θ	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
methane	-	-	0.0400	0.0008	0.6583	-	-	0.2084	0.0294

nitrogen	-	-	0.0698	0.0036	0.6660	-	-	0.3195	0.0477
carbon_dioxide	0.0805	0.1667	0.0244	0.0009	0.6073	0.2721	0.5922	0.1002	0.0160
ethane	-	-	0.0046	-	0.6441	-	-	-	-
propane	0.2381	0.2887	0.0009	0.0004	0.6015	0.3594	0.9398	0.0472	0.0035
butane	-	-	-	-	-	-	-	-	-
isobutane	0.3793	0.2307	0.0002	0.0003	0.6288	0.4450	0.9295	0.0531	0.0036
pentane	-	-	-	-	-	-	-	-	-
isopentane	0.3788	0.2758	0.0053	0.0006	0.6241	0.4042	0.9394	0.0467	0.0037
hexane	-	-	-	-	-	-	-	-	-
heptane	0.4259	0.2617	0.0032	0.0002	0.4850	0.4779	0.9357	0.0657	0.0041
isopentane	-	-	-	-	-	-	-	-	-
hexane	0.3782	0.2521	0.0081	0.0006	0.6541	0.4031	0.8686	0.0436	0.0033
heptane	-	-	-	-	-	-	-	-	-
octane	0.4552	0.2255	0.0047	0.0003	0.6160	0.4998	0.8723	0.0586	0.0038
nonane	-	-	-	-	-	-	-	-	-
decane	0.5107	0.2154	0.0056	0.0003	0.6243	0.5583	0.8513	0.0559	0.0032
hydrogen	-	-	-	-	-	-	-	-	-
oxygen	0.5255	0.2067	0.0044	0.0002	0.5773	0.5939	0.8374	0.0567	0.0031
carbon_monoxide	-	-	-	-	-	-	-	-	-
hydrogen_sulfide	0.5616	0.1912	0.0024	0.0001	0.5203	0.6405	0.8431	0.0597	0.0032
argon	-	-	-	-	-	-	-	-	-
decane	0.5791	0.1902	0.0034	0.0001	0.5360	0.6397	0.8110	0.0555	0.0028
hydrogen	-	-	-	-	-	-	-	-	-
oxygen	0.0584	0.0068	0.0927	0.0005	0.7498	0.0648	0.2465	0.5305	0.0076
carbon_monoxide	-	-	-	-	-	-	-	-	-
hydrogen_sulfide	0.0495	0.1969	0.0470	0.0008	0.7289	0.0540	0.6250	0.1550	0.0181
argon	0.0845	0.4184	0.0124	0.0003	0.0901	0.0952	0.6949	0.1441	0.0196
methane	-	-	-	-	-	-	-	-	-
nitrogen	0.1825	0.1930	0.0237	0.0009	0.5939	0.1978	0.7232	0.0671	0.0118
carbon_dioxide	-	-	-	-	-	-	-	-	-
ethane	0.0142	0.2525	0.0770	0.0039	0.7169	0.0150	0.5671	0.3316	0.0560

Table 6. Modified Entropy Scaling parameters for pure substances.

Substances	Entropy Scaling			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
methane	0.1165	-0.0419	0.2611	-0.0545
nitrogen	0.0782	-0.0838	0.3744	-0.0963
carbon_dioxide	-0.2614	0.6853	-0.2334	0.0374
ethane	-0.3649	0.9105	-0.3254	0.0459
propane	-0.4541	1.0203	-0.3767	0.0528

butane	-0.5748	1.1565	-0.4375	0.0606
isobutane	-0.4234	0.9647	-0.3464	0.0487
pentane	-0.8168	1.4677	-0.5767	0.0792
isopentane	-0.5902	1.1328	-0.4167	0.0570
hexane	-0.4438	0.9517	-0.3575	0.0489
heptane	-0.5724	1.0851	-0.4051	0.0533
octane	-0.6911	1.2058	-0.4488	0.0580
nonane	-1.0096	1.5818	-0.5946	0.0760
decane	-0.7458	1.2536	-0.4634	0.0583
hydrogen	1.2180	-3.3635	3.4071	-0.8932
oxygen	0.1225	-0.0640	0.3062	-0.0751
carbon_monoxide	0.2528	-0.3281	0.4940	-0.1200
hydrogen_sulfide	-0.0386	0.2196	0.1282	-0.0508
argon	0.1039	-0.0820	0.3940	-0.1008

Table 7. Helmholtz and Entropy Scaling AADs for *Chung* and *SAFT* calculation method.

Substance	Reference	N_{data}	T range (K)	P range (MPa)	Helmholtz Scaling		Entropy Scaling		Modified Entropy Scaling
					AAD (%) <i>Chung</i>	AAD (%) <i>SAFT</i>	AAD (%) <i>Chung</i>	AAD (%) <i>SAFT</i>	AAD (%) <i>Chung</i>
methane	[46]	2935	90.68 - 450	0.01 - 70	1.36	1.32	2.66	2.67	1.25
nitrogen	[43]	2714	63.151 - 704	0.01 - 100	1.54	1.55	2.55	2.40	1.51
carbon_dioxide	[43]	1566	216.59 - 598	0.01 - 100	1.40	2.06	3.13	4.06	2.08
ethane	[43,47-49]	1451	91 - 500	1e-6 - 60	2.89	2.58	4.63	4.40	2.05
propane	[43]	3247	85.525 - 596	1.72e-10 - 100	5.01	4.03	4.99	4.52	2.80
butane	[43]	2597	134.9 - 574.89	6.791e-7 - 100	4.50	3.42	4.98	4.37	2.56
isobutane	[43]	2825	113.73 - 570	2.289e-8 - 100	4.02	2.71	4.04	3.65	1.86
pentane	[43]	2565	143.47 - 593.47	7.803e-8 - 100	5.13	3.73	8.23	7.38	3.05
isopentane	[43]	187	113 - 495	1.02e-10	6.67	4.37	4.02	3.45	2.31

		3		-100					
hexane	[43]	270 2	177.83 - 597.83	1.19e-6 - 100	2.31	1.68	3.43	3.05	2.48
heptane	[43]	273 8	182.55 - 592.55	1.743e-7 - 100	3.51	1.88	3.23	2.95	2.50
octane	[43]	237 0	216.37 - 568.37	2.075e-6 -100	3.83	2.11	3.89	3.24	1.64
nonane	[43]	266 6	219.7 - 599.7	4.44e-7 - 100	5.51	3.91	6.27	5.41	2.28
decane	[43]	290 3	243.5 - 673.5	1.404e-6 - 100	4.32	2.22	4.77	4.06	1.90
hydrogen	[43]	144 3	13.957- 594	7.36e-3 - 100	2.17	3.01	4.19	4.37	8.56
oxygen	[43]	153 5	55-595	1.79e-4 - 80	1.46	1.42	2.69	2.74	1.31
carbon_m onoxide	[43]	236 1	68.16- 498.16	0.01 - 100	1.84	3.76	2.92	5.41	2.16
hydrogen_ sulfide	[43]	153 8	188 -598	0.01 - 100	3.63	4.16	5.59	6.17	3.59
argon	[43]	154 6	84 -595	0.01 - 100	1.20	1.08	2.31	2.22	1.32
				Promedi o	3.28	2.69	4.13	4.03	2.48
				Maximu m	6.67	4.37	8.23	7.38	8.56
				Minimu m	1.20	1.08	2.31	2.22	1.25
				%AAD Global	3.42	2.70	4.19	4.02	2.37

3.2. Evaluation of mixing rules based on binary mixtures

We analyzed an asymmetric binary mixture composed of methane + n-decane in the whole composition range, to evaluate the performance of the different mixing rules considered. Table 8 shows %AADs of all the data points considered for the binary methane decane system, using the Chung and SAFT methods for Helmholtz, entropy and entropy modified approaches.

Table 8. %AADs of all the data considered for the binary methane + n-decane system, for methods and approach used.

References	[50,51]	
N_{exp}	438	
T range (K)	293.15-393.15	
P range (MPa)	0.1-140	
Mixing Rule	AAD Chung (%)	AAD SAFT (%)

Helmholtz Approach		
H-MR1	113.56	8567.32
H-MR2	94.89	3012.87
H-MR3	18.20	3687.35
H-MR4	11.63	1003.82
H-MR5	8.23	719.14
H-MR6	40.62	64.45
H-MR7	1760.00	2.38E+06
H-MR8	9.28	42.89
H-MR9	1380.00	2.28E+06
H-MR10	1.74E+06	3.58E+12
H-MR11	42.38	13.60
Entropy Scaling		
S-MR1	17.25	17.52
S-MR2	28.96	24.68
S-MR3	37.45	36.24
S-MR4	34.83	61.17
S-MR5	28.36	37.34
S-MR6	14.21	23.67
S-MR7	34.69	28.15
Modified Entropy Scaling		
S-MR1	18.07	-
S-MR2	14.28	-
S-MR3	28.06	-
S-MR4	112.60	-
S-MR5	13.27	-
S-MR6	48345.83	-
S-MR7	128.26	-

Using the Chung calculation method for Helmholtz scaling, the lowest AAD deviation was 8.23% for the H-MR5 mixing rule. For the same method and the entropy approach, the lowest deviation was observed for the S-MR6 rule with a value of 14.21%. The lowest AAD value obtained by the modified entropy scaling method was 13.27%, using the mixing rule S-MR5. Meanwhile, for the SAFT calculation method, we obtained the lowest deviation was 13.60% for the H-MR11 mixing rule. For the entropy approach and SAFT method, the lowest deviation was 17.52% for the S-MR1 mixing rule. In general, the lowest deviations are obtained using the Chung method in the Helmholtz and Entropy approach for asymmetric binary mixture considered.

In table 8, huge sensitivity in AAD results is observed with respect to the method used to obtain the pure-component parameter values of σ , ε/k_B and m (Chung method or SAFT method). In the entropy scaling approach, the reference term of the residual entropy scaling factor (s^{res}) does not depend on the parameters that vary between the Chung and SAFT methods (σ , ε/k_B and m), making the entropy scaling approach less sensitive to changes in these parameters. On the other hand, the sensitivity of the results to the method used (Chung or SAFT) is higher in the Helmholtz scaling approach, due to the direct dependence of scaling factor (\bar{A}^*) on the parameters (σ , ε/k_B and m). Note that in (eq 12), \bar{A}^* is

expressed as a difference between the total molar Helmholtz energy (\bar{A}) and the contribution of hard spheres (\bar{A}_{hs}). Calculating \bar{A}_{hs} term requires the $\sigma, \varepsilon/k_B$ and m parameters, making the Helmholtz scaling approach much more sensitive to parameter changes.

The shape of molecules also affects the sensitivity of the results, as non-spherical molecules (with longer chains) have a greater sensitivity to the method used (Chung or SAFT) than spherical molecules (with shorter chains of low molecular weight). The values of these parameters can vary significantly depending on the method used for their calculation (Chung or SAFT) based on the non-sphericity of the molecules (Table S3 in supplementary material significant differences in the parameter ε/k_B are observed depending on the method employed.).

Table 9. Parameters comparison between the Chung method and the SAFT method, for methane and decane, employing the Helmholtz scaling approach.

Method	Compound	Helmholtz scaling parameters				
		a	b	c	d	θ
Chung	Methane	-0.0186	-0.2922	0.0369	0.0009	0.6307
	Decane	-0.1582	-0.5514	-0.0416	-0.0045	1.0277
SAFT	Methane	-0.0389	-0.2863	0.0400	0.0008	0.6583
	Decane	-0.5791	-0.1902	-0.0034	-0.0001	0.5360

Table 9 shows the values of the pure-component parameters (eq 18) for methane and decane obtained using Helmholtz scaling and the Chung and SAFT methods. Note that the values of the fitting parameters for methane are very similar for the Chung and SAFT methods. On the other hand, for decane, the values of the parameters a , b , c , d and θ are quite different depending on the method (Chung or SAFT) due to the high degree of non-sphericity of the molecule.

This sensitivity extends to mixture systems, depending on the mixing rule used. The differences in the deviations presented when using one method or another will be reflected in different ways, increasing or neutralizing errors depending on the case. In addition to all the above, Helmholtz scaling has an additional parameter, theta, compared to entropy-based approaches. Note that, for Decane, this parameter has again very different values with the Chung and SAFT methods (table 9), which deepens the sensitivity when dealing with different mixing rules. An example of the sensitivity of the theta parameter in the Helmholtz approach is shown in the [supplementary material](#). The modified entropy approach exhibits higher sensitivity than the entropy approach, because in the former, the dimensionless viscosity has a dependence on the reduced dimensionless entropy (eq 9).

3.2.1. Chung method

Figure 9 shows the behavior of the different mixing rules considered in this work, using Chung calculation method for Helmholtz scaling approach.

Figure 9 shows that some mixing rules such as H-MR7, H-MR9, H-MR10 are not suitable for the binary system studied over the whole pressure range. Furthermore, a similar behavior is observed for the H-MR7 and H-MR9 (almost superposed), since both rules are

similar in their mathematical structure, differing in that H-MR7 uses m_i parameters of PC SAFT and H-MR9 uses molecular weights.

The rules H-MR1, H-MR2, H-MR6, H-MR11 have a better performance than the previous rules, but still show considerable deviations. The best behaviors were presented by the mixing rule H-MR3, H-MR4, H-MR5, H-MR8. Based on the results obtained at this step, and the %AAD presented in Table 7, we consider for the study of multicomponent mixtures the mixing rules that show the best performance, i.e., H-MR3, H-MR4, H-MR5, H-MR8 and also the rule H-MR11 used by Goncalves. Figure 10 shows only the best mixing rules.

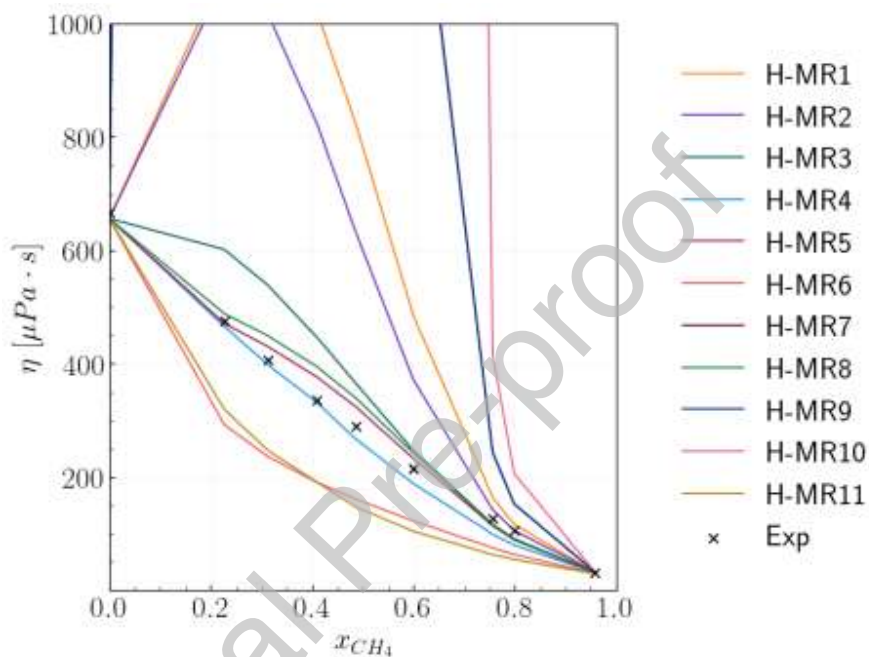


Figure 9. Mixing rules behavior for Helmholtz Scaling using Chung calculation method, for methane + n-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

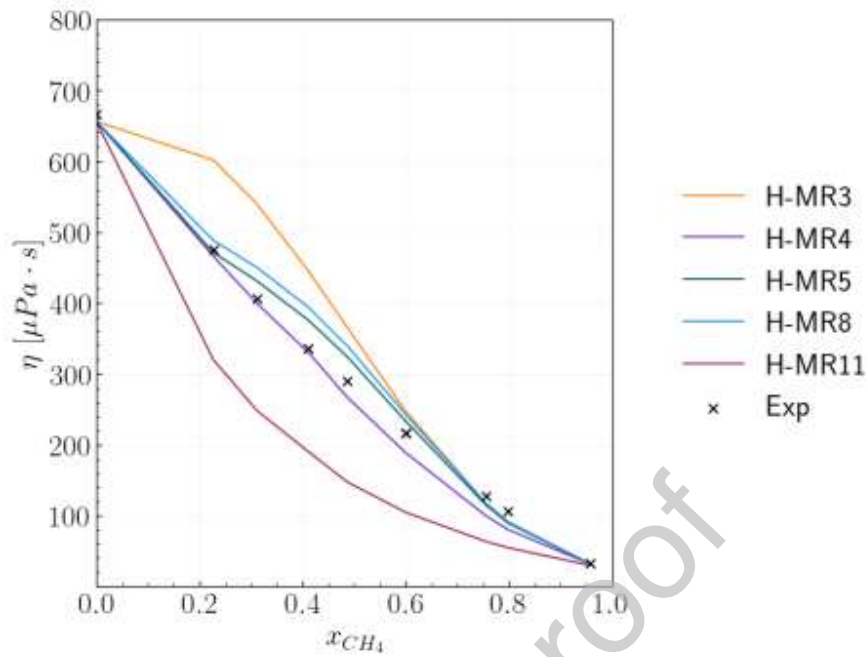


Figure 10. Better performance mixing rules for Helmholtz Scaling using Chung calculation method, for methane + n-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

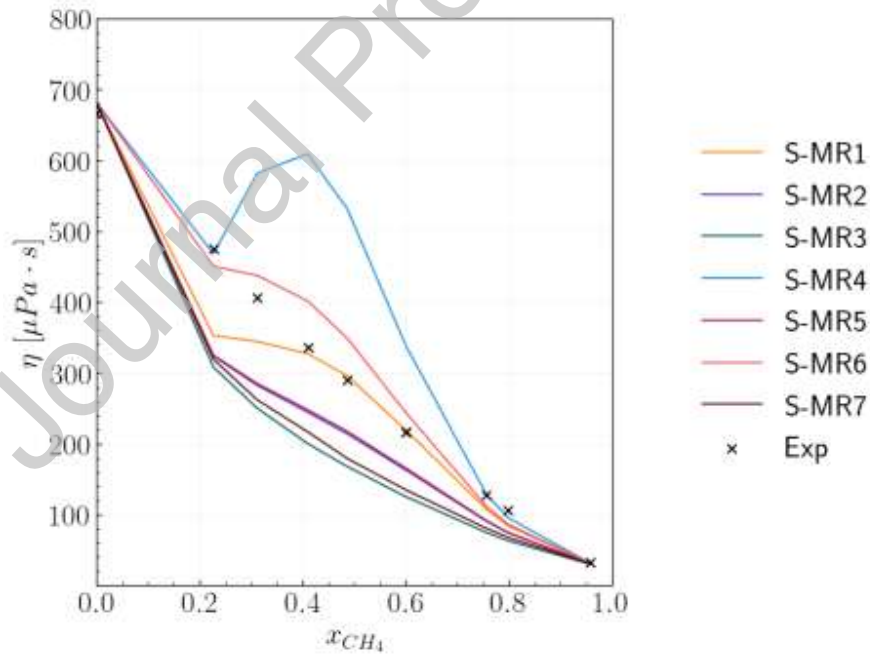


Figure 11. Mixing rules behavior for Entropy Scaling using Chung calculation method, for methane-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

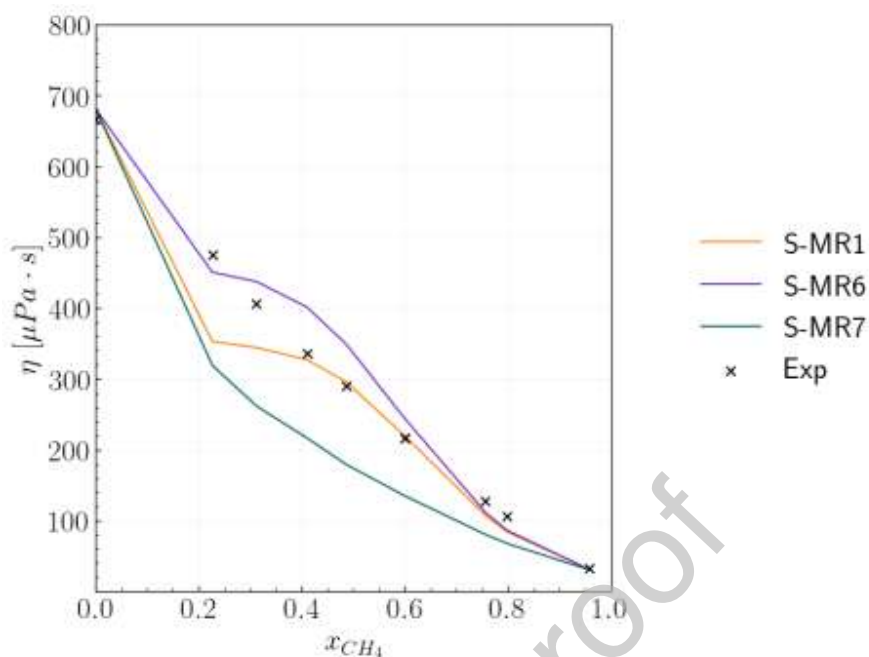


Figure 12. Better performance mixing rules for Entropy Scaling using Chung calculation method, for methane-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

Figure 11 shows the behavior of the different mixing rules considered in this work, using Chung calculation method for Entropy scaling approach. We observe that most mixing rules show a similar (nonlinear) behavior. Mixing rules S-MR1, S-MR6 and S-MR7 were selected for studies of multicomponent systems, and their predictions for this binary system are shown separately in figure 12. S-MR7 was used by Lötgering-Lin et al, so we consider it to compare results.

3.2.2. SAFT method

Figure 13 shows the behavior of the different mixing rules considered in this work, using SAFT calculation method for Helmholtz scaling approach described in this work. It is observed that only one mixing rule H-MR11 (the one proposed by Gonçalves et al.) has an acceptable fit with the experimental data, while the rest of the mixing rules present high deviations. Based on this analysis and the global deviations in Table 8, we select mixing rule H-MR11 to evaluate the SAFT calculation method with the Helmholtz scaling approach for multicomponent mixtures.

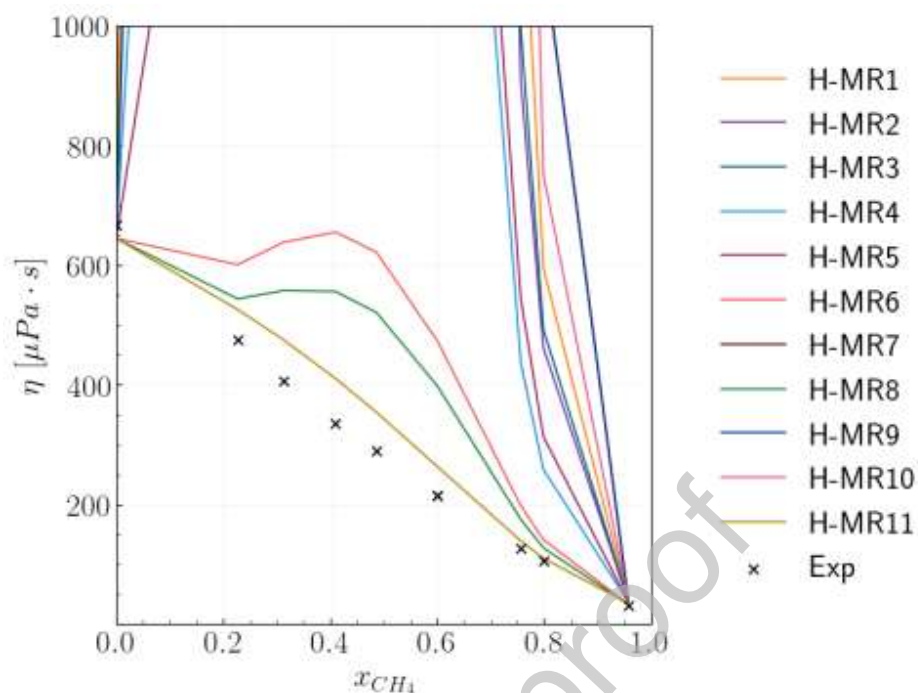


Figure 13. Mixing rules behavior for Helmholtz Scaling using SAFT calculation method, for methane-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

Figure 14 shows the behavior of the different mixing rules using SAFT calculation method for Entropy scaling approach. The binary system with the SAFT method presents similar behavior compared to the Chung method. Quantitatively, according to the Table 8, the SAFT method with entropy scaling presents lower values of %AAD.

Mixing rules S-MR1 and S-MR7 were selected for studies of multicomponent systems, like with the Chung calculation method.

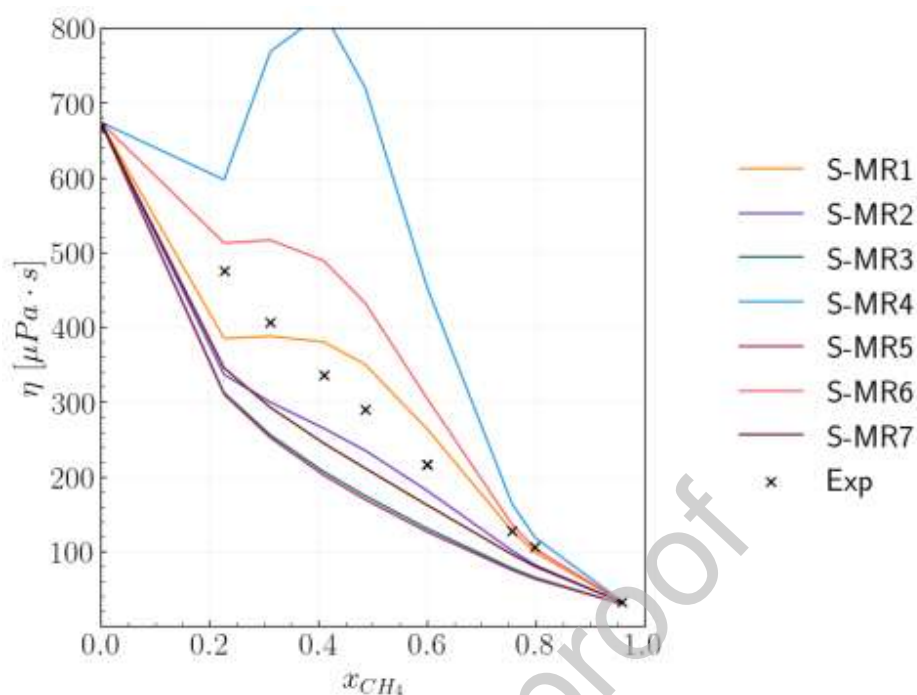


Figure 14. Mixing rules behavior for Entropy Scaling using SAFT calculation method, for methane-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

Figure 15 shows the behavior of the different mixing rules considered in this work, using Chung calculation method for modified entropy scaling approach. We observe that most mixing rules show a similar (nonlinear) behavior. Mixing rules S-MR1, S-MR2, S-MR5 and S-MR7 were selected for studies of multicomponent systems. S-MR7 was used by Lötgering-Lin et al, so we consider it to compare results.

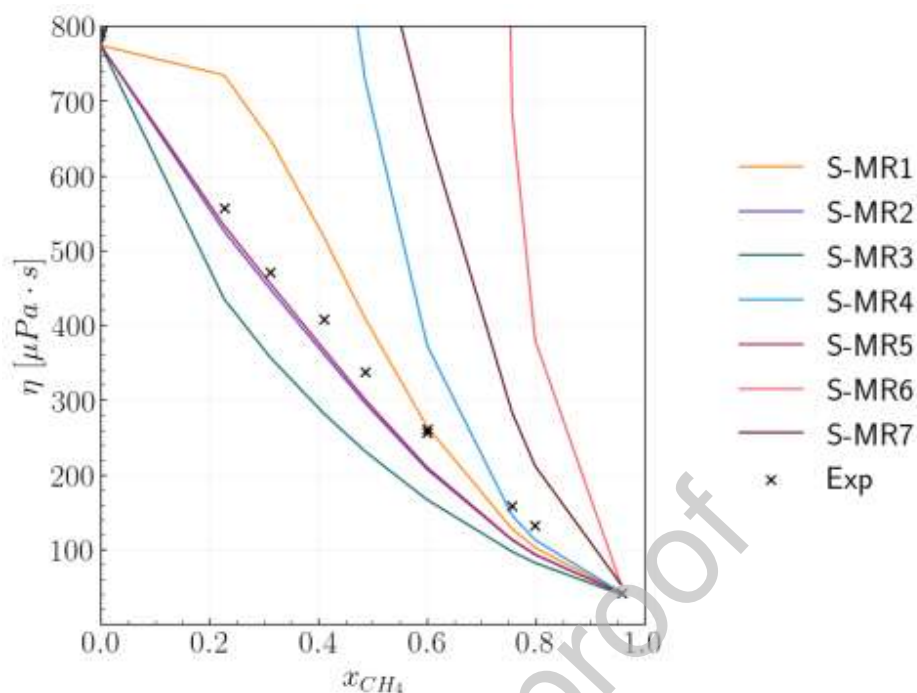


Figure 15. Mixing rules behavior for Entropy Scaling using SAFT calculation method, for methane-decane system to 60 MPa and 353.15 K. Symbols represent experimental data [50,51], while solid lines represent the results obtained using the mixing rules equations presented in table 8.

3.3. Evaluation of mixing rules based on natural gas mixtures

Viscosity values for seventeen selected natural gas mixtures were predicted with Helmholtz scaling and entropy scaling approaches, using also both calculation methods denoted as Chung and SAFT in this work, previously explained. In mixture viscosity prediction, no adjustment of model parameters is required. The results for mixtures are based on the mole fraction weighted pure-component parameters, with residual entropy and Helmholtz free energy values being obtained from the GERG 2008 equation of state. We consider the same natural gas mixtures studied by Mairhofer [52] with compositions include table 10 presents the composition of the seventeen natural gas mixtures evaluated.

In mixtures that contain components not included in the GERG-2008 model, such as neopentane, toluene, benzene, xylene, and methylcyclopentane, or when their mole fraction is very low (e.g., helium or water), these components are ignored and the mole fractions of the remaining components are adjusted to add up to 100%. For the gas condensate, NG17, components heavier than decane are combined with the decane mole fraction. The range of composition of the natural gas mixtures considered was 0.70 to 0.92 mole fraction of methane. Table 11 summarizes the mixing rules evaluated for each approach and calculation method used.

Table 12 presents the number of data, the temperature and pressure range and the percentage of methane for each of the natural gas mixtures evaluated. The temperatures and pressure range from 241 K to 473 K and 0.095 to 138 MPa, respectively.

For some mixtures, significant molar compositions of N₂, CO₂, Ethane, Propane, and Decane were found, with maximum values of molar composition of 9.8%, 4.4%, 14%, and 9.2%, respectively.

Table 10. composition of natural gas mixtures considered mol/mol. The reported values are renormalized where the composition originally reported does not sum to 100%.

Substance	N G 1	NG 2	N G 3	NG 4	NG5	N G 6	NG7	NG8	N G -9	N G 0	N G 11	N G 12	N G 13	NG1 4	N G 15	N G 16	N G 17
References	[53]	[53]	[54]	[54]	[54]	[5]	[56]	[56]	[56]	[57]	[57]	[58]	[58]	[58]	[58]	[59]	[59]
Methane	0.8515	0.9045	0.8049	0.8478	0.851783	0.8484	0.901650	0.800504	0.9292	0.895	0.8484	0.7173	0.8633	0.807646	0.9146	0.8883	0.6962
Nitrogen	0.035	0	0.0661	0.0371	0.034994	0.0505	0.007587	0.006604	0.0101	0.0115	0.0909	0.0101	0	0.048038	0.0055	0.0106	0
Carbon dioxide	0.0234	0	0.0439	0.02245	0.022982	0.0066	0.017948	0.021913	0.0101	0.0774	0.0145	0.0104	0.0302	0.009007	0.0107	0.0224	0
Ethane	0.0554	0.0584	0.0502	0.0558	0.055344	0.0808	0.063081	0.093112	0.0404	0.0661	0.0341	0.0101	0.0608	0.087069	0.0303	0.0518	0.1314
Propane	0.0201	0.0211	0.0188	0.0196	0.020109	0.0005	0.008010	0.049656	0.0054	0.0053	0.0006	0.0803	0.0204	0.029023	0.0104	0.0164	0.0919
Butane	0.0059	0.0064	0.0057	0.0055	0.006126	0	0.000643	0.012797	0.0008	0.0092	0.0013	0.0009	0.0048	0.017013	0.0005	0.0027	0.0243
Isobutane	0.004	0.0041	0.0038	0.0041	0.004013	0	0.000446	0.007191	0.0026	0.0086	0.0001	0.0077	0.0043	0	0.0067	0.0016	0.0067
Pentane	0.0015	0.0016	0.0014	0.0015	0.001411	0	0.000044	0.002500	0.0000	0.0000	0.0000	0.0000	0.0000	0.001301	0.0000	0.0000	0.0000
Isopentane	0.0017	0.0021	0.0019	0.0021	0.001711	0	0.000054	0.002557	0.0005	0.0057	0.0004	0	0	0	0	0.0004	0.0044
Hexane	0	0	0	0	0	0	0.000014	0.001793	0.0000	0.0000	0.0000	0.0000	0.0000	0.000600	0.0000	0	0.0056
Heptane	0	0	0	0	0	0	0.000005	0.001010	0.0000	0.0000	0.0000	0.0000	0.0000	0.000300	0.0000	0	0.0006

Octane	0.0015	0.0016135	0.0015	0.0015	0.001521506	0	0.000001	0.000197105	0	0.00004	0	0	0	0	0	0	0.0063
Nonane	0	0	0	0	0	0	0	0.00086046	0	0.00001	0	0	0	0	0	0	0.0042
Decane	0	0	0	0	0	0	0	0.00063034	0	0.00001	0	0	0	0	0	0	0.00173
Hydrogen	0	0	0	0	0	0	0	0.00010005	0	0.00001	0	0	0	0	0	0	0
Oxygen	0	0	0	0	0	0	0	0	0	0.00042	0.00001	0	0	0	0	0	0
Carbon_monoxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hydrogen_sulfide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Helium	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Argon	0	0	0	0	0	0	0.000514038	0	0	0	0	0	0	0	0	0	0

Table 11. mixing rules evaluated for each approach and calculation method.

Method	Approach		
	Helmholtz	Entropy	Modified Entropy
Chung	H-MR3, H-MR4, H-MR5, H-MR8, H-MR11	S-MR1, S-MR6, S-MR7	S-MR1, S-MR2, S-MR5, S-MR7
SAFT	H-MR11	S-MR1, S-MR7	---

Table 12. molar composition of methane, temperatures and pressure ranges and number experimental data points of natural gases evaluated.

	Reference	N exp	T range [K]	P range [MPa]	CH4 (mol/mol)
NG1	[53]	248	250–450	10–65	0.85
NG2	[53]	248	250–450	10–65	0.90

NG3	[54]	248	250–450	10–65	0.80
NG4	[54]	248	250–450	10–65	0.85
NG5	[54]	246	250–450	10–65	0.85
NG6	[55]	40	241.09–454.97	0.242–14.04	0.85
NG7	[56]	44	263.35–303.43	4.46–25.11	0.90
NG8	[56]	34	262.86–304.43	13.31–25.31	0.80
NG9	[56]	45	262.96–303.64	4.95–25.24	0.92
NG10	[57]	224	260–320	0.095–20.07	0.90
NG11	[57]	224	260–320	0.095–20.23	0.84
NG12	[58]	33	310.93–444.26	4.826–55.158	0.72
NG13	[58]	30	310.93–444.26	1.379–27.579	0.86
NG14	[58]	26	344.26–444.26	1.379–17.237	0.81
NG15	[58]	27	310.93–444.26	2.758–55.158	0.91
NG16	[59]	28	323.15–473.15	34.6–138	0.89
NG17	[59]	28	323.15–473.15	41.4–138	0.70

Good results were obtained in predicting experimental viscosity data for natural gas mixtures. Table 13 shows the deviations obtained, as % AAD for each of the Helmholtz and entropy scaling approaches, and both calculation methods (Chung and SAFT) used in this work. Considering the data for all natural gas mixtures, the Helmholtz approach exhibited its lowest average absolute deviations (2.73% AAD) when coupled with the SAFT method and H-MR11 mixing rule. In the case of the entropy approach, the lowest AAD value was observed for the SAFT method and S-MR7 mixing rule with a value of 2.72%. In turn, the best performance with the modified entropy approach using the Chung method was observed for the S-MR7 mixing rule, with AAD of 3.12%. Tests were conducted by applying the SAFT method to the modified entropy approach, but the deviations increased. The natural gas mixture NG8 exhibits higher deviations, as shown in table 14. A first sight, one possible cause could be the low methane content in that particular gas composition. However, other mixtures with similar methane content, such as NG14 and NG17, show lower deviations, despite being at different pressure and temperature conditions, as indicated in table 12.

Table 14 presents a comparison of the results obtained in this study, with respect to values calculated using other models [60] for the same experimental viscosity data. For all studied natural gas mixtures, lower deviations were found compared to those reported by Mairhofer. Out of a total of seventeen natural gas mixtures studied, nine of them showed lower deviations in this work, compared to alternative models, as shown in table 15. These nine natural gas mixtures were obtained using the Helmholtz approach coupled with the SAFT method and H-MR11 mixing rule (five mixes), the Helmholtz approach coupled with the Chung method and H-MR4 mixing rule (one mix), and the modified entropy scaling approach using the Chung correlations with the S-MR1 mixing rule (three mixes).

Mixtures of sour natural gas were also analyzed, with varying compositions of H₂S, as reported in the work of Mairhofer [52]. Table 16 presents the composition of each sour gas mixture and the predicted viscosity values in this study compared to alternative models [60]. For most sour gas mixtures, lower deviations were found compared to those reported

by Mairhofer, except for the SNG6 mixture, which has a molar composition of methane (67.71%) and H₂S(7.08%). In comparison to other mixtures, such as SGN4, which has a lower molar percentage of methane (44.47%) and in this work exhibits lower deviations than the SNG6 mixture. Probably, the higher H₂S content of SNG4 mixture (49.35%) can explain this observation. Better results for the SNG1, SNG2, SNG3, and SNG4 mixtures were obtained in this study compared to the alternative approaches referenced in Table 16. On the other hand, it is important to highlight the improvement in deviations for the SNG7 and SNG8 mixtures, which had the highest deviation values in Mairhofer's work (57.3% and 43.35%, respectively). In this study, these deviations decreased to values of 43.7% and 37.4% for SNG7 and SNG8, respectively. This improvement in deviations for the sour gas mixtures SNG7 and SNG8, with lower content of key light compounds (CH₄ and H₂S), is achieved using the modified entropy scaling approach with the S-MR7 mixing rule. Table S4, available in the supplementary material, displays the results of all mixing rules and approaches applied to the sour gas mixtures.

Table 13. AAD (%) for natural gases evaluated with the Helmholtz and entropy approaches, considering the Chung and SAFT calculation methods.

Substance	Helmholtz Scaling					Entropy Scaling					Modified Entropy Scaling				
	Chung					SAFT	Chung			SAFT		Chung			
	Method					Method	Method			Method		Method			
	H-MR3	H-MR4	H-MR5	H-MR8	H-MR11	H-MR1	S-MR1	S-MR6	S-MR7	S-MR1	S-MR7	S-MR1	S-MR2	S-MR5	S-MR7
AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	AAAD (%)	
NG1	5.12	5.16	4.94	4.76	5.86	3.23	3.89	3.98	3.92	3.12	3.05	4.21	4.54	4.53	3.64
NG2	4.26	4.63	4.44	4.41	5.77	2.73	3.47	3.53	3.09	2.81	2.47	3.90	4.20	4.19	4.46
NG3	3.79	3.63	3.36	3.09	4.04	2.80	2.67	2.70	3.03	2.63	2.80	2.31	2.55	2.53	6.91
NG4	5.04	5.07	4.85	4.65	5.75	3.13	3.77	3.85	3.81	3.04	2.97	4.06	4.39	4.38	3.91
NG5	4.93	4.96	4.75	4.56	5.67	3.03	3.67	3.76	3.67	2.92	2.84	3.97	4.30	4.28	3.93
NG6	1.63	1.69	1.64	1.66	1.63	1.87	1.29	1.25	1.40	1.44	1.60	0.90	0.99	0.98	1.25
NG7	4.45	4.55	4.65	4.59	4.93	3.48	5.80	5.88	5.57	4.90	4.63	5.40	5.63	5.61	1.60
NG8	8.12	8.85	8.49	8.37	11.05	5.02	9.52	9.65	9.18	6.92	6.51	7.45	7.93	7.92	6.36

NG9	3.8 5	3.8 9	3.9 4	3.8 8	4.18	2.93	5.3 8	5.4 4	5.1 6	4.5 6	4.3 2	3.4 3	3.5 9	3.5 8	1.2 4
NG10	1.2 3	1.2 2	1.1 3	1.1 4	1.22	1.93	1.4 0	1.4 1	1.4 3	1.7 7	1.9 0	0.9 2	0.9 8	0.9 7	2.3 5
NG11	1.3 0	1.4 8	1.3 7	1.4 6	1.43	2.17	1.1 3	1.1 4	1.1 6	1.5 4	1.6 0	0.8 2	0.8 5	0.8 6	1.6 5
NG12	1.1 7	0.9 4	1.0 3	1.1 2	1.57	4.06	1.2 0	1.2 3	1.5 4	2.5 3	3.3 0	2.8 0	3.2 3	3.2 1	10. 57
NG13	1.6 6	1.7 5	1.9 9	1.9 7	1.94	1.03	2.2 8	2.3 0	2.0 3	1.3 1	1.1 9	3.1 2	3.5 7	3.5 5	1.6 2
NG14	2.2 8	2.2 8	2.5 1	2.4 9	2.34	1.75	2.7 5	2.7 5	2.5 5	1.8 4	1.7 9	3.3 2	3.7 8	3.7 5	2.0 6
NG15	4.4 3	4.6 1	4.7 2	4.6 9	5.07	3.05	4.8 1	4.8 4	4.6 2	3.6 4	3.4 1	5.0 7	5.4 1	5.4 0	3.6 2
NG16	3.3 2	3.4 8	3.3 8	3.2 2	4.05	1.74	6.0 1	5.9 8	5.6 9	6.5 4	6.2 5	2.4 4	2.3 3	2.3 3	8.5 0
NG17	10. 97	13. 79	11. 69	11. 49	21.4 3	1.48	4.5 1	4.9 5	4.8 2	5.2 6	2.4 8	6.9 7	8.8 3	8.7 6	25. 14
Global %AADs	3.8 0	3.9 1	3.7 3	3.6 2	4.54	2.74	3.1 5	3.2 1	3.1 5	2.8 0	2.7 2	3.1 2	3.3 9	3.3 8	4.1 7

Table 14. presents the best Average Absolute Deviation (%AAD) values for natural gas mixtures obtained in this study, as well as the values for alternative viscosity models obtained in previous studies [60].

	Refere nce	N G 1	N G 2	N G 3	N G 4	N G 5	N G 6	N G 7	N G 8	N G 9	N G 10	N G 11	N G 12	N G 13	N G 14	N G 15	N G 16	N G 17
This work		3. 05	2. 48	2. 31	2. 97	2. 84	0. 90	1. 60	5. 02	1. 24	0.9 2	0.8 2	0.9 4	1.0 3	1.7 5	3.0 5	1.7 4	1.4 8
Mair hofer	[52]	3. 47	3. 35	2. 76	3. 36	3. 23	2. 12	5. 09	9. 06	4. 64	1.4 7	1.4 8	4.1 4	2.8 9	3.7 3	4.7 5	5.6 7	4.5 8
ADE L	[61]	4. 02	2. 03	8. 07	4. 38	4. 21	2. 44	1. 55	1. 39	1. 02	1.8 3	4.4 4	-	-	-	-	-	-
LGE	[58]	7. 42	9. 58	3. 51	7. 03	7. 57	3. 06	7. 73	10 .7 7	7. 16	1.9 4	5.9 2	-	-	-	-	-	-
HMS	[62]	19 .6 5	17 .4 1	18 .1 9	19 .8 2	19 .9 5	-	-	-	-	-	-	-	-	-	-	-	-
CKB	[63]	7. 61	3. 76	9. 27	9. 64	9. 42	9 9	7. 75	28 .2 7	7. 44	9.1 5	12. 87	-	-	-	-	-	-
Sanja ri	[64]	2. 88	2. 48	1. 93	2. 96	2. 49	2. 97	4. 79	4. 26	5. 23	2.8 6	2.1 2	-	-	-	-	-	-
EF- V1	[65]	-	-	-	-	-	6. 5	-	6. 3	9. 7	-	-	3.2	8.3	8.8	7.5	-	-

EF-V2	[66]	-	-	-	-	-	1.8	-	1.7	2.1	-	-	4.1	3.1	4.4	3.5	-	-
Supertrapp	[67]	5.86	3.92	6.7	5.57	5.96	2.08	2.34	1.37	-	-	-	-	-	-	-	-	-
CLS	[5,68]	4.68	3.46	5.4	4.21	4.72	-	-	-	-	-	-	-	-	-	-	-	-
LBC	[69]	3.6	3.58	4.13	3.4	3.65	-	-	-	-	-	-	-	-	-	-	2.8	9.8
Pedersen	[70,71]	2.5	1.59	2.89	2.32	2.5	-	-	-	-	-	-	-	-	-	-	6.9	6.3
Novak	[21]	4.6	4.5	2.2	4.6	4.6	-	-	-	-	-	-	-	-	-	-	-	-
LGE-1	[58]	-	-	-	-	-	6.91	7.03	6.47	-	-	-	-	-	-	-	-	-
LGE-2	[58]	-	-	-	-	-	5.16	7.43	4.64	-	-	-	-	-	-	-	-	-
LGE-3	[72]	-	-	-	-	-	1.63	1.2	0.82	-	-	-	-	-	-	-	-	-
LGE-4	[73]	-	-	-	-	-	6.39	6.47	5.94	-	-	-	-	-	-	-	-	-
Schlely	[57]	-	-	-	-	-	4.57	8.63	4.04	-	-	-	-	-	-	-	-	-
Lucas	[74]	-	-	-	-	-	4.75	8.78	4.28	-	-	-	-	-	-	-	-	-
VW-F	[75]	-	-	-	-	-	9.99	3.67	-	-	-	-	-	-	-	-	-	-
VW-S	[75]	-	-	-	-	-	10.1	4.45	-	-	-	-	-	-	-	-	-	-
HW	[76]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.4	8.5

Table 15. Natural gas mixtures in this study showed that better AAD values compared to all other alternative viscosity models presented in Table 14.

	CH4 mol/mol	AAD (%)	Scaling Approach	Method	Mixing Rule
NG6	0.85	0.90	modified entropy	Chung	S-MR1
NG10	0.90	0.92	modified entropy	Chung	S-MR1
NG11	0.84	0.82	modified entropy	Chung	S-MR1
NG12	0.72	0.94	Helmholtz	Chung	H-MR4
NG13	0.86	1.03	Helmholtz	SAFT	H-MR11
NG14	0.81	1.75	Helmholtz	SAFT	H-MR11
NG15	0.91	3.05	Helmholtz	SAFT	H-MR11
NG16	0.89	1.74	Helmholtz	SAFT	H-MR11
NG17	0.70	1.48	Helmholtz	SAFT	H-MR11

Table 16. Mole Fractions, Temperature, Pressure, Experimental Viscosity (η_{exp}) and AAD (%) of the Studied Sour Gas Samples [60].

Mixture	SG1	SG2	SG3	SG4	SG5	SG6	SG7	SG8
H2S	0.0057	0.0002	0.226	0.4935	0.7003	0.0708	0.2816	0.0034
CO2	0.0214	0.0148	0.005	0.0308	0.0865	0.0096	0.0608	0.6352
N2	0.0051	0.001	0.0046	0.0266	0.0092	0.0064	0.0383	0.0386
methane	0.8002	0.7424	0.7561	0.4447	0.2024	0.6771	0.4033	0.1937
ethane	0.09	0.1148	0.0071	0.0023	0.0016	0.0871	0.0448	0.0303
propane	0.0435	0.0554	0.0006	0.0006	0	0.0384	0.0248	0.0174
isobutane	0.0055	0.0059	0.0002	0.0002	0	0.005	0.006	0.0033
n-butane	0.0137	0.022	0.0002	0.0003	0	0.0156	0.0132	0.0093
isopentane	0.004	0.0068	0	0.0002	0	0.0056	0.0079	0.0039
n-pentane	0.0051	0.0118	0	0.0001	0	0.0082	0.0081	0.0047
n-hexane	0.0042	0.0127	0	0.0003	0	0.0083	0.0121	0.0051
heptane+	0.0016	0.0122	0	0	0	0.0656	0.0991	0.0551
T/K	348.71	388.71	352.59	322.04	352.59	364.26	394.26	377.04
P/MPa	14.479	17.926	34.474	17.237	9.404	32.192	28.889	33.267
η_{exp}/cP	0.0172	0.0191	0.03	0.03	0.022	0.042	0.1	0.09
CKB-D [16,77]	1.16	-0.52	3.33	10	13.64	33.33	56	40
LGE [58]	0.58	-5.24	-3.33	-20.00	18.18	14.29	10	-118.8
DS [78]	2.33	-4.19	6.67	3.33	9.09	26.19	55	41.11
Lucas [74]	-1.16	-7.85	3.33	6.67	9.09	21.43	53	38.89
LBC [69]	-23.26	-33.51	20	33.33	22.73	11.9	58	7.78
MPR-EOS [79,80]	-16.28	-30.89	-3.33	-86.67	-13.64	-14.29	12	14.44
Mahirhofer [52]	-2.86	-6.15	2.78	-4.69	0.13	0.68	57.3	43.35
This work	0.17	1.30	2.19	1.00	1.29	3.89	43.67	37.41

We analyzed two binary mixtures: Carbon Dioxide + Methane and Carbon Dioxide + Decane, as studied by Goncalves et al.[32]. Table 17 demonstrates a decrease in the average absolute deviations (AAD) values for the binary mixtures obtained in this study compared to those reported in that publication. For both binary mixtures, the best results were achieved using the modified residual entropy method with the S-MR1 mixing rule for the Carbon Dioxide + Methane system and S-MR5 for the Carbon Dioxide + Decane mixture. This highlights how certain mixing rules can improve results based on the asymmetry of the studied mixtures.

Table 17. Binary mixture systems investigated by Goncalves et al [32].

Substance 1	Substance 2	Composition range mol/mol	References	N_{exp}	AAD (%) Helmholtz scaling by Goncalves	AAD (%) Entropy scaling by Goncalves	AAD (%) this work, modified entropy scaling
Carbon Dioxide	Methane	0.243 - 0.755	[81]	128	6.26	10.21	1.680
Carbon	Decane	0.15 - 0.85	[82]	63	23.95	49.14	18.20

Dioxide							
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Accurate viscosity predictions were found for natural gas mixtures and sour gas applications. Among the 15 combinations of approaches, methods, and mixing rules included in table 13, the global AAD considering all of the studied natural gas mixtures did not exceed 4.54%. It is important to emphasize that the obtained results demonstrate the significant role of mixing rules in viscosity value predictions for mixtures with low methane content. Results for all combinations methods, mixing rules and scaling approaches, can be found in table S5 in supplementary material.

4. Conclusions

In general, in combination with GERG 2008 EoS, all three approaches demonstrated reliable predictions of natural gas viscosity.

This work showed the influence of the selection of mixing rules for both Helmholtz and entropy scaling approaches, illustrating how they can have an enormous effect on viscosity prediction, especially in low and medium methane concentrations. For Helmholtz scaling, the H-MR11 mixing rule with the SAFT method demonstrated the best performance. In the case of the residual entropy approach, the S-MR7 mixing rule with the SAFT method showed better results, and the modified entropy scaling approach performed better with the S-MR1 mixing rule. The performance of the best mixing rule for the entropy approach is excellent in mixtures due to the deviations being better than those observed for pure parameters.

Once each approach is evaluated using its best mixing rule, there is no approach that clearly and systematically gives better results than the others. AAD values obtained for entropy and Helmholtz scaling approaches were 2.72% and 2.74%, respectively. The modified entropy scaling approach presented an AAD value of 3.12%. Helmholtz energy scaling does not offer significant improvements over entropy scaling approaches, despite having an additional adjustable parameter. Furthermore, Helmholtz energy scaling is highly sensitive to the choice of mixing rule and may not work at all with certain "reasonable" mixing rules (table 8, H-MR1 with SAFT method). Moreover, it is a more complex method as it requires an additional model for the hard sphere reference.

Although on average across the studied mixtures, both entropy and Helmholtz Scaling approaches yielded lower deviations than modified entropy, when analyzing individual fluid cases, there are instances where modified entropy provides the best results (6 out of the 17 natural gas mixtures). Furthermore, comparing the results with previous studies, better results were obtained for 9 out of the 17 natural gas mixtures.

For pure components, the modified entropy approach yielded better results, and this advantage could be further exploited by developing a mixing rule that reflects this improvement. However, although some approaches perform better for pure compounds, it does not necessarily translate to better performance in mixtures.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: