

Residual Entropy Model for Predicting the Viscosities of Dense Fluid Mixtures

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Abstract

In this work, we have investigated the monovariate relationship between reduced viscosity and residual entropy in pure fluids and in binary mixtures of hydrocarbons and hydrocarbons with dissolved carbon dioxide. The mixtures considered were octane + dodecane, decane + carbon dioxide and 1,3-dimethylbenzene (*m*-xylene) + carbon dioxide. The reduced viscosity was calculated according to the definition of Bell, while the residual entropy was calculated from accurate multi-parameter Helmholtz-energy equations of state and, for mixtures, the multi-fluid Helmholtz energy approximation. Mono-variant dependence of reduced viscosity upon residual molar entropy was observed for the pure fluids investigated and, by incorporating two scaling factors (one for reduced viscosity and the other for residual molar entropy), the data were represented by a single universal curve. To apply the method to mixtures, the scaling factors were determined from a mole-fraction weighted sum of the pure-component values. This simple model was found to work well for the systems investigated. The average absolute relative deviation (AARD) was observed to be between 1 % and 2 % for pure components and a mixture of similar hydrocarbons. Larger deviations, with AARDs of up to 15 %, were observed for the asymmetric mixtures but this compares favourably with other methods for predicting the viscosity of such systems. We conclude that the residual-entropy concept can be used to estimate the viscosity of mixtures of similar molecules with high reliability and that it offers a useful engineering approximation even for asymmetric mixtures.

1. Introduction

Viscosity is one of the most important properties influencing the performance of chemical processes, especially in connection with pressure drops and heat and mass transfer. In oil exploration and production, viscosity is one of the key parameters determining the selection of production techniques and the design of processing facilities. However, despite its importance in many processes, there is presently no well-founded theoretical method for predicting the viscosity of dense fluids and empirical methods are often unreliable, especially under high-temperature and/or high-pressure conditions.

Several models for predicting the viscosity of dense fluids have been proposed. For petroleum systems, the Lohrenz-Bray-Clarke (LBC) method is widely used.¹ In the LBC method, the reduced excess viscosity is expressed as a function of reduced density for reservoir oils and gases in what amounts to a corresponding-states treatment. Other corresponding-states treatments have been developed, including the TRAPP model of Ely and Hanley² and the models of Pedersen et. al.³ and Aasberg-Petersen et al.⁴ Although useful, these methods employ empirical functions to account for density dependence and involve uncertain mixture critical parameters. A more theoretically-based approach was followed by Galliero et. al.⁵ based on molecular dynamics (MD) simulations where, for simple fluids such as methane, ethane, propane, argon, nitrogen, oxygen and carbon dioxide, the molecular parameters were deduced from the experimental critical temperature and volume. Other works on predicting viscosities include using friction theory,^{6, 7} free-volume theory,⁸⁻¹⁰ thermodynamic scaling,^{11, 12} the Dymond-Assael (DA) hard-sphere model¹³⁻²² and the Vesovic- Wakeham (VW) model.²²⁻²⁶ The applications of such models have been widely explored, especially for pure components and mixtures of similar substances.^{12, 14-20, 22, 24-31} Some approaches offer acceptable results but others are unsatisfactory especially for asymmetric mixtures and/or extreme conditions.²¹ Entropy scaling (or residual entropy) models offer an interesting and promising alternative approach.

The entropy scaling approach, originally put forward by Rosenfeld³² in 1975, states that the complex temperature and density dependence of the reduced viscosity and the reduced self-diffusion coefficient can be collapsed into a mono-variant function of the residual entropy. The residual entropy is defined for specified temperature T and molar density ρ as follows:

$$S^r(T, \rho) = S(T, \rho) - S^{\text{id}}(T, \rho) \quad (1)$$

where $S(T, \rho)$ is the molar entropy and $S^{\text{id}}(T, \rho)$ is the molar entropy of the hypothetical ideal gas at the same temperature and molar density. The entropy scaling approach is a hypothesis and is not based on an exact theory; therefore, it cannot be derived from first principles. The underlying physics, and the associated concept of isomorphic invariance, has been discussed by Dyre³³ who also reviewed molecular simulation results that exemplify the working of the approach. Dzugutov³⁴ also used molecular dynamics simulations to demonstrate that the self-diffusion coefficient of monatomic fluids, reduced to dimensionless form, was a *universal* function of the residual molar entropy only. In non-monoatomic fluids, it has been established that entropy scaling also applies but that the dimensionless transport properties do not follow exactly the same universal relation; instead, they exhibit a substance-specific but mono-variant dependence upon residual entropy.³⁵⁻³⁷ Goel et. al.³⁸, also using molecular dynamics simulations, tested the residual-entropy scaling relationship for the diffusivity and viscosity of

Lennard-Jones chain fluids, restricted to short chains that do not show significant entanglement. He concluded that the residual-entropy scaling associated with the transport properties shows a simple but strong dependence on chain length. It has been confirmed in other simulation work that this mono-variant dependence applies to more complex substances such as the n-alkanes³⁹⁻⁴¹ and hard dumbbell-shaped particle.³⁶ The analysis has also been applied to the experimental data for water.^{35, 42, 43} Loetgering-Lin and Gross⁴⁴ presented a group contribution method for the correlation and prediction of pure-component viscosities involving nonpolar, polar, and self-associating components. They used the PCP-SAFT equation of state for the residual entropy and represented the reduced viscosity by a summation over functional groups involving three parameters per group. A similar approach was used by the same group to predict thermal conductivity⁴⁵⁻⁴⁷ and self-diffusion coefficients⁴⁸ of pure substances using the group contribution method. They showed that the transport properties of these systems could be predicted well even in the absence of a large experimental database.

A modified entropy-scaling approach for viscosity was proposed by Bell and Laesecke⁴⁹ wherein a dimensionless residual entropy per unit volume was used as the scaling variable and a reference fluid was used to establish the functional dependence of reduced viscosity upon that variable. The method was applied with some success over the whole fluid region to a family of ten refrigerant fluids. Recently, Bell⁵⁰ investigated the relationship between reduced viscosity and residual entropy for molecular fluids including argon, methane, CO₂, SF₆, refrigerant R134a, refrigerant R125, methanol and water by introducing an appropriate density scaling. It was concluded that the viscosity of a dense fluid could be predicted within about 20% by using a universal scaling approach along with scaling parameters. A comprehensive overview of the application of the entropy scaling can be found in a review by Dyre.³³

Literature reports pertaining to the viscosity-entropy relation of mixtures are limited and restricted to mixtures of similar components.⁵¹⁻⁵³ Novak⁵¹ studied the viscosity of the methane-ethane system and came to a conclusion that a new entity-based scaled viscosity model correlated well the pure components and their corresponding mixtures to a single semi-logarithmic function. Delage-Santacreu et al.⁵² explored the application of entropy scaling to the viscosity of model fluids, including mixtures that interact according to the Mie potential. A simple logarithmic mixing rule was used to estimate the viscosity of mixtures from pure component values. Loetgering-Lin et al. applied an entropy-scaling model, based on their earlier work on pure substances,⁴⁴ to mixtures of real fluids.⁵³ In their paper, they considered almost 140 pure substances and 566 mixtures of various complexity and used molecular dynamic simulations and PCP-SAFT to develop a mixture model for viscosity and residual entropy, respectively. Nevertheless, the mixtures considered were mainly of similar molecules. Fouad and Vega^{54, 55} applied a similar approach to the viscosities of hydrofluorocarbon and hydrofluoroolefin refrigerants and their mixtures. Entropy scaling based on the PC-SAFT equation has also been used to predict the viscosity of hydrocarbon mixtures and diesel fuels at several extreme conditions by Rokni et al.⁵⁶ In their work, two calculated or measured properties were used as the inputs and, in comparison with experimental data, average mean absolute percent deviations of 12.2% for hydrocarbon mixtures and 21.4% for diesel fuels.

In this study, we first explore the application of highly-accurate Helmholtz equations of state for the calculation of residual entropy and the subsequent correlation of reduced viscosity for pure substances. We introduce scaling factors to reduce the data to a universal function. We then apply the method to mixtures based on the multi-fluid Helmholtz-energy approximation for the mixture residual entropy and simple mixing rules for the scaling factors. In our work, the compounds of interest are aliphatic and aromatic hydrocarbons and their mixtures with CO₂. We have tested these methods in comparison with experimental mixture viscosities in the temperature range from (200 to 500) K and at pressures up to 200 MPa.

2. Theoretical Background

We begin with a review of the methods to reduce the viscosity to dimensionless form as well as the method to calculate residual entropy according to the multi-fluid Helmholtz energy approximation.

2.1 Reduced Viscosity

According to the original model proposed by Rosenfeld,³² the dimensionless viscosity η^* was defined in terms of the thermal velocity $(k_B T/m)^{1/2}$ and the number density n as follows:

$$\eta^* = \frac{\eta n^{-2/3}}{(m k_B T)^{1/2}}, \quad (2)$$

where m is the mass of one molecule and k_B is Boltzmann's constant. This definition of reduced viscosity is illustrated in Fig. 1(a), where we plot data for pentane in the following ranges of temperature T and pressure p : $200 \leq T/\text{K} \leq 550$ K and $0.1 \leq p/\text{MPa} \leq 50$. These data were taken from a correlation⁵⁷ of experimental data that has an estimated expanded relative uncertainty ($k = 2$) of 4 %. It can be seen that $\log(\eta^*)$ is a very-nearly linear function of residual molar entropy in the dense-fluid region. However, in the low-density region ($-S^*/R \leq 1.0$), $\log(\eta^*)$ is divergent. To counter this issue, Novak⁵⁸⁻⁶⁰ proposed an alternative definition of reduced viscosity,

$$\eta^* = \eta/\eta_0, \quad (3)$$

in which η_0 is the zero-density viscosity of the fluid. For pure substances, Novak obtained η_0 from the Chapman-Enskog formula:

$$\eta_0 = \frac{5\sqrt{m k_B T / \pi}}{16\sigma^2 \Omega^{*(2,2)}}, \quad (4)$$

where σ is the characteristic molecular diameter and $\Omega^{*(2,2)}$ is a dimensionless collision integral, typically estimated from the Lennard-Jones potential.^{61, 62} Fig. 1(b) illustrates this definition of reduced viscosity, again for the case of pentane, and shows that the $\log(\eta^*)$ goes smoothly to zero as $S^*/R \rightarrow 0$. In his work,⁵⁹ Novak showed that a small amount of data was sufficient to obtain a correlation that could then be applied to determine the viscosity in the entire fluid region.

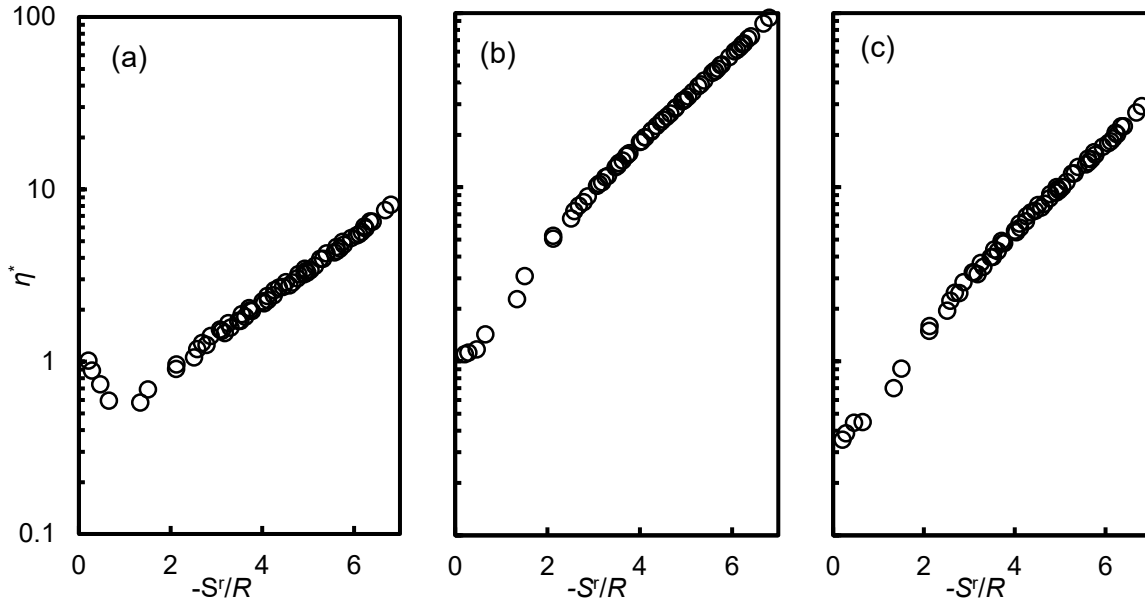


Figure 1 Reduced viscosity η^* and residual entropy (S^r/R) for n-pentane: (a) based on Rosenfeld³²; (b) based on Novak⁵⁸; (c) based on Bell⁵⁰

Bell⁵⁰ proposed another approach in order to eliminate the divergence of the reduced viscosity in the zero-density limit. Based on the theory of Rosenfeld,⁶³ according to which the transport properties should be proportional to the residual entropy raised to the power of $-2/3$ in the dilute gas, the reduced viscosity of Eq. (2) was multiplied by $(-S^r/R)^{2/3}$ to give the following definition:

$$\eta^* = \frac{\eta n^{-2/3}}{(mk_B T)^{1/2}} \left(-\frac{S^r}{R} \right)^{2/3} = \frac{\eta \rho^{-2/3} N_A^{1/3}}{(MRT)^{1/2}} \left(-\frac{S^r}{R} \right)^{2/3}. \quad (5)$$

Here, ρ is molar density, M is the molar mass, T is temperature, R is the gas constant and N_A is Avagadro's constant. Fig. 1(c) shows that this definition also yields an approximately mono-variant relationship. In a subsequent paper by Bell et al.,⁶⁴ the same approach was applied to analyse the viscosity, thermal conductivity and self-diffusion coefficients of Lennard-Jones 12-6 fluids. Further discussion of the behaviour of the scaled viscosity in the limit of zero-density for different types of molecules can be found in Bell et al.⁶⁵ Other alternatives have also been proposed to eliminate the divergence at low densities however, despite success in eliminating the divergence, these somewhat compromise the mono-variant scaling in the compressed liquid region.^{44, 49, 51, 53, 58-60}

In this work, we adopt Bell's definition of reduced viscosity and our model was then developed without making any assumption about the form of interaction between molecules.⁶⁴

2.2 Residual Entropy

Fundamental equations of state, expressed in terms of the Helmholtz energy, have been developed for many fluids.⁶⁶ In these formulations, the dimensionless Helmholtz energy of a pure component is separated into ideal-gas and residual parts:

$$\alpha(T, \rho) = \alpha^{\text{id}}(T, \rho) + \alpha^{\text{r}}(T, \rho) \quad (6)$$

where $\alpha = A/RT$ and A is molar Helmholtz energy. The residual molar entropy is then given by,

$$S^{\text{r}}/R = \tau \left(\partial \alpha^{\text{r}} / \partial \tau \right)_{\delta} - \alpha^{\text{r}}, \quad (7)$$

where τ and δ are the inverse reduced temperature and the reduced density, respectively, defined as follows:

$$\tau = T_r/T \quad (8)$$

and

$$\delta = \rho/\rho_r. \quad (9)$$

For pure fluids, the reducing temperature T_r and reducing density ρ_r are the critical temperature T_c and critical density ρ_c , respectively.

For a mixture, the basic structure of equation (6) is retained. The ideal-gas part is given exactly by

$$\alpha^{\text{id}} = \alpha^{\text{id}}(T, \rho, \mathbf{x}) = \sum_{i=1}^N x_i \alpha_i^{\text{id}}(T, \rho) + \sum_{i=1}^N x_i \ln x_i, \quad (10)$$

where N is the number of components and x_i is the mole fraction of component i . The residual part is generally approximated as follows:

$$\alpha^{\text{r}}(\tau, \delta, \mathbf{x}) = \sum_{i=1}^N x_i \alpha_i^{\text{r}}(\tau, \delta) + \Delta \alpha^{\text{r}}(\tau, \delta, \mathbf{x}), \quad (11)$$

where \mathbf{x} is the vector of mole fractions. The first term in Eq. (11) represents a corresponding-states approximation while the second term, $\Delta \alpha^{\text{r}}$, is a departure function that can be used to improve the representation of the properties of specific mixtures. For the mixtures considered in this work, no binary-specific departure functions have been developed and $\Delta \alpha^{\text{r}} = 0$.

The inverse reduced temperature and reduced density of the mixture are given as before by Eqs (8) and (9) but the reducing parameters are now functions of composition as follows:

$$T_r(\mathbf{x}) = \sum_{i=1}^N x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} T_{c,j})^{0.5} \quad (12)$$

and

$$\frac{1}{\rho_r(\mathbf{x})} = \sum_{i=1}^N x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8} \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \quad (13)$$

Here, $T_{c,i}$ and $\rho_{c,i}$ are the critical temperature and density of component i and $\beta_{T,ij}$, $\beta_{v,ij}$, $\gamma_{T,ij}$ and $\gamma_{v,ij}$ are a set of adjustable binary parameters. Note that, while $\gamma_{T,ij} = \gamma_{T,ji}$ and $\gamma_{v,ij} = \gamma_{v,ji}$, $\beta_{T,ij} = 1/\beta_{T,ji}$ and $\beta_{v,ij} = 1/\beta_{v,ji}$. A more details explanation on this method can be found in the

original work of Lemmon,⁶⁷ and in connection with the GERG-2004⁶⁸ and GERG-2008⁶⁹ equations of state.

In the present work, the values of the binary parameters β_T , β_V , γ_T and γ_V were all taken from the REFPROP database⁷⁰ and the values are given in Table 1. For CO₂ + decane, the parameters come from the GERG-2008⁶⁹ models. For CO₂ + *m*-xylene, optimised parameters are not available and the values used were those reported for CO₂ + octane.⁶⁹ The values for octane + dodecane are unpublished data taken from the REFPROP database.⁷⁰ Calculations of $S^r(T,\rho)$ were also carried out using the REFPROP software.

Table 1. Mixing parameters for mixtures involved in this work

Mixtures	octane (1) + dodecane (2)	CO ₂ (1) + <i>m</i> - xylene (2)	CO ₂ (1) + decane (2)
β_T	0.99884	1.02969	1.02003
β_V	1.00000	1.02617	1.00015
γ_T	1.02500	1.07446	1.14551
γ_V	1.00000	1.10404	1.18339

3. Entropy Scaling Model for Pure Fluids and Mixtures

The objective of this study was to devise an entropy-scaling model for the viscosity of mixtures based on the definition of reduced viscosity proposed by Bell combined with accurate models for the residual entropy. We first consider the case of pure fluids and then, by introducing simple mixing rules, extend the approach to the mixtures of interest.

3.1 Pure fluids

In this work, five pure components were studied: decane, 1,3-dimethylbenzene (*m*-xylene), CO₂, dodecane and octane. The viscosity data for CO₂ was taken from a precise correlation having an estimated expanded relative uncertainty ($k = 2$) of approximately 3 %⁷¹ as well as experimental data from Iwasaki and Takahashi⁷². The viscosity data of octane, decane, dodecane and *m*-xylene were original experimental data measured in our laboratory^{18, 73-75} with estimated relative uncertainties of 2 %. These data span temperatures from (298 to 473)K and pressures from (0.1 to 200) MPa. Additional experimental data were added for from several previous works: octane⁷⁶, decane^{77, 78}, dodecane⁷⁹ and *m*-xylene^{30, 80}. The criterion for selecting the hydrocarbons were based upon the availability of both reliable wide-ranging viscosity data and a wide-range Helmholtz equation of state.

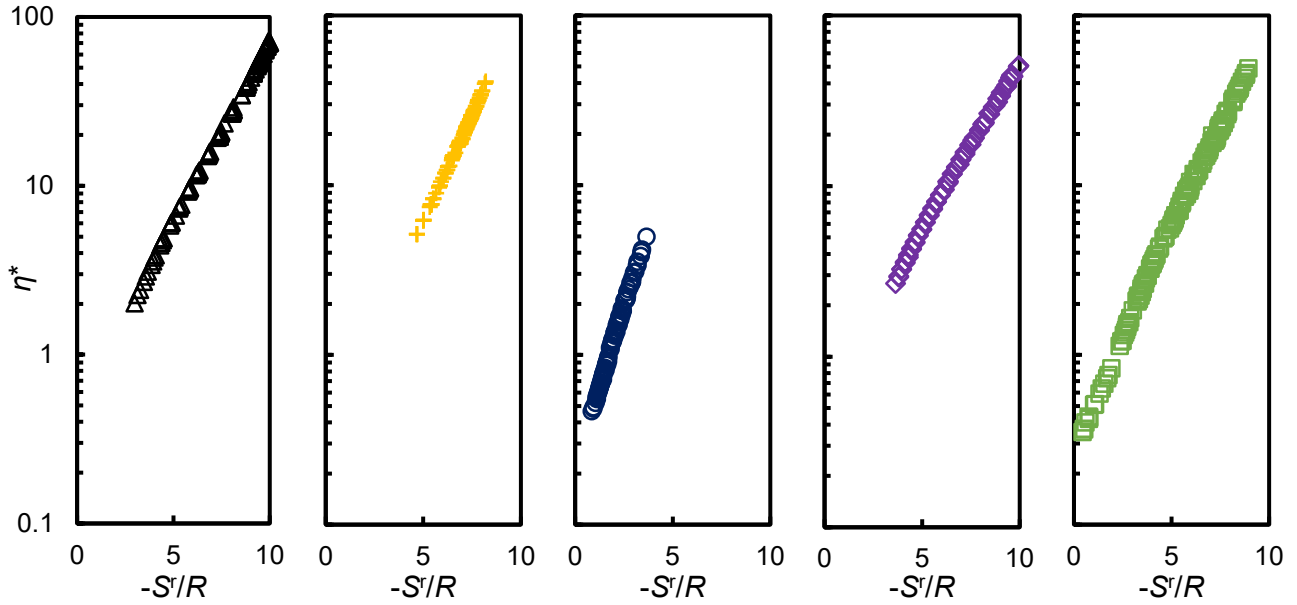


Figure 2 Reduced viscosity η^* and residual molar entropy (S^r/R) for pure fluids: \triangle , decane; $+$, *m*-xylene; \circ , CO_2 ; \diamond , dodecane; \square , octane.

For each substance, reduced viscosities were calculated from Eq. 5 while the residual molar entropy was calculated from the relevant Helmholtz equation of state⁸¹ via Eq. 6. Figure 2 shows the reduced viscosities of the pure components plotted against residual molar entropy. To a good approximation, the data for each substance fall approximately on a single curve, demonstrating the expected mono-variant relationship over an extended range of temperature and pressure. On the semi-logarithmic scale of the plot, these mono-variant relationships happen to be nearly linear but different from one substance to the next.

Table 2. Scaling parameters for each substance

Substance	h	R_η
decane	1.000	1.000
<i>m</i> -xylene	0.8309	0.6792
CO_2	0.6370	0.5483
dodecane	1.0901	1.1037
octane	0.9045	0.8681

In order to reduce all of the data to a single universal curve, we introduce two scale factors: a horizontal factor h , which scales the residual molar entropy, and a vertical factor R_η , which scales the reduced viscosity. The latter is incorporated into our definition of η^* as follows:

$$\eta^* = \frac{\eta \rho^{-2/3} N_A^{1/3}}{R_\eta (MRT)^{1/2}} \left(-\frac{S^r}{R} \right)^{2/3}. \quad (14)$$

Since the data for decane span the widest range of residual molar entropy, we selected this substance as a reference fluid to which we assigned the scaling factors $h = 1$ and $R_\eta = 1$.

However, this choice is arbitrary. The universal correlation (which is slightly non-linear on a semi-log scale) was then represented by the polynomial function

$$\ln \eta^* = \sum_{i=0}^3 c_i \left[-S^r / (hR) \right]^i . \quad (15)$$

The parameters c_i , together with the values of h and R_η , for each substance other than decane were optimised in a global regression that minimised the following objective function:

$$\Theta = \frac{1}{N} \sum_{i=1}^N \left(\frac{\eta_{i,\text{exp}} - \eta_{i,\text{fit}}}{\eta_{i,\text{exp}}} \right)^2 \quad (16)$$

where $\eta_{i,\text{exp}}$ is an experimental datum and $\eta_{i,\text{fit}}$ is the value calculated from Eq. (15) with the best-fit parameters. The scaling factors so determined for each substance are given in Table 2 while the coefficients c_i are given in Table 3 together with the absolute average relative deviation Δ_{AAD} and the maximum absolute relative deviation Δ_{MAD} for all data. These metrics are defined by

$$\Delta_{\text{AAD}} = \sum_i \left| \frac{\eta_{i,\text{exp}} - \eta_{i,\text{fit}}}{\eta_{i,\text{exp}}} \right| \quad (17)$$

and

$$\Delta_{\text{MAD}} = \text{Max} \left| \frac{\eta_{i,\text{exp}} - \eta_{i,\text{fit}}}{\eta_{i,\text{exp}}} \right| . \quad (18)$$

Figure 3 shows the scaled experimental data in comparison with the universal function and illustrates the generally excellent mono-variant representation. The deviations of the data from the model, shown for each substance separately in Figure 4, are all within a band of $\pm 10\%$. With this finding, we concluded that, by an appropriate scaling, the experimental data for each component can be collapsed onto a single curve relating reduced viscosity to residual molar entropy.

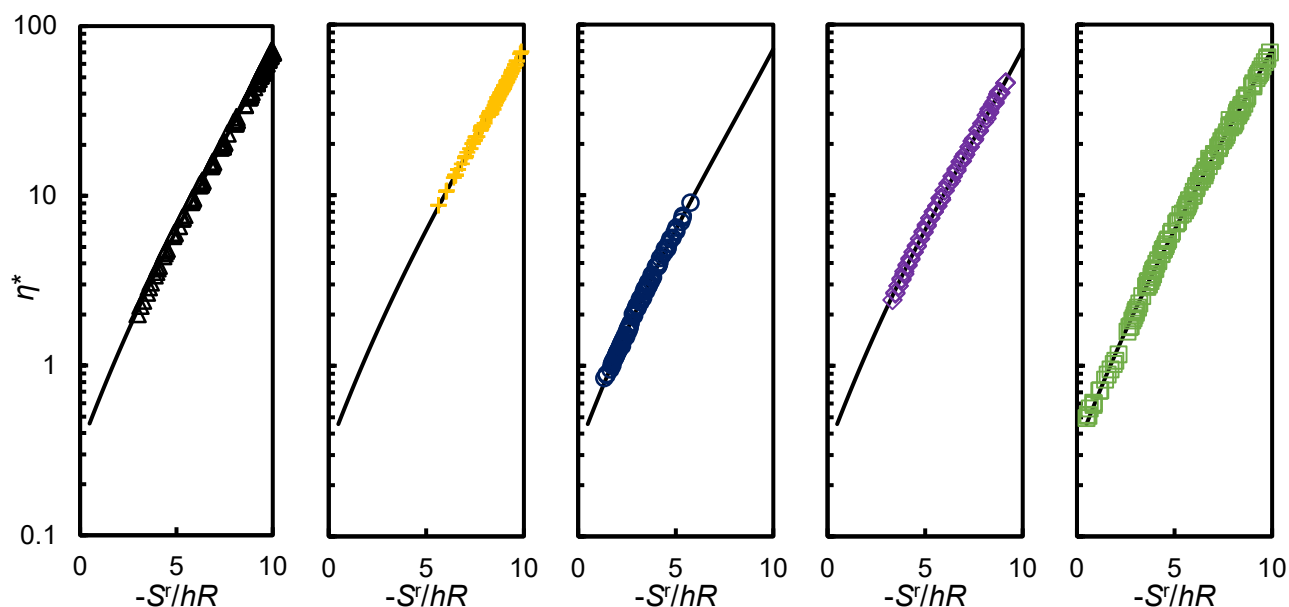


Figure 3 Scaled reduced viscosity η^* against scaled residual entropy (S^*/hR) for each pure substance: \triangle , decane; $+$, *m*-xylene; \circ , CO_2 ; \diamond , dodecane; \square , octane. The solid line represents Eq. 15.

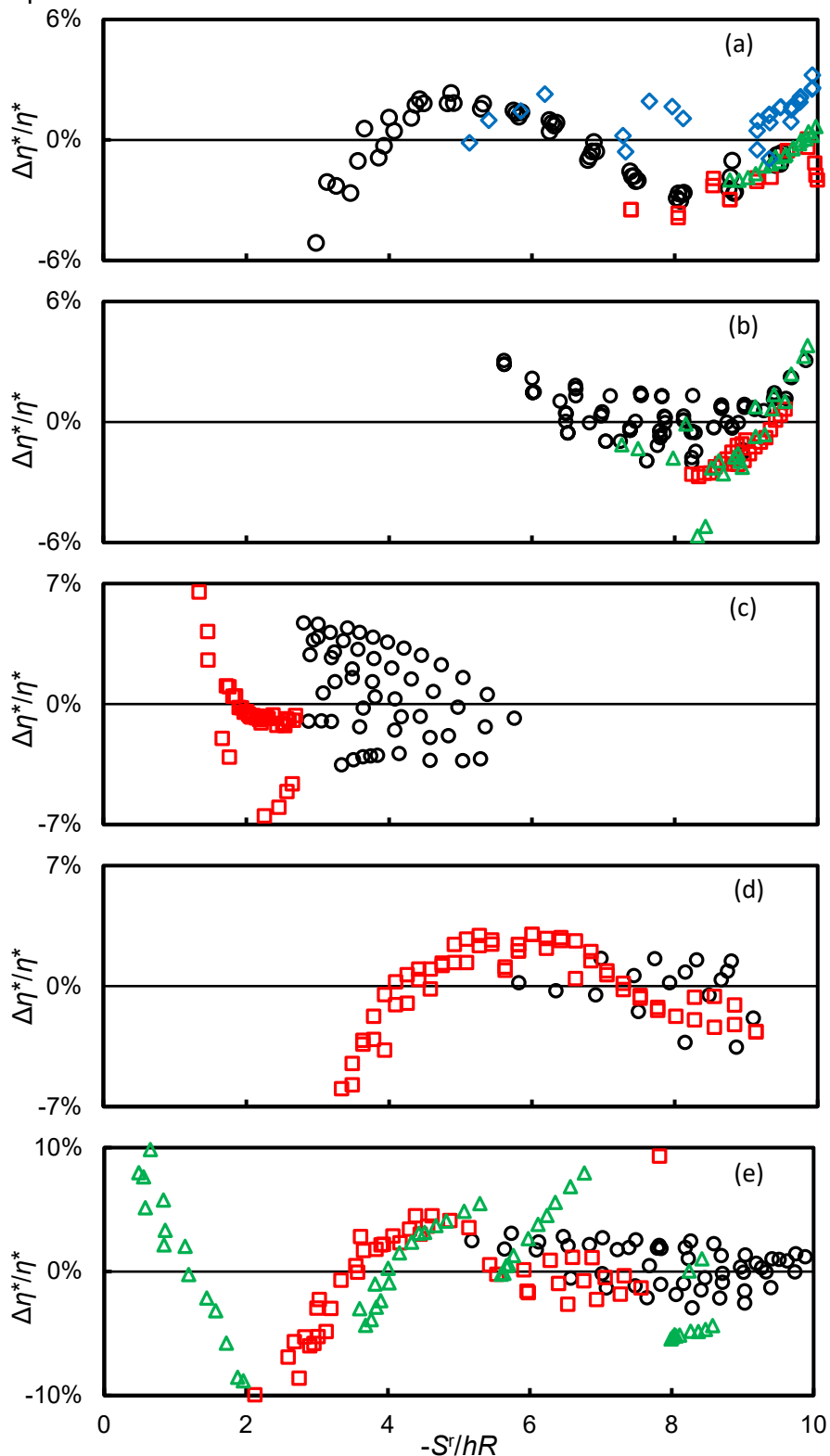


Figure 4 Relative deviations $\Delta\eta^*/\eta^*$ of the scaled reduced viscosity from the values estimated from equation (15) for each component: (a) decane: \circ , Liu et al.⁷⁴; \square , Caudwell et al.¹⁸; \triangle , Assael et al.⁷⁷; \diamond , Carmichael et al.⁷⁸ (b) *m*-xylene: \circ , Caudwell et al.¹⁸; \square , Assael et al.³⁰; \triangle , Et-tahir et al.⁸⁰ (c) CO_2 : \circ , Fenghour et al.⁷¹; \square , Iwasaki and Takahashi⁷² (d) dodecane: \circ , Caudwell et al.¹⁸; \square , Assael et al.³⁰; \triangle , Et-tahir et al.⁸⁰ (e) octane: \circ , Caudwell et al.¹⁸; \square , Assael et al.³⁰; \triangle , Et-tahir et al.⁸⁰

Caudwell et al.^{73, 75}; □, Yang et al.⁷⁹ (e) octane: O, Caudwell et al.¹⁸; □, Badalyan and Rodchenko⁷⁶; △, Stephen and Heckelberger.⁸²

Table 3. Coefficients of equation 15 and statistical parameters for the universal correlation

i	C_i
0	-1.12478
1	0.70260
2	-0.02813
3	1.1865×10^{-3}
Δ_{AAD}	1.9%
Δ_{MAD}	9.9%

3.2 Application to Mixtures

In order to apply the model to mixtures, one simply needs a means of determining the molar mass M in Eq. (14) and the scaling factors h_{mix} and $R_{\eta,mix}$ that apply. These can of course be fitted to experimental data but, to obtain a predictive model, we postulate the simplest possible mixing rules as follows:

$$M_{mix} = \sum_i x_i M_i \quad (19)$$

$$h_{mix} = \sum_i x_i h_i \quad (20)$$

$$R_{\eta,mix} = \sum_i x_i R_{\eta,i} \quad (21)$$

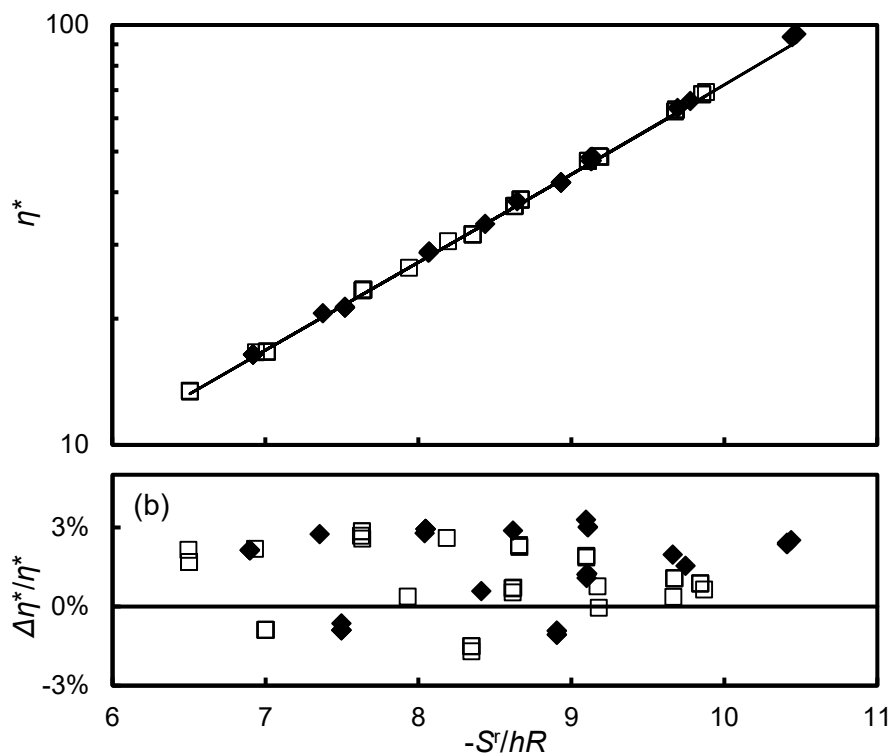


Figure 5 Scaled reduced viscosity η^* (a) and relative deviations $\Delta\eta^*/\eta^*$ (b) for octane (1) + dodecane (2) system as a function of scaled residual entropy: □, $x_1 = 0.743$; ◆, $x_1 = 0.434$.

An initial test of this postulate is provided by a comparison with data for a mixture of two hydrocarbons having similar characteristic. Due to the availability of wide-ranging and precise experimental data at more than one mixture composition, the (octane + dodecane) system was chosen for this test.⁷³ Figure 5 compares the experimental data with the model and shows reasonable agreement with absolute average relative deviation of 2%.

A more severe test of the approach is provided by data for asymmetric mixtures, for example hydrocarbon liquids with dissolved CO₂. Two such mixtures are considered here, namely (CO₂ + decane) and (CO₂ + *m*-xylene). The experimental viscosity data for the (CO₂ + decane) system were those of Cullick et al.⁸³ while those for the (CO₂ + *m*-xylene) system were taken from a recent study carried out in our laboratory.⁸⁴ All data considered fall in the homogeneous liquid region. A complication arises in the latter case because the binary parameters in the MFHEA have not been optimised for the (CO₂ + *m*-xylene) system. Therefore, the calculated residual entropy, based on the parameters from Table 1, might not be as reliable as in the other cases. To test the accurate of the equation-of-state model, we compare in Figure 6 the reported experimental densities⁸⁴ with those predicted by the model. Here, we plot the relative differences $\Delta\rho/\rho$, where $\Delta\rho = \rho(\text{experimental}) - \rho(\text{predicted})$. The analysis of the viscosity data was then restricted to those state points for which $|\Delta\rho/\rho| \leq 5\%$. Figures 7 and 8 compare the viscosity data for these two systems with the model. Clearly, the deviations are larger in these cases, particularly for (CO₂ + decane) where a few points deviate by more than 30%. The three most discrepant points relate to the highest composition of CO₂ at a temperature of 403 K. It is also observed that the model systematically underestimates the experimental data for both systems.

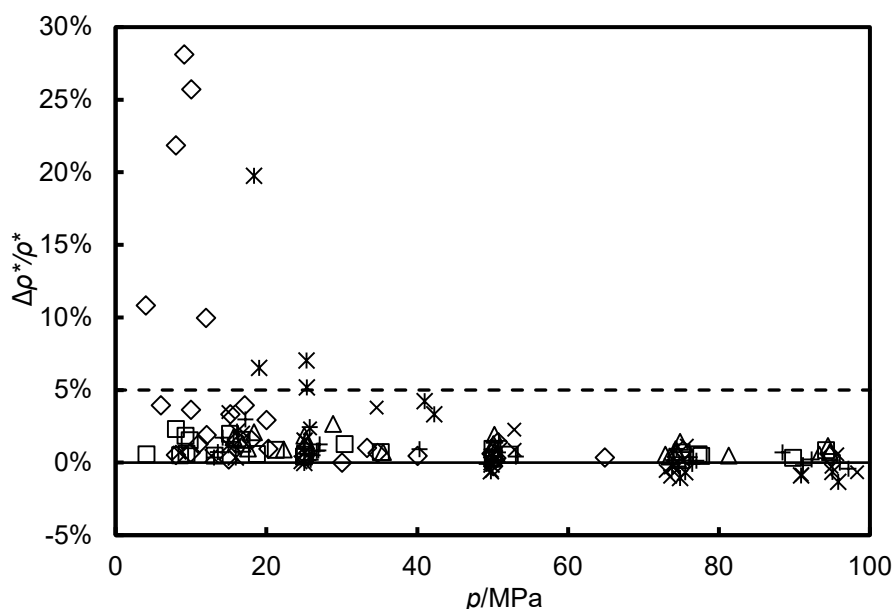


Figure 6 Density deviation as a function of pressure for CO₂ (1) + *m*-xylene (2). Data points above the dashed line was not considered in this work.

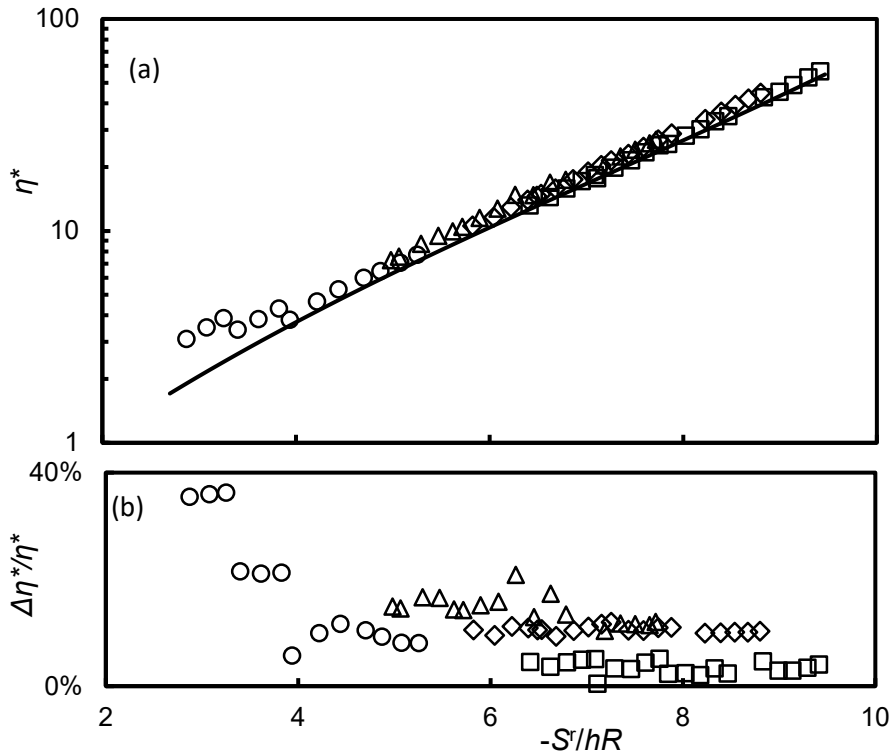


Figure 7 Scaled reduced viscosity η^* (a) and relative deviations $\Delta\eta^*/\eta^*$ (b) for CO_2 (1) + decane (2): \square , $x_1 = 0.15$; \diamond , $x_1 = 0.30$; \triangle , $x_1 = 0.51$; \circ , $x_1 = 0.85$. Solid line in (a) represents the predicted values.

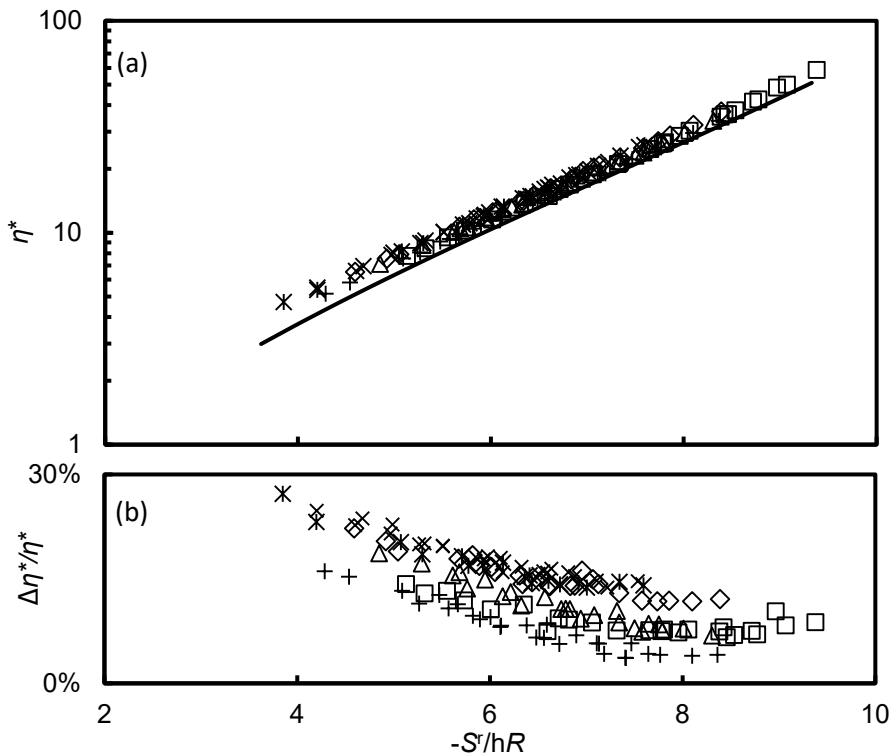


Figure 8 Scaled reduced viscosity η^* (a) and relative deviations $\Delta\eta^*/\eta^*$ (b) for CO_2 (1) + *m*-xylene (2): \square , $x_1 = 0.19$; \diamond , $x_1 = 0.38$; \triangle , $x_1 = 0.46$; +, $x_1 = 0.51$; x, $x_1 = 0.62$; *, $x_1 = 0.65$. Solid line in (a) represents the predicted values.

3.3 Discussion

The method proposed in this work has the potential to be a universal model, at least for the class of non-polar and non-associating fluids consider in this paper. The approach is contingent upon the availability of an accurate method for calculating the residual molar entropy of pure fluids and mixtures. The use of multi-parameter Helmholtz-energy models limits the approach to the 100 or so pure substances for which such models have so far been developed and to mixtures of these for which the binary parameters β_T , β_V , γ_T and γ_V , and any necessary binary-specific departure functions, have been adequately determined. Of course, other equation of state models, such as SAFT approaches,⁵³ could be used but the multi-parameter Helmholtz-energy models are preferred.

The scaling used to map the reduced viscosity onto a universal curve is somewhat similar to that in the hard-sphere theory of Dymond and Assael (DA) wherein a scaled reduced viscosity is represented as a universal function of a reduced molar volume. However, whereas the reducing molar volume in the DA theory is a function of temperature, the scaling factors in the present method are constants for a given substance. This means that only a limited amount of viscosity data is required to determine the scaling parameters. The performance of the present method appears to be excellent for pure substances and competitive with correlation models that involve many more parameters. When applied to mixtures, larger deviations are observed and it is not clear if these reflect inaccuracies in the prediction of the mixture residual entropy, limitations of the simple linear mixing rules used for the scaling factors, or both. Nevertheless, we consider the results encouraging and worthy of further investigation.

Referring to Fig. 3, one can observe that data points at $-S^*/R < 2$ are included. These points are located near the critical point or in the supercritical region and, in Fig. 4, they show greater and somewhat systematic deviations from the correlation. If one considers only those points at $-S^*/R \geq 2$ then a better fit can be obtained with an AAD of 1.5% and MAD of 7.8%.

In this work, we adopted the simplest possible expression for the molar mass of the mixture appearing in Eq. (14). As discussed by Galliero et al.,⁸⁵ several other rational possibilities exist including: (1) a quadratic model

$$M_{\text{mix}}^{1/2} = \sum_i \sum_j x_i x_j M_{ij}^{1/2}, \quad (22)$$

in which M_{ij} is the reduced molar mass ($1/M_{ij} = 1/M_i + 1/M_j$); (2) a linear square-root model

$$M_{\text{mix}}^{1/2} = \sum_i x_i M_i^{1/2}, \quad (23)$$

and (3) a log-linear square-root model

$$\ln M_{\text{mix}}^{1/2} = \sum_i x_i \ln M_i^{1/2}. \quad (24)$$

To test the effect of these different assumptions, we have made additional calculations with each of these alternative definitions for M_{mix} and, in Table 4, we compare the results in terms of the AAD and MAD statistics. However, these different rules do not offer any improvement, being either the same or slightly worse than the results obtained with Eq. (19) for M_{mix} . Galliero

et al.,⁸⁵ also considered a mixing rule for M_{mix} containing adjustable parameters but we prefer to avoid introducing additional parameters.

Table 4. Summary of the AADs and MADs for several mixing rule equations referred from Galliero et al.⁸⁵

Mixture	Equation (19)		Equation (22)		Equation (23)		Equation (24)	
	AAD	MAD	AAD	MAD	AAD	MAD	AAD	MAD
octane + dodecane	2%	4%	2%	4%	2%	4%	2%	4%
decane + CO ₂	11%	36%	16%	41%	13%	38%	15%	40%
<i>m</i> -xylene + CO ₂	13%	28%	17%	32%	14%	29%	16%	31%

4. Conclusion

In this work, we developed a prototype universal relation between reduced viscosity and the residual molar entropy. We evaluate the residual entropy from multi-parameter Helmholtz-energy equation of state that are known to be accurate for pure substances. For mixtures, a multi-fluid Helmholtz-energy approximation is used for the same purpose. The model incorporates two system-dependent scaling parameters and is therefore correlative for pure fluids. The simple linear mixing rules proposed render the method predictive for mixtures.

The method was able to correlate the viscosity of CO₂ and several hydrocarbon liquids over wide ranges of temperature and pressure with average absolute relative deviations of less than 2 % and maximum absolute relative deviations of less than 10 % for all components investigated. When applied to mixtures, larger deviations were observed that appear to increase with the molecular asymmetry of the system. Determining the origin of these deviations is a topic for further research. The methods proposed here should be capable of extension to other transport properties such as the self-diffusion coefficient and the thermal conductivity.

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