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Entropy Scaled Viscosities of Water and Some Alkanols Using a Cubic EoS

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The present modelling work introduces the application of the residual-entropy scaling approach to adequately represent the dynamic viscosity of water and some alkanols (methanol, ethanol, 1-propanol and 1-butanol) over wide temperature and density ranges. Both unreduced and reduced viscosity forms (total viscosity, Rosenfeld and dilute gas) were examined and compared. A cubic equation of state (Soave-Redlich-Kwong or Peng-Robinson or Peng-Robinson-Stryjek-Vera) was used to estimate sufficiently accurate residual entropy data needed by the present scaling procedure. The resulting modelling approach was successfully validated during the representation of experimental dynamic viscosities of the aforementioned pure fluids covering wide ranges of temperature (from the triple the triple point of the fluid up to 1,000 K) and pressures (from 0.1 up to 1,000 bar).

* 1. Introduction

Dynamic viscosity plays a crucial role in the design and optimization of industrial processes. However, experimental data for transport properties are often scarce or restricted to narrow ranges of pressure, temperature, and composition, particularly for complex systems. To address these limitations, various predictive approaches have been developed, including corresponding states principles (Ely et al., 1981), free volume theory (Burgess et al., 2012), friction theory (Quiñones et al., 2000), and thermodynamic scaling based on density (Pensado et al., 2008).

Residual-entropy scaling (Rosenfeld, 1977) has proven especially effective in correlating transport properties, such as viscosity, with the residual entropy of the system, reducing the dependence on pressure and temperature. While this approach has been extensively applied with SAFT-type equations of state (Melfi et al., 2024), studies by Dehlouz et al. (2024) and Macías-Salinas et al. (2023) have also demonstrated its applicability with cubic equations of state for liquid-phase systems, including ionic liquids and deep eutectic solvents.

This work builds on these findings by extending residual-entropy scaling with cubic equations of state (SRK, PR, and PRSV) to a diverse range of substances, including water, methanol, ethanol, 1-butanol, and 1-propanol, evaluating its performance across broad pressure and temperature ranges.

* 1. Description of the Model

First introduced by Rosenfeld (1977), residual-entropy scaling reduces the dependence of transport properties, such as viscosity, diffusion constant and thermal conductivity, from two variables (pressure and temperature) to a single variable: the residual entropy. Pressure and temperature are implicitly accounted for through the residual-entropy. Consequently, an accurate equation of state is required to calculate the residual entropy with sufficient precision, ensuring proper scaling. As mentioned previously, various authors have applied this modeling approach using SAFT-type equations of state, such as PC-SAFT, SAFT VR-Mie, PCP-SAFT, and ePC-SAFT, for a wide range of pure substances and their mixtures, achieving satisfactory results. However, one of the objectives of this work is to demonstrate that this scaling can be successfully performed using simple, practical, and widely adopted cubic equations of state in the industry, specifically SRK, PR and PRSV. Residual entropy (or departure entropy) is the difference between the entropy of the system and the entropy of the ideal gas at the same temperature and density:

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|  | (1) |

For a cubic equation of state explicit in pressure, such as SRK, PR and PRSV, it can be obtained using the following expression:

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|  | (2) |
|  | (3) |

Where is the molar density, is the temperature, is the derivative of the attractive parameter, is the van der Waals co-volume, is the gas constant, , for PR and PRSV and , for SRK.

* + 1. Reference Viscosity

The residual-entropy scaling for the dynamic viscosity of fluids can be described by the following equation:

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|  | (4) |

Where is a reference viscosity, refers to a scaling function, and and are the calculated viscosity and residual entropy at the absolute temperature and molar density of interest, respectively. Formally, the residual-entropy scaling uses macroscopically reduced units (Dyre, 2018), as presented in the original paper by Rosenfeld through the following equation:

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|  | (5) |

Where is the molecular mass, is the Boltzmann constant, is the absolute temperature and is the number density calculated from the molar density , using the equation of state. If is expressed in units of , then:

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|  | (6) |
|  | (7) |
|  | (8) |

Where is the molecular weight in g/mol and is Avogadro’s number, is the Boltzmann constant in J/K and is the absolute temperature in K.

Some authors (Lötgering-Lin et al., 2018) have proposed using the Chapman-Enskog equation to improve scaling within the gas-like region. In this work, the specific modification proposed by Chung et al. (1988) will also be analyzed:

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|  | (9) |
|  | (10) |
|  | (11) |
|  | (12) |

Where is the molecular weight in g/mol, is the absolute temperature in K, is the critical temperature in cm3/mol, is the Neufeld’s collision integral, is a reduced temperature, is the critical temperature in K, is a correction factor that accounts for the nonsphericity, polarity, and hydrogen bonding of the substance, is the acentric factor, is the dimensionless dipole moment and is a substance-specific constant as reported by Chung et al. (1988). In this work, is assumed to be unity.

Lastly, the third reference viscosity, as performed by Melfi et al. (2024) and Macías-Salinas et al. (2023), will be unity, meaning that the scaling will be performed using the total dynamic viscosity directly.

* + 1. Scaling function

As previously mentioned, the present modeling approach reduces the viscosity dependence to be solely a function of residual entropy. Therefore, a mathematical expression is required to best describe this relationship. In this work, a third-degree polynomial within an exponential function is used:

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|  | (13) |

Where , , , and are the model parameters specific to each component and model variation (combination of cubic equation of state, alpha function, and reference viscosity)

* 1. Results and discussion

In order to evaluate the model's performance, dynamic viscosity data for water, methanol, ethanol, 1-butanol, and 1-propanol were used within a pressure range up to 1,000 bar (up to 3,000 bar for water) and a temperature range up to 1,000 K. The specific range, number of data points, and sources for each component are detailed in Table 1.

Table 1: Experimental reference data for the fluids examined in this work

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| --- | --- | --- | --- | --- |
| Component | N | T, K | P, bar | Source |
| Water | 799 | 273.16 – 1073.1 | 0.0061165 – 3,000 | NIST Webbook (2019) |
| Methanol | 217 | 180 – 620 | 0.1 – 1,000 | NIST Webbook (2023) |
| Ethanol | 1252 | 268.1 – 612.2 | 0.8150 – 980.66 | Dortmund Data Bank |
| 1-butanol | 1297 | 186.15 – 473.15 | 0.8150 – 980.66 | Dortmund Data Bank |
| 1-propanol | 1042 | 153.15 – 546.15 | 0.8150 – 982 | Dortmund Data Bank |

The input parameters required for this work are provided in Table 2. Additionally, the model fitting is performed using the following minimization procedure:

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|  | (14) |

Where is the objective function, represents the experimental dynamic viscosity, and denotes the scaling potential .

Table 2: Single-component physical properties required as inputs for the model

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| --- | --- | --- | --- | --- | --- | --- |
| Component | Mw, g/mol | Tc, K | Pc, bar | vc, cm3/mol |  |  |
| Water | 18.0153 | 647.096 | 220.64 | 55.9481 | 0.3443 | -0.6635 |
| Methanol | 32.0419 | 512.6 | 81.035 | 116.2791 | 0.5625 | -0.16816 |
| Ethanol | 46.069 | 516.2 | 63.8348 | 168 | 0.635 | -0.03374 |
| 1-butanol | 74.1228 | 562.9 | 44.1777 | 274 | 0.59 | 0.33431 |
| 1-propanol | 60.0959 | 536.7 | 51.6758 | 218 | 0.624 | 0.21419 |

The model's performance was evaluated using the Average Absolute Deviation (AAD):

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|  | (15) |

A summary of the results obtained, in terms of AAD, for the different variations of the present model is provided in Table 3.

Table 3: Results Overview

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| --- | --- | --- | --- | --- |
| Component | Reference Viscosity | SRK AAD% | PR AAD% | PRSV AAD% |
| Water | Unity, | 14.02 | 13.776 | 13.546 |
| Rosenfeld, Eq(5) | 49.887 | 49.728 | 47.629 |
| CE, Eq(9) | 6.9122 | **6.6587** | 7.3969 |
| Methanol | Unity, | 8.5280 | 8.8439 | 6.9747 |
| Rosenfeld, Eq(5) | 43.648 | 43.536 | 37.312 |
| CE, Eq(9) | 5.4527 | 5.7645 | **4.2624** |
| Ethanol | Unity, | 3.0369 | 3.3217 | 3.1593 |
| Rosenfeld, Eq(5) | 3.2598 | 3.5067 | 3.2383 |
| CE, Eq(9) | **2.2279** | 2.5320 | 2.3584 |
| 1-butanol | Unity, | 3.2406 | 3.7136 | 6.1769 |
| Rosenfeld, Eq(5) | **2.2883** | 2.7127 | 5.1587 |
| CE, Eq(9) | ***2.2915*** | 2.7359 | 5.3514 |
| 1-propanol | Unity, | 4.1912 | 4.6589 | 6.1878 |
| Rosenfeld, Eq(5) | 4.8669 | 5.0316 | 6.6678 |
| CE, Eq(9) | **3.2895** | 3.6725 | 5.2945 |

Table 3 highlights, in bold, the best model variations in terms of AAD for each studied compound. Figures 1–6 present the vs vs surfaces obtained from the model and experimental data (a), along with the scaling curve and scaled experimental viscosities (b), for the best variations of water, methanol, ethanol, 1-butanol, and propanol, respectively.

Both the AAD values and graphical representations demonstrate that the present modeling approach accurately represents the dynamic viscosity of the studied compounds, with some exceptions for water and 1-butanol, which are discussed later. The best results were generally obtained using the SRK cubic equation of state and the CE reference viscosity. Conversely, the viscosity scaling originally proposed by Rosenfeld yielded the poorest results, except for 1-butanol, where it provided the best AAD value. However, it is important to note that the scaling curve observed for 1-butanol (Figure 5b) deviates from typical trends seen in other compounds. This is also reflected in the calculated saturated viscosities (Figure 5a), which exhibit an atypical pronounced drop. Therefore, while Rosenfeld's approach yields the best numerical results for 1-butanol, the use of the CE reference viscosity is still recommended. The PR and PRSV equations of state rarely showed significant improvements over SRK.

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| a) | b) |

Figure 1: a) Experimental & calculated viscosities vs T & P for Water. b) Scaled experimental viscosities & resulting scaling for Water.

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| --- | --- |
| a) | b) |

Figure 2: a) Experimental & calculated viscosities vs T & P for Methanol. b) Scaled experimental viscosities & resulting scaling for Methanol.

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| --- | --- |
| a) | b) |

Figure 3: a) Experimental & calculated viscosities vs T & P for Ethanol. b) Scaled experimental viscosities & resulting scaling for Ethanol.

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| a)  Gráfico  El contenido generado por IA puede ser incorrecto. | b)  Gráfico, Gráfico de líneas  El contenido generado por IA puede ser incorrecto. |

Figure 4: a) Experimental & calculated viscosities vs T & P for 1-Propanol. b) Scaled experimental viscosities & resulting scaling for 1-Propanol.

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| --- | --- |
| a) | b) |

Figure 5: a) Experimental & calculated viscosities vs T & P for 1-Butanol. b) Scaled experimental viscosities & resulting scaling for 1-Butanol.

Gráfico

Descripción generada automáticamente

Figure 6: *Model (SRK-Soave/CE) limitation in capturing the viscosity minimum of water at high pressures (0.1 – 3000 bar) and low temperatures (273.15 – 303.15 K)*.

Moreover, Figure 1b shows that the scaled experimental viscosities exhibit atypical behavior, forming multiple U-shaped curves in the high residual-entropy region (highlighted by the red circle). This phenomenon corresponds to the so-called anomalous region of water. Within this region, spanning approximately from 0 to 30 °C, viscosity exhibits a minimum as pressure increases from 0.1 to 3,000 bar. Figure 6 illustrates that this anomalous region could not be adequately represented by the present model. None of the model variations successfully capture this behavior.

* 1. Conclusions

This work demonstrates that residual-entropy scaling, originally proposed by Rosenfeld, can be effectively applied using simple and widely adopted cubic equations of state, such as SRK, PR, and PRSV. Among them, SRK provided the most accurate results, making it the preferred choice for viscosity modeling. Additionally, the CE reference viscosity function proved to be the most reliable, offering superior performance compared to Rosenfeld's original scaling. These equations of state, while less complex than SAFT-type models, provide satisfactory results for modeling dynamic viscosity across various compounds, offering a practical and efficient tool for industrial applications.

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