

A new Corresponding States model for the estimation of thermophysical properties of long chain *n*-alkanes[☆]

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Abstract

The interest in phase equilibrium and thermophysical properties of mixtures containing long chain hydrocarbons is increasing. Despite the industrial interest of these systems, the available experimental data are scarce, while new models are required.

Corresponding States Theory has been used with success for the estimation of properties of pure components and mixtures of small molecules. This work shows how this theory can be extended to the evaluation of liquid density, vapour pressure and viscosity of long chain molecules in a broad temperature range, based on information of lower members of the same homologous series.

Results for the *n*-alkane series showed that this new model is able to predict liquid density, vapour pressure and viscosity with percent average absolute deviations of 0.44, 0.52, and 3.15%, respectively.

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1. Introduction

As a result of the systematic demand for new products, the nature and number of the different chemicals in which we may be interested in is increasing considerably. In fact, in a short period of time, the chemical industry has changed from the production of a tiny number of small molecules to the large-scale production of a huge number of chemicals with broad compositional, structural and size differences.

This product-driven production forced fast changes in the chemical industry for which the chemist and the chemical engineer had to find rapid solutions. Because the experimental measurement of

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thermophysical properties is an expensive and time-consuming procedure, the alternative is to develop models from which the required properties with the desired accuracy could be obtained.

The *Corresponding States Principle* is the most versatile approach for equilibrium and transport properties. It has been used successfully for equilibrium properties, such as vapour pressure [1–5], liquid density [1,4,6,7] or surface tension [1,8–10] and transport properties, such as viscosity [1,11–14] and thermal conductivity [1]. In spite of their simplicity, *Corresponding States* models are able to produce very accurate estimates based on a small amount of experimental information. If we still add the strong theoretical basis behind *Corresponding States Principle* we can justify any effort in studying and developing such models.

In this work, a new *Corresponding States* model recently proposed for the estimation of the surface tension of the series of the *n*-alkanes [10] is extended to the prediction of other three properties: vapour pressure, liquid density and viscosity. It is shown that it is possible to use a similar framework to predict all these properties in a broad range of the liquid region and for both the lighter and heavier components of the series.

2. Corresponding States Principle

The *Corresponding States Principle* was initially proposed by van der Waals who observed that the reduced version of his equation of state is the same for all fluids. Although the establishment of this principle was originally made only on an empirical basis, subsequent studies in statistical mechanics and kinetic theory have confirmed its theoretical foundations [15–20]. Today, many generalised equations of state are examples of applications of this principle.

In its original form, the *Corresponding States Principle* expressed the reduced compressibility factor of a target fluid in terms of a universal function of two parameters, the dimensionless temperature and molar volume:

$$Z_{rj}(T_r, V_r) = Z_{r0}(T_r, V_r) \quad (1)$$

$$T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c} \quad (2)$$

where Z is the compressibility factor (PV/RT), and the subscripts ‘r’ and ‘c’ stand for reduced and critical property, and ‘j’ and ‘0’ for target and spherical reference fluid, respectively.

Experimental evidence has shown that this two-parameter *Corresponding States* is only obeyed by the noble gases and nearly spherical molecules, such as methane, nitrogen and oxygen. To extend this theory to a broader range of fluids, additional characterisation parameters have been introduced to account for the non-conformalities. Two main approaches have been applied in this parameterisation: the first performs a multi-parameter Taylor series expansion of the property of interest about the parameters; the second approach is to extend the simple two-parameter *Corresponding States Principle* at its molecular origin. The end result is a *Corresponding States* model that has the same mathematical form as the simple two-parameter model, but the definitions of the dimensionless volume and temperature are more complex, involving the so-called *shape factors* [17].

An additional third parameter, the Pitzer acentric factor (ω), was introduced [5] to generalise the scope of the *Corresponding States Principle* to include fluids whose force fields slightly depart from those of the

original spherical symmetry. Reduced pressure was used instead of reduced volume due to the uncertainty usually ascribed to the measurement of critical volumes:

$$Z_{rj}(T_r, P_r, \omega) = Z_{r0}(T_r, P_r) + \omega Z_r(T_r, P_r) \quad (3)$$

where Z_{r0} has the same meaning as in Eq. (1) and Z_r is a function that represents the departure from the spherical symmetry. In a Taylor series expansion, this function represents the derivative $\partial Z/\partial \omega$. In spite of the analytic formalism of Eq. (3), values for the functions Z_{r0} and Z_r were only presented in tabular form by Pitzer et al.

With the advent of cheaper and faster computers, Lee and Kesler [21] proposed an analytical framework for this three-parameter *Corresponding States* replacing the derivative in the Taylor series expansion with its finite difference:

$$Z_{rj}(T_r, P_r, \omega) = Z_{r0}(T_r, P_r) + \frac{\omega_j}{\omega_1} [Z_{r1}(T_r, P_r) - Z_{r0}(T_r, P_r)] \quad (4)$$

where the subscript '1' represents a reference fluid with $\omega > 0$.

Although this new formalism contained a correction for the departure from the spherical symmetry, some problems arose in the description of polar or asymmetric systems. Since Eq. (4) still contains a spherical reference fluid ($\omega = 0$), large interpolations/extrapolations were frequent in the description of real systems. Another problem was related with the widespread use of methane as the spherical reference fluid. Because methane has a reduced triple point temperature relatively high compared with the majority of the hydrocarbons, some low temperature calculations would result in the extrapolation of the methane equation of state introducing considerable errors in the predicted data.

After Teja and co-workers [4,6,8,11,22,23], the spherical reference fluid in Eq. (4) was relaxed. Hence, both reference fluids could be similar to the evaluating fluid. Several thermophysical properties were estimated according to this new formalism with very good predictive results.

3. Model

As reported in Section 2, one of the most accurate and well-known *Corresponding States* frameworks for thermophysical property estimation is the one proposed by Teja and co-workers based on a Taylor series expansion of the reduced property of the target fluid in terms of the Pitzer acentric factor.

As shown before, the series is usually truncated beyond the first derivative, giving a linear function:

$$X_r = X_{r1} + \frac{\omega - \omega_1}{\omega_2 - \omega_1} (X_{r2} - X_{r1}) \quad (5)$$

where X_r represents the reduced property of interest, ω the Pitzer acentric factor and the subscripts '1' and '2' the two reference fluid properties at the same reduced conditions as the target fluid. In all cases, good agreement with experimental data was obtained in the range of fluids covered by the two references. However, considerable deviations can be found if the reference fluids are far apart in the series from the target fluid, either interpolating or extrapolating (Figs. 1–3). In an attempt to correct for these deviations, and based on the dependence of the desired properties with chain length presented in Figs. 1–3, the Taylor series expansion of the reduced property was carried out to the second-order term, yielding the following equation that was previously applied for the description of the surface tension of pure *n*-alkanes [10]:

$$X_r = X_{r1} + D_1(\omega - \omega_1) + D_2(\omega - \omega_1)(\omega - \omega_2) \quad (6)$$

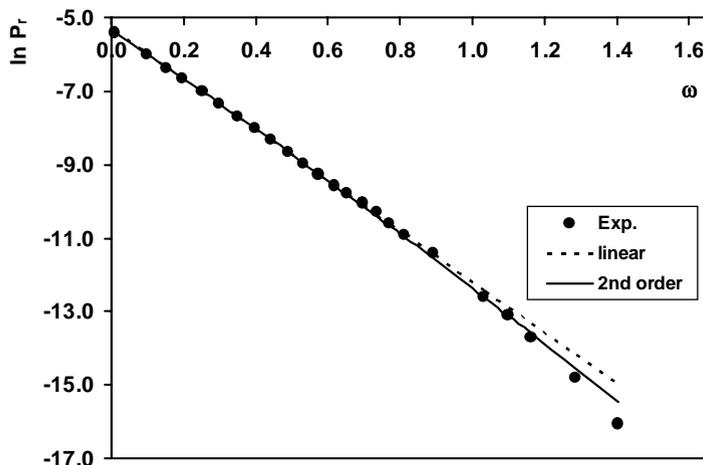


Fig. 1. Reduced vapour pressure (P_r) as a function of the acentric factor (ω) at $T_r = 0.5$.

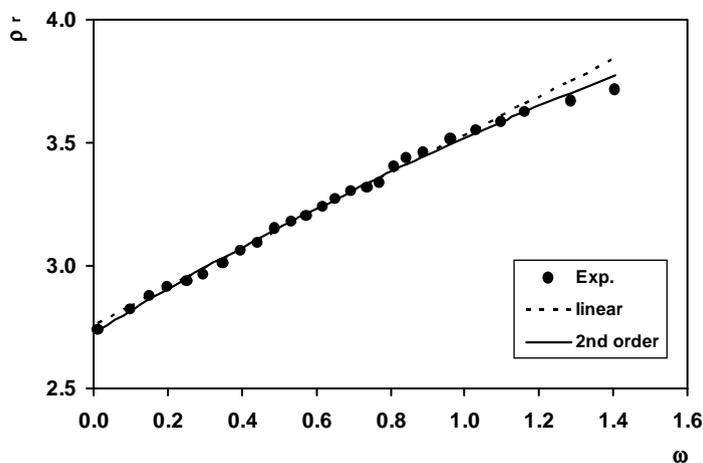


Fig. 2. Reduced liquid density (ρ_r) as a function of the acentric factor (ω) at $T_r = 0.5$.

$$D_1 = \frac{X_{r2} - X_{r1}}{\omega_2 - \omega_1}, \quad D_2 = \frac{[(X_{r3} - X_{r1})/(\omega_3 - \omega_1)] - [(X_{r2} - X_{r1})/(\omega_2 - \omega_1)]}{\omega_3 - \omega_2} \quad (7)$$

Note that a third reference fluid has to be introduced. A quadratic dependence on the acentric factor for heavy alkanes was previously used with success by Morgan and Kobayashi [3] to correlate vapour pressures and heats of vaporisation.

4. Results and discussion

The linear Teja approach and the second-order perturbation model proposed in Section 3 were evaluated for liquid density, vapour pressure and viscosity of n -alkanes from methane up to n -hexatriacontane.

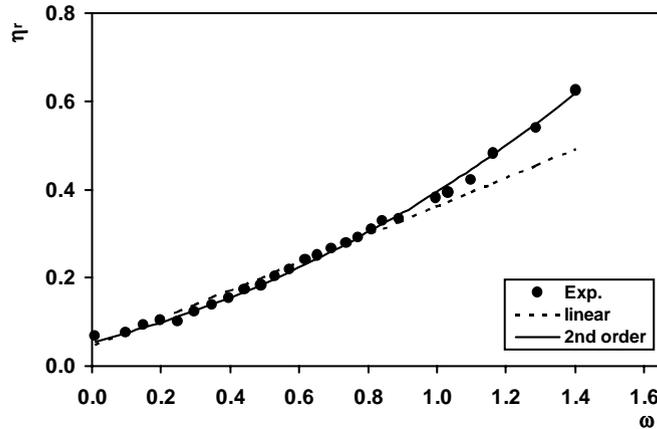


Fig. 3. Reduced viscosity (η_r) as a function of the acentric factor (ω) at $T_r = 0.5$.

For better data consistency, only the information presented on the DIPPR database [24] was selected. The reported correlations were used when reliable and enough experimental information was available. For some of the components, the correlating parameters were refitted to assure a good data description in the full range of temperatures used in this study, using the following equations, the same as those considered on the DIPPR database:

$$P \text{ (bar)} = \exp \left(A + \frac{B}{T} + C \ln T + DT^E \right) \times 1.0 \times 10^{-5} \quad (8)$$

$$\eta \text{ (mPa s)} = \exp \left(A + \frac{B}{T} + C \ln T + DT^E \right) \times 10^3 \quad (9)$$

$$\rho \text{ (mol cm}^{-3}\text{)} = \frac{A}{B^{1+[1-(T/C)]^D}} \times 10^3 \quad (10)$$

where T is the absolute temperature and A – E are correlating parameters.

Table 1 presents the studied n -alkanes for each property. A collection of reduced temperatures covering a broad range of the liquid region was selected for evaluation, starting at $T_r = 0.45$, close to the triple point of methane, and ending at $T_r = 0.75$. The higher limit for the reduced temperature was established to avoid the extrapolation to higher temperatures of the correlating equations.

Experimental critical properties were used, when available [25]. Correlations were assessed for those n -alkanes for which there is no experimental data. Critical temperature was obtained from the correlation

Table 1
Studied n -alkanes

Property	n in C_nH_{2n+2}
Vapour pressure	1:18, 20, 24, 26, 28, 32, 36
Liquid density	1:20, 22, 24, 26, 28, 32, 36
Viscosity	1:20, 23, 24, 26, 28, 32, 36

Numbers represent the n in C_nH_{2n+2} .

Table 2
Selected reference systems

Property	Reference system	
	Linear model	Second-order perturbation
Vapour pressure	C ₄ H ₁₀ /C ₁₂ H ₂₆	CH ₄ /C ₉ H ₂₀ /C ₂₆ H ₅₄
Liquid density	C ₄ H ₁₀ /C ₁₂ H ₂₆	CH ₄ /C ₁₅ H ₃₂ /C ₂₆ H ₅₄
Viscosity	C ₂ H ₆ /C ₁₅ H ₃₂	C ₂ H ₆ /C ₈ H ₁₈ /C ₁₈ H ₃₈

of Tsionopoulos [26], critical pressure from that of Magoulas and Tassios [27], critical volume from Marano and Holder [28] and the Pitzer acentric factor from Han and Peng [29].

Pressure and density were reduced using the critical pressure and volume:

$$P_r = \frac{P}{P_c} \quad (11)$$

$$\rho_r = V_c \rho \quad (12)$$

The natural logarithm of P_r was taken as X_r in Eqs. (5)–(7). Viscosity was reduced according to the following equation:

$$\eta_r = \frac{\eta V_c^{2/3}}{MW^{1/2} T_c^{1/2}} \quad (13)$$

Table 3
Correlating coefficients of the reference fluids to be used with Eqs. (8)–(10)

<i>n</i> -Alkane	Property	Correlation coefficient				
		<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>
CH ₄	Liquid density	2.9214	0.28976	190.56	0.28881	
	Vapour pressure	39.205	−1324.40	−3.4366	3.102 × 10 ^{−5}	2.0
C ₂ H ₆	Viscosity	−7.0046	276.380	−0.6087	3.111 × 10 ^{−18}	7.0
C ₄ H ₁₀	Liquid density	1.0677	0.27188	425.12	0.28688	
	Vapour pressure	66.343	−4363.20	−7.0460	9.451 × 10 ^{−6}	2.0
C ₈ H ₁₈	Viscosity	−7.7310	979.376	−0.5460		
C ₁₂ H ₂₆	Liquid density	0.3554	0.25551	658.00	0.29368	
	Vapour pressure	137.47	−11976.0	−16.698	8.091 × 10 ^{−6}	2.0
C ₁₅ H ₃₂	Liquid density	0.2844	0.25269	708.00	0.30786	
	Vapour pressure	135.57	−13478.0	−16.022	5.614 × 10 ^{−6}	2.0
	Viscosity	−2.9196	1196.57	−1.2470		
C ₁₈ H ₃₈	Viscosity	−2.3884	1280.02	−1.3112		
C ₂₆ H ₅₄	Liquid density	0.1624	0.24689	819.00	0.34102	
	Vapour pressure	155.64	−20116.0	−17.616	2.673 × 10 ^{−18}	6.0

Table 4
Percent average absolute deviation (%AAD) of the linear and second-order models as a function of reduced temperature

Reduced temperature	%AAD of the reduced property					
	Liquid density		Vapour pressure		Viscosity	
	Linear	Second order	Linear	Second order	Linear	Second order
0.45	0.66	0.50	1.29	0.87	11.19	4.47
0.50	0.63	0.47	1.01	0.59	8.18	3.69
0.55	0.62	0.44	0.82	0.42	6.63	3.11
0.60	0.63	0.42	0.67	0.36	5.97	2.34
0.65	0.65	0.39	0.56	0.42	5.86	2.09
0.70	0.68	0.40	0.52	0.44	6.12	2.54
0.75	0.71	0.45	0.57	0.55	6.62	3.79
Average	0.65	0.44	0.78	0.52	7.22	3.15

where MW represents molecular weight and η the viscosity (mPa s). Another reducing equation for viscosity, involving the critical pressure instead of the critical volume, can also be used [13,14], but our studies showed that it did not improve the results.

Although it would be theoretically possible to choose the same reference system to evaluate all properties, a small error in one or more of the reference fluids could mislead the results. Because of that, reference systems were selected for each property and model, so that they gave the smallest overall deviation. These reference systems are presented in Table 2 and the corresponding correlating coefficients to be used with Eqs. (8)–(10) are reported in Table 3.

It should be noted that with the second-order perturbation model methane can be used as the first reference fluid while the choice of a heavier member is required for the Teja approach. Basically, the

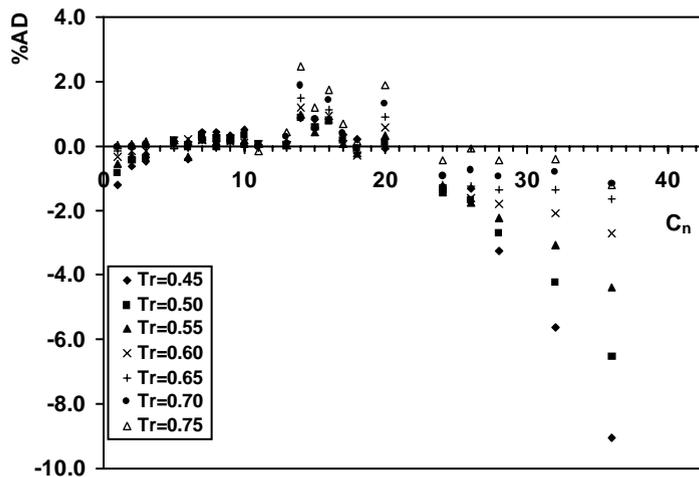


Fig. 4. Average deviation of the reduced vapour pressure predicted with the linear perturbation model as a function of the chain length of the n -alkane.

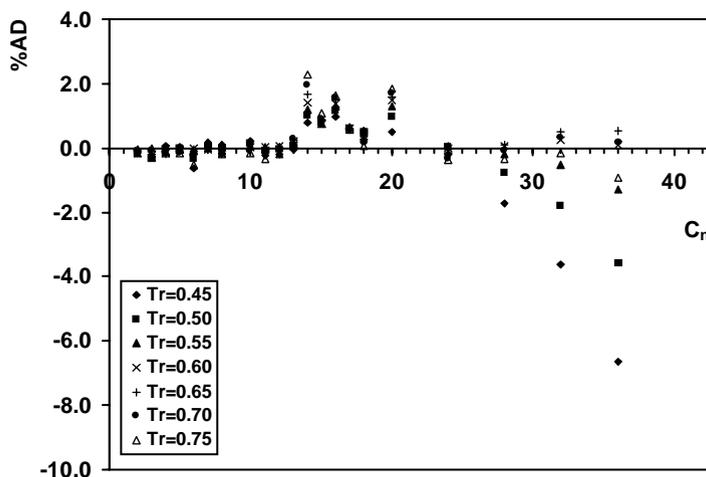


Fig. 5. Average deviation of the reduced vapour pressure predicted with the second-order perturbation model as a function of the chain length of the n -alkane.

second-order perturbation uses a lighter, an intermediate and a heavier member to represent the entire series.

Figs. 1–3, showing the reduced properties as a function of the acentric factor at a reduced temperature of 0.5, clearly evidence that a linear perturbation cannot describe the behaviour of the heavier n -alkanes. The introduction of a second-order perturbation is required for an adequate description of the properties of heavy n -alkanes.

Results are presented in Table 4 as a function of reduced temperature only. No pressure effects were considered at this point. This table shows how the introduction of the second-order term of the Taylor series expansion improves the prediction of all the reduced properties at all the studied reduced temperatures.

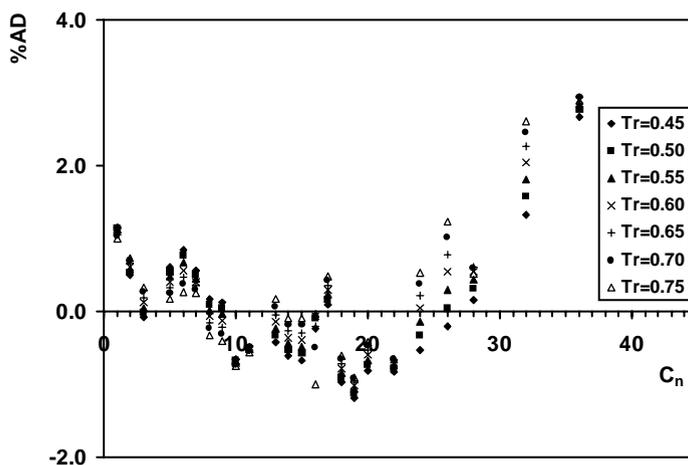


Fig. 6. Average deviation of the reduced liquid density predicted with the linear perturbation model as a function of the chain length of the n -alkane.

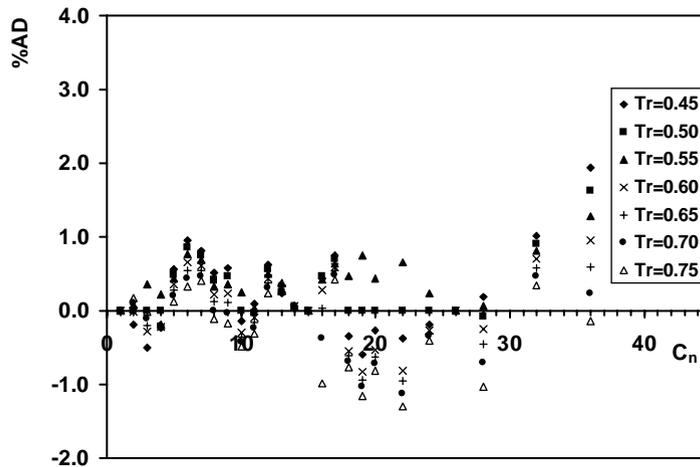


Fig. 7. Average deviation of the reduced liquid density predicted with the second-order perturbation model as a function of the chain length of the n -alkane.

The average improvements over the linear approach are 32% for liquid density, 33% for vapour pressure and 56% for viscosity.

Some trends in the deviations with reduced temperature reported in Table 4 can be ascribed to uncertainties propagating from the experimental measurements to the reference fluid correlating equations. Measurements at higher temperatures are typically more uncertain, and properties, such as vapour pressure and viscosity, often present greater uncertainty at low temperatures due to the difficulties in measuring smaller vapour pressures and the sharp increase of viscosity with the proximity of the melting point.

Figs. 4–9 illustrate the percent average deviation of the estimated reduced properties as a function of the chain length of the n -alkane. It can be seen that the linear approach proposed by Teja and co-workers has

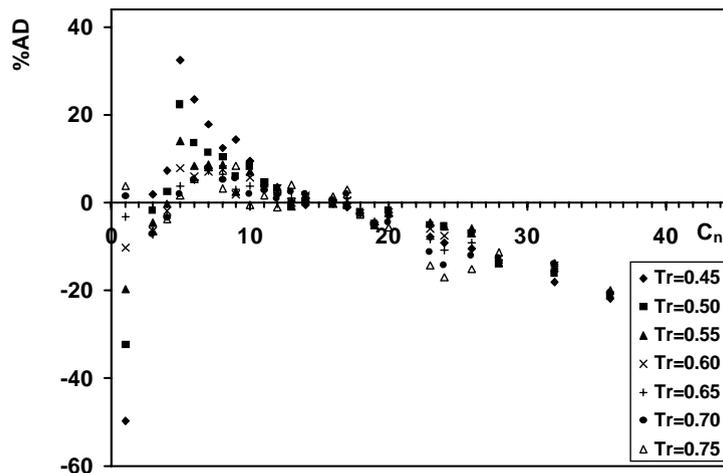


Fig. 8. Average deviation of the reduced viscosity predicted with the linear perturbation model as a function of the chain length of the n -alkane.

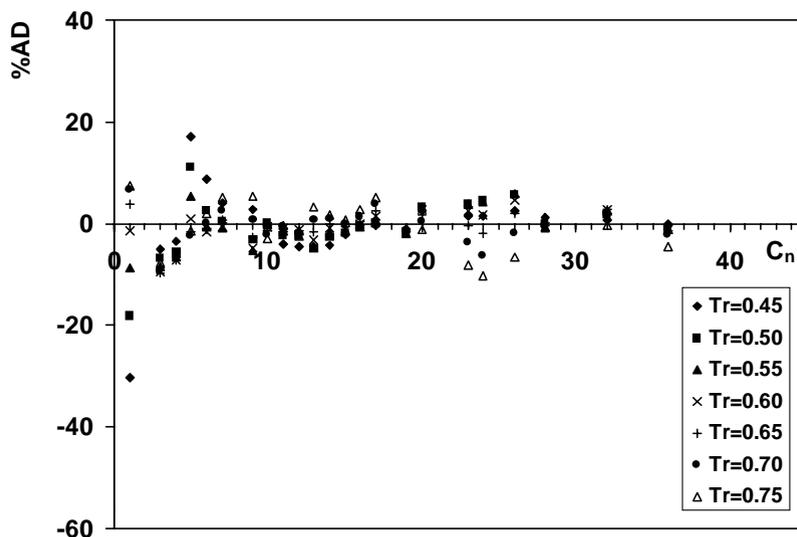


Fig. 9. Average deviation of the reduced viscosity predicted with the second-order perturbation model as a function of the chain length of the n -alkane.

some limitations for the heavier n -alkanes and that the average deviation decreases considerably around the reference fluid, confirming that this model is not able to predict the trend in the reduced property, as shown before in Figs. 1–3.

The second-order perturbation model shows a more random distribution of the deviations. Some higher values can be observed for liquid density and vapour pressure at the last studied members of the series, but still the deviations are smaller than those from the linear approach.

In both models, the highest deviations are found for the lowest and highest reduced temperatures, except for viscosity where the highest deviations are mainly from the lowest reduced temperature. As mentioned before, this should be the result of the higher uncertainties in the corresponding experimental measurements, coupled with the smaller amount of data usually found in these regions that can make the correlating equations less accurate in these zones.

From Figs. 1–9 and Table 4, it can thus be concluded that if the evaluation of all the series of the n -alkanes using the linear perturbation model is required we should use, at least, two sets of reference systems. Using the new second-order perturbation just one reference system is enough.

5. Conclusions

A new *Corresponding States* model was proposed for the estimation of vapour pressures, liquid densities and viscosities of the series of the n -alkanes. This model is predictive and only uses experimental information from the reference fluids and the critical properties of the target fluid.

The inclusion of the second-order term in the Taylor series expansion of the reduced property about the Pitzer acentric factor has proved to improve the predicting abilities of the *Corresponding States Principle* for the entire n -alkane series, particularly for the heavier components.

A list of reference systems was proposed for each property. Using this new second-order perturbation framework only one reference system should be enough to predict the entire *n*-alkane series. Since this model is mathematically able to represent the reduced property as function of the acentric factor, it is expected to interpolate/extrapolate better than the linear approach presented before.

Although this new model is presented here to predict the pure *n*-alkane properties, it shall also give better results in the prediction of mixtures, especially for asymmetric mixtures, since in those cases the property is very sensitive to the composition and the linear approach shall perform large interpolations/extrapolations.

List of symbols

A–E	correlating parameters in Eqs. (8)–(10)
MW	molecular weight
<i>P</i>	pressure (bar)
<i>R</i>	gas constant
<i>T</i>	absolute temperature (K)
<i>V</i>	molar volume (cm ³ mol ⁻¹)
<i>X</i>	thermophysical property
<i>Z</i>	compressibility factor

Greek letters

η	viscosity (mPa s)
ρ	liquid density (mol cm ⁻³)
ω	Pitzer acentric factor

Subscripts

0	spherical reference fluid
1, 2, 3	non-spherical reference fluids
c	critical property
<i>j</i>	target fluid
r	reduced property

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