Predicting the viscosity of *n*-alkane liquid mixtures based on molecular description

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Abstract

A new model has been developed to predict the viscosity of liquid, *n*-alkane mixtures. It represents a mixture by a single pseudo-component characterized by an appropriate molecular weight and calculates the viscosity by means of the modified, extended hard-sphere model (EHS) that makes use of an universal function relating reduced viscosity to reduced volume. For mixtures that contain *n*-alkanes with a similar number of carbon atoms, the molecular weight of the pseudo-component is simply given by the molecular weight of the mixture. For more asymmetric mixtures, the choice of the molecular weight is a function of the difference in the number of carbon atoms, between the longest and the shortest chain. The proposed model is a precursor of a new family of models that do not require the knowledge of detailed composition of the mixture, but still take advantage of the underlying molecular description. The developed model, named 1-component Extended Hard-Sphere (1-cEHS), predicted, in general, the viscosity of binary and multicomponent *n*-alkane mixtures with uncertainty of 5%, even when the mixtures contain very long *n*-alkanes. For highly asymmetric binary mixtures of alkanes the predictions deteriorated, but improved for highly asymmetric multicomponent mixtures indicating that the presence of the intermediate alkane species leads to a better prediction.

We have also tested two other viscosity models, the extended hard sphere (EHS) and Vesovic-Wakeham (VW), that also rely on kinetic theory to provide the molecular description, but require a full compositional specification of the mixture. They can also predict the viscosity within 5%, but the presence of the long chain *n*-alkanes in a mixture as well as the high asymmetry, leads to deterioration of the prediction.

Keywords

Alkanes; Hard-Sphere Theory; Liquid; Viscosity; Mixtures

1. Introduction

In numerous industrial applications that involve the flow of fluids, knowledge of the viscosity is an essential pre-requisite for good design and optimal operations [1,2]. The plethora of conditions and fluids of interest, primarily mixtures, precludes relying on experimental means alone. The experimental data has to be supplemented by models that can predict the viscosity of fluids as a function of temperature, pressure and composition. The development of generic, predictive models is best achieved if such models have some basis in the underlying physical theory. This ensures reliability and accuracy with well-defined estimates of uncertainty that are essential for any engineering applications. For dilute gases, where only the binary molecular interactions are present, it is possible not only to establish a rigorous molecular description of the viscosity, but also to make use of it to compute the viscosity directly from precise, ab initio intermolecular potentials. At low pressure, in the limit of zero density, we are now in position to calculate the viscosity of gases consisting of simple molecules, both pure and mixtures, with an uncertainty commensurate with the best experimental measurements over a wide temperature range [3–9].

The situation for liquids is markedly different as the underlying theory of viscosity is incomplete. Consequently a number of different approximate approaches have been taken to model viscosity resulting in numerous models available in literature. They range from the purely empirical and correlative, where the experimental data used govern both the form and predictive power of the model, to semi-theoretical, where approximations made allow for sufficient simplification. Although kinetic theory would be a natural choice for the development of the theoretical basis, a lack of a proper generalization of the Boltzmann equation for liquids has hampered progress and led to other formulations based on approaches that do not necessarily take molecular description as the starting point. Successful viscosity models have been proposed based on the corresponding states theory [10–17], free-volume concept [18–21], the friction theory [22–26], the relationship with

residual entropy [27–30], density scaling [31–33], the effective carbon number approach [34,35] and the expanded fluid based approach [36–38] among others.

In this work we limit our investigation to modelling viscosity of liquids based on a molecular approach using the kinetic theory as our starting point. For liquids and dense fluids in general the only tractable solutions developed to date are based on the assumption that the molecules interact as hard spheres and that their collisions are uncorrelated. The resulting Enskog equation [39] for the viscosity of a dense hard-sphere fluid has formed the basis for several semi-theoretical approaches, two of which in particular have found practical application: the Assael and Dymond (AD) approach [40,41] and the Vesovic-Wakeham (VW) model [42–45]. The former was initially developed for pure species and subsequently extended to mixtures, while the latter is the model for predicting the mixture viscosity based on the knowledge of the viscosity of pure species making up the mixture. In line with most methods for predicting the thermophysical properties, both models make use of mixing rules to evaluate a limited number of mixture parameters. Although the VW mixing rules are theoretically based, unlike the AD ones and most others used in viscosity models, one still requires a detailed composition of the mixture. For compositionally well-defined mixtures this is not an issue, as this is a readily available information. However, for most fluids of industrial interest (oil, heavier refinery fractions, coal liquids, pharmaceutical) that may contain a large number of components, isomeric species or ill-defined large species, this is not the case. In this instance a different formulation is required which forfeits the full compositional formulation and usually relies on describing the mixture in terms of pseudo-components.

Here, we present a novel molecular model that represents the viscosity of the multicomponent mixture by a viscosity of a single pseudo-component which is characterized by an appropriate molecular weight. The model is based on the extended hard-sphere (EHS) approach [46,47], and hence retains the best available description in terms of the underlying

molecular theory. It is important to point out that in this work we use the term pseudo-component in its most generic form implying not a real component, used to simplify the compositional description of the mixture. The concept of the single pseudo-component used here is thus different from concepts with pseudo-components as used in oil and gas processing (sub-surface and surface) or product design and development where the pseudo-component applications are not solely based on molecular weight and are often used for estimation of a wider range of properties. A number of empirical methods [34,35] have also used a single pseudo-component concept, defined by an effective carbon number rather than molecular weight, to predict the viscosity of oil and coal liquids with some success, but require at least a single viscosity measurement to obtain the effective carbon number.

We have tested the proposed model by validating it against a data set consisting of viscosity of liquid, *n*-alkane mixtures and have compared its performance to the performance of the EHS and VW models, the other two viscosity models that have basis in kinetic theory. The choice of *n*-alkane mixtures as a first test of the validity and accuracy of the proposed model was made for a number of reasons. Normal alkanes are one of the important classes of constituents of oil and are ubiquitous in petroleum and chemical processes. There exist numerous experimental viscosity data for *n*-alkane mixtures of low uncertainty, covering wide range of mixture composition and to a certain extent temperature and pressure. Presence of long-chain *n*-alkane species in the mixture will increase viscosity significantly, thus providing a stern test of the models. Normal alkanes structurally resemble long chains made up of ($-CH_2$) units and thus are ideal to test the usefulness of models consisting of chain-like molecules that are predominantly used in Molecular Dynamics simulations. Finally, *n*-alkanes are usually used as a precursor to developing models to predict the viscosity of fluids encountered in the petrochemical and chemical industries, where more complex molecular structures of hydrocarbon or non-hydrocarbon species may prevail.

In section 2 we summarize the EHS model focusing on its most relevant features and use it as the basis for presenting the new model for mixtures. We complete the section by briefly summarizing the VW model. In section 3 we compare the three models in their ability to predict the viscosity of liquid mixtures, containing *n*-alkane species. The comparison covers, binary mixtures, multicomponent mixtures, mixtures containing long-chain *n*-alkanes, and mixtures containing light *n*-alkanes.

2. Methodology

2.1 The Extended Hard-Sphere Model with traditional mixing rules

The recently proposed extended hard-sphere model [46,47] is the latest modification of the original hard-sphere model of Assael, Dymond and their collaborators [40,41]. The original method was developed to predict the viscosity of pure fluids by postulating that the reduced viscosity, η^*, is an universal function of the reduced molar volume, $V^* = V_m/V_0$. In applications to real fluids the molar core volume, V_0, is a weakly temperature-dependent adjustable parameter. Recently, a slight modification of the extended hard-sphere model [47] was proposed in order to ensure that the model can adequately describe the viscosity of pure, long chain *n*-alkanes up to tetratetracontane (*n*-$C_{44}H_{90}$) within ±5 % at atmospheric pressure and temperatures below 400 K. As this model forms the basis of the developments presented in this work, we will briefly summarize its main features.

The essence of the model is the universal correlation of the form,

$$\log_{10}(1+\Delta\eta^*) = \sum_{i=1}^{7} a_i/(V^*)^i \quad , \tag{1}$$

where the coefficients a_i are given in the original work. The reduced excess viscosity, $\Delta\eta^*$, is defined by Ciotta et al. [46],

$$\Delta\eta^* \equiv \frac{16}{5}(2N_A)^{1/3}\left(\frac{\pi}{MRT}\right)^{1/2} V_m^{2/3}\left(\frac{\eta-\eta^{(0)}}{R_\eta}\right), \tag{2}$$

where V_m is the molar volume, M is the molar mass, N_A is Avagadro's constant, R is the gas constant, R_η is the roughness factor and $\eta^{(0)}$ is the zero-density viscosity. For *n*-alkanes the molar core volumes are represented by the following empirical correlations in terms of temperature T and carbon number n for *n*-hexane to *n*-tetratetracontane [46,47],

$$V_o\ (cm^3.mol^{-1}) = 117.874 + 0.15(-1)^n - 0.25275\,\theta + 0.000548\,\theta^2 \\ -4.246\times10^{-7}\theta^3 + (n-6)(1.27 - 0.0009\,\theta)(13.27 + 0.025\,n) \quad (3)$$

where $\theta = T$/K. The temperature range of the correlations for core molar volume is limited to $110 \le T/\mathrm{K} \le 400$. The expressions for lighter *n*-alkanes (methane to *n*-pentane) are of similar form and are available in literature [40,48]. The roughness factor is given by [47],

$$R_\eta = 0.995 - 0.0008944n + 0.005427n^2 \qquad n < 17, \quad (4)$$

$$R_\eta = 2.6380 + 0.157(n - 18) \qquad n \ge 17. \quad (5)$$

In order to apply the extended hard-sphere model to predict the viscosity of mixtures one requires mixing rules. Traditionally, the simple, mole average mixing rules for the molar core volume and the roughness factor, as originally proposed by Assael and Dymond [41], are utilized, namely,

$$V_{\mathrm{o,mix}} = \sum_{i=1}^{N} x_i V_{\mathrm{o},i} \quad (6)$$

$$R_{\eta,\mathrm{mix}} = \sum_{i=1}^{N} x_i R_{\eta,i}\ . \quad (7)$$

Eqs (1-5, 6-7) represent the Extended Hard-Sphere (EHS) model that has the claimed uncertainty of approximately 5% , based on the analysis of pure fluids [40,46,47]. It is worth pointing out that the EHS model [46,47] was developed using only viscosity data, unlike the original AD model [40,41] which could also predict the thermal conductivity and self-diffusion coefficients of *n*-alkanes within 5%.

2.2 The Extended Hard-Sphere Model using Molecular weight as a proxy

In order to enhance the extended hard-sphere model we postulated that what distinguishes one *n*-alkane molecule from another is its molecular weight and nothing else, as far as the

prediction of the liquid viscosity is concerned. Certainly the nature of Eqs. (1-5) would support this assumption, notwithstanding the small contribution at liquid densities of the zero-density viscosity term. Hence, we replace the need for mixing rules, Eqs (6-7), by evaluating the mixture viscosity using Eqs (1-5) and replacing the molecular weight of a pure species by the molecular weight of the mixture ($M = \sum_i^N x_i M_i$).

The use of molecular weight of a mixture as a proxy yields a good agreement between predicted and experimental values, as will be demonstrated later, but deviations increase with increasing asymmetry of the mixture. Hence, we propose a slight modification to the evaluation of the roughness factor as shown by the following equations,

$$R_\eta = (0.995 - 0.0008944n + 0.005427n^2)\left(\frac{M_{\text{av.}}}{M}\right)^{0.15} \qquad n < 17\ , \tag{8}$$

$$R_\eta\ =\ (2.6380 + 0.157(n - 18))\left(\frac{M_{av.}}{M}\right)^{0.15} \qquad n\ \geq 17\ , \tag{9}$$

where $M_{\text{av.}}$ is defined as,

$$M_{\text{av.}} = \left(\sum_i^N x_i M_i^\alpha\right)^{1/\alpha} \tag{10}$$

and *n* is calculated from the average molecular weight, $M_{\text{av.}}$, by using a standard relationship between the number of carbon atoms and the molecular weight of *n*-alkane,

$$n\ = (M_{\text{av.}} - 2.01588)/14.02658\ . \tag{11}$$

The parameter α in Eq. (10) is given by,

$$\ln \alpha\ =\ (\Delta C)^k\ \ln\ (\Delta C)\ ,$$

$$k\ =\ -0.5 \quad \Delta C\ \leq 30\ , \tag{12}$$

$$k\ =\ -0.25 \quad \Delta C\ > 30\ ,$$

where ΔC, which takes into account the asymmetry of mixture, is the difference of the carbon number of the largest and the smallest species of the mixture. We note that the second term in Eq. (3), can only be evaluated for integer values of *n*. Hence, when application of Eq. (11) results in a non-integer value of *n*, we round-off to the nearest integer in order to evaluate $(-1)^n$ term. For values of $\Delta C < 5$ the roughness factor obtained using Eqs. (8) and (9), is numerically approximately the same as the one obtained from Eqs. (4) and (5). Eqs (1-3, 8-12) represent the new model which we term 1-component Extended Hard-Sphere (1-cEHS) model.

As no mixture data were used to tune Eqs. (8-12) nor does the equation contain any adjustable parameter, this model, like the previous one, is fully predictive.

2.3 The VW model

The VW method [42–45] has been developed to evaluate the mixture viscosity. It is founded on the kinetic theory of the hard-sphere fluid [39] and has been recently extended to incorporate the shape of the molecules by representing them as chains of equally-sized, tangentially-joined, rigid spherical segments [44,45]. It is assumed that the collision dynamics in such a fluid can be approximated by instantaneous binary collisions involving spherical segments belonging to different chains. In its most advanced form the VW model takes Enskog formulation for a pure fluid [39] as its starting point and represents the viscosity of each species making up the mixture as,

$$\eta_i = \tilde{\eta}_i^{(0)}\left[\tilde{\chi}_i^{-1} + \tilde{\alpha}_i\tilde{\rho} + 1.205\tilde{\alpha}_i^2\,\tilde{\chi}_i^2\tilde{\rho}^2\right], \tag{13}$$

where ρ is the molar density and $\eta^{(0)}$ is the viscosity in the limit of zero density. The quantity χ is the radial distribution function at contact, while α is a parameter proportional to the excluded volume per molecule. The symbol tilde is used to indicate that each quantity is

defined for a segment, rather than a molecule. The interested readers are referred to Ref. [45] for a detailed exposition of the VW model. Here, for brevity we summarize just the main features of the model. In order to render the Enskog formulation viable for the description of the real fluids, the VW method treats the radial distribution function of each species in the mixture as adjustable. It obtains the value of $\tilde{\chi}_i$, as a function of temperature and density, by ensuring that Eq. (13) reproduces the viscosity of each pure species constituting the mixture of interest. By constraining the radial distribution function to be a continuous, monotonically increasing function of density, it is possible to obtain a unique and internally consistent value of parameter $\tilde{\alpha}_i$ at each temperature of interest [44,45]. It is important to stress that although $\tilde{\alpha}_i$ and $\tilde{\chi}_i(\rho)$ determined in this fashion are unique, they are effective parameters. In the process of using them to reproduce the viscosity of each species, the link between the two, in terms of the hard-sphere diameter, has been broken. In essence, the VW method postulates that in order to reproduce the experimental viscosity by means of a hard-sphere model one needs to use one effective size of the molecule for the excluded volume and another for the collisional dynamics [49].

In order to be able to calculate the viscosity of a mixture, we need to relate the properties of the pure species to those for the mixture. In the VW model this is achieved by making use of mixing rules that are thermodynamically consistent and based on the expressions for the hard sphere fluid [43,45]. No empiricism is introduced at the level of mixing rules and consequently the VW method has no adjustable parameters and requires no dense mixture viscosity data. However, it does require the knowledge of viscosity of each pure species. In line with the previous work we have used published correlations for *n*-alkanes for this purpose [50–54]. For *n*-alkanes where no accurate and reliable correlations are available, we have made use of the recent generic method specifically developed for long *n*-alkanes [47]. The claimed uncertainty of the VW model for liquid mixtures is of the order of 5% [43,45].

3. Results and Discussion

In this section, we evaluate the new model (1-cEHS) by validating it against extensive data on the viscosity of *n*-alkane mixtures. Simultaneously, we reassess the VW model and validate the EHS model that has not been tested previously for mixtures. The evaluation is performed using the data sets that pertain to binary and multicomponent mixtures, as well as data sets that contain long-chain and light *n*-alkanes.

3.1 Binary mixtures

Literature search indicated that the viscosity of binary *n*-alkane mixtures has been measured for at least 146 different systems, providing ample data for validation purposes. The available data set consists of approximately 4483 data points covering a range of temperature (100 – 473 K) and pressure (0.1 – 506 MPa). Unsurprisingly, the vast majority of the measurements have been reported at atmospheric pressures and near room temperature. We start our analysis by examining the capability of the three models to predict the viscosity of liquid binary mixtures at ambient pressure. For this purpose we have collated the data measured by Aucejo et al. [55], Cooper and Asfour [56], Chevalier et al. [57] and Wu et al. [58] that consists of 747 data points that cover the temperature range from 293 to 313 K. We have supplemented this data set by the measurements of Knapstad et al. [59], Dixon [60], Trevoy and Drickamer [61], and Wakefield et al. [62,63] to enlarge the range of temperature in the evaluation, (288 to 338 K). The overall data consists of all possible binary mixtures, consisting of *n*-alkanes ranging from *n*-pentane to *n*-hexadecane, apart from: (i) *n*-$C_{13}H_{28}$ with *n*-C_5H_{12} to *n*-C_7H_{16} and *n*-C_9H_{20}; (ii) *n*-$C_{14}H_{30}$ with *n*-C_5H_{12} and *n*-$C_{11}H_{24}$; (iii) *n*-$C_{15}H_{32}$ with *n*-C_5H_{12} to *n*-C_7H_{16}, *n*-C_9H_{20} and *n*-$C_{12}H_{26}$; (iv) *n*-$C_{16}H_{34}$ with *n*-$C_{13}H_{28}$ and *n*-$C_{15}H_{32}$. Inclusion of the other available measurements [64–70] would neither increase the temperature range nor provide data on a new binary mixture. Furthermore, our analysis indicates that some of these measurements can be shown to exhibit deviations larger than expected when compared with other researchers data on the same mixtures.

The average and maximum deviations in predicting the viscosity by the three models (1-cEHS, EHS and VW) are summarized in Table 1. As the overall data set consists of 90 mixtures, we have presented the analysis based on the value of the parameter ΔC, which takes into account the asymmetry of mixture, and as discussed previously is the difference between the carbon number of the largest and smallest species in the mixture.

Table 1. Comparison of the prediction of the viscosity of binary mixtures at atmospheric pressure by using three models.

ΔC	N	$T_{min} - T_{max}$, K	1-cEHS		EHS		VW	
			AAD[a] %	MD[b] %	AAD[a] %	MD[b] %	AAD[a] %	MD[b] %
1	117	293 - 298	2.1	6.2	2.3	6.0	1.3	-4.5
2	153	293 - 333	1.7	4.6	2.0	4.7	1.2	-4.2
3	110	293 - 313	1.9	4.2	2.1	4.1	1.1	-3.6
4	90	293 - 313	1.4	3.5	1.7	4.6	1.6	-5.9
5	84	293 - 335	1.5	-5.2	1.5	3.6	2.1	5.7
6	71	288 - 323	1.2	-4.3	1.6	4.1	2.8	6.6
7	54	293 - 335	1.4	-6.0	1.3	2.8	3.4	6.5
8	30	298 - 338	1.0	2.8	1.8	4.2	3.6	7.3
9	15	298 - 335	1.5	-5.2	1.3	-3.3	4.9	8.0
10	14	293 - 333	3.3	-4.5	0.8	-1.9	6.3	10.3
11	9	298 - 298	7.4	-10.5	2.2	-3.9	5.1	7.1
	747		***1.7***	***-10.5***	***1.8***	***6.0***	***2.0***	***10.3***

[a] AAD, The Average Absolute Deviation=$^{100}/_{N}\sum|(\eta_{cal}-\eta_{exp})/\eta_{exp}|$; [b]MD – Maximum deviation

The results in Table 1 indicate that all three models are capable of representing the viscosity of binary mixtures at atmospheric pressure equally well with Average Absolute Deviation (AAD) of 1.7-2.0%. Based on the data in Table 1 alone, the bias of 1-cEHS, EHS and VW model is 0.8%, 1.6% and 0.9%, respectively, while the overall uncertainty, estimated as the combined expanded uncertainty with a coverage factor of 2, is 4.1%, 4.1%, 5.6%, respectively. This is in line with the claimed uncertainty, of approximately 5%, of the VW and EHS models.

As a way of example, Figures 1 and 2 show the deviations in predicting the viscosity measured by Aucejo et al. [55] by means of the VW model and 1-cEHS model. The deviations for data of other workers and for the EHS model follow the similar pattern. As illustrated in Figure 1 and highlighted before by de Wijn et al. [45], for mixtures with high asymmetry ($\Delta C > 9$) the accuracy of the VW model deteriorates. We observe a similar trend for 1-cEHS model, (see Figure 2), but in this case only the deviations for C_5H_{12}-$C_{16}H_{34}$ mixture are outside the 5% range, exhibiting a maximum deviation and bias of 10.5% and -7.4%, respectively. The deviations produced by means of the EHS model exhibit a very weak dependence on an asymmetry of the mixture with maximum deviation and bias of 3.9% and -2.1%, respectively for C_5H_{12}-$C_{16}H_{34}$ mixture.

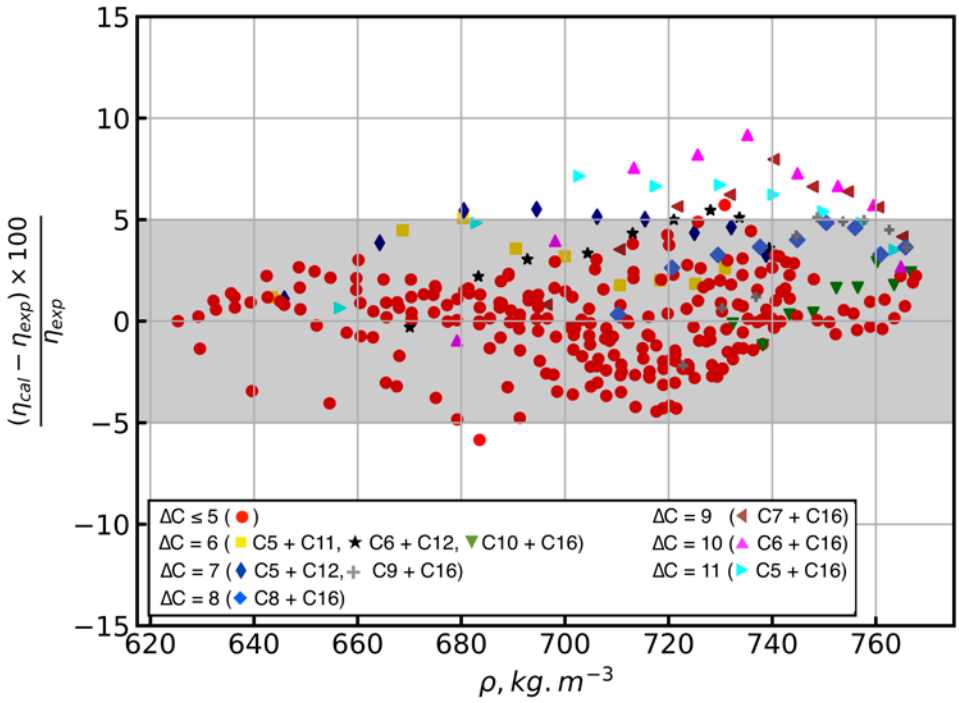

Figure 1. Percentage deviations $\left[100\left(\eta_{\mathrm{cal}}-\eta_{\mathrm{exp}}\right)/\eta_{\mathrm{exp}}\right]$ of the experimental data measured by Aucejo et al. [55] from the calculated values by means of the VW model as a function of density. For convenience we have used the notation Cn to represent *n*-C_nH_{2n+2} alkane.

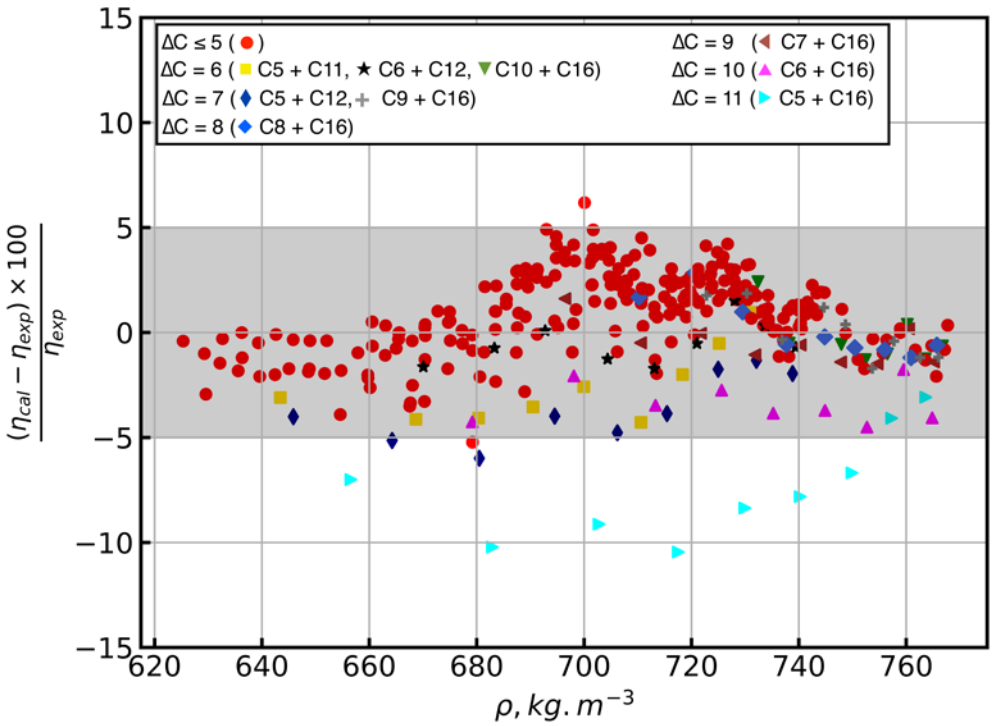

Figure 2. Percentage deviations $\left[100\left(\eta_{\mathrm{cal}} - \eta_{\mathrm{exp}}\right)/\eta_{\mathrm{exp}}\right]$ of the experimental data measured by Aucejo et al. [55] from the calculated values by means of the 1-cEHS model as a function of density. For convenience we have used the notation Cn to represent *n*-C_nH_{2n+2} alkane.

It is well-known that the viscosity can be very sensitive to the value of the density [1], especially in regions of the phase space where the viscosity increases rapidly with the density. However, even at ambient conditions the uncertainty in density can lead to large changes in viscosity. Figure 3 illustrates the viscosity deviations for (*n*-C_5H_{12} + *n*-C_8H_{18}) mixture measured by Baruffet et al. [71] who did not measure density as part of the experiment. If the densities are estimated using Refprop [72], the viscosity predicted by for instance the VW model, deviates by as much as 15.4%, from the experimental values, while if the densities are estimated by assuming that the mixture is ideal, the largest absolute deviation is approximately 8.5%. If however, the densities are estimated using the density measurements reported by Aucejo et al. [55], who measured the same mixture at nearly the same conditions, the predicted viscosity is within 3% of the experimental value. This is considerable improvement, bearing in mind that the difference between two ways of

estimating density is not larger than 1.6% and 3.1% for ideal mixture and Refprop, respectively. The result highlights the importance of supplementing the viscosity models with thermodynamic models capable of accurately estimating the mixture density.

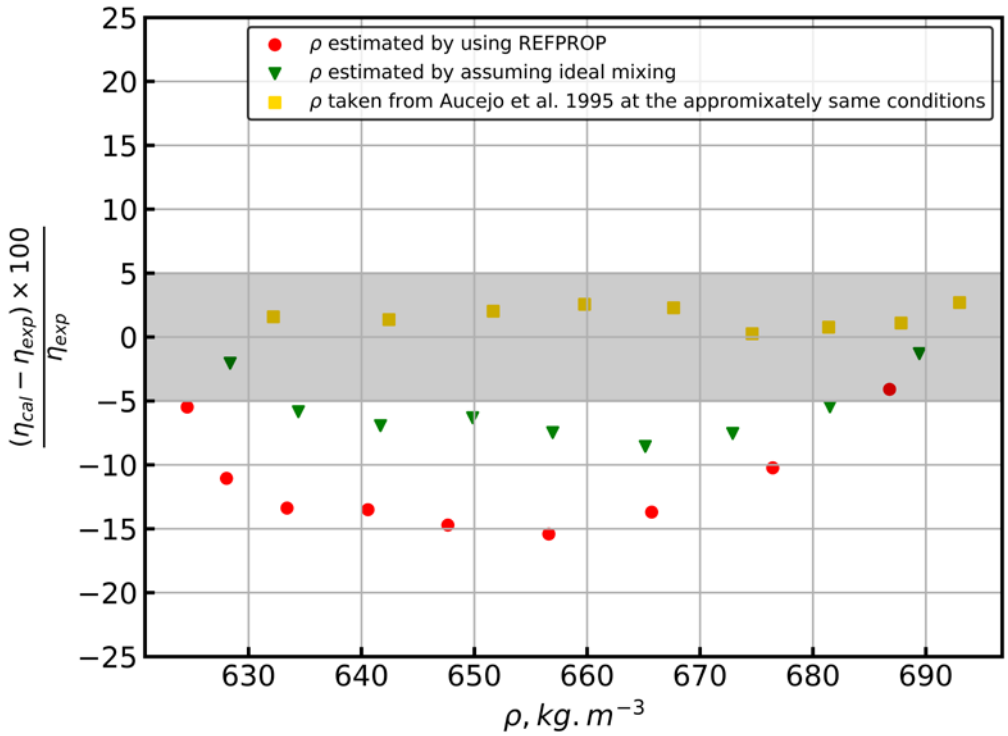

Figure 3. Viscosity deviations of *n*-C_5H_{12} + *n*-C_8H_{18} mixture from Barrufet measured data [71] with the use of different density values. The viscosity is estimated by using the VW approach.

At pressures higher than ambient only a few workers have measured the viscosity of liquid binary mixtures [71,73–83]. Based on our analysis of the available data we have limited further consideration to data measured by Assael et al. [74,75], Dymond et al. [78–80], Caudwell et al. [76] and Peleties [83]. These data were all measured in what are considered to be primary instruments [84], the experimental density data have been reported and the other viscosity data measured in the same viscometers agree well with the mixture data measured by other workers at ambient conditions and with the reference viscosity correlations for pure species. Assael et al. [74,75] have performed the measurements of the viscosity of (*n*-C_6H_{14} + n-C_7H_{16}), (*n*-C_7H_{16} + *n*-C_9H_{20}), (*n*-C_7H_{16} + *n*-$C_{10}H_{22}$) and (*n*-C_7H_{16} + *n*-$C_{11}H_{24}$) mixtures in the vibrating wire viscometer in the temperature range (288 - 333 K) and

pressure up to 72 MPa. Caudwell et al. [76] and Peleties [83] have performed the measurements on (n-C_8H_{18} + n-$C_{12}H_{26}$) mixture, also using the vibrating wire viscometer, in the temperature range (323 - 423 K) and (298 - 447 K), respectively and pressures up to 200 MPa. Dymond et al. [78–80] performed extensive measurements on (n-C_6H_{14} + n-$C_{12}H_{26}$), (n-C_6H_{14} + n-$C_{16}H_{34}$) and (n-C_8H_{18} + n-$C_{12}H_{26}$) mixtures using falling body viscometer in the temperature range (298 - 373 K) and pressures up to 500 MPa. The uncertainty of the measured viscosity values is in the range 0.5 – 2.0%, as quoted by the authors.

In order to help with the analysis we have divided the data in three pressure ranges: (i) 0.1-75 MPa; (ii) 75 - 200 MPa and (iii) above 200 MPa. Both EHS and 1-cEHS models are based on the general expression for V_0, Eq. (3), that is valid for n-alkanes in the range n-C_6H_{14} – n-$C_{44}H_{90}$. It has been observed [47] that as the pressure increases above 30-75 MPa, the viscosity prediction of the EHS model, with the general expression for V_0, deteriorates. Unlike the EHS model with individual V_0 correlations [46] which is accurate up to higher pressures. In order to avoid this particular deficiency of the EHS and 1-cEHS model adversely affecting the validation procedure the analysis is performed in two different pressure ranges. The reason for considering data in the third pressure range ($P \geq$ 200 MPa) separately, is driven by the requirements of the VW model that uses pure species viscosity as input. For some of the species present in the mixtures of interest, namely n-C_8H_{16} and n-$C_{12}H_{26}$ the recommended correlations [53,54] only extend up to pressures of 200 MPa. Hence, the need to limit the analysis of the mixture data, by the VW model, to pressures below this value.

Table 2 summarizes AAD and MD obtained by the three models, for binary mixtures where the data were measured below 75 MPa. The good agreement, within approximately 5% claimed uncertainty, is observed for all three models, apart from the predictions of the VW model for the system (C_6H_{14} + $C_{16}H_{34}$) with the highest asymmetry (ΔC = 10) where we

observe a systematic bias of 6.3% and MD of 13.9%. It is interesting to note that the extrapolation of 1-cEHS and EHS models to higher temperatures (T > 400 K) does not seem to adversely affect their predictions.

Table 2. Comparison of the prediction of the viscosity of binary mixtures at pressure below 75 MPa by using three models.

	No. of data	$T_{min} - T_{max}$, K	1-cEHS		EHS		VW	
			AAD %	MD %	AAD %	MD %	AAD %	MD %
C6-C7[a] [74]	63	288 - 323	1.8	-2.4	1.5	-2.1	0.9	-1.5
C7-C9 [74]	66	293 - 333	1.1	2.8	1.0	-2.3	2.2	-3.0
C7-C10 [85]	61	291 - 323	0.6	-1.6	0.8	-1.9	3.6	-5.4
C7-C11 [75]	68	297 - 332	0.9	-1.9	1.5	-3.3	1.4	-3.3
C8-C12 [76]	23	323 - 423	1.7	3.0	2.4	4.3	2.0	-3.5
C8-C12 [83]	21	298 - 447	1.4	-2.6	1.8	3.6	1.6	-4.2
C8-C12 [78]	9	298 - 373	1.8	-4.0	2.0	-3.8	1.8	3.2
C6-C12 [78]	6	298 - 373	3.7	-6.9	2.1	-3.5	3.1	-6.9
C6-C16 [79]	28	283 – 378[b]	1.5	-2.5	1.1	4.0	6.0	13.5
C6-C16 [80]	77	298 - 373	1.9	-8.1	1.6	-6.8	6.5	13.9
	422	***283 - 447***	***1.4***	***-8.1***	***1.4***	***-6.8***	***3.1***	***13.9***

[a]For brevity we use abbreviation Cn to indicate *n*-C_nH_{2n+2}; [b]saturation line

Table 3 summarizes AAD and MD obtained by the three models, for binary mixtures for the data measured above 75 MPa. We observe that the VW model predicts the viscosity data at high pressure within its claimed uncertainty of 5%, notwithstanding already discussed deterioration for systems of high asymmetry. The 1-cEHS and EHS models exhibit

progressively worsening predictions as the pressure increases or for temperatures above 400 K. This indicates that the universal correlations, Eq (1), would require further refinement for high densities, especially if it is to be used in conjunction with generic expressions for V_0.

Table 3. Comparison of the prediction of the viscosity of binary mixtures at pressure above 75 MPa by using three models.

	No. of data	$P_{min} - P_{max}$, MPa	1-cEHS		EHS		VW	
			AAD %	MD %	AAD %	MD %	AAD %	MD %
C8-C12 [76]	38	79 – 201[a]	3.6	-7.3	1.7	-5.9	1.1	-2.2
C8-C12 [76]	14	79 – 201[b]	5.5	-10.1	4.1	-9.0	1.1	2.3
C8-C12 [83]	12	100 – 137[c]	2.5	-4.4	1.9	3.4	1.2	2.3
C8-C12 [83]	4	100 – 137[d]	5.2	-6.2	3.4	-4.3	0.6	1.0
C8-C12 [78]	11	94 - 197	3.4	-10.8	2.9	-10.4	3.0	3.9
C8-C12 [78]	18	202 - 505	8.0	21.5	8.0	23.2	-	-
C6-C12 [78]	7	96 - 177	10.2	-12.7	6.1	-9.8	1.0	2.0
C6-C12 [78]	11	203 - 455	12.8	-17.4	8.7	-13.5	-	-
C6-C16 [80]	38	77 - 199	5.5	-10.8	3.0	-8.6	3.9	10.8
C6-C16 [80]	44	201 - 502	7.1	18.6	5.8	24.7	-	-
	197	***77 - 505***	***6.0***	***21.5***	***4.3***	***24.7***	***2.1***	***10.8***

[a] $323 \leq T/K \leq 373$; [b] $T/K = 423$; [c] $298 \leq T/K \leq 398$; [d] $T/K = 447$;

3.2 Liquid multicomponent mixtures

Table 4 summarizes, to the best of our knowledge, the experimental measurements of the viscosity of multicomponent *n*-alkane mixtures reported in the literature, [63,76,79,86–94] detailing the temperature and pressure ranges, number of data points measured, and the technique employed to perform the measurements. We have restricted the data to

encompass only investigations where the density is reported alongside the viscosity, in order to avoid uncertainties due to density prediction. However, we have not eliminated the data obtained in non-primary viscometers, as we did when we dealt with the binary mixtures, in order to retain the widest possible choice of mixtures in the validation data set. Overall, the data set contains measurements on 15 mixtures consisting of 233 data points covering a wide range of temperature (288 – 448 K) and pressure (0.1 – 160 MPa).

Table 4. Summary of the experimental viscosity data on multicomponent *n*-alkane mixtures

Systems	Technique employed[a]	No. of data	$T_{min} - T_{max}$, K	$P_{min} - P_{max}$, MPa	Ref.
C3 + C8 + C12	VWire	53	323 – 373	20 – 103	[76]
C6 + C7 + C8 + C12	VWire	36	298 – 448	1.3 – 160	[91]
C6 + C8 + C12 + C16	FB	6	288 – 358	$P_{sat.}$	[79]
C6 + C8 + C16	FB	11	288 – 378	$P_{sat.}$	[79]
C6 + C10 + C12 + C16	C	10	303 – 308	0.1	[63]
C6 + C14 + C16	C	15	298 – 298	0.1	[89]
C7 + C8 + C9	C	5	293 – 313	0.1	[93]
C7 + C8 + C11 + C13	C	28	293 – 313	0.1	[92]
C7 + C8 + C11 + C13 + C15	C	7	298 – 298	0.1	[92]
C7 + C8 + C12 + C16	C	10	308 – 313	0.1	[92]
C7 + C9 + C12 + C16	C	10	303 – 308	0.1	[63]
C7 + C10 + C13 + C16	C	10	308 – 313	0.1	[92]
C8 + C10 + C11 + C15	C	10	308 – 313	0.1	[92]
C8 + C11 + C13 + C15	C	10	308 – 313	0.1	[92]
C8 + C14 + C16	C	12	293 – 298	0.1	[94]

[a] *C - capillary; VWire - vibrating wire; FB - falling body.*

Figures 4-6 illustrate the deviations in predicting the viscosity of studied multicomponent mixtures for pressures below 75 MPa, by means of the 1-cEHS, EHS and VW models, respectively, while Table 5 summarizes AAD and MD obtained by using the three models.

We observe that the 1-cEHS model predicts most of the data within 5% with AAD of 1.3%. Only for the (C_6H_{14} + C_7H_{16} + C_8H_{18} + $C_{12}H_{26}$) mixture [91] do the predictions deteriorate, at lower density, with the maximum deviation of 8.4% (see Figure 4). For pressures higher than 75 MPa, as already discussed for binary mixtures, the predictions of the 1-cEHS model deteriorate further and the viscosity of the discussed quaternary system (C_6H_{14} + C_7H_{16} + C_8H_{18} + $C_{12}H_{26}$) is predicted with AAD of 3.1%, Bias of -2.9% and MD of -10.7%. Although this is unacceptably high, the prediction is on par with the predictions of the EHS and VW models for the same system (see Table 5).

The prediction based on the EHS model, illustrated in Figure 5, is on average worse than those by the 1-cEHS model, with AAD of 2.0%. Apart from the quaternary mixture (C_6H_{14} + C_7H_{16} + C_8H_{18} + $C_{12}H_{26}$) at low density [91], the EHS model also fails to predict the (C_3H_8 + C_8H_{18} + $C_{12}H_{26}$) mixture [76] within 5%. For pressures higher than 75 MPa, the prediction of the EHS model deteriorates further for this particular ternary mixture [76], while the prediction of the viscosity of the quaternary mixture [91] is similar to that of the 1-cEHS model.

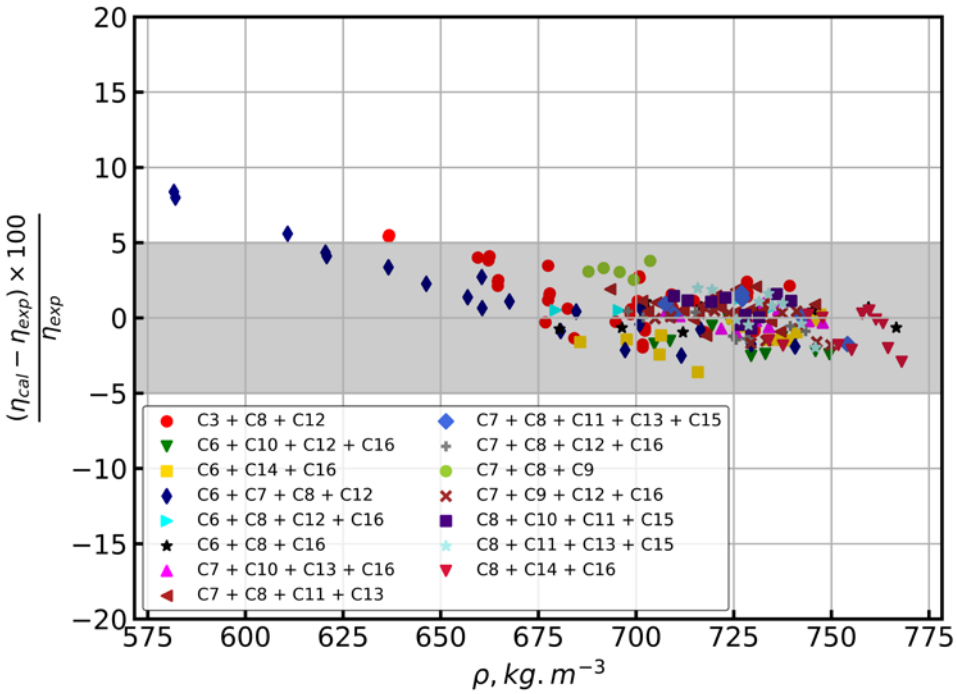

Figure 4. Percentage deviations $[100(\eta_{\text{cal}} - \eta_{\text{exp}})/\eta_{\text{exp}}]$ of the experimental data for multicomponent mixtures below 75 MPa, from the calculated values by means of the 1-cEHS model as a function of density.

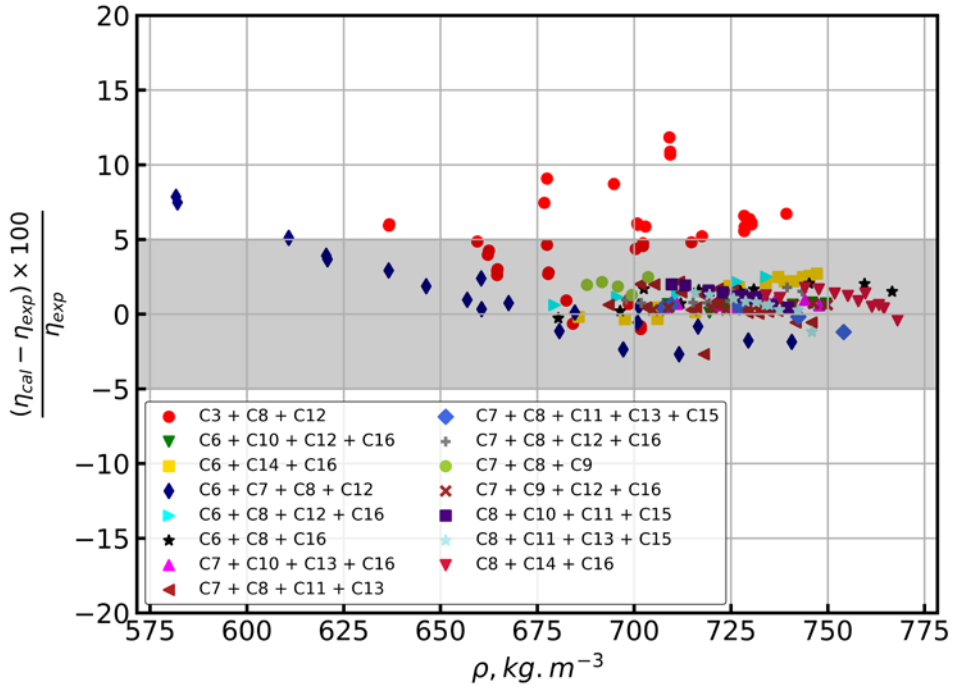

Figure 5. Percentage deviations $[100(\eta_{\text{cal}} - \eta_{\text{exp}})/\eta_{\text{exp}}]$ of the experimental data for multicomponent mixtures below 75 MPa, from the calculated values by means of the EHS model as a function of density.

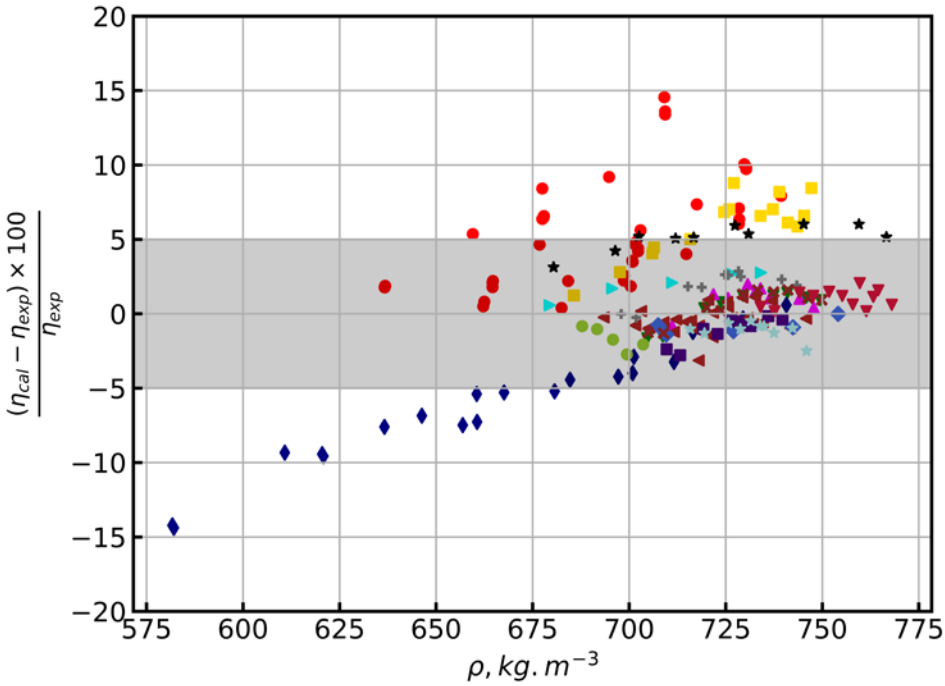

Figure 6. Percentage deviations $[100(\eta_{\mathrm{cal}} - \eta_{\mathrm{exp}})/\eta_{\mathrm{exp}}]$ of the experimental data for multicomponent mixtures below 75 MPa, from the calculated values by means of the VW model as a function of density. For the legend refer to Figure 5.

Table 5. Comparison of the prediction of the viscosity of multicomponent mixtures by using three models

Systems	No. of data	$P_{min} - P_{max}$, MPa	1-cEHS		EHS		VW	
			AAD %	MD %	AAD %	MD %	AAD %	MD %
At the pressure below 75 MPa								
	204	0.1 - 63	*1.3*	*8.4*	*2.0*	*11.8*	*3.1*	*14.6*
At the pressure above 75 MPa								
C3 + C8 + C12	13	80 – 103	1.6	2.9	6.3	14.7	12.3	19.9
C6 + C7 + C8 + C12[a]	11	80 – 155 [b]	3.1	-10.7	3.1	-10.8	4.3	-14.5
C6 + C7 + C8 + C12	5	80 – 160 [c]	1.2	-2.4	1.3	-2.7	8.5	-10.2

[a] *outlier at T= 398 K and P=157 MPa removed.* [b] *298 ≤ T/K ≤ 398.* [c] *T/K = 448*

The VW model predicts the viscosity below 75 MPa with AAD of 3.1% and while the predictions are good for systems where ΔC between successive *n*-alkanes is less than 5, for more asymmetric mixtures (C_3H_8 + C_8H_{18} + $C_{12}H_{26}$), containing higher proportion of the lightest species, deviations up to 10-15% are observed (see Figure 6).

3.3 Mixtures containing long-chain n-alkane

Table 6 summarizes the experimental measurements reported in the literature of the viscosity and density of mixtures that contain long-chain (n > 18) *n*-alkane species. All the available measurements [16,61,88,95] were carried out at atmospheric pressure in the temperature range (293 – 343 K) and consist of 215 data points. Although the asymmetry of these mixtures is high, all three models predict the viscosity reasonably well and there is no major differences between the predictions for each mixture. The AAD for this set of data for 1-cEHS, EHS and VW model is 4.5%, 4.8% and 3.8%, respectively, while the maximum deviation is between 24-27%. As a way of example, Figure 7 illustrates the deviation of experimental data from the predictions of the 1-cEHS model. We observe that the deviations increase with asymmetry and that for mixtures where ΔC > 15 they exceed 5%. The quaternary mixture (C_6H_{14} + C_8H_{18} + $C_{10}H_{22}$ + $C_{24}H_{50}$) measured by Wakefield et al. [88] shows the largest deviations which at the highest density reach -25%. The measurements at this density correspond to the mixture that contains the smallest amount of C_6H_{14} and $C_{10}H_{22}$ ($x_{C6} = x_{C10} = 0.1$). Interestingly the 1-cEHS model predicts the binary mixture (C_8H_{18} + $C_{24}H_{50}$) measured in the same apparatus and in a similar range of density within 5%. The other two models also exhibit the largest deviations for this mixture at high densities.

Table 6. Summary of the experimental viscosity data on mixtures containing long-chain *n*-alkane species

Systems	Technique Employed [a]	No. of data	T_{min} - T_{max}, K	Ref.
C7 + C18	C	3	298 – 335	[61]
C7 + C20	RB	24	293 – 343	[95]
C7 + C22	RB	19	303 – 343	[95]
C7 + C24	RB	15	313 – 343	[95]
C8 + C24	C	15	318 – 338	[88]
C10 + C20	RB	24	293 – 343	[16]
C10 + C22	RB	20	303 – 343	[16]
C10 + C24	RB	16	313 – 343	[16]
C16 + C20	RB	25	293 – 343	[95]
C20 + C24	RB	3	323 – 343	[95]
C6 + C8 + C10 + C24	C	13	318 – 338	[88]
C7 + C20 + C24	RB	20	303 – 343	[95]
C10 + C20 + C24	RB	18	303 – 343	[16]

[a] *C capillary, RB rolling-body*

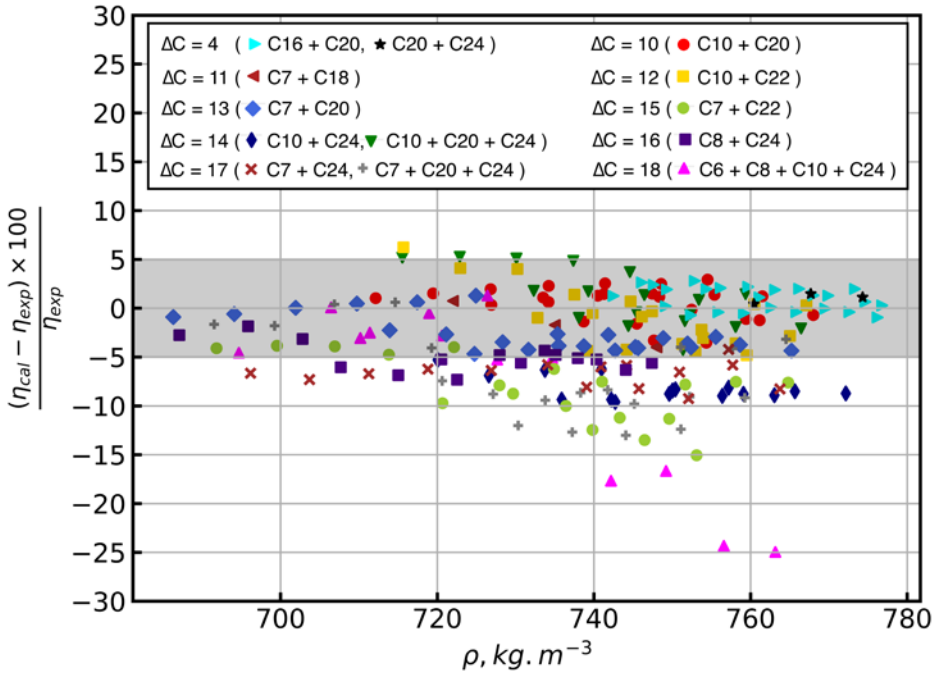

Figure 7. Percentage deviations $[100(\eta_{\mathrm{cal}} - \eta_{\mathrm{exp}})/\eta_{\mathrm{exp}}]$ of the experimental data for mixtures containing long chain n-alkanes, from the calculated values by means of the 1-cEHS model as a function of density.

Aasen et al. [96] have also performed extensive viscosity measurements of mixtures that contain the long chain *n*-alkane species. The measurements were performed in the oscillating-cup viscometer at 0.3 MPa in the temperature range (368 – 464 K) for three binary systems ($C_{10}H_{22}$ + $C_{44}H_{90}$; $C_{10}H_{22}$ + $C_{60}H_{122}$; $C_{22}H_{46}$ + $C_{60}H_{122}$), two ternary systems (C_6H_{14} + $C_{10}H_{22}$ + $C_{60}H_{122}$; $C_{10}H_{22}$ + $C_{22}H_{46}$ + $C_{60}H_{122}$) and one quinary system ($C_{10}H_{22}$ + $C_{22}H_{46}$ + $C_{32}H_{66}$ + $C_{44}H_{90}$ + $C_{60}H_{122}$). No experimental density data are reported, but the authors estimated the mixture density with the claimed accuracy of 0.5%, by assuming an ideal mixing. Based on experimental data available for mixtures listed in Table 6 we estimate that the underprediction in density introduced by neglecting the excess volume can be as high as 1%. This would result in underprediction of viscosity in the range of 4-11%, for mixtures measured by Aasen et al. [96], with the sensitivity increasing with an increase in the magnitude of viscosity.

For binary systems that are highly asymmetric we observe large deviations for all three methods. The most accurate prediction is given by the 1-cEHS model with AAD, Bias and MD of 10.7, -4.8 and -20.9%, respectively. However, for ternary and quinary mixtures which are less asymmetric, the prediction of 1-cEHS and VW models improves markedly. Figures 8 and 9 illustrate the experimental and predicted viscosity data as a function of density for ($C_{10}H_{22}$ + $C_{22}H_{46}$ + $C_{60}H_{122}$) and ($C_{10}H_{22}$ + $C_{22}H_{46}$ + $C_{32}H_{66}$ + $C_{44}H_{90}$ + $C_{60}H_{122}$), respectively. The 1-cEHS, EHS and VW models reproduce the measured data for these two mixtures with MD of -4.2%, -38% and -18%, respectively. The agreement observed for the 1-cEHS model is remarkable in view of complexity of the mixture, uncertainty in density and in measured viscosity. In no smaller measure it is a result of the proposed modification of the roughness factor, Eqs. (8) and (9), that captures very well the behaviour of the viscosity of mixtures containing long-chain *n*-alkane species.

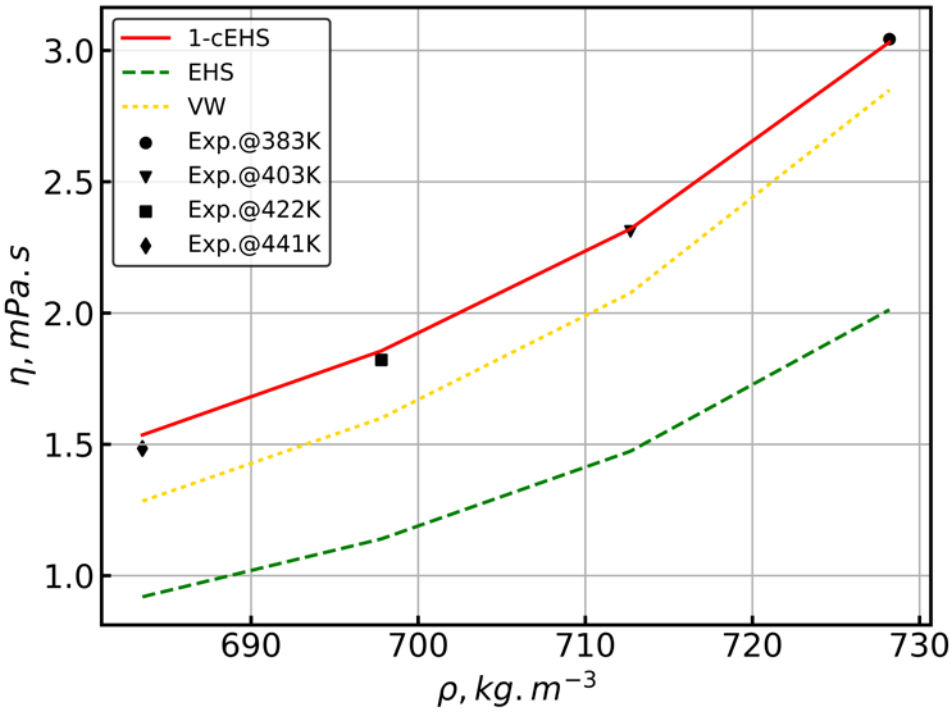

Figure 8. Comparison of the viscosity as a function of density predicted by the three models and the measured data [96] for $C_{10}H_{22}$ + $C_{22}H_{46}$ + $C_{60}H_{122}$ mixture

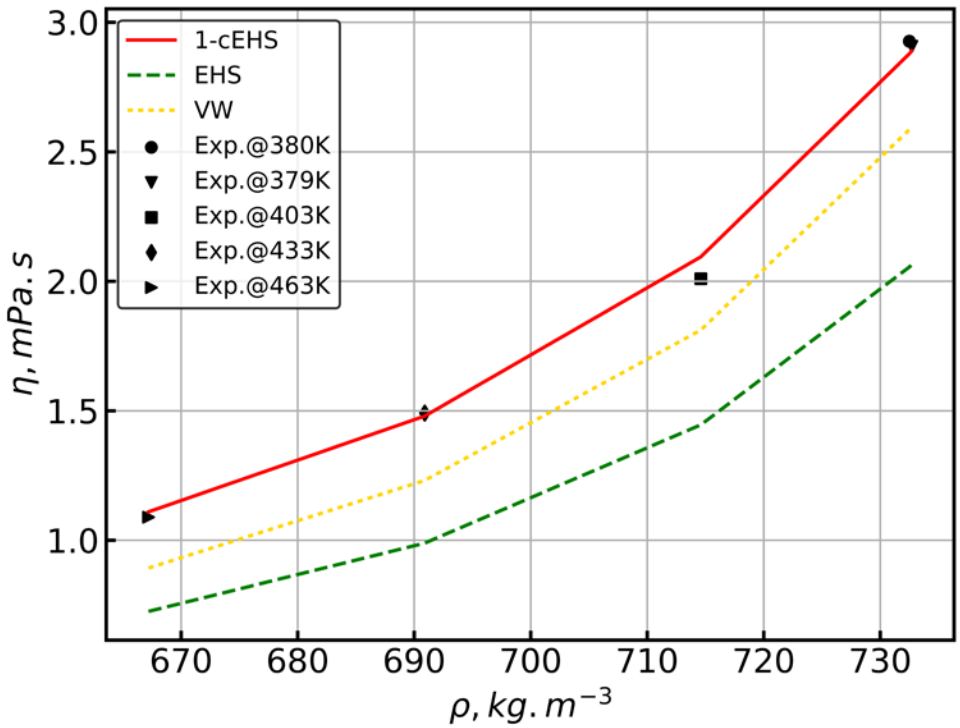

Figure 9. Comparison of the viscosity as a function of density predicted by the three models and the measured data [96] for $C_{10}H_{22}$ + $C_{22}H_{46}$ + $C_{32}H_{66}$ + $C_{44}H_{90}$ + $C_{60}H_{122}$ mixture

3.4 Binary asymmetric mixtures containing methane

As the final test of the predictive capability of the three models, we examine the viscosity of liquid mixtures whereby a small molecule is dissolved in the pure liquid which is made up of large molecules. In particular, we focus on (CH_4 + $C_{10}H_{22}$) and (CH_4 + $C_{16}H_{34}$) mixtures that are well characterized experimentally in a wide range of temperature and pressure by the number of workers [83,97–100]. Such mixtures are not only of industrial interest, but also of scientific interest as the presence of even small amount of light component can reduce the viscosity substantially [101]. The large difference in viscosity between pure components, one of them being gaseous at the mixture temperature and pressure, puts additional demands on predicting the viscosity by molecular means.

We have already reported on the prediction for (CH_4 + $C_{10}H_{22}$) mixture by the VW model. The deviations are large, with an AAD of 5.4% and MD of 14% when comparison is made with

the data of Audonnet and Padua [97]. Furthermore, we observed a systematic trend with density which indicates that refinement of the mixing rule within VW-chain model is necessary for highly asymmetric alkane mixtures of this type. The 1-cEHS model also has difficulties in predicting the experimental viscosity of this mixture, as illustrated in Figure 10, displaying an AAD of 6.6% and MD of 18%. Surprisingly, the EHS model performs rather better than the other two and reproduces the data with an acceptable AAD of 2.5% and MD of 7.2%. The comparison with the data of other authors who have measured (CH_4 + $C_{10}H_{22}$) mixture [83,98,99] shows similar trends and similar values of AAD and MD for the three models investigated.

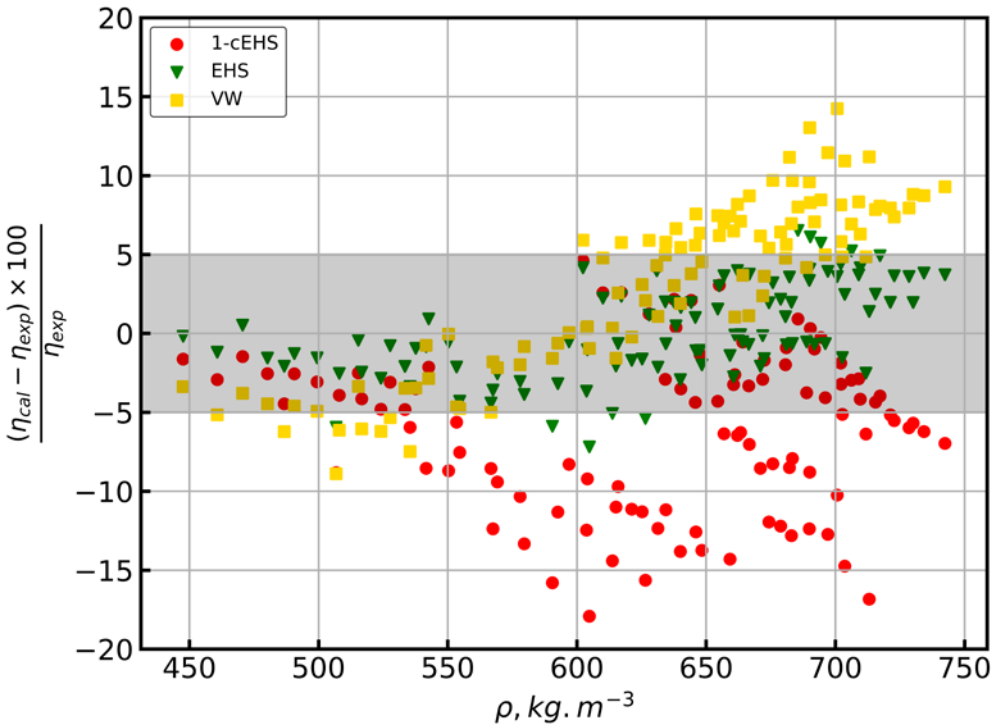

Figure 10. Percentage deviations $[100(\eta_{\mathrm{cal}} - \eta_{\mathrm{exp}})/\eta_{\mathrm{exp}}]$ of the experimental data (CH_4 + $C_{10}H_{22}$) measured by Audonnet et al. [102] from the calculated values by means of the 1-cEHS model as a function of density.

Mohammed et al. [100] performed measurements on the (CH_4 + $C_{16}H_{34}$) mixture with the vibrating wire viscometer in the temperature range (298 - 473 K) and pressure up to 80 MPa. Figure 11 illustrates the deviation of experimental data from the prediction of the three models. We have limited our analysis to temperatures below 400 K in order to test the 1-

cEHS and EHS models within their temperature range. We observe that the VW model overpredicts the measured values over the whole range of interest with the deviations increasing with the density and the mole fraction methane, reaching as high as 60%.

The 1-cEHS and EHS models perform better with AAD of 10.0 and 6.4% respectively, bias of -7.6 and 4.3%, respectively and the maximum deviation of approximately -24.0% and 16.3%, respectively. It is interesting to note that at low mole fractions of methane the 1-cEHS model performs better than the EHS model, while at the higher mole fraction the reverse is true, see Figure 11.

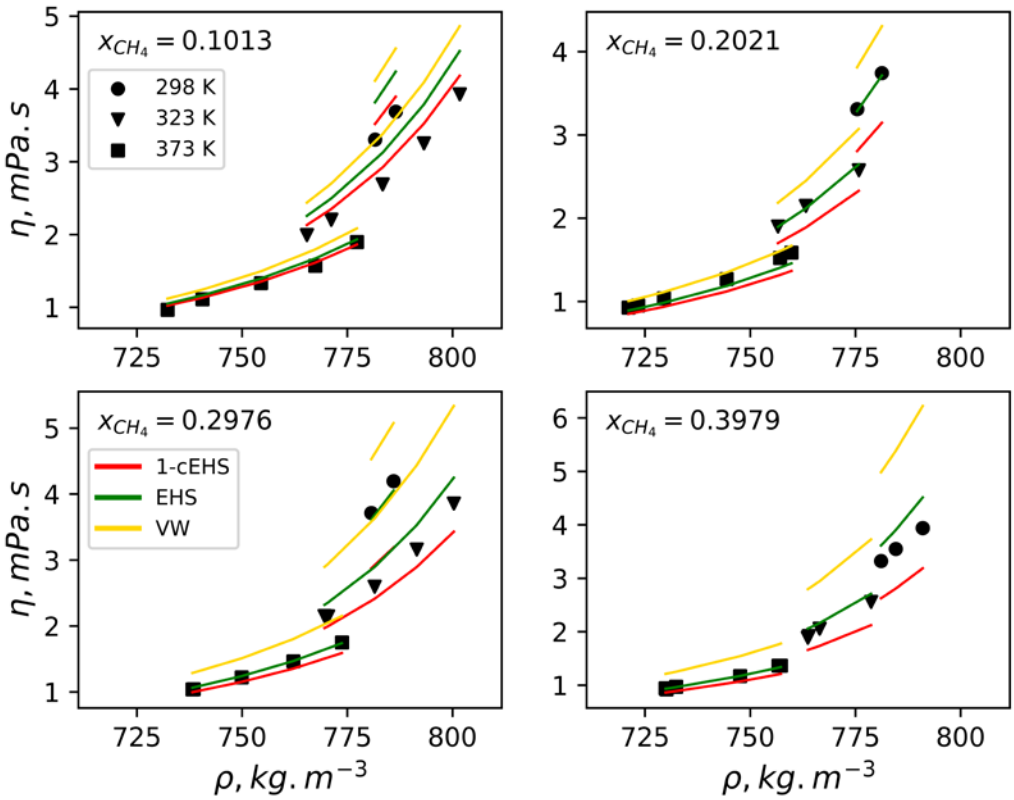

Figure 11. Comparison of the viscosity as a function of density predicted by the three models and the measured data [100] for $CH_4 + C_{16}H_{34}$ mixture

4. Conclusions

An extended hard-sphere model is used as the basis for developing the new model to predict the viscosity of liquid mixtures consisting of *n*-alkanes. We postulate in this work that the molecular weight of an *n*-alkane governs its viscosity and that the viscosity of the multicomponent mixture can be represented by a viscosity of a single pseudo-component, within the EHS model. The pseudo-component is characterized by an appropriate molecular weight. For mixtures that contain *n*-alkanes with a similar number of carbon atoms, the molecular weight of the pseudo-component is simply given by the molecular weight of the mixture. For more asymmetric mixtures, the choice of the molecular weight is a function of the difference in the number of carbon atoms between the longest and shortest chain (ΔC). Although the proposed method does not completely eliminate the need for the detailed compositional specification of the mixture, it goes a long way to setting up a model that can deal with industrially relevant fluids where the detailed composition is not available. Most of these fluids have generic relationships between the different components present which can be incorporated into procedures for estimating the molecular weight of the pseudo-component for viscosity calculations discussed herein.

The focus of the present communication was not to explore the extension of the model in this direction, but rather to validate the postulate that a single pseudo-component would suffice to represent the viscosity of the mixture. For this purpose the developed model is tested against a plethora of data that pertain to binary and multicomponent mixtures, as well as mixtures that contain long-chain and light *n*-alkanes. The developed model, named 1-component Extended Hard-Sphere (1-cEHS), predicted, in general, the viscosity of binary and multicomponent *n*-alkane mixtures with uncertainty of 5% even when the mixtures contain very long *n*-alkanes. For highly asymmetric binary mixtures with $\Delta C > 9$ the prediction deteriorates and for highest asymmetry ($\Delta C = 50$) deviations of up to 20% are observed. However, this is a perennial problem in the field of viscosity prediction and most

available methods will struggle to predict the viscosities of such mixtures, as the viscosity changes with the composition and density are rather large. Nevertheless, the prediction of the 1-cEHS model improves for highly asymmetric multicomponent mixtures, indicating that the presence of the intermediate species alleviates the problem. This bodes well for the application of the developed model to predict the viscosity of industrially relevant mixtures where intermediate species are often present. The work on testing the concepts presented in this paper for naphthenic and aromatic structural groups present in oil is currently under way.

It is prudent to currently limit the applications of the 1-cEHS model to pressure and temperature below 75 MPa and 400 K, respectively, as the universal correlation which is fundamental to the EHS model needs further modification when more plentiful data for viscosity of pure species at these conditions become available.

We have also tested the two other viscosities models (EHS and VW) that relay on kinetic theory to provide the molecular description. Both of them incorporate mixing rules and require a full compositional specification of the mixture. For binary and multicomponent mixture consisting of similar *n*-alkanes both models can predict the viscosity within 5%. For more asymmetric mixtures the VW model exhibits larger deviations than the 1-cEHS model, while the EHS exhibits a reverse trend. The inclusion of long chain *n*-alkanes causes problems for both models, with the unacceptable high deviations in some cases.

The work has also touched upon the importance of supplementing the viscosity models with thermodynamic models capable of accurately estimating the mixture density. This is an essential prerequisite for accurate viscosity predictions, especially in the regions where viscosity is sensitive to density and compositional changes.

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