Measurements and modelling of the viscosity of six synthetic crude oil mixtures

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Abstract

The viscosity and density are reported for six synthetic mixtures, composed of up to 13 components, designed to match a light, dead crude oil of API 32° and molar mass of approximately 184 $g \cdot mol^{-1}$. The measurements were made in the liquid region at temperatures between (323 and 398) K and in the pressure range from 1 MPa to 70 MPa**.** The viscosity was measured with a vibrating-wire viscometer, while the density was measured by means of a vibrating U-tube densimeter. The density and viscosity data have expanded relative uncertainties of 0.12% and 1.2%, respectively with a coverage factor of 2.

We have used the measured viscosity data to test the predictive power of the four viscosity models, the extended hard sphere (EHS), one-component EHS (1-cEHS), three-component EHS (3-cEHS) and Vesovic-Wakeham (VW), that have their basis in kinetic theory and the molecular description of the fluid. Two of the models (EHS and VW) require full compositional description of the mixture, while the other two belong to a new family of models which dispense with full compositional characterization, but retain molecular description. On average the EHS and VW models predict the viscosity data with lower deviations than 1-cEHS and 3-cEHS models, but all four models represent the data with uncertainty of 5-10%.

Keywords

Synthetic oil; Alkanes; Cycloalkanes; Alkylbenzenes; Hard-Sphere Theory; Liquid; Viscosity; Mixtures

1. Introduction

An accurate thermophysical characterization of reservoir fluids and their derivatives is an important pre-requisites for reliable and optimal operations in the petroleum industry, both in the upstream and downstream sections. One of the problems the industry faces in this regard is the variety and compositional complexity of different process streams. Reservoir fluids in particular and some of their derivatives are complex mixtures consisting of numerous species, ranging from simple *n*-alkanes and their isomers to poorly characterized asphaltenes. The situation is particularly serious for viscosity [1] as, under certain conditions encountered in petroleum exploitation and processing, it can be very sensitive to changes in temperature, density and composition, making viscosity prone to larger uncertainty than other thermophysical properties. Although it is possible to measure the viscosity of the sample of interest, the variety of conditions, issues with representative samples and ensuring reliable operations of the viscometers makes this a costly way of obtaining routine data. Furthermore, interpolating and extrapolating such data to all the conditions of interest, so that it can be used in the process and reservoir simulators, is fraught with difficulties. The current trend is to supplement carefully-measured data on selected samples with development of predictive and versatile models, that have been validated, and that can provide accurate and reliable values.

For thermodynamic properties, we have a range of tools at our disposal that are based on strong underlying fundamentals [2] and that can provide reliable values. For viscosity, the complete theory in the liquid state is still lacking and that has resulted in a number of different approximate approaches that are based on kinetic theory [3–7], corresponding states theory [8–15], free-volume concepts [16–19], friction theory [20–24], residual entropy scaling [25–28], density scaling [29–31], effective carbon number approach [32,33] and the expanded fluid based approach [34–36] among others. Although some of the models are better suited than others for petroleum engineering applications, we are still

lacking a comprehensive comparison against reliable experimental data in order to ascertain their accuracy and the range of validity. Moreover, most of the models require compositional data as one of the inputs. For reservoir fluids, full compositional characterization is not always possible, due to the large number of components, isomeric species and ill-defined large species, and the standard approach in the petroleum industry is to characterize the fluid mixture in terms of a number of pseudo-components. The choice of components and the properties of the heavy fraction are optimized to a great extent by matching the predicted phase equilibria envelope with a measured one. However, the pseudo-component description of a given fluid based on thermodynamic consideration is usually not transferrable from the upstream to downstream processing units nor is it transferrable to viscosity models; thus requiring additional fluid characterization. We have recently developed viscosity models [37,38], based on the hard-sphere molecular formulation, that forfeit the full compositional input and use a pseudo-component description, characterized by molar mass, to predict the viscosity of a mixture. We do not expect such models to be as accurate as the ones where detailed composition is one of the inputs, as we have sacrificed accuracy for versatility by making use of pseudo-components. However, the validation against comprehensive experimental data on mixtures consisting of *n*-alkanes, alkylbenzenes and cycloalkanes indicates that such models can predict the experimental viscosity data to within 5-10%. This level of accuracy would suffice for a large number of petroleum applications, hence these models, with further development, are serious contenders for providing accurate and reliable values of the viscosity of crude oil and refinery streams.

The objective of this work is two-fold. First, to measure the density and viscosity of six synthetic crude oil mixtures and provide benchmark data that can be used for validating the existing and new equations of state (EoS) and viscosity models. Second, to test the predictive power of the four viscosity models that have their basis in kinetic theory and the

molecular description of the fluid. Two of the models require a full compositional description of the mixture, while the other two belong to a new family of models which dispense with compositional characterization in favour of the pseudo-component approach.

In section 2 we describe the experimental procedure, viscometer used and how the mixtures were chosen and prepared. In section 3 we briefly outline the models used, while in section 4 we present the experimental density and viscosity measurements and compare the four models in their ability to predict the viscosity of the six mixtures studied.

2. Experimental

2.1 Apparatus

The measurements were carried out using the apparatus described in detail by McBride-Wright et al. [39]. This apparatus comprised a laboratory built vibrating-wire viscometer and a commercially-available vibrating-tube densimeter (Anton Paar, model DMA HPM) connected together with a laboratory built magnetically-coupled circulation pump in a loop. Fluids were injected into this loop from a set of high-pressure syringe pumps (Quizix, model Q5000-20k) and valves were provided to permit draining, flushing and evacuating the apparatus. The pressure was measured by means of pressure transducer located in the circulation loop. Two different transducers were used in this work. For the measurements on oil samples A and B, an analogue transducer (Honeywell TJE, full-scale 104 MPa) was used while, for the remaining measurements, a digital transducer (Keller, model 33X, full-scale 100 MPa) was employed; the expanded uncertainty of the measured pressure at 95% probability was 0.1 MPa with the former and 0.05 MPa with the latter.

The temperatures of both the densimeter and the viscometer were regulated by means of a thermostatic circulating silicone oil bath (Huber, PetitFleur Tango). The oil was circulated through the internal heat exchanger of the densimeter and through a fluid jacket enclosing the pressure vessel that contained the viscometer. The temperature of the densimeter was measured by means of a calibrated platinum resistance thermometer (PRT) inserted into a thermowell in the cell block, while that of the viscometer was measured with a second calibrated PRT inserted into a thermowell bored in the wall of the pressure vessel. Although the circulating oil lines were well insulated, slightly different temperatures were measured in the two instruments. The uncertainty of the each temperature reading at 95% probability was 0.05 K.

In the present work, the viscometer was fitted with a gold-plated tungsten wire with a nominal radius of 0.05 mm. The precise value of wire radius R and the vacuum decrement

Δ_0 of the instrument were determined in calibration measurements with ambient air and methylbenzene at T = 298.15 K and p = 0.1 MPa. Measurements of Δ_0 were also carried out at other temperatures in the range of the present study and, except at one temperature, the results were all between (3 and 4) x 10^{-5}. However, the results at temperatures close to 323.15 K were reproducibly higher at about 15 x 10^{-5}. This anomalously-high vacuum decrement might indicate that the viscometer capsule was not firmly held inside the pressure vessel at that temperature. A mean value Δ_0 = 6 x 10^{-5} was used in the analysis and a sensitivity analysis showed that the relative effect on the measured viscosities of varying Δ_0 within the observed range was ≤ 0.5%. The expanded relative uncertainty of the viscosity at 95% probability was 1.2%.

The densimeter was calibrated prior to the start of this work according to the physical model of May et al. [40,41] according to which the density is related to the period of oscillation τ by the equation

$$\rho = \frac{\left(\rho_{\mathrm{M}}/S_{00}\right)}{\left(1+\alpha_V t+\beta_V p\right)}\left[\left(\frac{\tau}{\tau_{00}\left(1+\varepsilon_{\tau 1}t+\varepsilon_{\tau 2}t^2\right)}\right)^2\left(1+\beta_\tau p\right)-1\right], \qquad (1)$$

where t is the Celsius temperature, p is the pressure and ρ_{M} is the density of the tube material. This model contains seven apparatus-specific parameters as follows: S_{00} is a geometric sensitivity factor, τ_{00} is the period of oscillation of the evacuated tube at t = 0°C, $\varepsilon_{\tau 1}$ and $\varepsilon_{\tau 2}$ are linear and quadratic temperature coefficients of the vacuum period, α_V and β_V are the temperature and pressure coefficients of the tube volume, respectively, and β_τ is the pressure coefficient of the tube's spring constant. In this work, the constraint β_V/β_τ = -3.87 was applied, based on previous calibrations of a group of similar densimeters including the one used in this work [40]. As a consequence of this constraint, the remaining parameters could be determined from measurements under vacuum and with one reference fluid over the full ranges of temperature and pressure. The calibration fluid chosen was

water and densities were calculated from the equation of state of Wagner and Pruss [42]. The expanded relative uncertainty of the density at 95% probability was 0.12%.

2.2. Selection and preparation of mixtures

The synthetic mixtures were synthesized to match a light, dead crude oil of API 32° and a molar mass of approximately 184 g·mol^{-1}. Initially the compositional distribution of the crude was generated in terms of the Single Carbon Number Groups (SCN) by employing a standard exponential distribution with C_{50+} as the heavy end [43]. The crude oil was then represented by 10 pseudo-components based on the SCN description, using the heaviest component, SCN28, to match the overall molar mass and thus API. The SCN components were replaced by the corresponding *n*-alkanes, thus generating synthetic mixture A. In an analogous fashion we synthesized mixture B consisting of five *n*-alkanes, but with *n*-eicosane ($C_{20}H_{42}$) being the heaviest *n*-alkane. The list of components making up each mixture is given in Table 1.

The choice of the pseudo-components was in part guided by the availability, cost and purity of the commercially available *n*-alkanes, but also by the constraint that the mixture had to be liquid, in the temperature and pressure range of the measurements. The latter influenced the choice and to a certain extent the amount of the heaviest *n*-alkanes present. In order to create synthetic mixtures with aromatic content we made some of the lighter SCN groups in the 10-pseudo component representation (mixture A) partially aromatic and then replaced them with real components. We achieved this by using methylbenzene (toluene), 1,4-dimethylbenzene (*p*-xylene) and 1-methylnaphtalene (MNP), in addition to *n*-alkanes already present in mixture A. In this fashion we created two new mixtures (mixture C and D) which differ in the total amount of aromatics present, namely 9.6 mass% and 18.8 mass%.

Mixture E was obtained by making SCN6 group, in prototype mixture C, purely naphthene and using cyclohexane to represent the naphthene components. It also consist of 13 components and in terms of Oil and Gas industry nomenclature PNA (ratios of paraffin, naphthene, and aromatic) for this synthetic mixture is 86.8 mass%, 3.6 mass% and 9.6 mass% which is well within observed PNA of real dead light oil. Finally, mixture F was designed to consist of only naphthene and *n*-alkanes species. It consists of 9-components, obtained by removing the aromatic species and making SCN6 and SCN7 groups naphthene. It contains 9.1 mass% of cyclohexane on par with mixture C which contains a similar amount of aromatic species. Although double-ring aromatics (MNP) are present in mixtures C to E, no polycyclic species were chosen because of their low solubility.

All the mixtures were designed by matching only the molar mass of the original light crude and hence they should not be seen as perfect matches for the light oil. On the contrary, the objective of this work was to provide a number of mixtures with different aromatic and naphthene content, that all have the same molar mass and oil-type compositional dependence, and that can be used to test different models, as a precursor for employing these models to predict the viscosity of real crude oil.

All of the pure components were obtained from Sigma-Aldrich, except for MNP which was supplied by Fluka Chemicals. As detailed in Table 1, the mass-fraction purities ranged from 97% to > 99%. Mixtures were prepared gravimetrically with the required mass of each component calculated from the desired final composition and the densities of the pure components such that the resulting volume was about 200 mL. The pure components were added sequentially, starting from the heaviest, to a glass bottle which was weighed on an analytical balance (Mettler-Toledo, full-scale 5100 g, resolution 0.001 g) before and after each addition. After the addition of the final component, a clean magnetic stirrer bar was placed in the bottle which was then sealed with a tight cap. The final composition was calculated from the actual masses of each component and the results are given in Table 1

together with the calculated mean molar mass of each mixture; these ranged from 182.2 to 184.5 g·mol^{-1}, as compared with a target value of 184.0 g·mol^{-1}. The mixtures were homogenised by stirring on a heated magnetic stirrer plate. Since six mixtures were found to be solid at ambient temperature, this operation was carried at a temperature of 50 °C, at which all mixtures were liquid.

Table 1

Mass fraction purities of the chemicals used and mass fractions of each species present in the six synthetic mixtures.

Components	Purity	A[#]	B[#]	C[#]	D[#]	E[#]	F[#]
cyclohexane	99%	--	--	--	--	0.0357	0.0914
n-hexane	99%	0.0372	0.0929	0.0371	0.0362	--	--
toluene	99%	--	--	0.0251	0.0395	0.0250	--
n-heptane	99%	0.0500	--	0.0222	0.0057	0.0217	--
n-octane	98%	0.0716	--	0.0394	0.0200	0.0398	0.0565
p-xylene	99%	--	--	0.0287	0.0466	0.0285	--
n-decane	99%	0.0946	0.1972	0.0739	0.0456	0.0739	0.0739
1-methylnaphthalene	97%	--	--	0.0421	0.1020	0.0422	--
n-dodecane	99%	0.1078	--	0.0854	0.0527	0.0848	0.1086
n-tetradecane	99%	0.0962	0.1149	0.0958	0.0957	0.0961	0.0958
n-hexadecane	99%	0.2684	0.3863	0.2778	0.2832	0.2798	0.2819
n-octadecane	99%	0.0725	--	0.0707	0.0705	0.0700	0.0774
n-eicosane	99%	0.0979	0.2267	0.0978	0.0982	0.0984	0.1104
n-octacosane	99%	0.1038	--	0.1040	0.1041	0.1041	0.1041
Molar mass (g.mol^{-1})		184.51	184.33	183.36	182.21	183.49	184.37
Mass fraction aromatics		--	--	0.0959	0.1881	0.0957	--
Mass fraction cyclohexane		--	--	--	--	0.0357	0.0914

[#]The expanded uncertain of the component mass fractions is 0.0001 with a coverage factor of 2.

The procedure to inject the synthetic mixtures into the system is very similar to the one employed for pure fluids [39], with the difference being the lack of degassing and the use of a heated inlet line to avoid wax precipitation. The fluid was transferred into the system by means of retracting and expanding the syringe pump, as described previously [44], until the system volume was completely full with the fluid, as judged by substantial increase of

pressure inside the system. The system was cleaned thoroughly after completing the measurements on a particular mixture and before injecting the new mixture. Initially, the system was flushed with hexane and then purged using nitrogen at 6 to 8 bar and with the temperature set to 10 to 20 degrees higher than the boiling point of the solvent. The system is then left under vacuum overnight, followed by cycles of 30 minutes of flushing with nitrogen and 10 minutes evacuation.

3. Modelling

As alluded to in the Introduction we used the measured data on six mixtures, representing dead light oil, to test the predictive capabilities of a number of models that have their basis in kinetic theory. In particular, we tested models that represent molecules as hard spheres, namely the Extended Hard-Sphere (EHS) model [45], the 1-component Extended Hard-Sphere (1-cEHS) model [37], 3-component Extended Hard-Sphere (3-cEHS) model [38] and Vesovic-Wakeham (VW) model [3–6]. Only a brief description of the models is given here and an interested reader is referred to the original publications for a detailed description and validation.

All three EHS models of interest to this work are based on a postulate that the reduced excess viscosity $\Delta\eta^*$ is an universal function of the reduced molar volume, V^*,

$$\log_{10}(1+\Delta\eta^*) = \sum_{i=1}^{7} a_i/(V^*)^i \tag{2}$$

as originally proposed by Assael and Dymond [45,46] and subsequently extended [7,47]. The reduced molar volume ($V^* = V_m/V_0$) is defined as the ratio of molar volume, V_m, and molar core volume, V_0, while the reduced excess viscosity, $\Delta\eta^*$, is defined as [45],

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

where M is the molar mass, N_A is Avogadro's constant, R is the gas constant, R_η is the roughness factor and $\eta^{(0)}$ is the zero-density viscosity. In applications to real fluids, molar core volume, V_0, is assumed to be temperature dependent and both V_0 and R_η are treated as adjustable, scaling quantities. It has been shown [45,46] that, with an appropriate choice of the scaling parameters, the viscosity of the plethora of pure fluids can be represented to within 5%. Furthermore, for a number of chemical families, in particular *n*-alkanes, it was possible to correlate the two scaling parameters as a function of molar mass.

In order to use the EHS models to predict the viscosity of a mixture, at a given temperature, density and composition, one requires a prior knowledge of V_0 and R_η. Traditionally [46] this was achieved by using simple, mole average, mixing rules,

$$V_{\mathrm{o,mix}} = \sum_{i=1}^{N} x_i V_{\mathrm{o},i} \tag{4}$$

$$R_{\eta,\mathrm{mix}} = \sum_{i=1}^{N} x_i R_{\eta,i} \ , \tag{5}$$

where the required values of the scaling parameters are obtained from the values of the pure species. In the rest of this work we refer to using these simple mixing rules, within the EHS scheme, as the EHS model.

Another approach, when dealing with mixtures, within the EHS scheme, is to dispense with the mixing rules all together and postulate that the mixture can be represented as a pseudo-component characterized by an effective molar mass. The recently developed 1-cEHS model [37] takes this approach. It was originally developed to estimate the viscosity of *n*-alkane mixtures by using V_0 and R_η expressions developed for pure *n*-alkanes [37] and replacing the molar mass of a pure species by the molar mass of the mixture. It was subsequently extended [38] to include mixtures that contain alkylbenzene and cycloalkane species by treating them as pseudo-alkanes, characterized simply by an effective molar mass. The effective molar mass was obtained by mapping V_o curves of alkylbenzenes and cycloalkanes onto the same V_0 curve of *n*-alkanes. The relevant relationships, between the effective and the real molar mass of non-alkane species, are given in the original reference [38]. In order to evaluate the mixture roughness factor, R_η, the 1-cEHS model makes use of the modified [37] expressions originally proposed for *n*-alkanes that include long-chain ones [7]. The modification involves using the weighted average molar mass, in addition to the mixture molar mass, as a correlating parameter,

$$M_{\mathrm{av}} = \left(\sum_i^N x_i M_i^{\alpha}\right)^{1/\alpha}. \tag{6}$$

The expression for parameter α, is given in the original publication [37] and is a function of ΔC, the difference between the carbon number of the largest and smallest molecule in the mixture. For mixtures where $\Delta C < 5$, the roughness factor can by estimated by replacing the weighted average molar mass, M_{av}, by the mixture molar mass. Thus, for more asymmetric mixtures, the 1-cEHS model still requires compositional information to estimate the value of M_{av}.

In order to eliminate the need for compositional information, we recently proposed the 3-cEHS model [38] wherein the mixture is characterized in terms of the chemical families present. For the purposes of characterizing light reservoir fluids encountered in the petroleum industry and for the synthetic crude oils measured in this work, we characterize a given mixture in terms of mole fraction of *n*-alkane, alkylbenzene and cycloalkane species. In the terminology of the petroleum industry, we create a three component pseudo-mixture consisting of alkane, aromatic and naphthene (cyclic) pseudo-components; each defined by its mole fraction ($x_{alk.}$, x_{aro} or $x_{cyc.}$) and its molar mass (M_{alk}, M_{aro} or M_{cyc}). The M_{av} is then estimated from,

$$M_{\mathrm{av}} = \left(x_{\mathrm{alk}} M_{\mathrm{alk}}^{\alpha} + x_{\mathrm{aro}} M_{\mathrm{aro}}^{\alpha} + x_{\mathrm{cyc}} M_{\mathrm{cyc}}^{\alpha}\right)^{1/\alpha} \tag{7}$$

The parameter ΔC, that is required in the expressions for estimating parameter α, is taken as ΔC=60 to represent generic oil. The sensitivity tests indicate that the parameter α is a weak function of ΔC for ΔC> 30. The influence on predicted viscosity is less than 0.3% by changing ΔC from 30 to 60.

We have carried out extensive validation tests on the three EHS models using the available experimental data on the compositionally well-defined mixtures consisting of *n*-alkanes, alkylbenzene and cycloalkane species [38]. Based on the deviations observed between the experimental and predicted data, the uncertainty of the predicted viscosity values is estimated to be in the region of 5-10%.

The final model that we used in this work is the VW model [3–6] that is also founded on the kinetic theory of the hard-sphere fluid [48]. In particular, it was designed to predict the viscosity of mixtures by means of the Enskog approach. Here we used the latest version specifically developed for *n*-alkane mixtures that represents molecules as chains of equally-sized, tangentially-joined, rigid spherical segments [5,6]. For brevity we summarize just the main features of the model and the interested readers are referred to Ref. [6] for details. 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 their value, as a function of temperature and density, by ensuring that the viscosity of each pure species, constituting the mixture of interest, is reproduced. In doing so, the VW model implicitly represents each molecule differently when performing calculations for the excluded volume and for the collisional dynamics [49], using two different effective molecular sizes.

To obtain the radial distribution function relevant for a mixture, it makes use of mixing rules, that are thermodynamically consistent and based on the expressions for the hard sphere fluid [4,6]. Thus, 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. The claimed uncertainty of the VW model for liquid mixtures is of the order of 5% [6,37] based on the comprehensive validation against the experimental data on the viscosity of *n*-alkane mixtures. In order to use the VW model to compute the viscosity of mixtures containing alkylbenzene and cycloalkane species we would need molecular description in terms of ring structures consisting of effective hard spheres. As such a molecular description is not available at present, we have modelled the alkylbenzene and cycloalkane species as effective spheres for the purposes of this work. The validity of this assumption,

that grossly oversimplifies the molecular structure, will be examined by the ability of the VW model to predict the viscosity of synthetic crude oil mixtures measured in this work.

4. Results and Discussion

The measurement of viscosity and density of six synthetic mixtures was carried out at four equally spaced nominal temperatures (323.15 K, 348.15 K, 373.15 K and 398.15 K) in the pressure range from 1 MPa to 70 MPa. The measured values, at a given temperature and pressure, are reported in Supplementary Material. Figure 1 illustrates the behaviour of density as a function of temperature and pressure for the mixture A. The behaviour of other mixtures follows a similar pattern (see Supplementary Material). We observe that, as expected, the density decreases with temperature and increases with pressure. The increase with pressure for all the mixtures studied is nearly linear with the largest curvature at the highest temperature. Figure 2 shows the behaviour of density as a function of pressure at a particular temperature for the six mixtures. The behaviour at other temperatures is similar. We observe that mixtures A and B, which contain only *n*-alkane species, have the lowest densities and that the density of two mixtures does not differ by more than 0.15% over the measured range. The latter illustrates that representation of this particular crude oil as either 10-pseudo-component mixture (mixture A) or 5-pseudo-component mixture (mixture B) is equivalent, as far the density predictions are concerned. The increase in aromatic and naphthene content leads to an increase in density, since in general the density of pure alkylbenzene and cycloalkane species is greater than that of equivalent *n*-alkanes. Mixture D, that has the highest content of non-alkane species ($x_{arom.}$= 0.289), displays the highest density, approximately 5.0% higher than density of mixtures A and B.

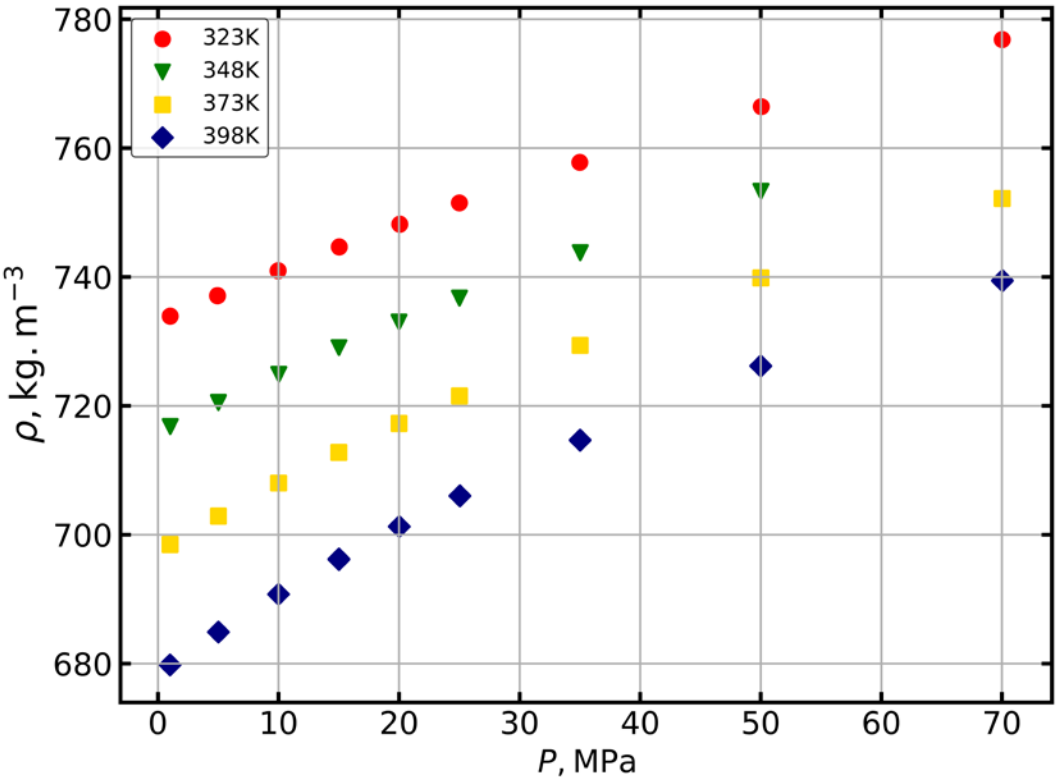

Figure 1: Density isotherms at (323, 348, 373 and 398) K as a function of pressure for the mixture A.

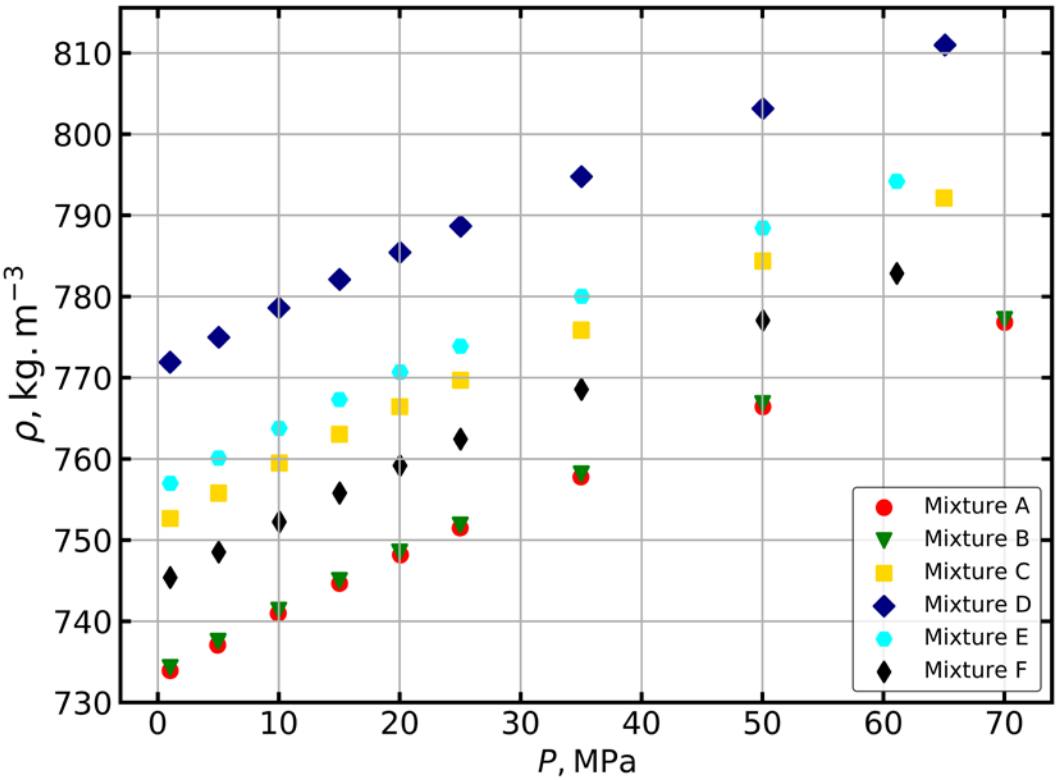

Figure 2: Density isotherms at 323 K as a function of pressure, for all six mixtures.

The measured densities have been correlated, for each mixture, by means of the modified Tait equation,

$$\rho = \rho_0 \left[1 - C \log\left(\frac{P+B}{0.1+B}\right)\right]^{-1} , \tag{8}$$

where ρ_0 and B are given by,

$$\rho_0 = \sum_{i=0}^{2} a_i \left(\frac{T}{273.15}\right)^i , \tag{9}$$

$$B = \sum_{i=0}^{2} b_i \left(\frac{T}{273.15}\right)^i , \tag{10}$$

and a_i , b_i and C are adjustable parameters, while ρ and P are in units of kg.m^{-3} and MPa, respectively. Table 2 lists the coefficients of the modified Tait equation for six mixtures. The

low AAD and MD indicate that the Eq. (10) can represent the measured density with a high level of precision.

Table 2

Coefficients of the modified Tait equation and Statistical Parameters for six mixtures

	A	B	C	D	E	F
a_0	864.091	866.177	884.593	915.826	965.843	890.531
a_1	-39.657	-44.544	-44.952	-61.453	-162.150	-65.994
a_2	-60.048	-57.257	-57.184	-51.504	-12.831	-48.743
b_0	325.962	162.997	165.862	188.116	256.631	292.392
b_1	-286.505	-42.151	-41.922	-45.720	-171.337	-229.117
b_2	63.818	-26.852	-26.912	-32.343	19.259	41.976
C	0.20	0.20	0.20	0.21	0.20	0.20
AAD (%)	0.01	0.02	0.02	0.03	0.02	0.02
MD (%)	0.04	-0.10	-0.08	0.11	-0.09	-0.07

Figure 3 illustrates the behaviour of viscosity as a function of pressure along four isotherms. For brevity, only results for the mixture A are shown as the other mixtures exhibit similar behaviour. The viscosity decreases with temperature and increases with pressure. The increase of viscosity with pressure, for all the mixtures studied, deviates from linearity at higher pressures, at all temperatures. Figure 4 shows the behaviour of viscosity as a function of density, for illustrative purposes at 323 K, for the six mixtures. We observe that among the six mixtures measured, *n*-alkane mixtures A and B, have the lowest viscosity. This is to be expected as *n*-alkanes tend to have a lower viscosity than alkylbenzenes and cycloalkanes. It is interesting to observe that there is a difference of about 3.0% in the measured viscosity between mixtures A and B, although both mixtures have the same nominal molar mass and density and pertain to represent the same light oil. This indicates the importance of adequately choosing the pseudo-components species and their overall number for the viscosity calculations.

Increase in aromaticity leads to increase in viscosity, as observed with mixtures C ($x_{arom.}$= 0.154) and D ($x_{arom.}$= 0.289). Nevertheless, the increase in the amount of cyclohexane has a more profound impact, as cycloalkane species tend to have higher

viscosity than alkybenzene species at the same conditions, and mixture F ($x_{cycl.}$= 0.2) displays the highest viscosity. Overall replacing 20% by volume of *n*-alkanes with 20% of cyclohexane, keeping the same molar mass of the mixture and oil-like composition distribution, has resulted in up to 10% increase in viscosity.

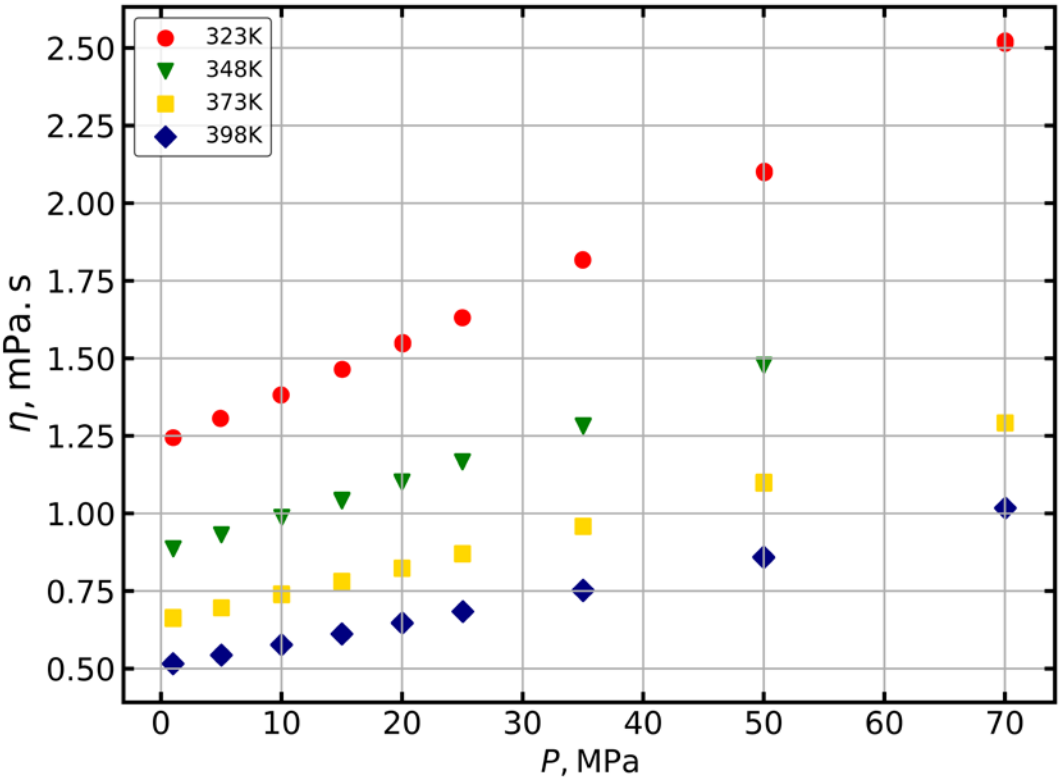

Figure 3: Viscosity as a function of pressure for the mixture A along four isotherms at (323, 348, 373 and 398) K

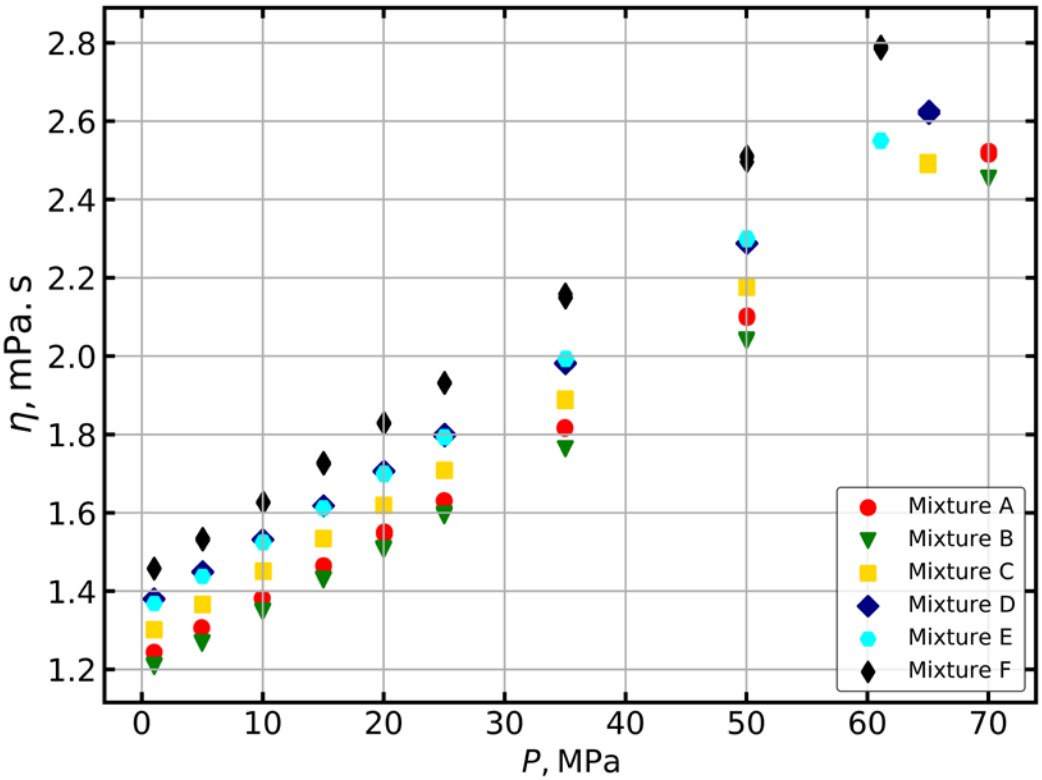

Figure 4: Viscosity at 323 K as a function of pressure for all six mixtures.

Figure 5 illustrates the deviations in predicting the measured viscosity by means of the three models employed in this work (EHS, 1-cEHS and VW) for two n-alkane mixtures A and B, while Table 3 summarizes the Average Absolute Deviation (AAD), Maximum Deviation (MD) and Bias for the three models. The 3-cEHS model was not employed for these mixtures as the model reduces to 1-cEHS model, if all the species belong to the same chemical family. We observe that overall, all three models underpredict the viscosity of mixture A with a Bias ranging from -3.8% for the VW and EHS models to –4.8% for the 1-cEHS model. The two models based on the full molecular description (VW and EHS) predict most of the data within ±5%, while 1-cEHS exhibits slightly larger deviations, that weakly increase with density, with the maximum deviation of -8.6%. Nevertheless, this is well within

the combined uncertainty quoted for the experimental data and the models. The viscosity of the mixture B, where the largest n-alkane species is n-eicosane, compared to n-octacosane in mixture A, is predicted more accurately by all three models with AAD ranging from 1.6% for EHS model to 3.1% for 1-cEHS model, and MD ranging from -4.8% for former to –6.8% for later model. Examining the combined results for the two n-alkane mixtures studied, the EHS model has the lowest overall AAD of 2.7% while the VW method gives a slightly larger deviation of 3.1%. What is very encouraging is that the 1-cEHS model which forgoes the full compositional description produces a good agreement with an overall AAD of 3.9% and MD of -8.6%.

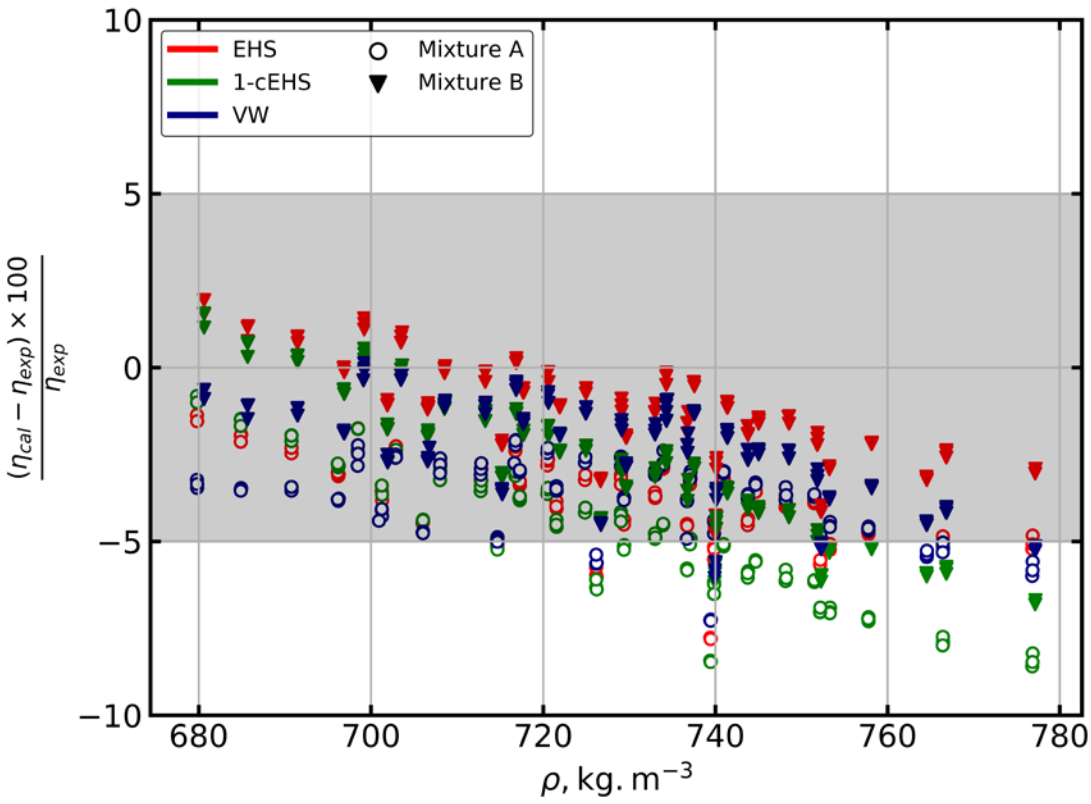

Figure 5: Deviations in predicting the viscosity of the mixtures A and B by using EHS, 1-cEHS and VW models.

Table 3

Summary of Average Absolute Deviation (AAD, %), Maximum Deviation (MD, %) and Bias (%) in predicting the viscosity of the mixtures by using EHS, 1-cEHS, 3-cEHS and VW models.

Models	Statistical parameters	A	B	C	D	E	F
EHS	AAD (%)	3.8	1.6	2.5	3.4	1.1	5.0
	MD (%)	-7.8	-4.8	-7.5	8.7	-3.7	-8.7
	Bias (%)	-3.8	-1.2	-2.0	3.2	0.1	-5.0
1-cEHS	AAD (%)	4.8	3.1	1.4	7.2	1.2	7.5
	MD (%)	-8.6	-6.8	-5.8	9.4	-3.2	-11.7
	Bias (%)	-4.8	-2.9	-1.1	7.2	-0.1	-7.5
3-cEHS	AAD (%)	-	-	6.2	4.6	1.8	7.6
	MD (%)	-	-	-10.7	6.8	-4.7	-11.8
	Bias (%)	-	-	-6.2	4.6	-1.5	-7.6
VW	AAD (%)	3.8	2.3	4.2	2.9	4.6	9.8
	MD (%)	-7.3	-6.1	-9.1	-6.3	-7.3	-14.9
	Bias (%)	-3.8	-2.3	-4.2	-2.9	-4.6	-9.8

AAD = $(100/N)\sum|(\eta_{cal}-\eta_{exp})/\eta_{exp}|$; Bias = $(100/N)\sum(\eta_{cal}-\eta_{exp})/\eta_{exp}$

We now turn our attention to the four mixtures that contain alkybenzene and cycloalkane species. Increase in aromaticity of the mixtures leads to increase in viscosity and Figure 6 illustrates the deviations in predicting the measured viscosity for two mixtures C and D, containing only alkybenzene and *n*-alkane species, while Table **3** summarizes the Average Absolute Deviation (AAD), Maximum Deviation (MD) and Bias. We observe that all four models are capable of predicting these two mixtures within their claimed uncertainty of 5-10%, as ascertained by previous validation against binary and multicomponent mixtures [38]. No systematic temperature or density trends are observed and although it would seem that the increase in aromaticity leads to a better prediction by the VW and 3-cEHS models and worse predictions by the EHS and 1-cEHS models, it would not be prudent to draw any general conclusions based on a study of just two synthetic oil mixtures. Overall, the EHS and VW models give a very good prediction of the viscosity for these two mixtures, with AAD of 3.0% and 3.6%, respectively and MD of 8.7% and -9.1%, respectively. This is especially encouraging result for the VW model that indicates, that at least for the content of aromatics found in crude oil, the use of the effective hard sphere, rather than a ring consisting of hard

spheres, is adequate to describe the single- and double ring alkylbenzenes present in oil. The two models, 1-cEHS and 3-cEHS, that do not rely on the full compositional description also produce a very good agreement with an overall AAD of 4.3% and 5.4%, respectively.

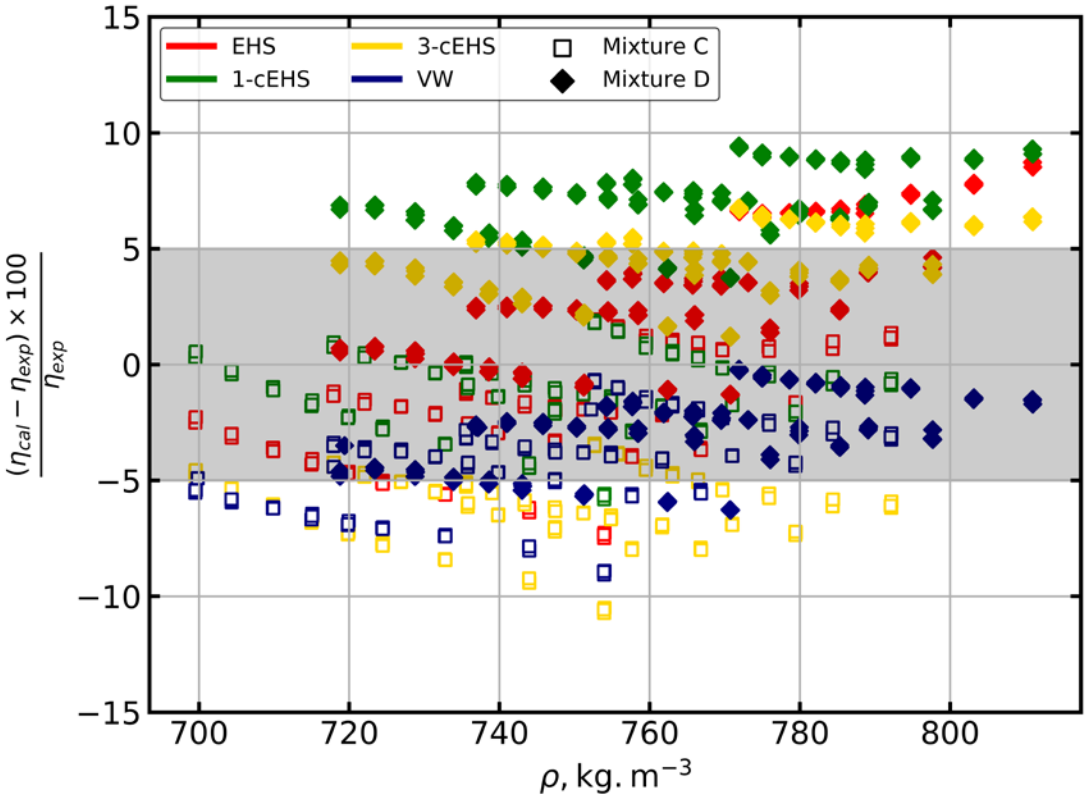

Figure 6: Deviations in predicting the viscosity of the mixtures C and D by EHS, 1-cEHS and 3-cEHS and VW models.

Reducing the amount of the alkylbenzene in mixture D and replacing it by cyclohexane, while keeping the same number of components results in a higher viscosity, as illustrated by mixture E in Figure 4. Figure 7 and Table 3 illustrate that the overall agreement between the measured and the predicted values has been improved and all four models predict the viscosity of mixture E surprisingly well. The EHS family of models displays a very low AAD ranging from 1.1% for the EHS model to 1.8% for the 3-cEHS model and no deviation exceeds ±5% limits, while the VW model displays higher deviations, on par to

those for mixtures C and D. Although the overall agreement is better than for mixtures C and D, the predictions of all four models display a discernable trend of increasing deviations with increasing density.

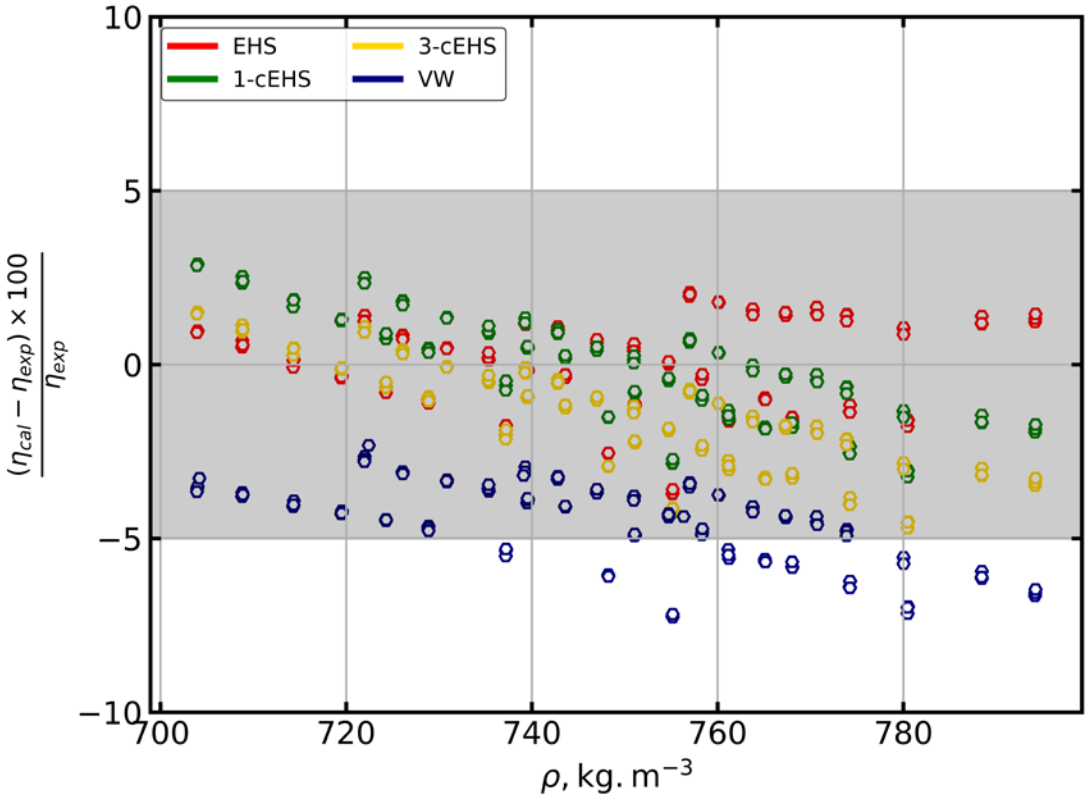

Figure 7: Deviations in predicting the viscosity of the mixtures E by EHS, 1-cEHS and 3-cEHS and VW models.

Finally we examine the mixture F which contains only cyclohexane, in addition to *n*-alkanes. Although it contains more than twice the amount of cyclohexane than the mixture E, in terms of the mole fraction, the total amount of non-alkanes does not exceed the amounts present in either mixture D or E. In terms of the mass fraction of non-alkane species it resembles mixture C (m_C=9.6%; m_F=9.1%) with cyclohexane replacing the alkylbenzene species. Nevertheless, as illustrated in Figure 8, we observe underprediction by all models with large deviations exhibiting a strong systematic downwards trend with increasing density.

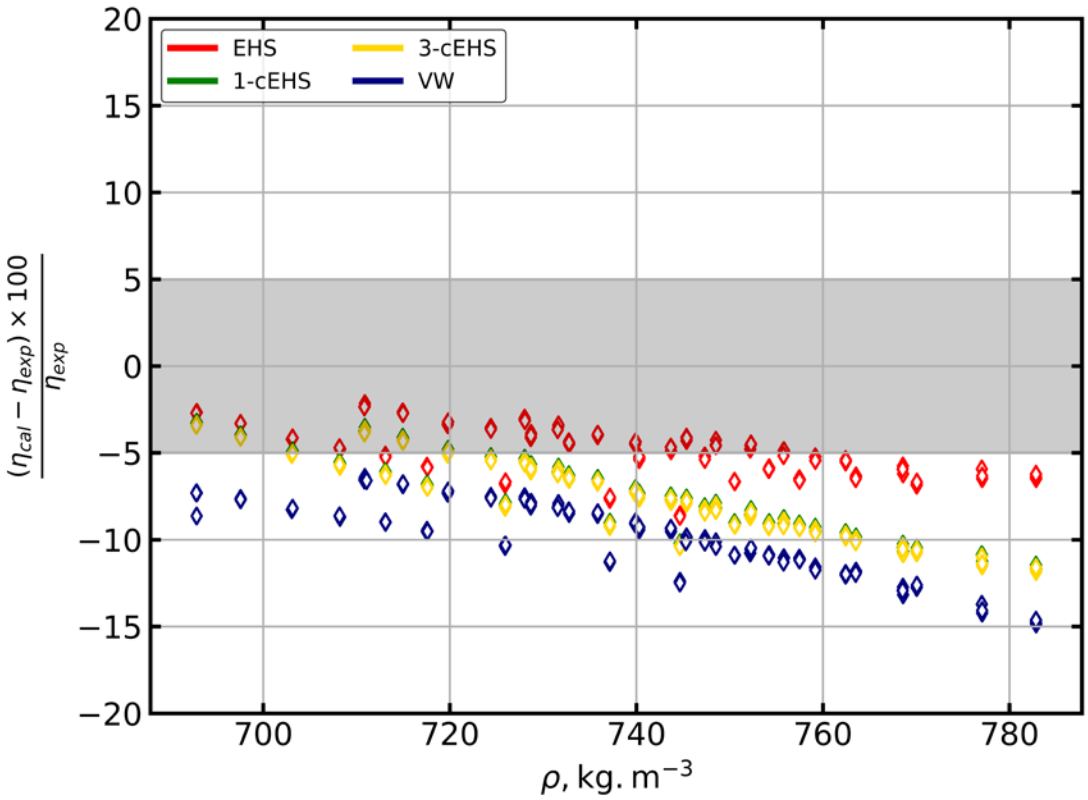

Figure 8: Deviations in predicting the viscosity of the mixture F by EHS, 1-cEHS, 3-cEHS and VW models.

The predictions of 1-cEHS and 3-cEHS have very similar characteristics, see Figure 8 and Table 3, with AAD of about 7.6% and MD of about -11.8%. The EHS model does marginally better with AAD of 5.0% and MD of -8.7%, while the VW model displays the worse predictions with AAD of 9.8% and MD of -14.9%. It is not clear why such large and systematic deviations are observed for this mixture. Especially as the validation of the EHS and 1-cEHS models against the available experimental data on the binary cyclohexane + *n*-alkane mixtures, consisting of more than 300 data points, indicated an agreement with AAD of 1.2% and 3.0%, respectively and overall MD of -7.9% [38]. One possible explanation is that this is a 9-component mixture with larger asymmetry than the mixtures C, D and E, as measured by the ΔC between successive components. We have previously observed that 1-

cEHS model improves with addition of intermediate components to a mixture [37]. The addition of cyclohexane is thus similar to adding a light component which for most available models causes the prediction deterioration [37].

The predicted viscosity is sensitive to density, as noted previously [38], with sensitivity increasing with increase in density and decrease in temperature. For the mixtures studied in this work, variation in density, within its claimed experimental uncertainty of 0.12%, will produce changes in viscosity of up to 1.6%. Although the viscosity changes are large they are not sufficient to explain the systematic increase in deviation with increasing density observed for the mixture F.

4. Conclusions

Measurements of viscosity and density were performed on six multicomponent, synthetic, liquid mixtures that were designed to match a light, dead crude oil, of different aromaticity, of API 32° and molar mass of approximately 184 $g \cdot mol^{-1}$. The mixtures consist of between 5 and 13 species belonging to *n*-alkane, cycloalkane and alkylbenzene families and the measurements were made at four temperatures (323.15, 348.15, 373.15 and 398.15) K in the pressure range from 1 MPa to 70 MPa**.** The viscosity was measured with a vibrating-wire viscometer, while the density was measured by means of a vibrating U-tube densimeter. The density and viscosity data have expanded relative uncertainties of 0.12% and 1.2%, respectively with a coverage factor of 2. The density data was correlated by means of modified Tait equation that reproduced the measured values with MD of 0.11%. The measured data provides benchmark data on mixtures representing synthetic crude oil that can be used for validating the existing and new Equations of State (EoS) and viscosity models.

We have made use of the measured data to test four viscosities models (EHS, 1-cEHS, 3-cEHS and VW) that rely on kinetic theory and underlying molecular description. Two of the models (EHS and VW) require a full compositional specification of the mixture and consequently incorporate mixing rules to evaluate mixture parameters. For two mixtures consisting of only *n*-alkane species both models on average predict the viscosity data well within their quoted uncertainty of ±5% with AAD of 2.7 and 3.1%, respectively and maximum deviation of -7.8%. For mixtures that contain alkylbenzene and cycloalkane species the EHS model retains a similar prediction capability, as measured by AAD, while deviations for the VW model increase slightly with overall AAD for mixtures C-E of 3.9% compared with AAD of 3.1% for *n*-alkane mixtures. The later can be ascribed to simplified modelling of alkylbenzene and cycloalkane species in the VW model where effective hard spheres where used to represent ring structures.

We have also tested the 1-cEHS and 3-cEHS models that belong to a family of new type of viscosity models that do not require a full compositional characterization of a mixture, as for quite a few fluids of industrial interest a detailed characterization is not available. In developing such models we have purposely sacrificed accuracy for versatility, as we have replaced the full compositional characterization by a knowledge of molar mass and mole fraction of each pseudo-component. For mixtures A-E the two models predict the viscosity with the overall AAD of 3.8% and MD of -10.7%. Although this is marginally worse than the prediction of the EHS and VW models, it demonstrates that these new type of models can predict reliably the viscosity of industrially relevant mixtures with reasonable accuracy and form a solid basis for further inclusion of species belonging to other chemical families.

None of the four models were able to adequately predict the viscosity of mixture F, displaying systematic trends of increasing deviations with increasing density, with MD ranging from -8.7% for EHS model to -14.9% for the VW model. It is not clear, at the moment, why this is the case, as mixture F is compositionally similar to other mixtures studied, being a 9-component mixture consisting of *n*-alkanes and cyclohexane. The previous work [38] on validation of the EHS type models indicated that mixtures consisting of *n*-alkanes and cyclohexane posed no specially difficulties.

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