

**Comparative Study of Viscosity Models on the Ternary System
Methylcyclohexane + cis-Decalin + 2,2,4,4,6,8,8-Heptamethylnonane up
to 100 MPa**

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Abstract

Recently, a comprehensive experimental study of the viscosity up to 100 MPa has been carried out on the ternary system composed of methylcyclohexane, cis-decalin, and 2,2,4,4,6,8,8-heptamethylnonane in order to provide data for asymmetrical hydrocarbon mixtures. Although not as complex as real petroleum fluids, the studied system is of interest for the evaluation of viscosity models for their potential application to the simulation of complex fluids with an asymmetrical molecular distribution. The measured data (1554 points) have been used in an extensive evaluation of the performance of seven different viscosity models applicable to

hydrocarbon fluids. These models range from empirical correlations, such as the self-referencing model and the commonly used LBC model in petroleum engineering, to recent approaches with a physical and theoretical background, such as the hard-sphere scheme, the free-volume model, and the friction theory. This comparative study shows that the evaluated models, except the LBC model, can represent the viscosity of the ternary system within an acceptable uncertainty for most engineering applications. However, the extension to real reservoir fluids may be more appropriate for some of the models, such as the free-volume and the friction theory, since these models are not limited to liquids and dense fluids, but are also applicable to gases, which is a required feature within the oil industry.

Key words: *density, equations of state, free-volume, f-theory, hard-sphere, hydrocarbon mixtures, modeling, pressure, viscosity*

1. Introduction

In the simulations of oil reservoirs or in the design of process and transport equipment the viscosity is an important fluid property. Although, experimental viscosity measurements are important, mathematical models play an even more important role, since they help to study the viscosity under operating conditions (temperature, pressure, and composition) in a fast and inexpensive way compared to carrying out experimental measurements. Consequently, reliable and accurate viscosity models are required, which can be applied under different operating conditions taking into account the effects of temperature, pressure along with compositional changes, which are common within the oil industry, as well as other industries. But experimental measurements are required in model development and evaluation. Due to their importance within the oil industry and the high-pressure conditions encountered in oil reservoirs, most experimental studies of the viscosity versus pressure and temperature have been performed on hydrocarbon fluids. Most of these studies have been performed on light or intermediate hydrocarbons, primarily paraffins, and their mixtures, whereas studies on highly branched hydrocarbons, polycyclic naphthenic and aromatic compounds as well as asymmetrical mixtures are less frequent, although petroleum and reservoir fluids are multicomponent mixtures composed of these types of chemical species.

Because of this, most of the compositional dependent viscosity models have been derived on the basis of paraffins and their mixtures.

Recently, a comprehensive experimental viscosity and density study was carried out for the ternary system composed of the highly branched alkane 2,2,4,4,6,8,8-heptamethylnonane and the two naphthenic compounds methylcyclohexane and cis-decahydronaphthalene (cis-decalin) in order to provide data on asymmetrical hydrocarbon mixtures. This study was performed in the temperature range 293.15 K to 353.15 K and up to 100 MPa for 37 different compositions [1-4]. These compositions are indicated as dots in the ternary diagram shown in Figure 1. For this ternary system a total of 1554 experimental viscosity values was obtained (42 for each of the pure compounds, 294 for each of the three binary systems, and 546 for the ternary). The viscosity was measured using a falling-body viscometer with an experimental relative uncertainty of $\pm 2\%$, whereas the uncertainty in the density measurement is reported to be $1 \text{ kg}\cdot\text{m}^{-3}$. Although not being as complex as real petroleum fluids, the studied system is of interest for the evaluation of viscosity models for their potential application to the simulation of complex fluids with an asymmetrical molecular distribution, such as oil accumulations exposed to biodegradation or alteration. These fluids have a higher content of naphthenic and heavy hydrocarbons, because biodegradation and alteration lead to the vanishing on decomposition of the intermediate “normal“ alkanes between C_6 and C_{16} .

In this work the measured data of this ternary system (1554 points) have been used to perform an extensive and comparative study and evaluation of the performance of seven representative viscosity models incorporating the effects of temperature, pressure, and composition. The considered models are applicable to hydrocarbon fluids and range from the simple classical mixing laws by Grunberg and Nissan [5] and Katti-Chaudhri [6] through empirical correlations, such as the self-referencing model [7] and the commonly used LBC model [8] in petroleum engineering, to recent approaches with a physical and theoretical background, such as the hard-sphere scheme [9,10], the free-volume model [11,12], and the friction theory [13,14]. These approaches, except the classical mixing laws, represent different ways of modeling the viscosity of pure compounds, whereas for mixtures, all approaches are totally predictive in the sense that only knowledge of the parameters characteristic of the pure compounds along with the composition are sufficient in order to predict the viscosity.

In order to analyze and evaluate the performance of the considered viscosity models, the following quantities defined below are used

$$\text{Deviation}_i = \frac{\eta_{calc,i} - \eta_{exp,i}}{\eta_{exp,i}} \quad (1)$$

$$\text{AAD} = \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} |\text{Deviation}_i| \quad (2)$$

$$\text{Bias} = \frac{1}{\text{NP}} \sum_{i=1}^{\text{NP}} \text{Deviation}_i \quad (3)$$

where NP is the number of experimental points, η_{exp} the experimental viscosity and η_{calc} the calculated viscosity. The AAD (absolute average deviation) indicates how close the calculated values are to the experimental values, while the quantity Bias is an indication of how well the calculated values are distributed around the experimental values. Further the quantity MxD referring to the absolute maximum deviation is used.

Further, pure component properties, such as the molecular weight and critical properties, are required in most of the models. The properties, which are used in this work, were taken from [15,16] and are given in Table I. The critical molar volume v_c of the pure compounds was estimated by the modified Benedict-Webb-Rubin equation of state by Soave [17] (SBWR). A comparison of the predicted densities of the pure compounds with experimental values [1-3] resulted in an AAD of 1.37% with a MxD of 2.37% for methylcyclohexane. For cis-decalin the obtained AAD and MxD are 0.57% and 1.28%, respectively, whereas for 2,2,4,4,6,8,8-heptamethylnonane the AAD and MxD are 1.96% and 4.11%, respectively. These results further show the satisfactory representation of the density of pure hydrocarbons by the SBWR EOS.

2. Classical Mixing Laws

Several mixing laws have been developed in order to calculate the viscosity of liquid mixtures. The objective of these mixing laws has been to

predict the viscosity of liquid mixtures using only the viscosity and density of the pure compounds along with the composition. Two of the more well-known mixing laws are the Grunberg and Nissan mixing law [5]

$$\ln(\eta_{mix}) = \sum_{i=1}^n x_i \ln(\eta_i) \quad (4)$$

and the Katti and Chaudhri mixing law [6]

$$\ln(\eta_{mix} v_{mix}) = \sum_{i=1}^n x_i \ln(\eta_i v_i) \quad (5)$$

where η is the viscosity, x the mole fraction, and v the molar volume defined as $v = M_w/\rho$ with M_w the molecular weight and ρ the density. Subscripts "mix" and "i" refer to the mixture and the pure compounds, respectively. For mixtures the molecular weight is defined as $M_{w,mix} = \sum x_i M_{w,i}$. These two viscosity mixing laws are totally predictive in the sense that only pure component properties are required. In this work, the viscosity calculations with the Katti-Chaudhri mixing law were performed using the experimental densities reported in [1-4] in order to obtain the molar volume of the pure compounds and the mixtures. The deviations obtained between the predicted viscosities and the experimental values are given in Table II for both mixing laws. The overall performance for these mixing laws on the ternary system is very satisfactory taking into account the simplicity of the mixing laws. Thus, the best performance of the Grunberg-Nissan mixing law is obtained at high temperature and low pressure i.e at low viscosity. This is also the

case for the Katti-Chaudhri mixing law. Further, the obtained deviations are within or close to the experimental uncertainty of 2% with the highest deviations found for mixtures composed of methylcyclohexane + 2,2,4,4,6,8,8-heptamethylnonane. However, despite that the experimental densities are incorporated as additional mixture information in the viscosity calculations with the Katti-Chaudhri mixing law, the simpler Grunberg-Nissan mixing law gives a better representation of the viscosity of this asymmetrical ternary system.

3. Self-Referencing Method

A completely different model is the self-referencing model [7] developed for estimating the viscosity of liquid petroleum fluids and dead oils under operating conditions using only the measured viscosity at atmospheric pressure for a given reference temperature T_0 , which is generally chosen to be close to room temperature. In this way, it is assumed that this measured reference viscosity value contains sufficient information about the studied fluid, and it is the reason why this method can be referred to as a self-referencing model. The method does not involve the molecular weight or any other physical properties or critical parameters. It can be applied without restriction indifferently to pure substances, synthetic mixtures or complex fluids, such as petroleum fluids, for which the method was originally developed. The method involves nine coefficients, which

have been adjusted using viscosity data of liquid n-alkanes and alkylbenzenes [7]. Based on this set of coefficients, the method can be used directly without further adjustment and can be considered general and predictive. The expression of this method is

$$\ln\left(\frac{\eta(P,T)}{\eta(0.1\text{ MPa},T_0)}\right) = (ay^2 + by + c)\ln\left(1 + \frac{P-0.1}{dy^2 + ey + f}\right) + (gy_0^2 + hy_0 + i)\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (6)$$

where

$$y = y_0 + (gy_0^2 + hy_0 + i)\left(\frac{1}{T} - \frac{1}{T_0}\right) \quad (7)$$

and $y_0 = \ln\eta(0.1\text{ MPa},T_0)$, with the temperature T in [K] and the pressure P in [MPa], when the following coefficients [7] are used

$a = 0.275832$	$d = 4.059832$	$g = 6.729026$
$b = 0.533739$	$e = 23.63475$	$h = 481.5716$
$c = 1.838385$	$f = 161.0261$	$i = 1278.456$

In this work the viscosity of the three pure compounds, the binary mixtures, and the ternary mixtures was calculated using the measured viscosity at 0.1 MPa and 293.15 K as the reference point for each fluid. The calculated values, excluding the reference points, were compared with the experimental values and the resultant AAD, MxD and Bias are given in Table III. The viscosity representations of methylcyclohexane, cis-decalin and their mixtures are satisfactory, taking into account the fact that the

prediction with the self-referencing method only requires the measured viscosity at atmospheric pressure and 293.15 K for each mixture. However, for 2,2,4,4,6,8,8-heptamethylnonane and its mixtures the representation of the viscosity with this method is less accurate with the highest deviations found at low temperature and at the highest pressures. An explanation may be that the coefficients in the model were adjusted only on alkylbenzenes and n-alkanes in the range n-heptane to n-octadecane, and not on branched molecules, such as the highly branched 2,2,4,4,6,8,8-heptamethylnonane, where a possible induced molecular interlinking effect may occur, when brought under pressure, resulting in an important reduction in the fluid mobility.

Recently, a modification of the self-referencing method has been proposed [18] in which the nine coefficients required in the model are obtained from the composition and the respective nine coefficients of the pure compounds by using the following simple mixing rule $\alpha_{\text{mix}} = \sum x_j \alpha_j$ with ($\alpha = a, b, \dots, i$). The nine pure component coefficients were fitted using the pure component viscosity values given in [1-3], with $T_0 = 293.15$ K as the reference temperature, and by first adjusting the three coefficient g , i , and h , which are directly related to the viscosity at 0.1 MPa. During this adjustment, it was observed that within the considered temperature range (293.15 – 353.15 K) the g coefficient can be put to zero for the three pure compounds. The adjusted coefficients are given in Table IV with the

modeling results given in Table V, which also contains the AAD, MxD, and Bias obtained for the binary and ternary mixtures by the self-referencing model using mixing rules for the model coefficients. The overall representation of the ternary system is very satisfactory and the AAD is within or close to the experimental uncertainty of 2%. The highest deviations are obtained at the lowest temperature and highest pressure. As it can be seen by estimating the coefficients in the self-referencing model using the pure compound coefficients, a significant improvement compared to the original model [7] is found and similar observations have been found for other petroleum related systems [18,19]. Further, this clearly shows, as suggested in the original article, that the use of the reference measurement point is important, because this measurement contains and provides useful information about the considered fluid.

4. The LBC Model

In petroleum engineering a commonly used empirical correlation based on the residual viscosity concept is the correlation by Jossi et al. [20], because it can be applied to both gases and liquids. However, this approach is generally referred to as the Lohrenz-Bray-Clark (LBC) correlation [8], because Lohrenz et al. introduced a procedure for calculating the viscosity of hydrocarbon mixtures and reservoir fluids using the same equation and coefficients originally derived by Jossi et al. [20] for pure fluids. This model

is a sixteenth degree polynomial in the reduced density, and due to this the viscosity estimations are highly dependent on the accuracy of the estimated reduced density $\rho_r = \rho/\rho_c$ or v_c/v . Here ρ_c is the critical density, whereas v_c is the critical molar volume. The LBC model is given below

$$\left[(\eta - \eta_0) \xi + 10^{-4} \right]^{1/4} = d_0 + d_1 \rho_r + d_2 \rho_r^2 + d_3 \rho_r^3 + d_4 \rho_r^4 \quad (8)$$

where η_0 is the dilute gas limit and ξ is the viscosity-reducing parameter defined as

$$\xi = \left(\sum_{i=1}^n x_i T_{c,i} \right)^{1/6} \left(\sum_{i=1}^n x_i P_{c,i} \right)^{-2/3} \left(\sum_{i=1}^n x_i M_{w,i} \right)^{-1/2} \quad (9)$$

where T_c and P_c are the critical temperature [K] and critical pressure [atm], respectively. Further, the calculated viscosity has the unit [mPa s] (cP), when the original d_i coefficients are used

$$\begin{aligned} d_0 &= 0.1023 & d_2 &= 0.058533 & d_4 &= 0.0093324 \\ d_1 &= 0.023364 & d_3 &= -0.040758 \end{aligned}$$

These coefficients were adjusted by Jossi et al. [20] using the following 11 pure compounds: argon, nitrogen, oxygen, carbon dioxide, sulfur dioxide, methane, ethane, propane, i-butane, n-butane, and n-pentane for reduced densities between 0.02 and 3.0.

In principle, the optimal performance with the LBC model should be obtained, when the experimental densities are used. Therefore, the experimental densities reported in [1-4] were used in conjunction with the calculation procedure originally derived for the LBC model [8] along with

the critical properties reported in the Table I. The obtained AAD, MxD, and Bias are given in Table VI. The performance of the LBC model is not satisfactory, since very large deviations are obtained for this asymmetrical ternary system. The viscosity is under predicted, since the Bias is negative and has the same numerical absolute value as the AAD. Further, it should be stressed that the deviations increase with increasing pressure or decreasing temperature, especially for viscous fluids. One explanation is that the model coefficients were adjusted on light fluids, and not on naphthenic and highly branched hydrocarbons – although these compounds are important constituents in petroleum and reservoir fluids.

An important property in the LBC model is the critical molar volume v_c due to the fact that the model is a sixteenth degree polynomial in the reduced density. Because of this, a common procedure within the oil industry in order to improve the viscosity calculations with the LBC model is to tune the critical molar volume of the considered fluid. However, since mixing rules were suggested for the critical molar volume in the LBC model [8], only a tuning of the critical molar volumes of the pure compounds was performed in order to improve the viscosity predictions. By minimizing the least squares, the critical molar volume of each pure compound was determined using the experimental densities and viscosities. For methylcyclohexane $v_c = 392.1 \text{ cm}^3 \cdot \text{mol}^{-1}$, while $v_c = 530.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ for cis-decalin and $v_c = 1018.8 \text{ cm}^3 \cdot \text{mol}^{-1}$ for 2,2,4,4,6,8,8-heptamethylnonane. The

resultant AAD, MxD, and Bias of the modeling of the pure compounds are given in Table VII, which also contains the results obtained for the binary systems and the ternary using the adjusted critical molar volumes. Although the tuned critical molar volumes of the pure compounds are around 10% higher than the values given in Table I, the performance of the LBC model is significantly improved (see Tables VI and VII). However, despite the tuning of the critical volumes of the pure compounds resulting in an improved performance of the LBC model, the obtained AAD and MxD are still higher than the resultant AAD and MxD reported for the other models considered in this work. Thus, it should be stressed that, in the case of mixtures, the performance of the LBC model could be further improved by directly tuning the critical density of each mixture. However, the model will no longer be considered predictive for mixtures.

Recently, a modification of the LBC model [21] has been proposed in which structural and thermal effects are introduced. The modified LBC model is given below

$$\left[(\eta - \eta_0) \xi + 10^{-4} \right]^{1/4} = h_0 + h_1 \rho_r + h_2 T_r^{q_2} M_w^{s_2} \rho_r^2 + h_3 T_r^{q_3} M_w^{s_3} \rho_r^3 + h_4 T_r^{q_4} M_w^{s_4} \rho_r^4 \quad (10)$$

where $T_r = T/T_c$ is the reduced temperature, and the h_i and q_i coefficients are given in [21]. In this model, the calculation procedure as well as the mixing rules is similar to those given for the original LBC model. For the considered ternary system, the calculated viscosities with the modified LBC

model were obtained using the experimental densities reported in [1-4] and with the required properties given from Table I. The experimental viscosities were compared with the calculated values resulting in the deviation results given in Table VIII. Although the performance of the modified LBC model are better than for the original LBC model (see Tables VI and VIII), significantly higher deviations are obtained with the modified LBC model compared to those obtained by the simple Grunberg-Nissan or Katti-Chaudhri mixing laws and the self-referencing model.

As it is the case with the original LBC model, the modified LBC model is also very dependent on the reduced density as well as the reduced temperature of the considered fluids. In order to optimize and improve the performance of the modified LBC model, a tuning of the critical molar volume as well as the critical temperature of each pure compound was performed using the experimental density and viscosity values. For methylcyclohexane $v_c = 386.7 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $T_c = 663.0 \text{ K}$, whereas for cis-decalin $v_c = 494.9 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $T_c = 1002.7 \text{ K}$, while $v_c = 929.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $T_c = 1045.8 \text{ K}$ for 2,2,4,4,6,8,8-heptamethylnonane. The resultant AAD, MxD, and Bias of the modeling of the pure compounds are given in Table IX.

For the optimal performance of the modified LBC model, the optimal critical temperature is significantly higher than the literature values reported in Table I. Further, these adjusted critical temperatures may not

have any physical meaning. In addition, the adjusted critical molar volumes are almost similar to the values given in Table I estimated by the SBWR EOS, except the tuned critical molar volume of methylcyclohexane, which is higher.

The tuning of the critical molar volume and the critical temperature of the pure compounds significantly improves the performance of the modified LBC model, but the deviations are still higher than those obtained for the other considered models in this work, except for the binary system composed of methylcyclohexane and cis-decalin. Further, the deviations increase with increasing viscosity.

5. Hard-Sphere Viscosity Scheme

This scheme [9,10] has been introduced for the simultaneous correlation of the self-diffusion, the viscosity, and the thermal conductivity of dense fluids over wide ranges of pressure and temperature. In this scheme, the transport properties of real dense fluids, expressed in terms of the reduced molar volume $v_r = v/v_0$ with v the molar volume and v_0 the hard-core molar volume, are assumed to be proportional to the exact hard-sphere values. For each reduced transport property universal curves have been determined as a function of v_r [10]. In this work, only the hard-sphere scheme introduced for viscosity estimation is described.

For rough spherical molecules at high densities, Chandler [22] showed that the self-diffusion coefficient and the viscosity could be related to the smooth hard-sphere values of the transport properties. This idea has been extended in [9,10] by assuming that a corresponding states relationship exists between the experimental transport properties of rough non-spherical molecules and the smooth hard-sphere values (subscript *shs*). Since, the experimental viscosity is proportional to the exact hard-sphere values, the following relation can be defined

$$\eta_{\text{exp}} = R_{\eta} \eta_{shs} \quad (11)$$

where the proportionality factor R_{η} is the roughness factor, which accounts for the roughness and non-spherical shape of the molecule.

However, in order to avoid calculating the viscosity directly, Dymond [23] found it convenient to express the viscosity as reduced quantities. Based on this, Dymond and Awan [9] derived the following expression relating the reduced smooth hard-sphere viscosity η_{shs}^* to the experimental value η_{exp}

$$\eta_{shs}^* = \frac{\eta_{\text{exp}}}{R_{\eta}} = 6.035 \cdot 10^8 \left[\frac{1}{M_w R T} \right]^{1/2} \frac{\eta_{\text{exp}} v^{2/3}}{R_{\eta}} \quad (12)$$

In order to determine R_{η} and v_0 for a given temperature a plot of $\log_{10}(\eta_{\text{exp}}^*)$ versus $\log_{10}(v)$ from the experiment is superimposed on a universal plot of $\log_{10}(\eta_{shs}^*)$ versus $\log_{10}(v/v_0)$ from the hard-sphere theory by vertical and

horizontal adjustments. The empirical expression for this universal curve is given below

$$\log_{10} \left[\frac{\eta_{\text{exp}}^*}{R_{\eta}} \right] = \sum_{k=0}^7 a_{\eta,k} (1/v_r)^k \quad (13)$$

with

$$\begin{array}{ll} a_{\eta,0} = & 1.0945 & a_{\eta,4} = & 797.6900 \\ a_{\eta,1} = & -9.26324 & a_{\eta,5} = & -1221.9770 \\ a_{\eta,2} = & 71.0385 & a_{\eta,6} = & 987.5574 \\ a_{\eta,3} = & -301.9012 & a_{\eta,7} = & -319.4636 \end{array}$$

The $a_{\eta,i}$ coefficients are universal, independent of the chemical structure of the compound. This has been verified by Baylaucq et al. [24,25]. It is generally assumed for pseudo-spherical molecules, such as n-alkanes, that v_0 is temperature dependent, whereas R_{η} is temperature independent [26].

In the case of methylcyclohexane and cis-decalin, no previous correlations have been given for v_0 and R_{η} . Due to this, a direct modeling of R_{η} and v_0 was carried out for each compound using the experimental viscosities and densities [1-3]. The estimation was performed with the following assumptions that R_{η} is temperature independent and the $a_{\eta,i}$ parameters are universal. Based on the estimated v_0 values at each temperature, the following expressions can be derived for methylcyclohexane

$$10^6 v_0 = 79.6874 + 0.0752363T + 1.51535 \cdot 10^{-4} T^2 \quad (13)$$

and for cis-decalin

$$10^6 v_0 = 155.894 - 0.182498T + 2.14956 \cdot 10^{-4} T^2 \quad (14)$$

where T is the temperature in [K] and v_0 in [$\text{cm}^3 \cdot \text{mol}^{-1}$]. The estimated value for the roughness factor R_η is 0.995974 for methylcyclohexane, which corresponds to a spherical molecule ($R_\eta = 1$) according to the definitions of R_η . R_η is a characteristic quantity related to the non-spherical shape of the molecule (see e.g. [26]). For cis-decalin the determined R_η value is 0.829246. The modeling resulted in an AAD of 0.75% for methylcyclohexane with a MxD of 2.74% and a Bias of 0.09%, whereas for cis-decalin the obtained AAD, MxD, and Bias are 1.75%, 8.33%, and – 0.20%, respectively.

For 2,2,4,4,6,8,8-heptamethylnonane, the following expression for v_0 is given [27]

$$10^6 v_0 = 272.252 - 0.2193951T + 1.54762 \cdot 10^{-4} T^2 \quad (15)$$

with $R_\eta = 0.898175$. The resultant AAD is 5.03% with a Bias of –3.69%, and a MxD of 28,2% obtained at 100 MPa and 293.25 K. These results are less satisfactory compared to those obtained for methylcyclohexane and cis-decalin. One reason can be the influence of the complex molecular structure of 2,2,4,4,6,8,8-heptamethylnonane on the viscosity. The deviation results for 2,2,4,4,6,8,8-heptamethylnonane found in this work are also higher than those obtained using the experimental values reported in [28] (AAD =

3.59%, Bias = -1.69%, and MxD = 23.8% found at 100 MPa and 293.25 K). For 2,2,4,4,6,8,8-heptamethylnonane, the experimental viscosity and density values at 100 MPa and 293.15 K reported in [1,3] are 22.77 mPa·s and 834.4 kg·m⁻³, whereas the values reported in [28] are 22.60 mPa·s and 836.1 kg·m⁻³, respectively. Although the difference between the density in [1,3] and [28] is only 0.20%, this difference has a very pronounced effect on the calculated viscosity value. By using the density value given in [1,3] at 100 MPa and 293.25 K the predicted viscosity is 16.35 mPa·s, whereas the calculated viscosity is 17.22 mPa·s when using the density value reported in [28]. The difference in the calculated viscosities is 5.32%, whereas the difference in the experimental viscosities is only 0.75%. The high sensitivity in the calculated viscosity with respect to the used molar volume (density) is due to the seven order polynomial as well as the exponential development in the reduced volume of the hard-sphere scheme.

In order to apply the hard-sphere scheme to mixtures, Assael et al. [29] introduced the following linear mixing rules

$$v_{0,mix} = \sum_{i=1}^n x_i v_{0,i} \quad ; \quad R_{\eta,mix} = \sum_{i=1}^n x_i R_{\eta,i} \quad ; \quad M_{w,mix} = \sum_{i=1}^n x_i M_{w,i} \quad (16)$$

The obtained AAD, MxD and Bias for the three binary systems and the ternary considered in this work are given in Table X. As it can be seen the highest AAD are found for mixtures containing 2,2,4,4,6,8,8-heptamethylnonane. For these mixtures the hard-sphere scheme over

predicts the viscosity, as indicated by the Bias. Further, the higher discrepancies found for these mixtures may be a result of the less satisfactory representation of the viscosity of 2,2,4,4,6,8,8-heptamethylnonane. However, the overall results are satisfactory, taking into account that for mixtures the viscosity predictions are totally predictive and only based on pure component properties. The performance of the hard-sphere scheme for this ternary system is better than the performance of the LBC models considered in this work, whereas the representation of the viscosity of this ternary system is less accurate compared to the results obtained with the self-referencing model with mixing rules (Table V).

6. Free-Volume Viscosity Model

Based on the free-volume concept, an approach has recently been proposed in order to model the viscosity of Newtonian fluids in the gaseous and dense states [11,12]. In this approach, the total viscosity η can be separated into a dilute gas viscosity term η_0 and an additional term $\Delta\eta$, in the following way

$$\eta = \eta_0 + \Delta\eta \quad (17)$$

The term $\Delta\eta$ characterizes the passage in the dense state and is connected to the molecular structure via a representation of the free volume fraction. In this model

$$\Delta\eta = \frac{\rho N_a \zeta L^2}{M_w} \quad (18)$$

where N_a is Avogadro's number, ζ the friction coefficient of a molecule, and L^2 an average characteristic molecular quadratic length. The friction coefficient ζ is related to the mobility of the molecule and to the diffusion process (diffusion of the momentum for viscosity). Moreover, the free volume fraction $f_v = v_f/v$ (with $v_f = v - v_0$, v the specific molecular volume and v_0 the molecular volume of reference or hard core volume) is for a given temperature T defined as

$$f_v = \left(\frac{RT}{E} \right)^{\frac{3}{2}} \quad (19)$$

by assuming that the molecule is in a state in which the molecular potential energy of interaction with its neighbors is E/N_a . Further, it has been assumed [11,12] that $E = E_0 + PM/\rho$ where the term $PM/\rho = Pv$ is related to the energy necessary to form the vacant vacuums available for the diffusion of the molecules and where $E_0 = \alpha\rho$ is the barrier energy, which the molecule has to exceed in order to diffuse.

Based on the empirical free-volume relation by Doolittle [30] (theoretically justified later [31,32]) for the viscosity, the following expression for the friction coefficient has been proposed [11,12]

$$\zeta = \zeta_0 \exp \left[\frac{B}{f_v} \right] \quad (20)$$

where B is characteristic of the free volume overlap. By inserting Eq.(20) into Eq.(18) leads to

$$\Delta\eta = \frac{\rho N_a L^2 \zeta_0 \exp(B/f_v)}{M_w} \quad (21)$$

The quantity ζ_0 has been defined [11,12] as

$$\zeta_0 = \frac{E}{N_a b_f} \sqrt{\frac{M_w}{3RT}} \quad (22)$$

where b_f is the dissipation length of the energy E .

The general expression of the free-volume viscosity model is obtained by combining Eqs.(17), (21), and (22) and given below

$$\eta = \eta_0 + \rho \ell \left(\frac{\alpha\rho + \frac{PM_w}{\rho}}{\sqrt{3RT M_w}} \right) \exp \left[B \left(\frac{\alpha\rho + \frac{PM_w}{\rho}}{RT} \right)^{3/2} \right] \quad (24)$$

where $\ell = L^2/b_f$ is homogeneous with a characteristic molecular length. This equation involves three physical parameters ℓ , α and B , which are characteristic of the molecule. The unit for the viscosity is [Pa·s], when all other units are kept in SI units. This model has been shown to accurately represent the viscosity behavior of various hydrocarbons over wide ranges of temperature and pressure in the gaseous, liquid and dense states.

The dilute gas viscosity η_0 can be obtained from any appropriate model. In this work, the model by Chung et al. [33] is used, since it is applicable of predicting the dilute gas viscosity of several polar and non-

polar fluids within an uncertainty of 1.5%. However, since the considered systems in this work are in the liquid state, any uncertainty in the dilute gas viscosity will not have any influence on the predicted total viscosity.

By using the experimental viscosity and density values given in [1-3], the three characteristic parameters in Eq.(24) were determined for methylcyclohexane, cis-decalin, and 2,2,4,4,6,8,8-heptamethylnonane, respectively. The fitted parameters are given in Table XI, whereas Table XII contains the modeling results.

In order to apply the free-volume model to mixtures, the following simple mixing rules have been proposed [34] in order to estimate the characteristic model parameters of mixtures based on the pure component parameters

$$\frac{1}{B_{mix}} = \sum_{i=1}^n \frac{x_i}{B_i} \quad ; \quad \ell_{mix} = \sum_{i=1}^n x_i \ell_i \quad (25)$$

It has been found that the variation of the specific energy parameter α with composition is approximately linear for the three binary systems considered in this work [1-3], which is probably linked to the fact that the considered ternary system is a very weakly interacting system. This leads to the writing of the following mixing rule in order to obtain the specific energy parameter of a mixture

$$\alpha_{mix} = \sum_{i=1}^n x_i \alpha_i \quad (26)$$

The viscosity predictions for the considered binary and ternary mixtures were performed using the above-mentioned mixing rules along with experimental densities [1-4]. A comparison of the predicted viscosities with the experimental values resulted in the AAD, MxD, and Bias presented in Table XII. The obtained results are very satisfactory, especially taking into account the simple structure of the model, since only three adjustable parameters are needed for each pure compound along with the experimental density of the fluid. Further, the obtained AAD are generally of the same order as the uncertainty reported for the experimental viscosities ($\pm 2\%$). By comparing the results obtained by the free-volume model (Table XII) with those obtained by the hard-sphere scheme (Table X), it can be seen that better results are obtained with the free-volume approach.

7. Friction Theory

Recently, starting from basic principles of mechanics and thermodynamics, the friction theory (*f-theory*) for viscosity modeling has been introduced [13]. In the *f-theory* the total viscosity can be written as

$$\eta = \eta_0 + \eta_f \quad (27)$$

where η_0 is the dilute gas viscosity and η_f the residual friction contribution.

The friction contribution is related to the van der Waals attractive and repulsive pressure terms, p_a and p_r , of an equation of states (EOS), such as the Peng and Robinson (PR) [35] or the Soave-Redlich-Kwong (SRK) [36]

EOS. These EOS are commonly used within the oil industry for phase behavior descriptions. Based on this concept, a general *f-theory* model [14] has been proposed with 16 universal constants and one adjustable parameter - a “characteristic” critical viscosity. For hydrocarbons with a simple molecular structure it has been shown that the *f-theory* models [13,14] consisting of a linear correlation on p_a and a quadratic correlation on p_r suffices to accurately represent the viscosity over wide ranges of temperature and pressure. However, in some cases, such as 2,2,4,4,6,8,8-heptamethylnonane, the molecular structure of the compound may induce an interlinking effect that results in an important reduction of the fluid mobility (high viscosity) when brought under pressure. For many of these systems, such dragging effects can be taken into account by a simple extension of the *f-theory* models with a third order p_r corrective term, as shown in [27,37]. A third order *f-theory* model can be written in the form

$$\eta_f = \kappa_a p_a + \kappa_r p_r + \kappa_{rr} p_r^2 + \kappa_{rrr} p_r^3 \quad (28)$$

where the kappa parameters are the temperature dependent friction coefficients.

In this work, the general *f-theory* model [14] with a third order repulsive correction term and in conjunction with the PR EOS has been used in order to achieve appropriate modeling of methylcyclohexane, cis-decalin, and 2,2,4,4,6,8,8-heptamethylnonane. This leads to the writing of the friction viscosity terms, Eq.(28), as

$$\eta_f = \eta^{GM} + \kappa_{rrr} p_r^3 \quad (29)$$

where η^{GM} is the friction viscosity term of the general model as defined in [14], whereas the κ_{rrr} coefficient is defined as

$$\kappa_{rrr} = d_2 (\exp(2\Gamma) - 1) (\Gamma - 1)^3 \quad (30)$$

with

$$\Gamma = \frac{T_c}{T} \quad (31)$$

and where d_2 is a component related parameter. The used dilute gas viscosity of the pure compounds has been obtained by the Chung et al. model [33]. All required pure component properties are given in Table I. With this *f-theory* approach, the modeling of the viscosity of the pure compounds requires the fitting of two parameters per compound: the characteristic critical viscosity η_c , used in the general *f-theory* model, and the d_2 constant. These two parameters were adjusted for each of the pure compounds considered in this work by a least-square fitting to experimental pure compounds viscosity values [1-3]. The adjusted parameters for the three pure compounds are reported in Table XIII, whereas the corresponding AAD, MxD, and Bias are given in Table XIV. In case of 2,2,4,4,6,8,8-heptamethylnonane and due to the use of more physical appropriate critical properties compared with the values reported in [27], led to the readjustment of the characteristic critical viscosity η_c , and the d_2 constant.

The viscosity predictions for the three binary systems and the ternary mixtures were performed in the following way: the dilute gas viscosity mixtures was estimated with the proposed mixing rule given in [13] which is based on the dilute gas viscosity of the pure compounds determined by the dilute gas viscosity model of Chung et al. [33]. The general PR *f-theory* model mixture contribution, η^{GM} , in Eq.(29) was treated according to the mixing rules proposed in [14], whereas the mixture third order friction coefficient, κ_{rrr} , was obtained with an exponential mixing rule [27] of the form

$$\ln(\kappa_{rrr,mix}) = \sum_{i=1}^n x_i \ln(\kappa_{rrr,i}) \quad (32)$$

In the PR EOS the regular van der Waals mixing rules were used without any binary interaction parameters.

A comparison of the predicted viscosities using this scheme with the experimental values was carried out, and the resultant deviations are reported in Table XIV. Given the kind of viscosity behavior this ternary system develops (see [1-4]), the obtained mixture results are satisfactory taking into account that they are obtained by a totally predictive method based on pure component properties and in conjunction with a simple cubic EOS. A comparison of the results given in Table XIV for the *f-theory* with those given in Table XII shows that the free-volume model gives better results, especially for the maximum deviation. One reason could be, as

already mentioned under the modeling of the ternary system 1-methylnaphthalene + n-tridecane + 2,2,4,4,6,8,8-heptamethylnonane [27], that the molecular structures of the components in the studied mixtures in this work may induce a possible interlinking effect, resulting in a higher viscosity as it is the case for mixtures containing 2,2,4,4,6,8,8-heptamethylnonane. This interlinking effect may be better related with the free volume than to a cubic EOS. However, an advantage of the *f-theory* is that it does not require the density of the considered fluid, and it is related to simple cubic EOS, which are commonly used in the petroleum industry as well as other industries.

8. Conclusion

An extensive evaluation of the performance of seven different viscosity approaches has been performed on the ternary system composed of methylcyclohexane, cis-decalin, and, 2,2,4,4,6,8,8-heptamethylnonane. For this system an extensive experimental study of the viscosity and density was recently carried out in the temperature range 293.15 K to 353.15 K and up to 100 MPa as a function of the composition, resulting in 1554 experimental data points for the viscosity. Although not as complex as real petroleum fluids, this ternary system is of interest for the evaluation of viscosity models for their potential application to the simulation of complex fluids with an asymmetrical molecular distribution, such as reservoir fluids

exposed to biodegradation or alteration. The considered models range from simple empirical correlations, such as the self-referencing model or the commonly used LBC model in petroleum engineering, to models with a physical and theoretical background, such as the hard-sphere scheme, the free-volume, and the friction theory. All these models are related to characteristic parameters and properties of the pure compounds. Further, they are totally predictive for mixtures.

It follows from the discussion that some simple predictive models, except the LBC model, are able to represent the viscosity of the ternary system within an acceptable and appropriate uncertainty for most applications within the oil industry. For comparison purposes, the deviations obtained with the Grunberg-Nissan mixing law, the self-referencing method with parameter mixing rules, the modified LBC model, the hard-sphere scheme, the free-volume model, and the *f-theory* model are shown versus the experimental values in Figure 2 for all T, P, x conditions of the ternary system (pure compounds, except for the Grunberg-Nissan mixing law, the binary and ternary mixtures) whereas Figures 3 and 4 show the obtained deviations versus pressure and temperature, respectively. For the studied ternary system, these figures reveal no significant fluctuation in the variation of the obtained deviations by a given model with temperature and pressure, except for the LBC correlation. The largest deviations for most of the models are obtained at the lowest temperature and highest pressure,

except for the self-referencing model. Further, these figures along with the corresponding tables show that the highest deviations are obtained for more viscous fluids, corresponding to mixtures containing 2,2,4,4,6,8,8-heptamethylnonane, which has a more pronounced viscosity increase when brought under pressure compared to the other involved compounds. The viscosity behavior of 2,2,4,4,6,8,8-heptamethylnonane is more complex to handle for the different models compared to the other involved compounds, see [1-3]. This may reflect more the higher deviations obtained by the considered models for the 2,2,4,4,6,8,8-heptamethylnonane containing mixtures than the general performance of the models, except the LBC model. Thus, it should be stressed that for a given fluid, the performance of a specific model can be improved, if the parameters or the model itself are readjusted or changed. In this case, the model will only be adequate for the considered system, and will no longer be considered as a general model.

Although the self-referencing model with parameter mixing rules gives the overall best performance for the considered ternary system, it can only be applied to liquids and dense fluids, but not gases, which are a common requirement within the oil industry. This is also the case for the mixing laws and the hard-sphere viscosity model. However from a fundamental point of view, the hard-sphere scheme as well as the free-volume model are interesting, because they give some insight on the microstructure of these complex fluids. But the variations of the density

versus pressure and temperature are required in these models. In the case of the hard-sphere scheme, the accuracy of the density has a pronounced influence on the estimated viscosity. The free-volume model and the friction theory are applicable to gases, liquids, and dense fluids, and due to this are more applicable within the oil industry. Moreover, the friction theory does not require the density, which is an advantage for practical use compared to the other methods. Further, the use of simple cubic EOS, which are commonly used within the oil industry, is also an advantage for applications within this industry. The widely used LBC model gives the largest maximum deviation and consequently fails to represent the viscosity of this ternary system, despite tuning, except for the modified LBC, which incorporates structural and thermal effects. Moreover the LBC model is also very dependent on the accuracy of the density. The performance of the simple mixing laws (Grunberg Nissan and Katti-Chaudhri) can be considered satisfactory due to their simplicity.

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List of Symbols

Latin Letters

B	Characteristic of the free-volume overlap.
b_f	Dissipative length.
E	Energy.
E_0	Barrier energy.
f_v	Free-volume fraction.
L^2	Average characteristic molecular quadratic length.
$\ell = L^2 / b_f$	Characteristic molecular length.
M_w	Molecular weight.
N_a	Avogadro's constant.
P	Pressure.
p_a	Attractive pressure term.
p_r	Repulsive pressure term.
R	Gas constant.
R_η	Roughness factor for viscosity.
T	Temperature.
T_c	Critical temperature.
v	Molar volume.
v_0	Hard-core volume.
v_f	Free volume.
v_r	Reduced molar volume.

x Mole fraction.

Greek Letters

Γ Defined in Eq.(31).

η Viscosity.

η_0 Dilute gas viscosity.

η_f Residual friction term.

κ_a Linear attractive friction coefficient.

κ_r Linear repulsive friction coefficient.

κ_{rr} Quadratic repulsive friction coefficient.

κ_{rrr} Third order repulsive friction coefficient.

ρ Density.

ρ_r Reduced density.

ξ Viscosity reducing parameter.

ζ Free-volume friction coefficient.

ω Acentric factor.

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	M_w [g·mol ⁻¹]	T_c [K]	P_c [MPa]	ω	v_c [cm ³ ·mol ⁻¹]
Methylcyclohexane	98.189	572.2	3.47	0.236	369.7
cis-Decalin	138.26	702.3	3.20	0.286	484.9
2,2,4,4,6,8,8-Heptamethylnonane	226.45	692.0	1.57	0.460	929.8

Table I. Pure component properties: M_w molecular weight, T_c critical temperature, P_c critical pressure, ω acentric factor and v_c critical molar volume.

	NP	AAD%	MxD%	Bias
<u>Grunberg-Nissan</u>				
Methylcyclohexane + cis-Decalin	294	2.18	7.71	1.51
Methylcyclohexane + HMN	294	9.98	15.4	-9.98
cis-Decalin + HMN	294	0.98	3.10	0.41
Methylcyclohexane + cis-Decalin + HMN	546	3.90	11.1	-3.82
<u>Katti-Chaudhri</u>				
Methylcyclohexane + cis-Decalin	294	2.02	7.17	1.26
Methylcyclohexane + HMN	294	15.3	22.0	-15.3
cis-Decalin + HMN	294	3.07	6.18	-3.07
Methylcyclohexane + cis-Decalin + HMN	546	8.56	17.5	-8.56

Table II. Results for viscosity predictions with the classical ideal mixing laws. HMN refers to 2,2,4,4,6,8,8-heptamethylnonane.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	41	5.32	11.4	-4.57
cis-Decalin	41	4.55	13.6	-3.80
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	41	19.4	43.1	-19.0
Methylcyclohexane + cis-Decalin	287	5.14	14.1	-4.80
Methylcyclohexane + HMN	287	15.4	41.8	-15.2
cis-Decalin + HMN	287	12.8	40.4	-12.5
Methylcyclohexane + cis-Decalin + HMN	533	12.0	37.6	-12.0

Table III. Results for viscosity predictions with the self-referring model using $T_0 = 293.15$ K as the reference temperature for each mixture.

	Methyl- cyclohexane	cis-Decalin	2,2,4,4,6,8,8- Heptamethylnonane
<i>a</i>	0	0.331972	1.28030
<i>b</i>	0.150266	0.383621	0.229255
<i>c</i>	1.93637	2.22826	4.97585
<i>d</i>	3.94327	11.8646	20.0657
<i>e</i>	22.0398	31.8285	40.0894
<i>f</i>	159.095	169.525	300.008
<i>g</i>	0	0	0
<i>h</i>	466.438	469.820	510.291
<i>i</i>	1327.87	1268.75	1300.05

Table IV. Pure component coefficients for the self-reference model.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	41	0.66	1.89	0.00
cis-Decalin	41	0.99	4.73	-0.01
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	41	1.45	6.72	-0.24
Methylcyclohexane + cis-Decalin	287	2.14	7.14	-0.14
Methylcyclohexane + HMN	287	2.91	12.9	-1.31
cis-Decalin + HMN	287	1.68	6.94	0.81
Methylcyclohexane + cis-Decalin + HMN	533	1.94	9.57	-0.73

Table V. Results for the viscosity prediction with the self-referencing model with mixing rules for the nine coefficients and with $T_0 = 293.15$ K as the reference temperature for each mixture.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	43.6	55.7	-43.6
cis-Decalin	42	67.2	84.2	-67.2
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	71.2	90.2	-71.2
Methylcyclohexane + cis-Decalin	294	54.6	81.2	-54.6
Methylcyclohexane + HMN	294	54.6	87.6	-54.6
cis-Decalin + HMN	294	66.3	89.1	-66.3
Methylcyclohexane + cis-Decalin + HMN	546	56.8	86.2	-77.0

Table VI. Results for viscosity predictions with the LBC model using experimental densities.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	4.05	13.7	-0.46
cis-Decalin	42	16.6	48.1	-3.77
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	21.6	64.5	-7.94
Methylcyclohexane + cis-Decalin	294	11.0	41.6	3.89
Methylcyclohexane + HMN	294	22.4	56.9	15.8
cis-Decalin + HMN	294	21.6	60.8	4.25
Methylcyclohexane + cis-Decalin + HMN	546	22.7	53.9	16.0

Table VII. Results for viscosity predictions with the LBC model using experimental densities and tuned v_c values.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	39.1	49.1	-39.1
cis-Decalin	42	49.9	69.2	-49.9
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	32.0	67.4	-32.0
Methylcyclohexane + cis-Decalin	294	43.4	66.1	-43.4
Methylcyclohexane + HMN	294	30.1	64.0	-30.1
cis-Decalin + HMN	294	35.2	66.4	-35.2
Methylcyclohexane + cis-Decalin + HMN	546	33.2	63.3	-33.2

Table VIII. Results for viscosity predictions with the modified LBC model using experimental densities.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	1.79	6.09	-0.30
cis-Decalin	42	2.92	15.6	-1.35
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	7.09	32.0	-2.39
Methylcyclohexane + cis-Decalin	294	2.76	11.6	0.62
Methylcyclohexane + HMN	294	6.97	26.8	5.27
cis-Decalin + HMN	294	8.68	27.3	6.36
Methylcyclohexane + cis-Decalin + HMN	546	9.38	20.7	8.69

Table IX. Results for viscosity predictions with the modified LBC model using experimental densities and tuned v_c and T_c values.

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	0.75	2.74	0.09
cis-Decalin	42	1.75	8.33	-0.20
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	5.03	28.2	-3.69
Methylcyclohexane + cis-Decalin	294	3.81	10.7	3.34
Methylcyclohexane + HMN	294	7.96	21.1	6.92
cis-Decalin + HMN	294	4.07	24.8	1.66
Methylcyclohexane + cis-Decalin + HMN	546	9.24	20.4	9.02

Table X. Results for viscosity predictions with the hard-sphere scheme.

	α [(J m ³) /(mole kg)]	B	l [Å]
Methylcyclohexane	69.5355	0.0133607	1.20024
cis-Decalin	103.800	0.0120304	0.749291
2,2,4,4,6,8,8-Heptamethylnonane	173.492	0.00778338	0.564770

Table XI. Characteristic parameters of pure compounds for the free-volume model

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	1.24	3.41	-0.02
cis-Decalin	42	1.22	3.77	-0.04
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	2.05	12.1	-0.58
Methylcyclohexane + cis-Decalin	294	3.67	10.3	3.58
Methylcyclohexane + HMN	294	5.03	12.6	4.92
cis-Decalin + HMN	294	1.62	11.3	-0.27
Methylcyclohexane + cis-Decalin + HMN	546	5.10	12.2	5.01

Table XII. Results for viscosity predictions with the free-volume model using experimental densities.

	η_c [μP]	d_2 [$\mu\text{P}/\text{bar}^3$]
Methylcyclohexane	403.312	$7.56912 \cdot 10^{-9}$
cis-Decalin	542.196	$8.07823 \cdot 10^{-9}$
2,2,4,4,6,8,8-Heptamethylnonane	360.028	$4.53230 \cdot 10^{-8}$

Table XIII. Characteristic critical viscosity η_c and third order PR friction constant d_2 .

	NP	AAD%	MxD%	Bias
Methylcyclohexane	42	3.72	10.1	-0.99
cis-Decalin	42	2.69	6.52	-0.39
2,2,4,4,6,8,8-Heptamethylnonane (HMN)	42	3.26	14.1	-0.39
Methylcyclohexane + cis-Decalin	294	6.78	17.2	6.40
Methylcyclohexane + HMN	294	5.94	17.8	-1.48
cis-Decalin + HMN	294	4.63	16.2	-4.41
Methylcyclohexane + cis-Decalin + HMN	546	4.81	18.8	-0.29

Table XIV. Results for viscosity predictions with the friction theory using the PR EOS.

Figure Captions

Figure 1. Ternary diagram representing the compositions as mole percent (dots) of the experimental viscosity and density study of the ternary system methylcyclohexane + cis-decalin + 2,2,4,4,6,8,8-heptamethylnonane reported in [1-4].

Figure 2. Performance of viscosity models shown as the deviation versus the experimental viscosity for all measured points of the pure compounds (except for the Grunberg-Nissan mixing law), the binary and ternary mixtures of the ternary system methylcyclohexane + cis-decalin + 2,2,4,4,6,8,8-heptamethylnonane. Experimental values reported in [1-4].

Figure 3. Performance of viscosity models shown as the deviation versus pressure for all experimental points of the pure compounds (except for the Grunberg-Nissan mixing law), the binary and ternary mixtures of the ternary system 1-methylcyclohexane + cis-decane + 2,2,4,4,6,8,8-heptamethylnonane. Experimental values reported in [1-4].

Figure 4. Performance of viscosity models shown as the deviation versus temperature for all experimental points of the pure compounds (except for the Grunberg-Nissan mixing law), the binary and ternary mixtures of the ternary system 1-methylcyclohexane + cis-decalin + 2,2,4,4,6,8,8-heptamethylnonane. Experimental values reported in [1-4].

Figure 1

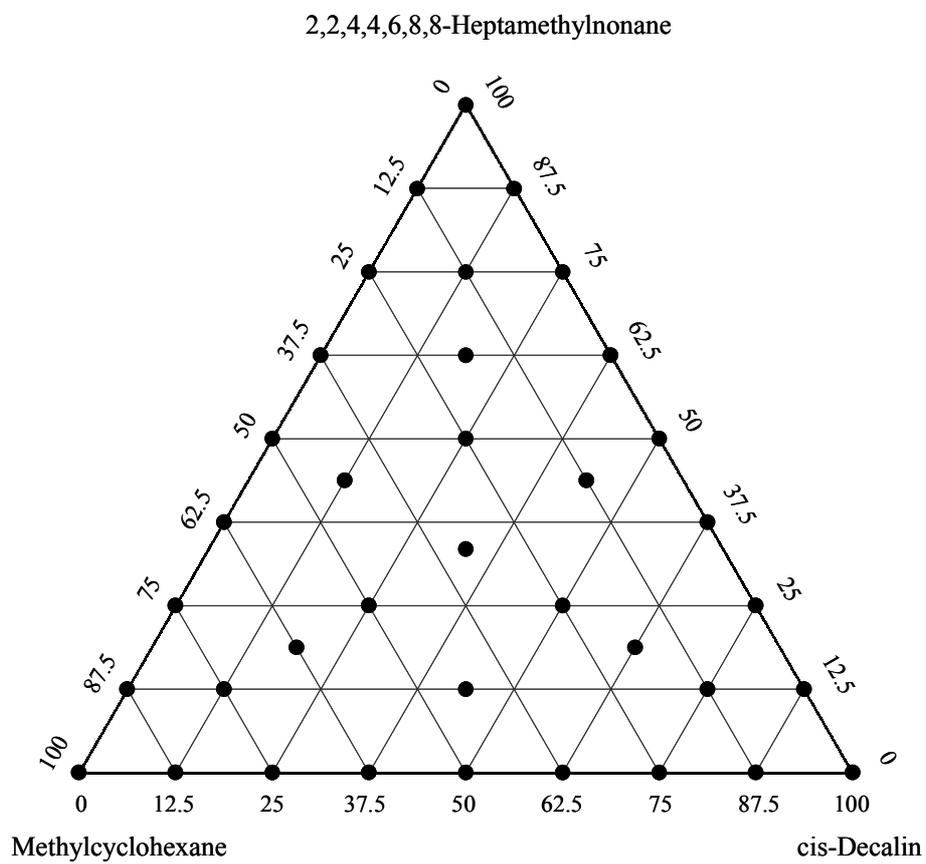


Figure 2

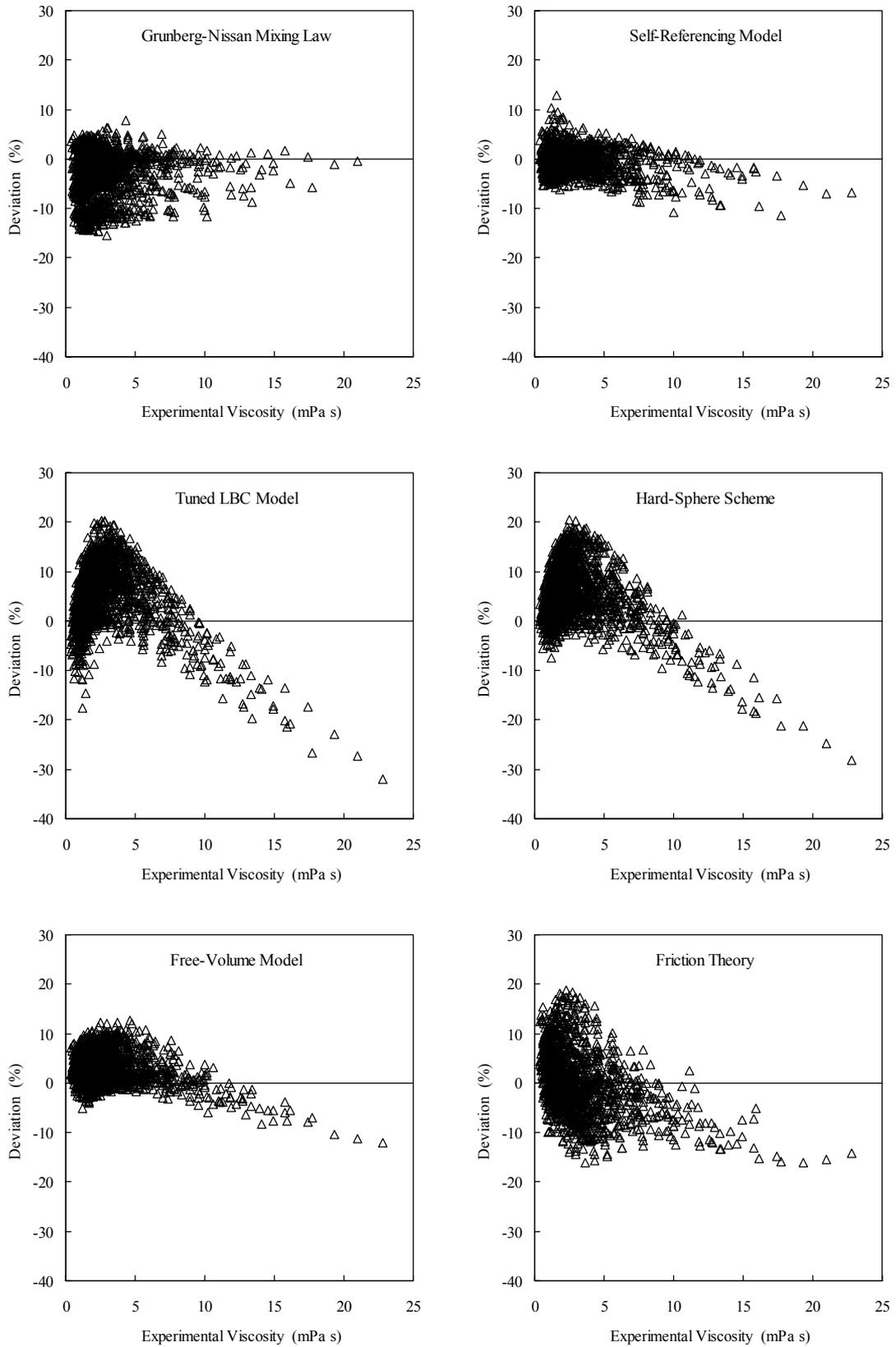


Figure 3

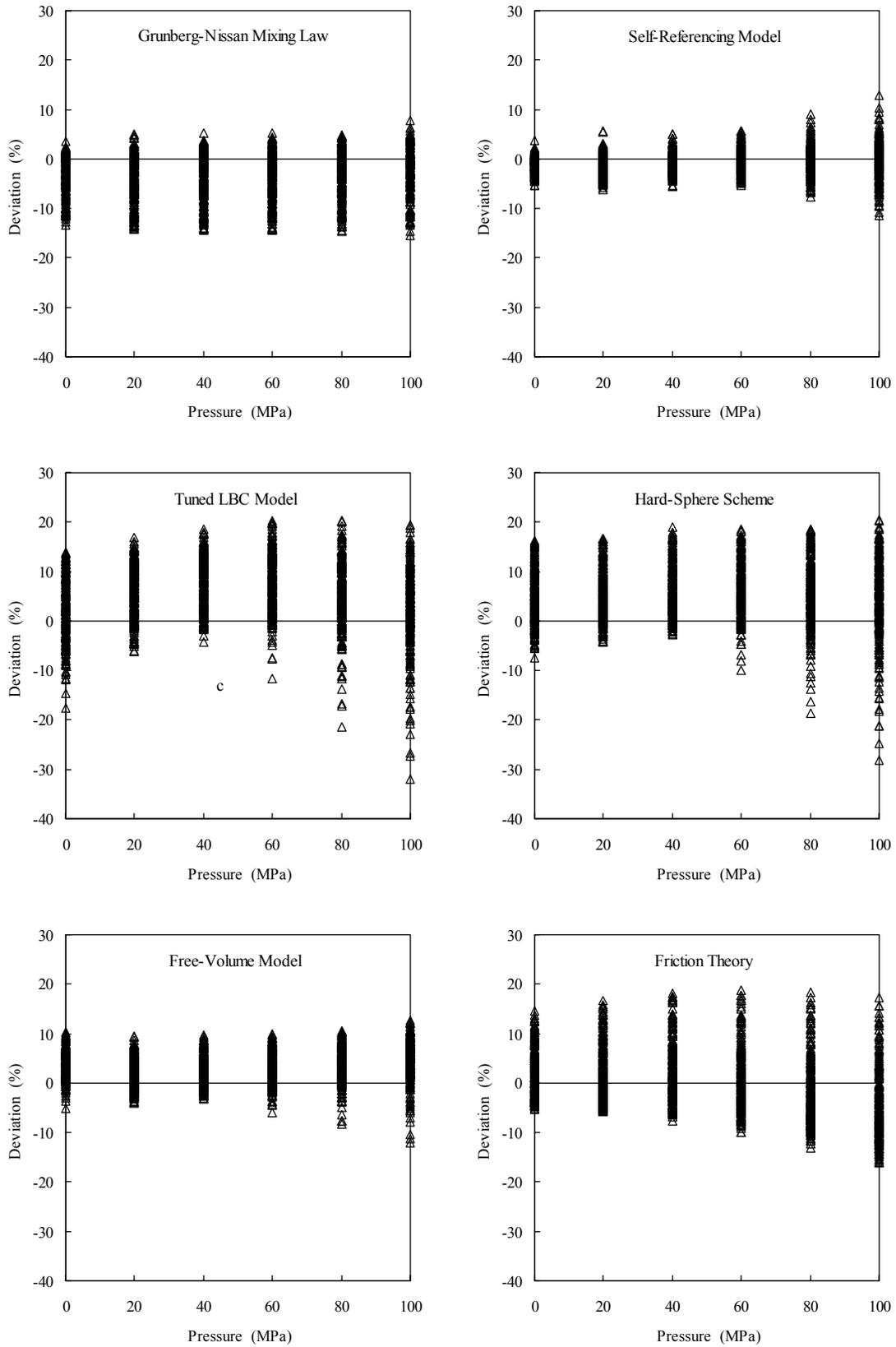


Figure 4

