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Prediction of the Viscosity of Supercritical Fluid Mixtures

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A method for predicting the viscosity of supercritical, multicomponent fluid mixtures, at any density, from the zero-density viscosity of pure components is presented. The method is based upon the results for a rigid-sphere model, suitably interpreted to apply to real fluids, and on the finding that the excess viscosity of pure supercritical fluids can be adequately described by a density function independent of temperature. The density range of the method extends to twice the critical density of the pure component with the smallest critical density. The only exception is for the methane-rich mixtures where the mixture density should not exceed 12000 $\mathrm{mol \cdot m^{-3}}$. The uncertainty ascribed to the predictions made by this method is of the order of $\pm 5\%$.

KEY WORDS: high pressure mixture; supercritical fluids; viscosity.

1. INTRODUCTION

A number of emerging, environmentally friendly technologies involve the extensive use of supercritical fluids [1]. For the process design to be optimal, an accurate and reliable knowledge of the thermophysical properties of supercritical fluids is prerequisite. The diversity of fluids and of conditions of interest precludes obtaining the relevant data by experimental means alone, thus requiring the development of prediction methods. The need for greater accuracy and internal consistency of predicted data favors prediction methods that are based on a solid theoretical framework and a stringent choice of primary data rather than those that are mere empirical correlations.

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One of the thermophysical properties of special interest to supercritical fluid technology is viscosity [1, 2]. The theoretical understanding of how the viscosity of a supercritical fluid behaves as a function of temperature and density is still limited [3]. Only in the regions of low density, corresponding to a dilute-gas limit, and near the critical point have sufficient advances been made to lead to the development of formal, theoretical descriptions of viscosity. Although the resulting theory, in most cases, does not allow for direct predictions, a small number of high-quality experimental data, when combined with theory, is often sufficient to enable accurate predictions. In all the other regions of phase space, the theoretical development is not yet at this stage. Invariably, the industrial processes involving supercritical fluids tend to operate at medium to high pressures away from the critical point, thus requiring the viscosity data in the regions where the theory is incomplete.

A number of prediction methods has been proposed both for the viscosity of pure supercritical fluids and of supercritical fluid mixtures at medium to high pressures [3, 4]. For pure fluids the most accurate are the prediction methods that rely on viscosity correlations based on critical analysis of the available viscosity data [3, 5, 6]. If such a correlation does not exist, one has to rely on more general methods [7] that are based on similarity in the behavior of viscosity as a function of density for a number of related fluids, and consequently incorporate, in one form or another, the corresponding-states principle [8]. For supercritical fluid mixtures the large number of possible component combinations and consequent lack of an extensive experimental database precludes the development of explicit correlations in most cases. The prediction methods that rely on a corresponding-states principle are still possible and useful [7, 9], but in general do not take advantage of any developments in kinetic theory and employ an empirical function to account for density dependence [7]. Furthermore, in order to estimate mixture critical parameters, these methods require mixing rules that, at least in principle, need to be optimized by recourse to experimental mixture viscosity data.

Recently, a new type of prediction method has been developed that has its basis in kinetic theory and consequently does not require any knowledge of the critical parameters of a mixture [3, 10, 11]. The method is based on rigid-sphere theory which is adequately modified to take into account the behavior of real supercritical fluids in a self-consistent manner. Comparison with the limited experimental data indicated that the method allows the evaluation of the viscosity of fluid mixtures to within a few percent [11]. Although accurate, the method requires a knowledge of pure-component viscosities as a function of density over the whole range of interest. This rather limits its applicability only to fluid mixtures made of components for which viscosity correlations are available. Furthermore, the method requires a knowledge of component viscosities at the molar density of the mixture. These are not always available, since there are circumstances in which the molar density of the mixture is such that one or more pure components of the mixture are in the two-phase region, at the mixture molar density.

In the present paper a modification of the method of Vesovic and Wakeham [10, 11] is presented whereby the limitations discussed above are removed. This is achieved by incorporating a recent development in representing the excess viscosity of a number of supercritical pure fluids by a single density-dependent function [12]. The new procedure is tested against experimental data for a wide variety of systems.

2. THEORY

2.1. Methodology of Vesovic and Wakeham

Only essential elements of the Vesovic and Wakeham (VW) methodology for calculating the mixture viscosity are presented here, and the reader is referred to the original publications [10, 11] for more detail. The viscosity of a supercritical fluid mixture, η, can be written in the form [11]

$$\eta = -\begin{vmatrix} H_{11} & \cdots & H_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix} + \kappa_{\text{mix}} \tag{1}$$

$$Y_i = x_i \left[1 + \sum_{j=1}^{N} \frac{m_j}{m_i + m_j} x_j \alpha_{ij} \bar{\chi}_{ij} \rho \right] \tag{2}$$

$$H_{ii} = \frac{x_i^2 \bar{\chi}_{ii}}{\eta_i^{(0)}} + \sum_{j \neq i} \frac{x_i x_j \bar{\chi}_{ij}}{2A_{ij}^* \eta_{ij}^{(0)}} \frac{m_i m_j}{(m_i + m_j)^2} \left[\frac{20}{3} + \frac{4m_j}{m_i} A_{ij}^* \right] \tag{3}$$

$$H_{ij} = -\frac{x_i x_j \bar{\chi}_{ij}}{2A_{ij}^* \eta_{ij}^{(0)}} \frac{m_i m_j}{(m_i + m_j)^2} \left[\frac{20}{3} - 4A_{ij}^* \right] \tag{4}$$

$$\kappa_{\text{mix}} = \frac{15}{5\pi} \rho^2 \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \bar{\chi}_{ij} \alpha_{ij}^2 \eta_{ij}^{(0)} \tag{5}$$

where ρ is the molar density and $\eta_i^{(0)}$, x_i, and m_i are the zero-density viscosity, mole fraction, and the molecular mass, respectively of species i. $\eta_{ij}^{(0)}$ is the zero-density interaction viscosity, while A_{ij}^* is a weakly temperature dependent function for the $i-j$ pair interaction. Both quantities are readily available from the analysis of experimental zero-density mixture viscosity data or can be obtained by means of the corresponding-states principle [13]. The parameter α_{ij} accounts for the mean free path shortening for an $i-j$ collision in the dense fluid, whereas $\bar{\chi}_{ij}$ is the pseudo-radial distribution function for the species i and j in the presence of all other species in the mixture. The pseudo-radial distribution function, $\bar{\chi}_{ij}$, is constructed by means of the following mixing rule which has no adjustable parameters,

$$\bar{\chi}_{ij}(\rho, T) = 1 + \frac{2}{5} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1) + \frac{6(\bar{\chi}_i - 1)^{1/3} (\bar{\chi}_j - 1)^{1/3}}{5[(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}]} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1)^{2/3} \tag{6}$$

while α_{ij} is obtained, for each isotherm, from

$$\alpha_{ij}(T) = \tfrac{1}{8}(\alpha_{ii}^{1/3} + \alpha_{jj}^{1/3})^3 \tag{7}$$

The pseudo-radial distribution function for a pure component i is calculated from the viscosity of the pure species

$$\bar{\chi}_i(\rho, T) = \frac{\beta}{2} \frac{(\eta_i - \rho\alpha_{ii}\eta_i^{(0)})}{\rho^2\alpha_{ii}^2\eta_i^{(0)}} \pm \beta \left[\left(\frac{\eta_i - \rho\alpha_{ii}\eta_i^{(0)}}{2\rho^2\alpha_{ii}^2\eta_i^{(0)}} \right)^2 - \frac{1}{\beta\rho^2\alpha_{ii}^2} \right]^{1/2} \tag{8}$$

where $\beta = 0.8299$ [11].

In general, the solution of Eq. (8) yields two roots, $\bar{\chi}_i^+$ and $\bar{\chi}_i^-$, corresponding to the positive and negative signs of the bracketed quantity in Eq. (8), respectively. To ensure the realistic physical behavior of the pseudo-radial distribution function, $\bar{\chi}_i$, obtained from Eq. (8), it is necessary to switch from $\bar{\chi}_i^-$ branch to $\bar{\chi}_i^+$ branch of the solution at some particular density ρ^* at which the two roots are equal. The switch-over density is obtained from the solution of the equation

$$\left.\frac{\partial\eta_i}{\partial\rho}\right|_T = \frac{\eta_i}{\rho} \tag{9}$$

If the switch-over density is chosen in this way, such that it marks a state where the density derivative of the viscosity, $(\partial\eta/\partial\rho)_T$, is equal to the kinematic viscosity, η/ρ, then the parameter α_{ii} can be determined uniquely, for a given isotherm, from

$$\frac{\eta_i}{\eta_i^{(0)}\alpha_{ii}\rho^*} = 1 + \frac{2}{\sqrt{\beta}} \tag{10}$$

This allows for a unique determination of the pseudo-radial distribution function $\bar{\chi}_i$, as a function of density at each isotherm for each pure component.

In order to evaluate the viscosity of a fluid mixture at a particular molar density, one first has to solve Eq. (9) for each pure component at the temperature of interest and then evaluate α_{ii} for each pure component by making use of Eq. (10). Then the construction of the pseudo-radial distribution function for each fluid at a given temperature is achieved using Eq. (8) with an appropriate change of the root from $\bar{\chi}_i^-$ to $\bar{\chi}_i^+$ at the switch-over density ρ^*. Equation (6) then permits evaluation of $\bar{\chi}_{ij}$ for each pair of molecules i and j. Thereafter, the application of Eqs. (1)–(5) with appropriate $\eta_{ij}^{(0)}$ and A_{ij}^* yields the viscosity of the supercritical fluid mixture at the selected temperature and molar density.

Hence, in order to evaluate the viscosity of the supercritical mixture, one only needs a knowledge of the two interaction parameters in the dilute gas limit, $\eta_{ij}^{(0)}$ and A_{ij}^*, together with the knowledge of the viscosity of all pure components. The viscosity of pure components has to be known as a function of density at each isotherm of interest, in order to be able to solve Eq. (9) for the switch-over density. The two interaction parameters can be estimated either from the experimental mixture viscosity data in the dilute-gas limit, or by means of the corresponding-states principle and, for most pair interactions, are readily available. The viscosity as a function of density of the well studied fluids is also readily available [3, 5, 6].

For fluids where the experimental measurements are scarce, there are no readily available correlations of viscosity and, therefore, no direct way to solve Eq. (9). Furthermore, even for well-studied fluids, the mixture properties might be required at the temperature and molar density where the pure component exhibits gas-liquid phase transition and its viscosity is not available as a smooth and continuous function of density. Under these circumstances the method described would have to rely on very approximate ways of solving Eq. (9) for some of the components in question and estimating the resulting supercritical mixture viscosity.

2.2. Modifications

It has been demonstrated recently [12], by making use of the best available experimental viscosity data, that the excess viscosity of a number of supercritical fluids (Ar, N_2, O_2, CO_2, CH_4, C_2H_6 and C_3H_8) is independent of temperature to within the quoted accuracy of the experimental data. Lack of reliable and extensive data precluded the investigation of other fluids, but there is no reason to believe that the other nonpolar supercritical fluids will behave differently. Moreover a single, general expression has been proposed, based on a corresponding-states principle representation, for the excess viscosity as a function of reduced density:

$$\Delta\eta_{\mathrm{corr}}(\rho) = \frac{1}{\xi} \sum_{i=1}^{n} b_i \left(\frac{\rho}{\rho_c}\right)^i \tag{11}$$

where ρ_c is the critical density and parameter ξ is given by

$$\xi = 1.202 \times 10^8 \left[\frac{T_c}{M^3 P_c^4}\right]^{1/6} \tag{12}$$

where M is the molecular weight in $\mathrm{kg \cdot mol^{-1}}$, P_c is the critical pressure in Pa, and T_c is the critical temperature in K. The optimum values of coefficients b_i are listed in Table I. The proposed overall correlation, Eq. (11), represents the viscosity of the supercritical fluids to within $\pm 5\%$. Nevertheless, at very high densities some systematic trends were observed for two of the fluids tested and high density data for methane did exhibit stratification leading to deviations larger than 5%. Thus, it was deemed necessary to limit the above representation to densities twice the critical density. With this limitation in place, the overall correlation is adequately accurate to incorporate it into the method for predicting the mixture viscosity of supercritical fluids.

The present modification of the VW method [11] consisted of replacing the viscosity of pure components by the viscosity calculated from the expression

$$\eta(T, \rho) = \eta^{(0)}(T) + \Delta\eta_{\mathrm{corr}}(\rho) \tag{13}$$

where $\eta^{(0)}$ is the viscosity in the zero-density limit and $\Delta\eta_{\mathrm{corr}}$ is the excess viscosity calculated from the expression given by Eq. (11). The zero-density

Table I. Coefficients b_i for the Representation of the Excess Viscosity, Eq. (11)

i	b_i
1	0.017143
2	1.70632
3	−2.52888
4	2.35935
5	−1.01337
6	0.17728

viscosity $\eta^{(0)}$ is still evaluated directly from the relevant correlations for a given component.

The advantages of the present methodology over the VW one [11] are threefold. First it allows the calculations of the viscosity of any pure component to densities twice the critical density independent of temperature. Thus, in a number of cases, this significantly increases the range of validity of mixture calculations without the need for any extrapolation procedures. Secondly, it allows the estimation of the viscosity of pure components where the viscosity as a function of density is not available. The only requirement is that the viscosity in the zero-density limit is known. Thirdly, under the circumstances that the mixture density is such that some of the components are in the two-phase region, the above formulation affords an elegant way of estimating the viscosity of a hypothetical pure component. Furthermore, the present method needs only the simplest input information, namely the behavior of the zero-density viscosity contribution for each pure component.

The disadvantage is that the present methodology can only be used to predict the viscosity of supercritical fluid mixtures and cannot be extended to cover vapor and liquid regions of the phase space.

3. RESULTS

The scarcity of reliable high-pressure measurements of the viscosity of supercritical fluid mixtures makes the proposed scheme, or any other scheme for that matter, very useful, but at the same time very difficult to test comprehensively. Since this scheme is a modification of an existing one [11] and since there have not been many measurements in the meantime, it was decided to test the present scheme against the same set of data that was used previously [10, 11]. The previously employed data sets were chosen on the basis of critically assessing all the available data, bearing in mind the need for each set to test a slightly different aspect of the proposed prediction methods.

It is customary to measure and report viscosities as a function of pressure at a given temperature. Most of the prediction methods work on the basis of predicting the viscosity at a given temperature and density. Thus, it is necessary to convert temperature, pressure pairs into the appropriate temperature, density pairs. In the case of pure fluids, this can be easily achieved by means of a single equation of state [4–6]. For mixtures, such a straightforward procedure is not possible and one has to evaluate the mixture density by means of different thermodynamic models [14]. For the purposes of this work we have employed a two-fluid reference model [15]. For the mixtures of interest to this work, the claimed accuracy is of the order of ± 0.5 to 1% at the most, which when translated into viscosity might result in an uncertainty of $\pm 1\%$ at the highest densities. In the rare cases where the investigators reported the measured densities, as well as the pressures, we have used their experimental density in preference to the calculated ones. Unless indicated otherwise, for a given mixture, all the densities have been calculated.

The interaction parameters $\eta_{ij}^{(0)}$ and A_{ij}^* at a given temperature can be obtained by analyzing the experimental mixture viscosity in the zero-density limit as a function of composition. Only for a very few mixtures is such information available, especially at more than one temperature. Thus, in order to make the present method applicable to the widest range of supercritical fluid mixtures, the interaction parameters $\eta_{ij}^{(0)}$ and A_{ij}^* were obtained from the readily available and reasonably accurate corresponding-states representation [13]. A consequence of this implementation is a marginal loss in accuracy of the proposed methodology.

Finally, the setting of an upper limit of twice the critical density on the validity of Eq. (11) implies that for each pure component this upper density limit should not be exceeded. The upper limit on the mixture density is then set by the requirement that it cannot exceed twice the value of the lowest pure component critical density.

3.1. The Viscosity of Air

There exists a large body of experimental data on the viscosity of air. The critical assessment of the data was undertaken by Kadaya and his coworkers [16] who also produced a correlation that is valid in the temperature range $200 \leqslant T/K \leqslant 1500$ up to pressures of 100 MPa. This still serves as the recommended representation of the viscosity of air and the values of viscosity obtained have an associated uncertainty of $\pm 2\%$ below 15 MPa rising to $\pm 3\%$ at the highest pressures. Thus, this representation offers a convenient and reliable means of testing the present prediction method.

Air has been treated as a three-component mixture ($x_{N_2} = 0.7841$; $x_{O_2} = 0.2066$; $x_{Ar} = 0.0093$) and the zero-density viscosity contributions, $\eta^{(0)}(T)$, of the pure components have been obtained from the currently recommended viscosities representations for N_2 [17], O_2 [18], and Ar [19]. The comparisons with the representation of Kadoya et al. [16] were performed over the range of densities up to twice the critical density for a number of supercritical isotherms ranging from 200 to 1000 K.

Figure 1 shows the deviation of the predicted viscosity values from the representation of Kadoya et al. as a function of density. The deviations exhibit a systematic increasing trend with increasing density. At pressures

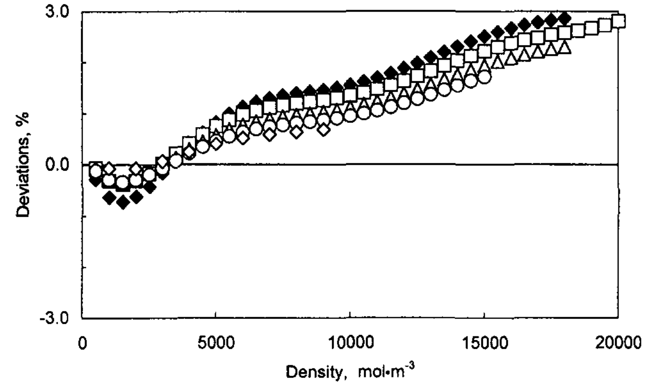

Fig. 1. Deviations, $[(\eta_p - \eta_{exp})/\eta_{exp}] \times 100\%$, of the predicted values, η_p, of the viscosity of air from the "experimental" values, η_{exp}, as a function of molar density, ρ. [(◆) $T = 200$ K; (□) $T = 300$ K; (△) $T = 400$ K; (○) $T = 500$ K; (◇) $T = 1000$ K].

below 15 MPa the deviations are within ±1.6%, increasing to 3.0% at the highest densities. Thus, the predicted viscosity values are just within the uncertainty ascribed to the correlation of Kadoya et al.. The systematic trend, observed in Fig. 1, is mainly a consequence of the approximations inherent in the present method, which require the excess viscosity to be independent of temperature and prescribe it in a specific analytical form. Nevertheless, comparison with a correlation, rather than directly with the experimental data, exaggerates the trend by forcing the deviations to be a smooth function of density. The present method performs marginally worse than the VW method [11] which also achieved remarkably good agreement by reproducing the data of Kadoya et al. [16] within their quoted uncertainty.

3.2. The Viscosity of Hydrogen-Methane Mixture

The viscosity of hydrogen-methane mixtures has been measured experimentally by Iwasaki and Takahashi [20] as a function of density along two isotherms for three different mixture compositions. The measurements have a claimed uncertainty of ±1.5%. The system is of particular interest to this work, since the viscosity data on hydrogen have not been used in developing the general correlation for the excess viscosity, Eq. (11). Thus, the present method has to rely on obtaining the relevant hydrogen parameters without recourse to any experimental information at moderate or high densities. The predictions of the hydrogen-methane mixture viscosity were obtained by application of the present method whereby the zero-density viscosity contributions, $\eta^{(0)}(T)$, of the pure components have been obtained from the currently recommended viscosity representations for H_2 [21] and CH_4 [22].

Figure 2 shows the deviations of the predicted viscosity values from the experimental ones as a function of density. The overall deviations are within ±2.0% which is again just outside the uncertainty ascribed to the experimental data. Nevertheless, the agreement can be termed very satisfactory, since the root-mean-square (rms) deviation from the experimental data is ±1.1% and only two predicted data points lie outside the ascribed uncertainty of the experimental data. The deviations of the present method are commensurable with those of the VW method which also predicted the experimental viscosity values within ±2.0% uncertainty limits.

3.3. The Viscosity of Hydrogen-Methane-Nitrogen Mixture

Viscosity measurements at moderate and high densities of ternary mixtures are very rare, with the exception of air which has been already discussed. Thus, the measurements made by Golubev and Petrov [23] on the hydrogen-methane-nitrogen mixture prove to be a valuable source of data for testing the prediction methods. The viscosity measurements were carried out at a number of isotherms for nitrogen-rich ($x_{H_2} = 0.247$; $x_{CH_4} = 0.198$; $x_{N_2} = 0.555$) and hydrogen-rich ($x_{H_2} = 0.625$; $x_{CH_4} = 0.170$; $x_{N_2} = 0.205$) mixtures for pressures up to 80 MPa. No uncertainty was

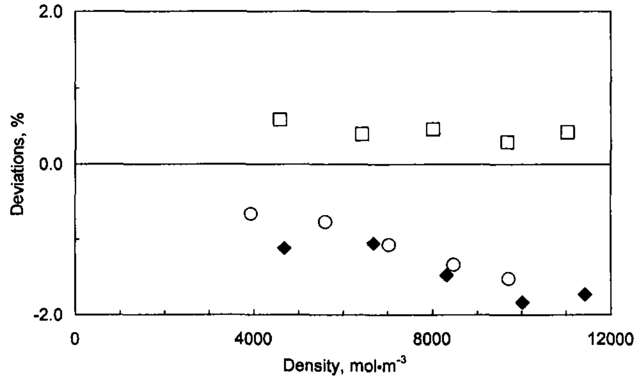

Fig. 2. Deviations, $[(\eta_p - \eta_{exp})/\eta_{exp}] \times 100\%$, of the predicted values, η_p, of the viscosity of CH_4-H_2 from the experimental values, η_{exp}, as a function of molar density, ρ. [(◆) $T = 298$ K; $x_{CH_4} = 0.552$; (□) $T = 298$ K, $x_{CH_4} = 0.359$; (○) $T = 348$ K, $x_{CH_4} = 0.552$].

ascribed to the data by the authors, but on the basis of examining [3, 5, 6] the other experimental data produced in the same laboratory, ±3 to 4% uncertainty limits would not be unreasonable. The zero-density viscosity contributions for the three pure components have been obtained from the correlations already mentioned [17, 21, 22].

Figure 3 shows the deviations of the predicted viscosity values from the experimental ones as a function of density. The data pertaining to the nitrogen-rich mixture along three isotherms extends to densities of 11000 mol · m^{-3}. The present method under-predicts the experimental data with an rms deviation of ±1.9%, the maximum deviation being −3.1%. This indicates reasonable agreement with the experimental data. Furthermore, the VW method [11] reproduced these data with the same accuracy, which leads to the conclusion that the approximations introduced in the present method have only a small effect on the deviations observed.

The data pertaining to the hydrogen-rich mixtures are also illustrated in Fig. 3. These data, along two isotherms, extend to much higher densities of 20300 mol · m^{-3}. The present method over-predicts the data with a root-mean-square deviation of ±2.8%, the maximum deviation being 6.9%. The deviations increase rapidly for densities higher than 12000 mol · m^{-3} and display an obvious systematic trend. This observation is not supported by the results obtained by means of the VW method [11], which reproduced the experimental data for the hydrogen-rich mixture within ±2%, with no systematic trend observed. The failure of the present method is entirely due to the failure of Eq. (11) to predict the excess

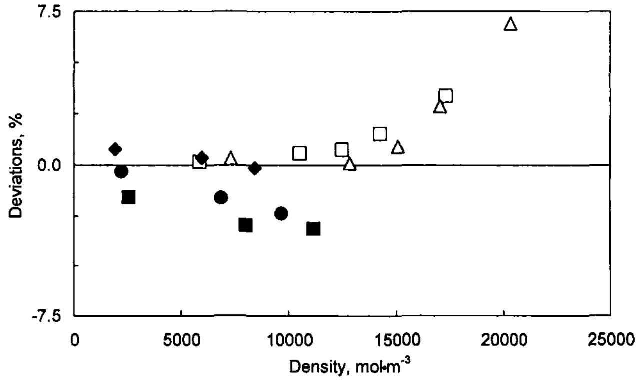

Fig. 3. Deviations, $[(\eta_p - \eta_{exp})/\eta_{exp}] \times 100\%$, of the predicted values, η_p, of the viscosity of CH_4-H_2-N_2 mixture from the experimental values, η_{exp}, as a function of molar density, ρ. [nitrogen-rich mixture: (◆) $T = 286$ K; (●) $T = 327$ K; (■) $T = 374$ K; hydrogen-rich mixture: (△) $T = 298$ K; (□) $T = 373$ K].

viscosity of methane at high densities. It has been observed [12] that the best methane excess viscosity experimental data show systematic stratification from the data for other fluids at reduced densities higher than 1.2, which for methane corresponds to 12000 $\mathrm{mol \cdot m^{-3}}$. At present, there is no theoretical reason for the observed methane behavior and in order not to degrade the general accuracy of the present method further, it is prudent to introduce the upper density limit for the methane-rich mixtures of 12000 $\mathrm{mol \cdot m^{-3}}$.

Following the aforementioned discussion it can be observed that the present method predicts the available data on the viscosity of the hydrogen-methane-nitrogen mixture up to densities of 12000 $\mathrm{mol \cdot m^{-3}}$ with an overall accuracy of ±3%. This level of accuracy is commensurate with the accuracy of the VW method [11] and is within the estimated uncertainty of Golubev and Petrov's experimental data [23].

3.4. The Viscosity of Methane-Propane Mixture

The viscosity of the methane-propane mixture is of interest to this work, since the range of temperatures and densities at which the measurements were performed encompasses the two-phase region of propane. Thus, some of the viscosity measurements can be used to test the prediction power of the present method at mixture densities where one of the pure components is in the two-phase region of the thermodynamic phase space.

The viscosity of the methane-propane mixture has been extensively measured by Giddings et al. [24] around the critical point including vapor, supercritical, and liquid regions. The claimed uncertainty of the data is ±0.5%. A critical assessment of the measurement technique and comparison of the Giddings and co-workers viscosity data for other fluids [3, 5, 6] with the data of other experimentalists led us to believe that a more realistic uncertainty would be ±2 to 3% [11]. The predictions of the methane-propane mixture viscosity were obtained by application of the present method whereby the zero-density viscosity contributions, $\eta^{(0)}(T)$, of the pure components have been obtained from the currently recommended viscosity representations for C_3H_8 [25] and CH_4 [22].

Figure 4 shows the deviations of the predicted viscosity values from the experimental ones as a function of density. The overall deviations are within ±4.0% with one data point being over-predicted by as much as 6%. This is outside the reassigned accuracy of the experimental data, but is well within the prediction of the VW method. The VW method predicts the data with a rms deviation of ±2.6%, while the present method does marginally better with an rms deviation of ±2.5%.

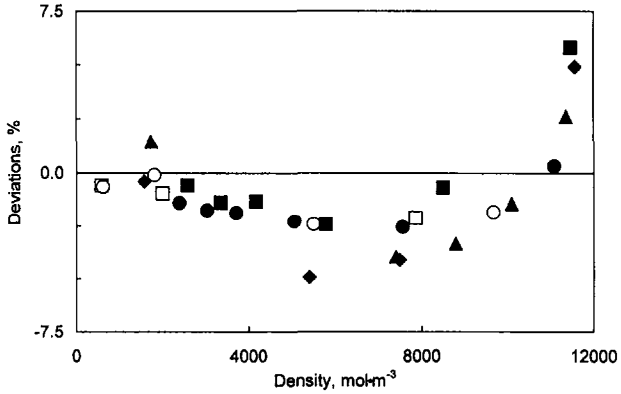

Fig. 4. Deviations, $[(\eta_p - \eta_{exp})/\eta_{exp}] \times 100\%$, of the predicted values, η_p, of the viscosity of CH_4–C_3H_8 mixture from the experimental values, η_{exp}, as a function of molar density, ρ. [(□) $T = 311$ K, $x_{CH_4} = 0.6139$; (○) $T = 311$ K, $x_{CH_4} = 0.7910$; (▲) $T = 378$ K, $x_{CH_4} = 0.2207$; (◆) $T = 378$ K, $x_{CH_4} = 0.3878$; (■) $T = 378$ K, $x_{CH_4} = 0.6139$; (●) $T = 378$ K, $x_{CH_4} = 0.7910$].

The critical temperatures of methane and propane are 190.5 and 369.8 K respectively, while the experimental data refers to two isotherms, namely 378 and 311 K. At the higher temperature, both pure components are above their critical temperatures and are therefore in the supercritical phase. At 311 K as the pressure is increased, propane undergoes a phase change and the vapor and liquid saturation densities are 648.1 and 10686 mol · m^{-3}, respectively. Although propane can exist between these two densities in a metastable state, the measurements of the viscosity of metastable fluids are not usually included in the development of general viscosity representations [3–6, 17–19, 22, 25]. As such, the viscosity of propane when plotted against the density, at 311 K, exhibits a discontinuity between 648.1 and 10686 mol · m^{-3}. Hence, if the properties of the mixture are required at such densities, the VW method [11] requires the construction of a hypothetical propane, which is equivalent to normal propane, but it does not undergo a phase change. The present method has no need for such a construction, since it evaluates all the excess properties from Eq. (11) which is a smooth and continuous function of density. It is therefore interesting to compare how well the present method predicts the viscosity under such conditions.

The five experimental points that correspond to these conditions are under-predicted by, on average, 2%, which is remarkably good. It is difficult to make any conclusions on the basis of such a small set of data, but the results are certainly encouraging.

3.5. The Viscosity of Nitrogen-Methane Mixture

An extensive investigation of the viscosity of the nitrogen-methane mixture has been carried out by Diller [26] both in the liquid and supercritical regions. The liquid region is of no interest here, since the present method, as such, cannot be extended to predict liquid viscosities. The data obtained in the supercritical region is of considerable interest, since some of it refers to an equimolar mixture, the properties of which are usually most difficult to predict. The ascribed uncertainty of the data in the supercritical region ranges from ±2% to ±4% near the critical region. The zero-density viscosity contributions for both pure components have been obtained by means of the already mentioned representations [17, 22], while the mixture densities have been taken from the experimental values quoted by Diller [26].

Figure 5 shows the deviations of the predicted viscosity values from the experimental ones as a function of density for the equimolar mixture ($x_{N_2} = 0.50115$; $x_{CH_4} = 0.49885$) for three isotherms. The available experimental data extend to densities of 19000 mol · m^{-3}, but the comparison is only performed at densities lower then 12000 mol · m^{-3} because of the upper limit imposed on pure methane as explained in Section 3.3.

The viscosity data along 250 K isotherm are predicted with an rms deviation of ±2.8%, the maximum deviation being 3.7%. This is outside the claimed uncertainty of the experimental data, but only marginally worse than the deviations obtained by using the VW method. The viscosity data along the 200 K isotherm is under-predicted by, on average, 6%.

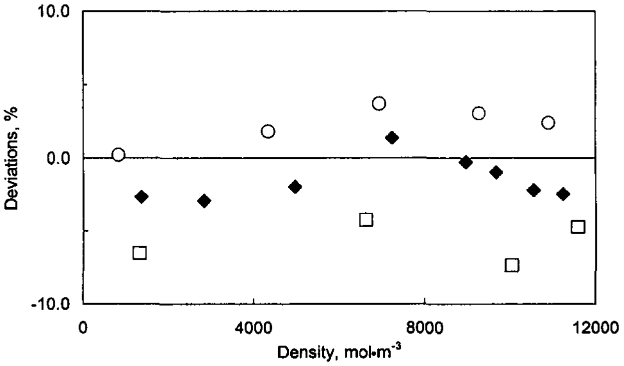

Fig. 5. Deviations, $[(\eta_p - \eta_{exp})/\eta_{exp}] \times 100\%$, of the predicted values, η_p, of the viscosity of CH_4-N_2 mixture from the experimental values, η_{exp}, as a function of molar density, ρ. [(◆) $T = 170$ K; (□) $T = 200$ K; (○) $T = 250$ K].

These are by far the largest average deviations observed for any system studied. Similar deviations from the experimental data are also observed if one were to employ the VW method [11]. It is instructive to observe that deviations do not show any obvious increasing or decreasing trend with density. Furthermore, the zero-density viscosity for this system has been extensively studied and is believed to be known with an accuracy of ± 1 to 2% [13] with which the present prediction methods are in agreement. If the experimental data for the 200 K isotherm were to be extrapolated to zero density the zero-density viscosity of the mixture would be underpredicted by about 5%. This leads us to believe that the experimental data along the 200 K isotherm might exhibit a systematic error.

The viscosity data along the 170 K isotherm is predicted with an rms deviation of ± 2.2%, the maximum deviation being -2.9%. This is within the claimed uncertainty of the experimental data taking into account that this isotherm is just 8 K above the critical temperature of the mixture. Furthermore, at this temperature, methane exhibits a phase change corresponding to a vapor saturation density of $2800\,\mathrm{mol \cdot m^{-3}}$ which implies that seven experimental data points are at densities that correspond to the two-phase region for methane. The present method does remarkably well in predicting the mixture viscosities at these densities with an rms deviation of ± 2%. Thus, this further strengthens the case that Eq. (11) is a very useful tool for predicting the excess viscosity at densities which correspond to the two-phase region of some of the pure components.

4. CONCLUSIONS

A generalization of the method for the evaluation of the viscosity of dense multicomponent fluids is presented and tested against experimental data. The modified method, capable of predicting the viscosity of supercritical, multicomponent mixtures, requires as input only the viscosity data of the pure components in the dilute-gas limit. The method requires no knowledge of mixture properties at high pressures, but it assumes that the excess viscosity of each pure component can be adequately described by a universal density function independent of temperature.

A set of experimental data has been chosen, following a critical assessment of the accuracy, range, and diversity of mixtures in order to validate the method. It has been shown that the present method reproduces most of the data with an uncertainty marginally worse than the claimed experimental uncertainty of the data. Nevertheless, the deviations are sufficiently small to lead to the conclusion that the present method is capable of predicting the viscosity of supercritical fluid mixtures with an accuracy adequate for most industrial requirements.

The limitations of the present method are related to the range of validity. The present method is only valid to densities twice the critical density of the pure component with the smallest critical density. Furthermore, for methane-rich mixtures, the maximum density should not exceed $12000\,\mathrm{mol \cdot m^{-3}}$. Within these limits the evidence presented indicates that the method is capable of predicting the viscosity of supercritical, multicomponent fluid mixtures within $\pm 5\,\%$.

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