Viscosity of Natural-Gas Mixtures: Measurements and Prediction[1]

M. J. Assael,[2, 3] **N. K. Dalaouti,**[2] **and V. Vesovic**[4]

New measurements of the viscosity of a natural-gas mixture are reported. The measurements were performed in a vibrating-wire viscometer, in the temperature range from 313 to 455 K at a pressure close to atmospheric and in the temperature range from 240 to 353 K at pressures up to 15 MPa. The uncertainty of the reported measurements is estimated to be $\pm 1\%$. The data were employed to validate further an existing method of predicting the viscosity of mixtures at high pressures.

KEY WORDS: natural gas; vibrating wire; viscosity.

1. INTRODUCTION

Although natural gas is widely used for both domestic and industrial use, very few measurements of its viscosity have been reported in the open literature [1–3]. The available data sets are further restricted, since in only a few cases are all the details of the experimental setup published, thus making it very difficult to judge the uncertainty and reliability of the published data. To our knowledge, only two investigators [1, 2] have reported measurements of the viscosity of natural-gas mixtures obtained in a well-characterized apparatus with an adequate uncertainty. The present measurements attempt to fill this gap.

Natural gas is a multicomponent fluid mixture, and the behavior of natural-gas transport properties thus represents a challenging test for developments in kinetic theory. The development of predictive methodology to

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[2] Faculty of Chemical Engineering, Aristotle University, 54006 Thessaloniki, Greece.

[3] To whom correspondence should be addressed.

[4] TH Huxley School of Environment, Earth Sciences and Engineering, Imperial College, London SW7 2BP, United Kingdom.

evaluate the viscosity of fluid mixtures relies heavily on the availability of accurate and reliable experimental data for validation purposes. The measurements reported in this work provide a very useful data set, especially since experimental viscosity data for multicomponent mixtures at moderate and high pressures are very scarce. In the context of this work the data are used to validate further the Vesovic and Wakeham (VW) scheme for predicting the viscosity of gas mixtures at high pressure [4–6]. The VW method is based on rigid-sphere theory, which is adequately modified to take into account the behavior of real fluids in a self-consistent manner.

2. VISCOMETER

The measurements of the viscosity of the natural-gas mixture were performed in a vibrating-wire viscometer, because of its high precision and the availability of a full theoretical background in interpreting the results. The viscometer has already been employed for the measurements of the viscosity of gas mixtures of nitrogen with water, methane with water [7], and refrigerant vapors [8].

The viscometer consists of a tungsten wire with a nominal diameter of 7μm. The upper end of the wire is kept in place by a chuck, insulated from the support plate by PTFE washers. At its lower end, the wire carries a weight of about 1.5 g, which keeps the wire under constant tension. The homogenous field of 1 T, in which the wire vibrates, is provided by two samarium–cobalt magnets, placed in a magnetic-steel shell. Electrical connections to the wire are made through the upper chuck and the bottom weight.

The wire motion is excited by the application of two pulses of opposite sign to the wire. In this way a symmetric oscillation is induced in the wire, and the wire performs a damped oscillating motion in the gas. The emf produced by the oscillatory motion of the wire in the magnetic field is amplified and then detected by an analog-to-digital (A/D) converter. The decay of the transverse vibrations, which conform to a damped sinusoidal oscillation, is fitted by an equation of the form

$$y = y_0 e^{(i - \Delta)\,\omega t} \tag{1}$$

where ω is the angular frequency and Δ is the logarithmic decrement of oscillation. The logarithmic decrement Δ is related to the properties of the fluid and the wire by the equation

$$\Delta = \frac{(\rho/\rho_{\mathrm{w}})\,k' + 2\Delta_0}{2[\,1 + (\rho/\rho_{\mathrm{w}})\,k\,]} \tag{2}$$

Here ρ_w is the density of the wire material, ρ is the density of the fluid, and Δ_0 is the logarithmic decrement in vacuum. The viscosity of the fluid, η, enters through the Reynolds number, Ω:

$$\Omega = \rho \omega R^2 / \eta \qquad (3)$$

In the equations above, k and k' are given by

$$k = -1 + 2 \operatorname{Im}(A) \qquad (4)$$

and

$$k' = 2 \operatorname{Re}(A) + 2\Delta \operatorname{Im}(A) \qquad (5)$$

where

$$A = (i - \Delta) \left\{ 1 + \frac{2K_1(s)}{sK_0(s)} \right\} \qquad (6)$$

and

$$s = [(i - \Delta)\,\Omega]^{1/2} \qquad (7)$$

The symbols K_0 and K_1 represent modified Bessel functions. The viscosity of the fluid can be determined by solving the above equations, provided that the density and the radius of the wire, R, and the fluid density are known.

3. EXPERIMENTAL

The measurements were performed in two parts.

(a) Initially the viscometer was placed in a specially designed oven and the measurements near atmospheric pressure (not exceeding 0.3 MPa) and from 313 to 455 K were performed.

(b) For the second set of experiments, the viscometer was placed in a high-pressure vessel in a thermostated bath capable of maintaining temperatures lower than room temperature, and measurements from 240 to 353 K and up to 15 MPa were performed.

The two ranges overlap each other, and the measurements performed in the common region were used as a further check of the accuracy and consistency of the reported experimental data.

3.1. Measurements Near Atmospheric Pressure

For the measurements in the temperature range from 313 to 455 K at pressures below 0.3 MPa, the viscometer was suspended from the top lid of a low-pressure vessel. The whole assembly was the same as the one used for the measurement of the viscosity of gas mixtures of nitrogen with water and methane with water [7]. The vessel was constructed from stainless steel, for a maximum working pressure of 5 MPa. Sealing was achieved by Viton O-rings. The two electrical connections came out of the pressure vessel by means of metal-sheathed wires. The pressure vessel was placed in a specially built cylindrical furnace. To ensure very good and stable temperature control, the furnace was made of three independent zones—the middle one, where the pressure vessel was placed, being the largest—each one controlled separately with an accurate PID controller (Jumo dTron 04). The temperature was recorded with two platinum resistance thermometers, placed on the top and the bottom part of the vessel, calibrated against a standard Tinsley platinum resistance thermometer certified to ± 1 mK (Class 1, NPL) with an uncertainty of better than ± 30 mK. All temperatures refer to ITS-90. The stability of the temperature over 1 h was better than 50 mK, and the maximum temperature difference between the top and the bottom of the vessel never exceeded 100 mK.

The vessel was filled with the natural gas mixture under vacuum, which was achieved by using an Edwards 1.5 rotary vacuum pump. The pressure was measured with a Druck PDCR 910 pressure transducer with an uncertainty of 0.001 MPa.

3.2. Measurements at Higher Pressures

For the pressure measurements in the temperature range from 240 to 353 K, the viscometer was placed in a pressure vessel and the whole assembly was the same as the one used for the measurements of the viscosity of refrigerants in the vapor phase [8]. The pressure vessel was made of stainless steel for a maximum working pressure of 100 MPa. Electrical contacts out of the pressure vessel were accomplished in the same way as in the previous case. The pressure vessel was sealed with Viton O-rings and was placed in a thermostated bath. A Julabo F81-MV external circulator was employed for controlling the temperature of the heat-transfer fluid, which in turn circulated inside the tubes that controlled the temperature in the bath. In this way, the temperature in the bath was very stable (± 10 mK) and the temperature gradients were kept within a tolerable level (< 100 mK). Above room temperature ethylene glycol was employed as both the

heat-transfer and the bath fluid, while below room temperature ethanol was used as the heat-transfer liquid and propanol as the bath liquid. The temperature was measured with three platinum resistance thermometers, embedded along the pressure vessel wall.

The platinum resistance thermometers employed were also calibrated over the whole temperature range as discussed previously, to an uncertainty of better than ± 20 mK. The pressure vessel was filled with natural gas under vacuum, while the pressure was measured with a Druck PTX 520 pressure transducer with an uncertainty of 0.01 MPa.

4. VISCOSITY PREDICTION

The viscosity of a fluid mixture, η, can be written in the form [4–6]

$$\eta = - \begin{vmatrix} H_{11} & \cdots & H_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{vmatrix} \bigg/ \begin{vmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{vmatrix} + \kappa_{\mathrm{mix}} \tag{8}$$

where

$$Y_i = x_i \left[1 + \sum_{j=1}^{N} \frac{m_j}{m_i + m_j} x_j \alpha_{ij} \bar{\chi}_{ij} \rho_{\mathrm{m}} \right] \tag{9}$$

$$H_{ii} = \frac{\chi_i^2 \bar{\chi}_{ii}}{\eta_i^{(0)}} + \sum_{j \neq i} \frac{x_i x_j \bar{\chi}_{ij}}{2 A_{ij}^* \eta_{ij}^{(0)}} \frac{m_i m_j}{(m_i + m_j)^2} \left[\frac{20}{3} + \frac{4 m_j}{m_i} A_{ij}^* \right] \tag{10}$$

$$H_{ij} = - \frac{x_i x_j \bar{\chi}_{ij}}{2 A_{ij}^* \eta_{ij}^{(0)}} \frac{m_i m_j}{(m_i + m_j)^2} \left[\frac{20}{3} - 4 A_{ij}^* \right] \tag{11}$$

$$\kappa_{\mathrm{mix}} = \frac{15}{5\pi} \rho_{\mathrm{m}}^2 \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \bar{\chi}_{ij} \alpha_{ij}^2 \eta_{ij}^{(0)} \tag{12}$$

In the above equations, ρ_{m} is the molar density and $\eta_i^{(0)}$, x_i, and m_i are the zero-density viscosity, mole fraction, and 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. 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,

$$\bar{\chi}_{ij}(\rho_{\mathbf{m}}, T) = 1 + \frac{2}{5} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1) + \frac{6(\bar{\chi}_i - 1)^{1/3}(\bar{\chi}_j - 1)^{1/3}}{5[(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}]}$$
$$\times \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1)^{2/3} \qquad (13)$$

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

$$\alpha_{ij}(T) = \tfrac{1}{8}(\alpha_{ii}^{1/3} + \alpha_{jj}^{1/3})^3 \qquad (14)$$

The pseudo-radial distribution function for a pure component i is calculated from the viscosity of the pure species, as described in a number of recent publications [4–6]. To construct a realistic pseudo-radial distribution function that monotonically increases with increasing density, one is constrained in the choice of parameter α_{ii}. In fact, at each temperature, the requirement that the pseudo-radial distribution function is a continuous function of the molar density uniquely determines the value of parameter α_{ii}. This, in turn, allows for a unique determination of the pseudo-radial distribution function, $\bar{\chi}_i$, as a function of the molar density at each isotherm for each pure component [4–6].

To evaluate the viscosity of the mixture, one needs a knowledge of the two interaction parameters in the dilute gas limit, $\eta_{ij}^{(0)}$ and A_{ij}^*, together with a knowledge of the viscosity as a function of the molar density of all pure components. 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.

5. RESULTS

5.1. Experimental Data

The natural-gas mixture was supplied by Air Liquide SA, Greece, certified to the following composition: CH_4 (84.84 mol%), C_2H_6 (8.40 mol%), C_3H_8 (0.50 mol%), N_2 (5.60 mol%), and CO_2 (0.66 mol%). The uncertainty in the composition quoted was less than 0.01%.

The measurements of the viscosity of the natural-gas mixture that cover the temperature range from 313 to 455 K at near-atmospheric pressure, and were performed with the viscometer placed in the furnace, are

Table I. Measurements of the Viscosity of a Natural-Gas Mixture (CH_4, 84.84 mol%; C_2H_6, 8.4 mol%; C_3H_8, 0.50 mol%; N_2, 5.60 mol%; CO_2, 0.66 mol%) Near Atmospheric Pressure

T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
312.724	0.242	1.702	11.97
333.649	0.251	1.655	12.57
352.673	0.256	1.592	13.11
375.619	0.266	1.557	13.79
394.167	0.264	1.470	14.31
414.577	0.271	1.437	14.83
434.776	0.267	1.346	15.36
454.968	0.273	1.317	15.85

listed in Table I. The measurements that cover the temperature range from 240 to 353 K as a function of pressure, and were performed with the viscometer placed in the thermostated bath, are listed in Table II.

As discussed in detail previously [8], the uncertainty of the measurements is estimated to be ± 1%, while their precision and their reproducibility are much better. The continuing good operation of the instrument was checked by measuring, before and after the present results, the viscosity of nitrogen in the fashion discussed elsewhere [8].

5.2. Predictions of the VW Method

The VW method works on the basis of predicting the viscosity at a given temperature and density. Thus, it is necessary to convert temperature, pressure experimental pairs into the appropriate temperature, density pairs. The density of the natural gas mixture was calculated by the AGA8-DX92 correlation of Jaeschke and Schley [9], which is based on an extended virial-type equation. The uncertainty of this correlation is ± 0.1% for the temperature range from 265 to 335 K and pressures up to 12 MPa and ± 0.3% for the other temperature and pressure ranges.

Viscosity values of the five pure components of the natural-gas mixture, required as input for the VW method, were obtained from the currently recommended viscosity representations for CH_4 [10], C_2H_6 [11], C_3H_8 [12], N_2 [13], and CO_2 [14]. The interaction parameters $\eta_{ij}^{(0)}$ and A_{ij}^*, at a given temperature, were obtained from the corresponding-states representation [15], which is based on an extensive analysis of the available experimental data on transport properties at low pressures.

Table II. Measurements of the Viscosity of a Natural-Gas Mixture (CH_4, 84.84 mol%; C_2H_6, 8.4 mol%; C_3H_8, 0.50 mol%; N_2, 5.60 mol%; CO_2, 0.66 mol%) as a Function of Pressure

T (K)	P (MPa)	ρ (kg·m^{-3})	η (μPa·s)
241.137	0.36	3.320	9.77
241.094	1.04	9.877	9.82
263.304	0.29	2.435	10.43
263.316	2.07	18.41	10.67
263.323	4.10	39.15	11.24
263.309	6.12	63.04	12.14
263.309	8.16	90.74	13.39
263.348	9.60	112.06	14.42
293.963	0.31	2.326	11.44
293.956	2.06	16.05	11.58
293.949	4.03	32.76	12.05
293.929	6.02	51.09	12.65
293.929	8.04	71.09	13.47
293.924	10.08	92.14	14.47
293.936	12.19	114.98	15.77
293.963	14.04	134.46	17.02
322.866	0.30	2.045	12.21
322.852	2.04	14.27	12.45
322.866	4.04	29.08	12.82
322.846	6.06	44.85	13.34
322.846	8.05	61.06	13.93
322.866	10.07	78.00	14.61
322.866	12.08	95.11	15.48
322.896	14.01	111.43	16.36
353.369	0.31	1.928	13.09
353.369	2.04	12.91	13.25
353.369	4.04	26.06	13.66
353.369	6.05	39.70	14.06
353.369	8.06	53.70	14.54
353.381	10.07	67.91	15.11
353.394	12.12	82.49	15.77
353.388	13.96	95.50	16.37

Figure 1 shows the deviation of the predicted viscosity values from the experimental data as a function of the molar density for the five isotherms studied in this work. The only systematic trends observed are at the lowest temperatures. The experimental data are predicted with an rms deviation of 1.5%. This is well within the combined accuracy of the VW method and of the experimental data. The deviations observed further validate the
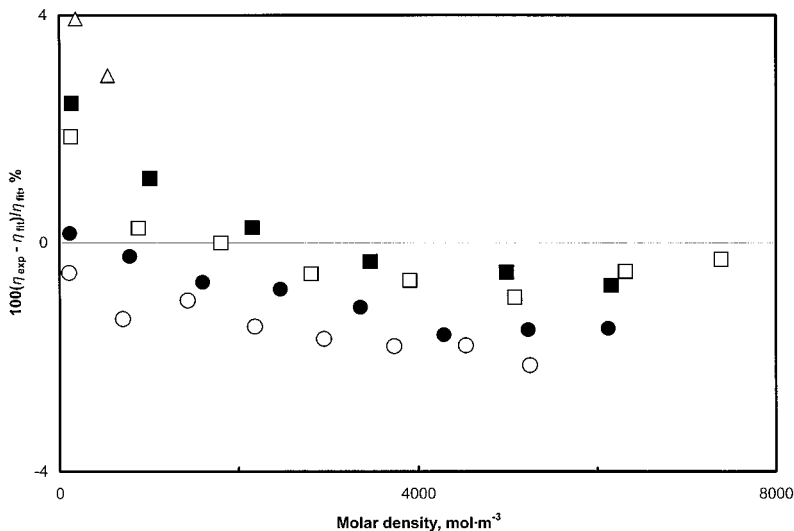
Fig. 1. Percentage deviations of the high-pressure viscosity measurements from the values predicted by the VW scheme: ($\bigcirc$) 353.4 K; ($\bullet$) 322.9 K; ($\square$) 293.9 K; ($\blacksquare$) 263.3 K; ($\triangle$) 241.1 K.
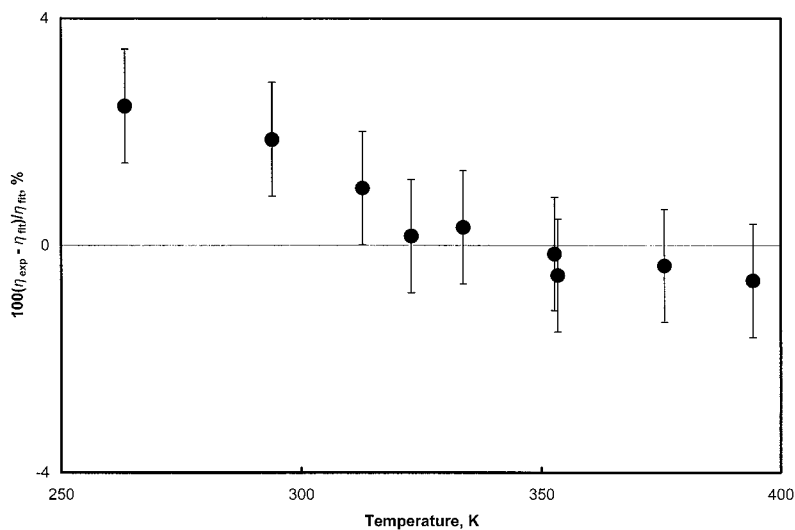

Fig. 2. Percentage deviations of the near-atmospheric-pressure viscosity measurements from the values predicted by the VW scheme.

VW method as a prediction method capable of predicting the viscosity of mixtures at moderate and high pressures with an estimated accuracy of $\pm 5\%$ [6].

Figure 2 illustrates the deviations of the predicted viscosity values from the experimental data as a function of temperature at the lowest pressure measured for each isotherm. In each case the pressure is sufficiently low, below 0.2 to 0.3 MPa, that the resulting viscosity is essentially the zero density viscosity, to within, at most, 0.6%. In the limit of zero density, the VW method reduces to the first-order kinetic theory expression for the mixture viscosity [16]. If these expressions are used in the predictive mode, where the first-order pure component viscosities are replaced by the experimental viscosities, the method is estimated to be accurate to ± 1 to 2% [16]. The absolute deviations observed in Fig. 2 are thus within the accuracy of the method. The temperature trend at low temperatures can be attributed to the higher uncertainty in measurements in that region.

6. CONCLUSIONS

The measurements of the viscosity of a natural-gas mixture were performed in a vibrating-wire viscometer. The experimental viscosity data are reported in the temperature range from 313 to 455 K at a pressure close to atmospheric and in the temperature range from 240 to 353 K at pressures up to 15 MPa. The uncertainty of the reported measurements is estimated to be $\pm 1\%$.

The predictions of the VW method for evaluating the viscosity of mixtures at high pressures were compared with the reported experimental data. The VW method performed remarkably well by reproducing all the available experimental data with an rms deviation of 1.5% and a maximum deviation of -3.8%. This further validates the method and supports the conclusion that the method is accurate to within 5%.

ACKNOWLEDGMENT

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