International Journal of Thermophysics, Vol. 23, No. 2, March 2002 (© 2002)

Viscosity Prediction of Natural Gas Using the Friction Theory

C. K. Zéberg-Mikkelsen,[1] S. E. Quiñones-Cisneros,[1, 2] and E. H. Stenby[1]

Received November 3, 2000

Based on the concepts of the friction theory (f-theory) for viscosity modeling, a procedure is introduced for predicting the viscosity of hydrocarbon mixtures rich in one component, which is the case for natural gases. In this procedure, the mixture friction coefficients are estimated with mixing rules based on the values of the pure component friction coefficients. Since natural gases contain mainly methane, two f-theory models are combined, where the friction coefficients of methane are estimated by a seven-constant f-theory model directly fitted to methane viscosities, and the friction coefficients of the other components are estimated by the one-parameter general f-theory model. The viscosity predictions are performed with the SRK, the PR, and the PRSV equations of state, respectively. For recently measured viscosities of natural gases, the resultant AAD (0.5 to 0.8%) is in excellent agreement with the experimental uncertainty ($\pm$ 1.0%). The AAD is found to be higher for older measurements (around 3.5%), due mainly to the higher experimental uncertainties and problems with some of the measurements. Overall, the results are satisfactory for most industrial applications related to natural gases.

KEY WORDS: f-theory; hydrocarbon; natural gas; petroleum fluid; prediction; viscosity.

1. INTRODUCTION

Because natural gas has become an important energy resource, an increasing demand for reliable and accurate physical properties of natural gases has arisen. One of these properties is the viscosity, which is required in many engineering disciplines, ranging from the simulation of gas production at reservoir conditions to the design and operation of necessary

---

[1] Center for Phase Equilibria and Separation Processes (IVCSEP), Department of Chemical Engineering, Technical University of Denmark, Building 229, 2800 Lyngby, Denmark.

[2] To whom correspondence should be addressed. E-mail: sec@kt.dtu.dk

0195-928X/02/0300-0437/0 © 2002 Plenum Publishing Corporation

transport equipment. Thus, the viscosity of a natural gas has to be evaluated for wide ranges of temperature, pressure, and composition. This requires simple and accurate models, which can take these changes into account. Currently, the most commonly used models for predicting the viscosity of natural gases are based on either empirical equations, the corresponding states principle, or the kinetic gas theory.

Recently, Quiñones-Cisneros et al. introduced the friction theory (f-theory) for viscosity modeling [1], which has been applied to the modeling of the viscosity of *n*-alkanes from low to high pressures over wide ranges of temperature. In the f-theory, the viscosity of dense fluids is approached as a mechanical property rather than a transport property. Thus, by linking the Amontons–Coulomb friction law to the van der Waals repulsive and attractive pressure terms, accurate viscosity estimates are obtained using simple cubic equations of state (EOS), as illustrated in Ref. 1. This is achieved because cubic EOSs are optimized for good pressure–temperature performance and therefore good viscosity–pressure performance can also be obtained, regardless of the accuracy of the estimated density. Based on the f-theory, Quiñones-Cisneros et al. further developed EOS-dependent general models [2] based on a corresponding states behavior and with only one optimized reducing parameter—a characteristic critical viscosity.

Since a viscosity estimation based on the f-theory can be linked to the repulsive and attractive pressure terms obtained from cubic EOSs. Because cubic EOS are widely used within the petroleum industry, an implementation of the f-theory can be easily performed. Thus the main aim of this work is to introduce an f-theory-based procedure for predicting the viscosity of hydrocarbon mixtures rich in one component, which is the case for natural gases.

2. FRICTION THEORY

In the friction theory for viscosity modeling [1], the total viscosity η is separated into a dilute gas viscosity term, η_0, and a residual friction term, η_f,

$$\eta = \eta_0 + \eta_\mathrm{f} \tag{1}$$

The dilute gas viscosity η_0 is defined as the viscosity in the zero density limit, while the residual term η_f is related to friction concepts of classical mechanics. According to the f-theory, the residual friction term of an *n*-component mixture can be expressed as

$$\eta_\mathrm{f} = \kappa_\mathrm{r} p_\mathrm{r} + \kappa_\mathrm{a} p_\mathrm{a} + \kappa_\mathrm{rr} p_\mathrm{r}^2 \tag{2}$$

where p_{a} and p_{r} are the van der Waals attractive and repulsive pressure contributions in the mixture. The repulsive and attractive pressure contributions can be obtained from simple cubic EOSs, such as the Soave–Redlich–Kwong (SRK) EOS [3], the Peng–Robinson (PR) EOS [4], or the modified Peng–Robinson EOS proposed by Stryjek and Vera [5] (PRSV), among others. The friction coefficients κ_{r}, κ_{a}, and κ_{rr} are obtained by the following mixing rules:

$$\begin{aligned}\kappa_{\mathrm{r}} &= \sum_{i=1}^{n} z_i \kappa_{\mathrm{r},\,i}\\ \kappa_{\mathrm{a}} &= \sum_{i=1}^{n} z_i \kappa_{\mathrm{a},\,i}\\ \kappa_{\mathrm{rr}} &= \sum_{i=1}^{n} z_i \kappa_{\mathrm{rr},\,i}\end{aligned} \tag{3}$$

with

$$z_i = \frac{x_i}{\mathrm{MW}_i^{\varepsilon}\mathrm{MM}} \tag{4}$$

and

$$\mathrm{MM} = \sum_{i=1}^{n} \frac{x_i}{\mathrm{MW}_i^{\varepsilon}} \tag{5}$$

where $\varepsilon = 0.30$. MW_i and x_i are, respectively, the molecular weight and the mole fraction of component i. The friction coefficients in Eq. (3), $\kappa_{\mathrm{r},\,i}$, $\kappa_{\mathrm{a},\,i}$, and $\kappa_{\mathrm{rr},\,i}$, can be estimated with the following model proposed in Ref. 1,

$$\begin{aligned}\kappa_{\mathrm{r},\,i} &= a_{0,\,i} + a_{1,\,i}[\exp(\Gamma_i - 1) - 1] + a_{2,\,i}[\exp(2\Gamma_i - 2) - 1]\\ \kappa_{\mathrm{a},\,i} &= b_{0,\,i} + b_{1,\,i}[\exp(\Gamma_i - 1) - 1] + b_{2,\,i}[\exp(2\Gamma_i - 2) - 1]\\ \kappa_{\mathrm{rr},\,i} &= c_{2,\,i}[\exp(2\Gamma_i) - 1]\end{aligned} \tag{6}$$

where

$$\Gamma_i = \frac{T_{\mathrm{c},\,i}}{T} \tag{7}$$

or by using the one-parameter general f-theory model [2]. The following expressions for the pure friction coefficients follow from the one-parameter general f-theory model,

$$\kappa_{\mathrm{r},i} = \frac{\eta_{\mathrm{c},i}\hat{\kappa}_{\mathrm{r},i}}{P_{\mathrm{c},i}}$$
$$\kappa_{\mathrm{a},i} = \frac{\eta_{\mathrm{c},i}\hat{\kappa}_{\mathrm{a},i}}{P_{\mathrm{c},i}} \tag{8}$$
$$\kappa_{\mathrm{rr},i} = \frac{\eta_{\mathrm{c},i}\hat{\kappa}_{\mathrm{rr},i}}{P_{\mathrm{c},i}^2}$$

where $\hat{\kappa}_{\mathrm{r},i}$, $\hat{\kappa}_{\mathrm{a},i}$, and $\hat{\kappa}_{\mathrm{rr},i}$ are reduced forms of the friction coefficients based on the two main reducing parameters: the critical pressures $P_{\mathrm{c},i}$ and characteristic critical viscosities $\eta_{\mathrm{c},i}$. The $\hat{\kappa}_{\mathrm{r},i}$, $\hat{\kappa}_{\mathrm{a},i}$, and $\hat{\kappa}_{\mathrm{rr},i}$ parameters are further separated into a critical isotherm contribution and a residual temperature-dependent contribution,

$$\hat{\kappa}_{\mathrm{r},i} = \hat{\kappa}_{\mathrm{r}}^{\mathrm{c}} + \Delta\hat{\kappa}_{\mathrm{r},i}$$
$$\hat{\kappa}_{\mathrm{a},i} = \hat{\kappa}_{\mathrm{a}}^{\mathrm{c}} + \Delta\hat{\kappa}_{\mathrm{a},i} \tag{9}$$
$$\hat{\kappa}_{\mathrm{rr},i} = \hat{\kappa}_{\mathrm{rr}}^{\mathrm{c}} + \Delta\hat{\kappa}_{\mathrm{rr},i}$$

For the temperature-dependent residual terms, the following empirical functions have been derived [2]:

$$\begin{aligned}
\Delta\hat{\kappa}_{\mathrm{r},i} &= \kappa_{\mathrm{r},0,0}(\Gamma_i - 1) + (\kappa_{\mathrm{r},1,0} + \kappa_{\mathrm{r},1,1}\psi_i)[\exp(\Gamma_i - 1) - 1] \\
&\quad + (\kappa_{\mathrm{r},2,0} + \kappa_{\mathrm{r},2,1}\psi_i + \kappa_{\mathrm{r},2,2}\psi_i^2)[\exp(2\Gamma_i - 2) - 1] \\
\Delta\hat{\kappa}_{\mathrm{a},i} &= \kappa_{\mathrm{a},0,0}(\Gamma_i - 1) + (\kappa_{\mathrm{a},1,0} + \kappa_{\mathrm{a},1,1}\psi_i)[\exp(\Gamma_i - 1) - 1] \\
&\quad + (\kappa_{\mathrm{a},2,0} + \kappa_{\mathrm{a},2,1}\psi_i + \kappa_{\mathrm{a},2,2}\psi_i^2)[\exp(2\Gamma_i - 2) - 1] \\
\Delta\hat{\kappa}_{\mathrm{rr},i} &= \kappa_{\mathrm{rr},2,1}\psi_i[\exp(2\Gamma_i) - 1](\Gamma_i - 1)^2
\end{aligned} \tag{10}$$

where

$$\psi_i = \frac{RT_{\mathrm{c},i}}{P_{\mathrm{c},i}} \tag{11}$$

3. DILUTE GAS VISCOSITY

The dilute gas viscosity in the f-theory can be estimated with the model proposed by Chung et al. [6], which is applicable for predicting the dilute gas viscosity of a number of polar and nonpolar fluids over wide ranges of temperature within an uncertainty of ±1.5%. This model is an empirical correlation derived from the Chapman–Enskog theory [7] and the reduced collision integral expression for the Lennard–Jones 12–6 potential of Neufeld et al. [8]. The model is given by

$$\eta_0 = 4.0785 \frac{\sqrt{\mathrm{MWT}}}{v_{\mathrm{c}}^{2/3}\Omega^*} F_{\mathrm{c}} \tag{12}$$

where the reduced collision integral Ω^* corresponds to

$$\Omega^* = \frac{1.16145}{T^*} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.16178}{\exp(2.43787T^*)} - 6.435 \times 10^{-4} T^{*0.14874} \sin\left(18.0323T^{*-0.76830} - 7.27371\right) \tag{13}$$

with

$$T^* = \frac{1.2593T}{T_{\mathrm{c}}} \tag{14}$$

For nonpolar fluids, the empirical expression for F_{c} reduces to

$$F_{\mathrm{c}} = 1 - 0.2756\omega \tag{15}$$

where ω is the acentric factor. The dilute gas viscosity obtained with Eq. (12) has units of μPa·s, when the temperature is in K and the critical volume v_{c} in $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$.

In general, when predicting the viscosity of vapors or supercritical fluids at high temperatures, the estimated dilute gas viscosity term becomes important. This is due to the fact that the dilute gas viscosity increases with increasing temperature, while the total viscosity of supercritical fluids under pressure decreases with increasing temperatures, as illustrated qualitatively in Fig. 1. The temperature and pressure conditions under which the viscosity of natural gases is required correspond to the conditions where the contribution of the dilute gas viscosity to the total viscosity becomes important. Because of this, the accuracy of the Chung et al. [6] dilute gas viscosity model has been further validated by comparing the predicted dilute gas viscosities obtained by Eq. (12) with values reported in the literature for methane [9, 10], ethane [11, 12], propane [13], *n*-butane [14], *i*-butane [15], *n*-pentane [16], *n*-hexane [17], *n*-heptane [16], carbon dioxide [10], and nitrogen [18] over wide ranges of temperature—all these compounds are found in natural gases. For each fluid, the resulting average absolute deviation (AAD) and maximum absolute

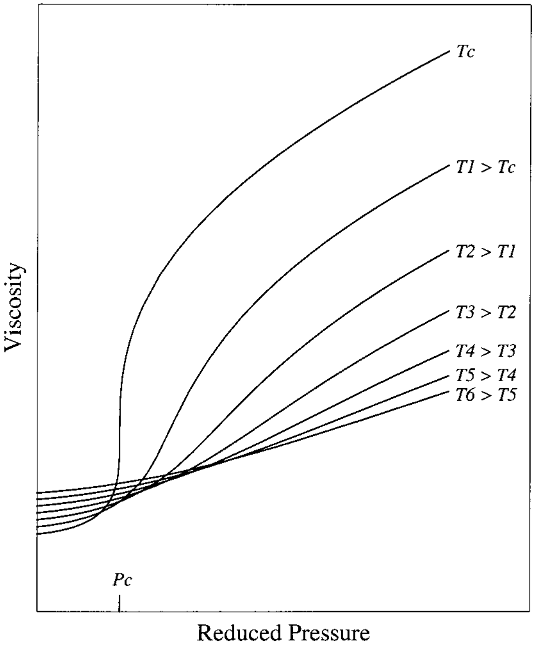

Fig. 1. Qualitative representation of the viscosity as a function of pressure for different temperatures in the supercritical region.

deviation (MxD), together with the temperature range and the uncertainty in the reported literature values, are listed in Table I. The Chung et al. dilute gas viscosity predictions were performed using the critical properties and parameters reported in Ref. 19. Further, the percentage deviations of the predicted dilute gas viscosities for each fluid as a function of reduced temperatures between 0.5 and 3.0 are shown in Fig. 2. Comparing the uncertainty of the reported literature values with the AAD given in Table I and the percentage deviations shown in Fig. 2, good agreement between the Chung et al. dilute gas viscosity model and the reported literature values is found. This is quite satisfactory for a general model which has been developed for calculations of dilute gas viscosities of different fluids over wide temperature ranges.

For natural gas mixtures, the mixture dilute gas viscosities are estimated with the following mixing rule proposed by Herning and Zipperer [20],

$$\eta_0 = \frac{\sum_{i=1}^{n} x_i \eta_{0,i} \mathrm{MW}_i^{1/2}}{\sum_{i=1}^{n} x_i \mathrm{MW}_i^{1/2}} \tag{16}$$

Table I. Performance of the Dilute Gas Viscosity Model [6]

	Ref. No.	NP[a]	T-range (K)	AAD (%)	MxD (%)	Reported uncertainty
Methane	[9]	31	100–400	0.56	2.97	3.0% $T < 270$ K 0.5% 270 K $< T <$ 400 K
	[10]	95	110–600	1.00	3.02	2.0%
Ethane	[11]	41	100–500	1.54	6.21	5.0% 100 K $< T <$ 250 K 1.5% 250 K $< T <$ 300 K 1.0% 300 K $< T <$ 375 K
	[12]	12	293–633	0.74	1.39	0.3%
Propane	[13]	14	297–625	1.29	1.53	0.3%
n-Butane	[14]	14	298–626	0.76	1.25	0.4%
i-Butane	[15]	10	298–627	1.35	1.89	0.4%
n-Pentane	[16]	7	323–623	0.65	0.93	0.3%
n-Hexane	[17]	9	363–623	0.52	0.72	0.3%
n-Heptane	[16]	7	353–623	0.19	0.63	0.3%
Carbon dioxide	[10]	71	200–600	1.67	2.41	2.0%
Nitrogen	[18]	87	120–600	1.41	2.90	2.0%

[a] Number of points.

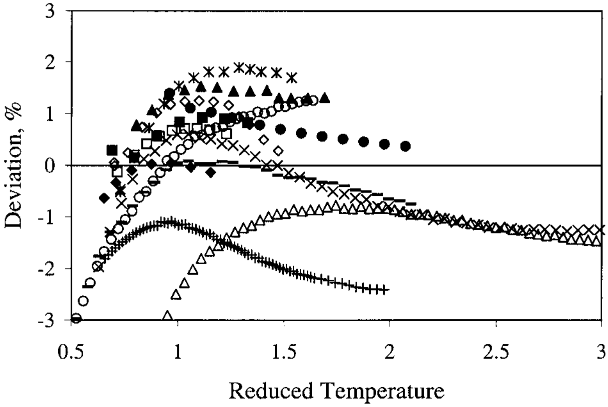

Fig. 2. Deviations, $(\eta_{\mathrm{calc}} - \eta_{\mathrm{r}})/\eta_{\mathrm{r}} \times 100\%$, of the dilute gas viscosities (η_{calc}) predicted by Eq. (12) from reported values in the literature (η_{r}). (×) Methane [9]; (–) methane [10]; (○) ethane [11]; (●) ethane [12]; (▲) propane [13]; (◇) *n*-butane [14]; (✱) *i*-butane [15]; (■) *n*-pentane [16]; (□) *n*-hexane [17]; (◆) *n*-heptane [16]; (+) carbon dioxide [10]; (△) nitrogen [18].

for multicomponent gas mixtures at low pressures. In this mixing rule, no additional information about the mixture properties is required, only the dilute gas viscosity, the molecular weight, and the mole fraction of the pure components.

The dilute gas viscosity of the binary mixture propane + *i*-butane [21] has been compared with the predicted values obtained with Eq. (16), resulting in an AAD = 1.06% and an MxD = 1.46%. This is better than the AAD and MxD for pure propane and *i*-butane, although higher than the reported uncertainty for the measurements (±0.4%). Further, the dilute gas viscosities of the binary mixtures methane + *n*-butane and methane + carbon dioxide have been predicted with Eq. (16) and compared with experimental values. For the binary system methane + *n*-butane [22], an AAD = 0.25% and an MxD = 0.44% are obtained, while for the binary methane + carbon dioxide system [22] the AAD and MxD are 1.59 and 2.47%, respectively. The AAD and MxD for the binary system methane + carbon dioxide are higher than for pure methane, but in agreement with the results obtained for carbon dioxide.

Since the total viscosity is separated into a dilute gas viscosity term and a friction term, any dilute gas viscosity model can be used. However, the Chung et al. [6] dilute gas viscosity model used in this work for pure components and the mixing rule of Herning and Zipperer [20] combines simplicity with sufficient accuracy for hydrocarbon multicomponent mixtures, such as natural gases. Nevertheless, if required, other models, such as those described in Ref. 19, can be incorporated for the dilute gas limit.

4. PURE METHANE

Since the mixture friction coefficients in Eq. (3) are estimated with mixing rules based on the friction coefficients of the pure components, they can be obtained by any combination of Eq. (6) and the general one-parameter f-theory model, provided that the same EOS is used. In the case of natural gases, which are multicomponent mixtures containing mainly methane (75 to 90 mol%), it will be advantageous to combine Eq. (6) for pure methane with the general one-parameter f-theory model for the remaining components. In this way, efficient and accurate viscosity predictions can be achieved. Thus, the seven constants required in Eq. (6) for methane have been estimated from a fit to a database containing smoothed points in the ranges of about 100 K to near 500 K and up to about 100 MPa. This database has been generated from published experimental points from the list of references for methane reported in Ref. 1. The derived recommended database, as well as the process followed in its derivation, are available in Ref. 23. The resulting parameters for methane

Table II. Friction Constants Multiplied by the Critical Pressure for Methane

EOS	$P_c a_0$ (μPa·s)	$P_c a_1$ (μPa·s)	$P_c a_2$ (μPa·s)	$P_c b_0$ (μPa·s)	$P_c b_1$ (μPa·s)	$P_c b_2$ (μPa·s)	$P_c c_0$ (μPa·s)
PR	0.238122	−0.576655	0.125629	−1.99172	−1.71568	0.532587	0.00206695
PRSV	0.247501	−0.571076	0.130641	−1.98158	−1.69746	0.534845	0.00205442
SRK	0.0514168	−0.208167	−0.426694	−2.47847	−1.94465	0.226937	0.00328076

are reported in Table II. Consistent with the results previously found [1] for the modeling of the recommended viscosity values of Vogel et al. for propane [24], a seven-parameter f-theory model can also provide accurate results for methane under wide ranges of temperature and pressure. In this case, compared with the smoothed methane data used for the fitting, AADs under 1% and a bias of about –0.15% are found for all seven-parameter f-theory models. In all cases, the MxD reaches near 10% around the critical point but remains under 3% outside the critical region. The seven-parameter f-theory models also show a satisfactory performance compared to the raw experimental data, giving an AAD and a bias of about 1.85% and 0.07% for all EOS models. Figure 3 represents a *T–P* deviation diagram showing the location of the more than 750 experimental points originally considered in the fitting process. From all the experimental points shown in Fig. 3, 2.9% are underpredicted and 3.6% are

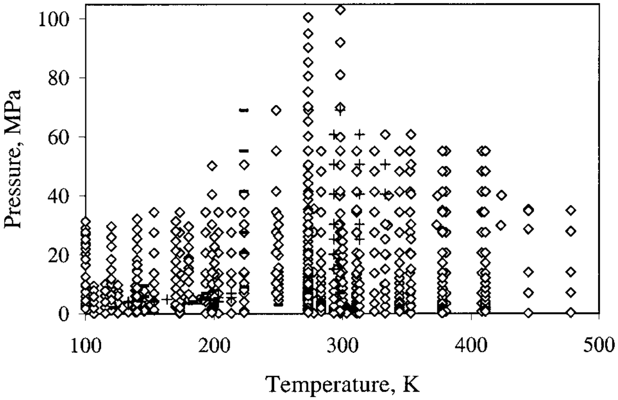

Fig. 3. Methane viscosity deviation, $(\eta_{calc} - \eta_{exp})/\eta_{exp} \times 100\%$, diagram for the f-theory PR seven-parameter model (η_{calc}) compared to experimental points (η_{exp}) from the database reported in Ref. 1. (+) Deviations above 5%; (◇) deviations between ±5%; (–) deviations under −5%.

overpredicted by more than 5%, while the remaining 93.5% of all points are within a deviation of ±5%. In fact, 70% of all points fall within a ±2% deviation. Furthermore, Fig. 3 shows no particular trend or bias with respect to temperature or pressure. Although all data in the ranges from 100 to 475 K and up to 100 MPa were used, consistent with the distribution of experimental points shown in Fig. 3, the recommended range of application of the f-theory methane models is up to 40 MPa from 100 to 200 K and up to 600 MPa from 200 to 500 K.

A further test of the f-theory models against other methane reference data has also been carried out. When the methane data recommended by Younglove and Ely [25] in the ranges between 100 and 600 K and pressures up to 100 MPa are considered, the results show an AAD and a bias of 1.43 and −0.18% for the PR EOS, 1.41% and −0.16% for the PRSV EOS, and 1.53 and −0.15% for the SRK EOS. A second test of the f-theory models has also been carried out against the more recent data recommended by Friend et al. [9], obtaining an AAD and a bias of 1.23 and −0.22% for the PR EOS, 1.22 and −0.22% for the PRSV EOS, and 1.25 and −0.26% for the SRK EOS. The performance of the PR EOS f-theory methane model compared to the Younglove and Ely [25] and the Friend et al. [9] recommended data is depicted in Figs. 4 and 5. These figures show that at high pressures the Younglove and Ely data have a trend to be overpredicted at practically all temperatures, while the

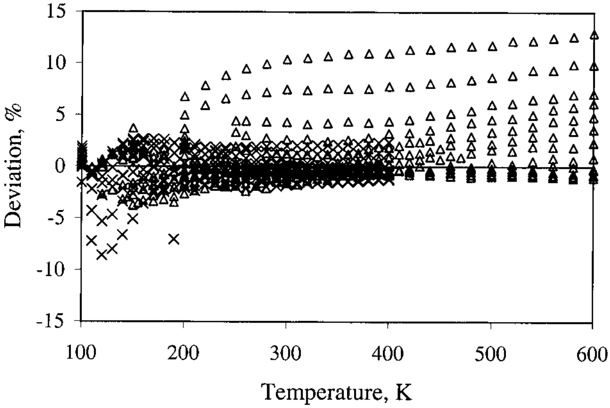

Fig. 4. Temperature deviation, $(\eta_{\mathrm{calc}}-\eta_{\mathrm{r}})/\eta_{\mathrm{r}}\times 100\%$, performance of the predicted methane viscosity by the f-theory PR seven-parameter model (η_{calc}) compared to recommended data points (η_{r}). (△) Recommended data of Younglove and Ely [25]; (×) recommended data of Friend et al. [9].

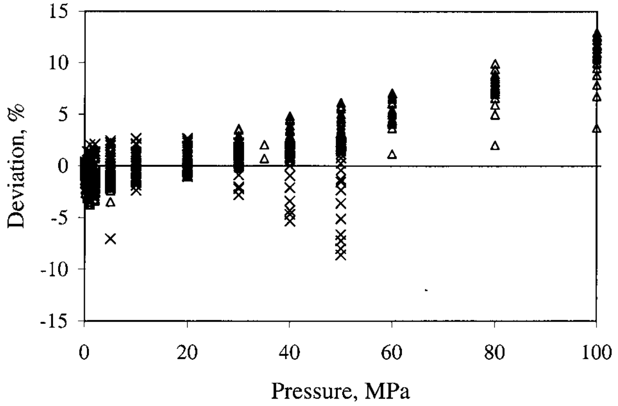

Fig. 5. Pressure deviation, $(\eta_{\text{calc}} - \eta_{\text{r}})/\eta_{\text{r}} \times 100\%$, performance of the predicted methane viscosity by the f-theory PR seven-parameter model (η_{calc}) compared to recommended data points (η_{r}). (△) Recommended data of Younglove and Ely [25]; (×) recommended data of Friend et al. [9].

Friend et al. data have an opposite trend at temperatures under 200 K. Nevertheless, the figures show good agreement between the f-theory methane models and the Friend et al. data for the range of application that is relevant to natural gases, above 200 K and up to 50 MPa, with deviations within ±3% in all cases.

5. RESULTS AND DISCUSSION

Despite the importance of natural gases, only a few accurate measurements covering only moderate ranges of temperature and pressure have recently been carried out [26, 27]. Other older measurements from the 1960s are reported in Ref. 28. Thus, six mixtures have been studied in this work and the corresponding compositions, along with the literature source, are listed in Table III. The components referred to as pentanes, hexanes, and heptanes in Ref. 28 have been taken as equivalent to *n*-pentane, *n*-hexane, and *n*-heptane, respectively. Also, because of its low concentration in mixtures 4 and 5, all of the helium present has been neglected by lumping it together with the nitrogen. Since at the temperature and pressure ranges relevant to this work, both helium and nitrogen have low viscosities of similar orders of magnitude, this lumping procedure does not introduce any significant errors.

Table III. Composition of Natural Gases in mol%

	Mixture 1 [26]	Mixture 2 [27]	Mixture 3 [28]	Mixture 4 [28]	Mixture 5 [28]	Mixture 6 [28]
Nitrogen	5.60	1.83		1.40	4.80	0.55
Carbon Dioxide	0.66		3.20	1.40	0.90	1.70
Helium				0.03	0.03	
Methane	84.84	94.67	86.33	71.71	80.74	91.46
Ethane	8.40	3.50	6.80	14.00	8.70	3.10
Propane	0.50		2.40	8.30	2.90	1.40
i-Butane			0.43	0.77		0.67
n-Butane			0.48	1.90	1.70	0.50
n-Pentane			0.22	0.39	0.13	0.28
n-Hexane			0.10	0.09	0.06	0.26
n-Heptane			0.04	0.01	0.03	0.08

Using the friction coefficient mixing rules, Eq. (3), with the pure methane friction coefficients obtained by the seven-parameter f-theory model, Eq. (6), and the friction coefficients of the remaining compounds given by the one-parameter f-theory general model, Eq. (8), the viscosity of the six natural gas mixtures is predicted with the SRK, the PR, and the PRSV EOS, respectively, and compared with experimental values. All of the required constants in the general one parameter f-theory model have been taken from Ref. 2, and for the EOS, the parameters have been taken from Ref. 19. The resultant AAD and MxD are reported in Table IV, clearly showing results of similar accuracy for the three EOS-based f-theory models. Additionally, a comparison of the results obtained with the f-theory

Table IV. Performance of the f-theory Viscosity Model

					SRK		PR		PRSV	
	Ref. No.	NP[a]	*T*-range (K)	*P*-range (MPa)	AAD (%)	MxD (%)	AAD (%)	MxD (%)	AAD (%)	MxD (%)
Mixture 1	[26]	40	241–455	0.24–14.0	0.79	2.74	0.76	2.67	0.78	2.68
Mixture 2	[27]	59	299–399	0.10–6.70	0.52	1.54	0.50	1.40	0.48	1.36
Mixture 3	[28]	30	311–444	0.14–27.6	3.53	5.51	3.46	5.27	3.48	5.27
Mixture 4	[28]	33	311–444	4.80–55.2	3.56	6.64	3.30	5.94	3.22	5.95
Mixture 5	[28]	26	344–444	1.40–17.2	3.56	6.44	3.47	6.24	3.47	6.23
Mixture 6	[28]	26	311–444	2.80–55.2	3.89	10.40	3.84	10.43	3.93	10.43

[a] Number of points.

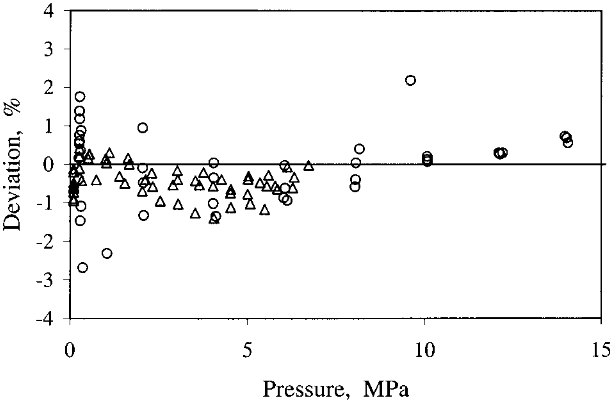

Fig. 6. Pressure deviation, $(\eta_{\text{calc}} - \eta_{\text{exp}})/\eta_{\text{exp}} \times 100\%$, performance of predicted natural gas viscosity using the f-theory with the PR EOS (η_{calc}) compared to experimental points (η_{exp}). (○) Table III, mixture 1 [26]; (△) Table III, mixture 2 [27].

approach in relation to other approaches leads to the work of Vesovic [29], where the same natural gas mixtures were also studied.

For mixture 1 [26] and mixture 2 [27], the AAD are in excellent agreement with the experimental values, which have an uncertainty of 1.0%. Figure 6 shows the deviations obtained for mixtures 1 and 2 with the PR f-theory model, where the largest deviations are found at low temperatures close to the dilute gas viscosity limit for mixture 1. Nevertheless, the deviations close to the dilute gas limit are still within the accuracy of the Chung et al. model [6] and of the experimental measurements. Further, Assael et al. [26] observed the same trend when they compared their measurements with the Vesovic and Wakeham (VW) model [30–32]. Overall, for mixture1, Assael et al. [26] obtained an AAD of 1.5% and an MxD = 3.8%, compared to the AAD of 0.76% and MxD of 2.67% obtained in this work with the PR EOS. For mixture 2, Vesovic [29] obtained an AAD of 0.7% and an MxD = 1.5% with the VW method, compared to the AAD of 0.5% and MxD of 1.4% obtained with the f-theory and the PR EOS.

For the older measurements, mixtures 3 to 6, larger deviations are obtained. These measurements, together with density measurements, were carried out in the mid 1960s by Lee et al. [28], who also modeled the measured data using a density-dependent empirical equation with an overall AAD of 2.7%. The overall AAD in this work is around 3.5% for mixtures 3 to 6. Mixture 6 contains more than 91 mol% methane, and it should therefore be expected that the predicted viscosities would be in good

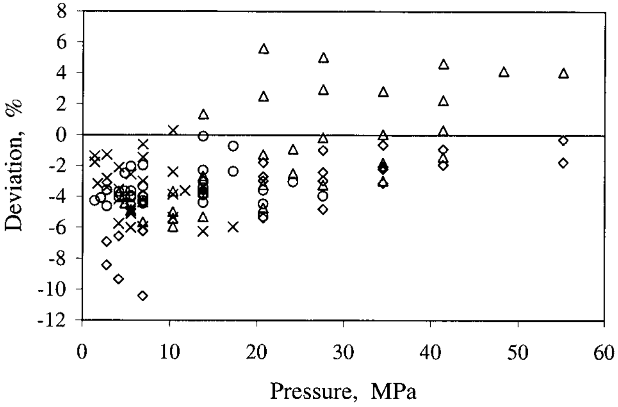

Fig. 7. Pressure deviation, $(\eta_{\text{calc}} - \eta_{\text{exp}})/\eta_{\text{exp}} \times 100\%$, performance of the predicted viscosity for the Lee et al. natural gas mixtures [28] using the f-theory with the PR EOS (η_{calc}) compared to experimental points (η_{exp}). (○) Table III, mixture 3; (△) Table III, mixture 4; (×) Table III, mixture 5; (◇) Table III, mixture 6.

agreement with the experimental data, similar to the results obtained for mixture 2 (94.7 mol% methane), but this is not the case. From the deviation plots shown in Figs. 7 and 8, large deviations are observed for mixture 6 at pressures below 10 MPa and temperatures above 400 K, while the other points have lower deviations, indicating problems with the

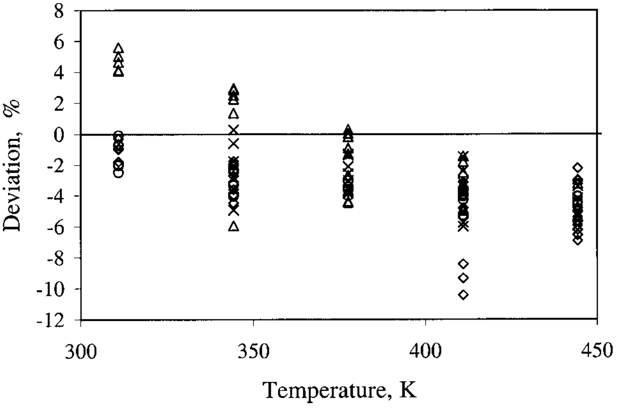

Fig. 8. Temperature deviation, $(\eta_{\text{calc}} - \eta_{\text{exp}})/\eta_{\text{exp}} \times 100\%$, performance of the predicted viscosity for the Lee et al. natural gas mixtures [28] using the f-theory with the PR EOS (η_{calc}) compared to experimental points (η_{exp}). (○) Table III, mixture 3; (△) Table III, mixture 4; (×) Table III, mixture 5; (◇) Table III, mixture 6.

high-temperature, lower pressure measurements—this is the main reason for the high AAD in mixture 6. The lowest AAD for the old measurements is found for mixture 4, which contains 71.7 mol% methane, but again, the largest deviations are found at the lowest pressures, as shown in Fig. 7. Basically the same problems with the Lee et al. [28] mixtures were found by Vesovic [29], where results of comparable accuracy and scatter were reported. However, it should be pointed out that although no particular trend with pressure is shown in Fig. 7, or with density in the Vesovic analysis [29], a clear deviation trend with temperature is found in Fig. 8 for the Lee et al. [28] mixtures. Therefore, since neither Fig. 3 nor Fig. 4 shows such a deviation trend with temperature for pure methane, it appears that the main source of deviation for mixtures 3–6 may be related to a temperature problem with the Lee et al. [28] measurements.

6. CONCLUSION

In this work, the friction theory approach for viscosity modeling [1, 2] has been extended to the viscosity prediction of natural gases. A scheme has been introduced by combining two f-theory models for the friction coefficients of the pure components. Since natural gases are multicomponent mixtures, containing mainly methane (75 to 90 mol%), an efficient and accurate scheme for predicting the viscosity of natural gases is obtained by using an accurate seven-constant f-theory model for the pure methane friction coefficients and the general one-parameter f-theory model for the friction coefficients of the remaining components. Based on this scheme, the viscosity of six natural gas mixtures has been predicted with the SRK, the PR, and the PRSV EOSs and compared with experimental values. For all of the f-theory models, it has been found that the most accurate, recently measured mixtures, 1 and 2, have resultant AADs (0.5–0.8%) in excellent agreement with the experimental uncertainty (±1.0). The maximum deviations are obtained at low temperatures and low pressures, and this can be ascribed to the uncertainty in the prediction of the dilute gas viscosity, which is within ±1.5% for the dilute gas viscosity model [6] used in this work. Thus, it is possible that a more accurate dilute gas viscosity model may slightly improve the low-pressure results. For the older measurements, mixtures 3–6, an overall AAD of about 3.5% is obtained, due to the higher experimental uncertainty in the measurements, but also due to problems with the measurements themselves, as found for mixture 6 at high temperatures and pressures below 10 MPa. Nevertheless, the results in this work are satisfactory for most applications related to the gas industry and compare favorably with the best results obtained with other approaches such as those reported in Ref. 29. A main advantage of the f-theory approach lies in the fact that it is not density dependent but, rather, pressure dependent. Therefore no accurate additional density modeling or experimental density information is required, as is the case for most of the viscosity models analyzed by Vesovic [29].

Furthermore, since the viscosities of the more accurate and recent measurements [26, 27] are predicted within the experimental uncertainty, it is also concluded that the results obtained for these mixtures better illustrate the application of this f-theory scheme for predicting the viscosity of natural gases.

Finally, because the f-theory can be linked to cubic EOSs, and such EOSs are widely used within the petroleum industry, this f-theory scheme for viscosity prediction of natural gases can be easily implemented. The only external input required for the f-theory approach presented here is the actual temperature, pressure, and composition of the mixture. This work, together with accurate viscosity modeling of reservoir oils [33], has shown that the f-theory can be a powerful tool in applications such as oil and gas reservoir simulations.

ACKNOWLEDGMENT

This work was accomplished within the European project EVIDENT under the JOULE Program, Contract No. JOF3-CT97-0034.

NOMENCLATURE

a_0, a_1, a_2	Repulsive friction constants in Eq. (6)
b_0, b_1, b_2	Attractive friction constants in Eq. (6)
c_2	Quadratic repulsive friction constant in Eq. (6)
F_c	Defined in Eq. (15)
MM	Defined in Eq. (5)
MW	Molecular weight ($g \cdot mol^{-1}$)
P	Pressure (MPa)
P_c	Critical pressure (MPa)
p_a	Attractive pressure term
p_r	Repulsive pressure term
R Gas	constant
T	Temperature (K)
T_c	Critical temperature (K)
T^*	Defined in Eq. (14)
v_c	Critical molar volume ($cm^3 \cdot mol^{-1}$)
x	Mole fraction
z	Mass weighted molar fraction defined in Eq. (4)

Greek Letters

Γ	Defined in Eq. (7)
η	Viscosity
η_0	Dilute gas viscosity
η_c	Characteristic critical viscosity
η_f	Residual friction term
κ_a	Linear attractive friction coefficient
κ_r	Linear repulsive friction coefficient
κ_{rr}	Quadratic repulsive friction coefficient
Ω^*	Reduced collision integral, defined in Eq. (13)
ω	Acentric factor
ψ	Defined in Eq. (11) ($\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)

REFERENCES

1. S. E. Quiñones-Cisneros, C. K. Zéberg-Mikkelsen, and E. H. Stenby, *Fluid Phase Equil.* **169**:249 (2000).
2. S. E. Quiñones-Cisneros, C. K. Zéberg-Mikkelsen, and E. H. Stenby, *Fluid Phase Equil.* **178**:1 (2001).
3. G. S. Soave, *Chem. Eng. Sci.* **27**:1197 (1972).
4. D.-Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.* **15**:59 (1976).
5. R. Stryjek and J. H. Vera, *Can. J. Chem. Eng.* **64**:323 (1986).
6. T.-H. Chung, M. Ajlan, L. L. Lee, and K. E. Starling, *Ind. Eng. Chem. Res.* **27**:671 (1988).
7. S. Chapman, T. G. Cowling, and D. Burnett, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (University Printing House, Cambridge, 1970).
8. P. D. Neufeld, A. R. Janzen, and R. A. Aziz, *J. Chem. Phys.* **57**:1100 (1972).
9. D. G. Friend, J. F. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* **18**:583 (1989).
10. R. D. Trengove and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **16**:175 (1987).
11. D. G. Friend, J. F. Ely, and H. Ingham, *J. Phys. Chem. Ref. Data* **20**:275 (1991).
12. S. Hendl and E. Vogel, *Fluid Phase Equil.* **76**:259 (1992).
13. E. Vogel, *Int. J. Thermophys.* **16**:1335 (1995).
14. C. Küchenmeister and E. Vogel, *Int. J. Thermophys.* **19**:1085 (1998).
15. C. Küchenmeister and E. Vogel, *Int. J. Thermophys.* **21**:329 (2000).
16. E. Vogel and B. Holdt, *High Temp. High Press.* **23**:473 (1991).
17. E. Vogel and T. Strehlow, *Z. Phys. Chem. Leipzig* **269**:897 (1988).
18. W. A. Cole and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **14**:209 (1985).
19. B. E. Poling, J. M. Prausnitz, and J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed. (McGraw–Hill, New York, 2000).
20. F. Herning and L. Zipperer, *Gas Wasserfach* **76**:49 (1936).
21. C. Küchenmeister, E. Vogel, and J. Baranski, *High Temp. High Press.* **33**:659 (2001).
22. J. Kestin and J. Yata, *J. Chem. Phys.* **49**:4780 (1968).
23. C. K. Zéberg-Mikkelsen, *Viscosity Study of Hydrocarbon Fluids at Reservoir Conditions: Modeling and Measurements*, Ph.D. thesis (Technical University of Denmark, Lyngby, 2001).
24. E. Vogel, C. Küchenmeister, E. Bich, and A. Laesecke, *J. Phys. Chem. Ref. Data* **27**:947 (1998).

25. B. A. Younglove and J. F. Ely, *J. Phys. Chem. Ref. Data* **16**:577 (1987).
26. M. J. Assael, N. K. Dalaouti, and V. Vesovic, *Int. J. Thermophys.* **22**:61 (2001).
27. H. Nabizadeh and F. Mayinger, *High Temp. High Press.* **31**:601 (1999).
28. A. L. Lee, M. H. Gonzalez, and B. E. Eakin, *J. Petrol. Tech.* **18**:997 (1966).
29. V. Vesovic, *Int. J. Thermophys.* **22**:415 (2001).
30. V. Vesovic and W. A. Wakeham, *Int. J. Thermophys.* **10**:125 (1989).
31. V. Vesovic and W. A. Wakeham, *Chem. Eng. Sci.* **44**:2181 (1989).
32. V. Vesovic, M. J. Assael, and Z. A. Gallis, *Int. J. Thermophys.* **19**:1297 (1998).
33. S. E. Quiñones-Cisneros, C. K. Zéberg-Mikkelsen, and E. H. Stenby, *Chem. Eng. Sci.* **56**:7007 (2001).