

# Viscosity measurements and correlations of binary mixtures: 1,1,1,2-tetrafluoroethane (HFC-134a) + tetraethylene glycol dimethylether (TEGDME)

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## Abstract

This paper reports viscosity data for the binary system 1,1,1,2-tetrafluoroethane (HFC-134a),  $x_1$ , +tetraethylene glycol dimethylether (TEGDME),  $1 - x_1$ . The measurements (200 data points) were obtained at various pressures (between 10 and 100 MPa) in the homogeneous liquid state from  $T = 293.15$ – $373.15$  K. The measurements have been carried out with a falling body viscometer for four molar fractions  $x_1 = (0.28, 0.44, 0.63 \text{ and } 0.88)$ . The density values of this system were interpolated from previous results obtained at the laboratory. All of the available viscosity data, including pure HFC-134a and pure TEGDME (both previously studied at the laboratory), have been correlated using several viscosity models (mixing rules, self-refracting model, hard-sphere theory, friction theory and free volume model). The resulting models are presented and discussed in this work.

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## 1. Introduction

During the past few years new refrigerants with better environmental performance, such as 1,1,1,2-tetrafluoroethane (HFC-134a,  $\text{CF}_3\text{CH}_2\text{F}$ ), have been proposed as alternative refrigerants to chlorofluorocarbons (CFCs). However, this transition into environmentally friendly alternative refrigerants requires the choice of suitable compatible lubricants. For that reason, the study (measurements and modeling) of the thermophysical properties of refrigerant + lubricant mixtures is required in helping for a better understanding of the behavior of these mixtures under various conditions of operation.

Polyalkylene glycol dimethyl ethers (PGDME),  $\text{CH}_3\text{O}-(\text{CH}_2)_n-\text{CH}_3$ , have been proposed as suitable lubricants for HFC-134a [1]. However, in spite of

their importance, there are only a few studies available in the literature on the thermophysical properties of the HFC-134a + PGDME system [2–6].

In this work, new ( $p$ ,  $x_1$ ,  $T$ ) measurements for four mixtures of HFC-134a + TEGDME,  $x_1 = (0.2769, 0.4433, 0.6333 \text{ and } 0.8797)$ , at temperatures between 293.15 and 373.15 K and pressures from 10 to 100 MPa are reported. A total of 200 experimental viscosity values have been measured. In addition, in sake of completeness, viscosity data previously obtained at the laboratory [5] for the mixture  $x_1 = 0.9290$  are also included. To the knowledge of the authors there is no previous studies on the viscosity of this system over wide ranges of temperature, pressure and composition.

The data obtained for the binary system in this work, combined with those previously obtained [5], have been used to test the ability of different mixing rules [7,8] and several models developed in the literature, which have different origin and theoretical background. The viscosity models used

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here were: the self-referencing method [9], the hard-sphere model [10–12], the friction theory ( $f$ -theory) [13,14] and the free volume model [15,16].

## 2. Experimental techniques and measurements

Measurements of the dynamic viscosity  $\eta$  for  $x_1$  HFC-134a +  $(1 - x_1)$  TEGDME have been carried out in the monophasic liquid state from  $T = 293.15$ – $373.15$  K in steps of 20 K. The studied HFC-134a (molar mass  $102.03 \text{ g mol}^{-1}$ ) has been provided by Gazechim Froid with a purity better than 99.94% and with a water content of no more than 24 ppm. The polyether TEGDME (molar mass  $222.28 \text{ g mol}^{-1}$ ) was obtained from Aldrich with a purity better than 99%.

In a previous publication [3], experimental density measurements for this system, from 10 to 60 MPa, and at the same temperatures have already been presented. For pressures between 60 and 100 MPa and the actual compositions used in this work the density has been extrapolated/interpolated using a Tait-type equation as described in [17].

The dynamic viscosity has been measured from 10 MPa to 100 MPa in steps of 10 MPa using a specially designed isobaric transfer falling-body viscometer [18]. For the viscometer used in this work, the viscosity is a function of the falling time ( $\Delta\tau$ ), the difference between the density of the falling body and the fluid ( $\Delta\rho$ ), and apparatus constants ( $a$ – $c$ ), according to the following working equation [18]:

$$\eta = a(\Delta\rho \Delta\tau)^2 + b(\Delta\rho \Delta\tau) + c \quad (1)$$

For the calibration constants in Eq. (1), measurements of the falling time for substances with known viscosity and density values, under similar ranges of ( $\Delta\rho \Delta\tau$ ) at the same pressure and temperature are required. For each fluid, the measurement of the falling time was repeated five times at thermal and mechanical equilibrium, with a reproducibility better than 1% – the final values are the averages of these measurements. The temperature and pressure uncertainties have been estimated to be  $\pm 0.5$  K and  $\pm 0.1$  MPa, respectively. The fluids chosen for the calibration were: toluene, decane and TEGDME. The falling time was measured for these three compounds for temperatures between 293.15 K and 373.15 K in steps of 20 K and from 10 MPa to 100 MPa in 10 MPa pressure intervals. In order to determine the constants in Eq. (1) the density and viscosity values were interpolated from published experimental data for toluene [19–21], decane [22–24] and TEGDME [25]. However, actual viscosity measurements are not available for all of the reference fluids in the entire studied ranges of temperature and pressure. Therefore, to minimize the uncertainty in the viscosity estimations, in addition to the previous interpolated viscosity values, the viscosity of the reference fluids were calculated using the hard-sphere model of Assael et al. [10–12] and the friction theory model of Quiñones-Cisneros et al. [13,14]. This method was also applied in recent publications concerning the dynamic viscosity of pure HFC-134a

[26] and mixtures of HFC-134a and TriEGDME or TEGDME at high content of HFC-134a [5].

Thus, one calibration curve was made for each temperature for each one of the three sets of reference fluids. As a result, up to three different viscosity estimations, for each one of the reference sets of viscosities, are derived for each measured temperature and pressure. The final experimental values for viscosity are the averages of the values obtained with the three methods.

The viscosity values obtained in this work for the HFC-134a + TEGDME system are presented in Table 1. Fig. 1

Table 1  
Dynamic viscosity,  $\eta$  (mPa s), for  $x_1$  1,1,1,2-tetrafluoroethane (HFC-134a) +  $(1 - x_1)$  tetraethylene glycol dimethylether (TEGDME)

$P$ (MPa)	$T$ (K)				
	293.15	313.15	333.15	353.15	373.15
$x_1 = 0.2769$					
10	3.132	2.001	1.406	1.038	0.832
20	3.378	2.197	1.533	1.133	0.907
30	3.669	2.395	1.664	1.229	0.986
40	3.992	2.601	1.800	1.328	1.069
50	4.341	2.816	1.941	1.431	1.156
60	4.710	3.043	2.086	1.539	1.247
70	5.095	3.282	2.236	1.653	1.342
80	5.495	3.535	2.391	1.773	1.441
90	5.907	3.803	2.549	1.900	1.545
100	6.329	4.088	2.712	2.035	1.654
$x_1 = 0.4433$					
10	2.335	1.527	1.097	0.834	0.662
20	2.537	1.674	1.195	0.908	0.720
30	2.765	1.824	1.297	0.984	0.783
40	3.014	1.978	1.402	1.064	0.850
50	3.282	2.140	1.512	1.147	0.921
60	3.568	2.310	1.624	1.233	0.994
70	3.871	2.490	1.741	1.323	1.069
80	4.191	2.680	1.861	1.415	1.147
90	4.527	2.881	1.984	1.510	1.226
100	4.877	3.094	2.111	1.609	1.307
$x_1 = 0.6333$					
10	1.514	1.046	0.774	0.609	0.471
20	1.679	1.151	0.845	0.665	0.524
30	1.851	1.260	0.922	0.725	0.577
40	2.031	1.374	1.003	0.788	0.631
50	2.219	1.493	1.087	0.854	0.685
60	2.414	1.616	1.173	0.921	0.739
70	2.617	1.745	1.260	0.990	0.794
80	2.827	1.878	1.349	1.061	0.849
90	3.045	2.016	1.438	1.132	0.904
100	3.269	2.159	1.529	1.205	0.960
$x_1 = 0.8797$					
10	0.557	0.412	0.321	0.256	0.195
20	0.613	0.460	0.364	0.299	0.234
30	0.671	0.506	0.405	0.336	0.268
40	0.733	0.553	0.444	0.370	0.300
50	0.796	0.600	0.483	0.404	0.330
60	0.863	0.647	0.522	0.436	0.360
70	0.932	0.695	0.561	0.469	0.390
80	1.003	0.744	0.600	0.501	0.419
90	1.077	0.794	0.640	0.533	0.448
100	1.154	0.845	0.681	0.565	0.478

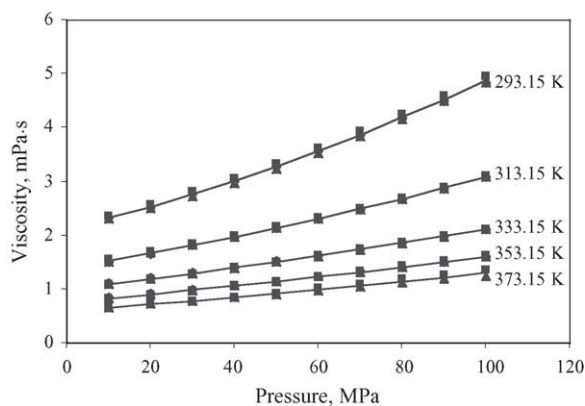


Fig. 1. Viscosity values for  $x_1$  HFC-134a +  $(1 - x_1)$  TEGDME for  $x_1 = 0.4433$  in the temperature range 293.15–373.15 K and pressures between 10 and 100 MPa using experimental data (♦), the hard-sphere model (▲) and the  $f$ -theory model (■) as reference values for the viscometer calibration constants.

shows the variation of  $\eta$  as a function of pressure for various temperatures at  $x_1 = 0.4433$ . It can be seen in Fig. 1 that the values obtained with the three methods are in good agreement; some discrepancies appear only in the region where no experimental data are available for the reference fluids (at the 373.15 K isotherm and above 60 MPa). The deviations between the viscosity values predicted using the different calibration curves (experimental data, hard sphere and friction theory) are in most cases of the order of 1–2%. However, for the 373 K isotherm and pressures above 60 MPa, due to the lack of reference data, the deviations between the calibration methods may reach higher values (of the order of 10 %). The uncertainty on the viscosity estimations is of  $\pm 2\%$  for the 293.15, 313.15 and 333.15 K isotherms (up to 100 MPa),  $\pm 3\%$  for the 353.15 K isotherm (up to 100 MPa) and  $\pm 4\%$  for the 373.15 K isotherm below 60 MPa. As stated before, the reader should be aware that for this last isotherm the difference between the calibration curves increased with pressure (above 60 MPa) reaching a difference of 9.32% at 100 MPa.

Fig. 2 displays the variations of viscosity versus  $x_1$  at  $T = 333.15$  K, where the viscosity values of the pure HFC-134a [26], pure TEGDME [25] and the mixture  $x_1 = 0.9290$

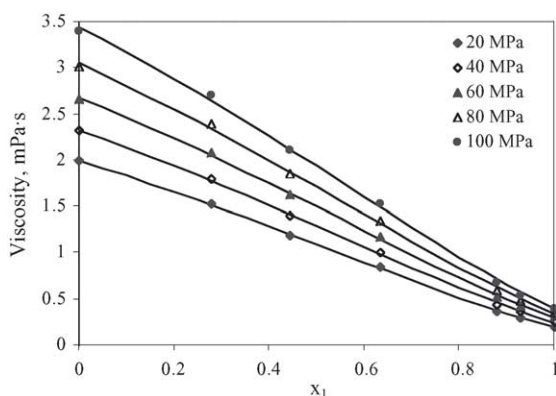


Fig. 2. Viscosity isobars as a function of composition at  $T = 333.15$  K.

[5] were taken from the literature. Similar behavior has been observed at the other studied temperatures.

### 3. Viscosity modeling

The data obtained for the binary system in this work, combined with those previously obtained at the laboratory [5], have been modeled using different viscosity approaches. These models only involve the viscosity data of the pure compounds of the mixture, except the self-referencing method, which requires one experimental value at each composition for the pressure and temperature of reference. For pure HFC-134a the previously measured viscosity data [26] in the temperature range of 273.15 to 373.15 K and pressures up to 140 MPa have been also considered (70 points). For pure TEGDME, experimental values between the temperatures of 293.15 and 353.15 K in steps of 20 K and pressures from 0.1 to 100 MPa were also taken from a previous study [25] (48 points). Taking into account the temperature and pressure intervals for which the viscosity of pure compounds is known, the prediction capabilities of the different models have been tested in the temperature interval of 293.15 to 353.15 K and over the pressure range of 10 to 100 MPa.

In order to compare the ability of the different models to predict the  $(p, \eta, T)$  behavior the following quantities are defined:

$$\text{ADD} = \frac{100}{n} \sum_{i=1}^n \left| \frac{\eta_{\text{cal}} - \eta_{\text{exp}}}{\eta_{\text{exp}}} \right|$$

$$\text{Bias} = \frac{100}{n} \sum_{i=1}^n \frac{\eta_{\text{cal}} - \eta_{\text{exp}}}{\eta_{\text{exp}}}$$

$$\text{MDev} = \max \left| \frac{\eta_{\text{cal}} - \eta_{\text{exp}}}{\eta_{\text{exp}}} \right|$$

where  $n$  is the total number of experimental points,  $\eta_{\text{exp}}$  the measured viscosity, and  $\eta_{\text{cal}}$  the value calculated using a given model.

#### 3.1. Mixing rules

A preliminary study has been carried out focusing on mixing laws. In the case of the Grunberg and Nissan mixing law [7],

$$\ln(\eta_{\text{mix}}) = \sum_{i=1}^n x_i \ln(\eta_i) \quad (2)$$

an absolute average deviation (ADD) of 32.91% a Bias of  $-32.91\%$  and a maximum deviation (MDev) of 55.62% are obtained. This model is very simple since no adjustable parameters are required, it only requires the viscosity of the pure compounds and the composition. The Grunberg–Nissan mixing law can be modified by introducing an adjustable param-

eter to better account for the interactions within the studied system:

$$\ln(\eta_{\text{mix}}) = \sum_{i=1}^2 x_i \ln(\eta_i) + x_1 x_2 d_{12} \quad (3)$$

By minimizing the average absolute deviation between the calculated and experimental data an adjustable parameter,  $d_{12} = 1.68$ , for Eq. (3) is obtained, resulting in an AAD = 15.53% a Bias = −6.73% and a MDev = 43.69%. The results are better but in such case the model is not anymore predictable.

Finally, the mixing rule proposed by Katti and Chaudhri [8] has also been tested. This mixing rule has the following expression:

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

where  $V_{\text{mix}}$  and  $V_i$  are respectively the molar volumes of the mixture and of the pure compounds. This mixing rule predicts the viscosity of the mixtures with an AAD of 38.04%, a Bias of −38.04% and a MDev of 61.60%. For the three mixing rules studied, (Eqs. (2)–(4)), the MDev was found at  $T = 293.15$  K,  $p = 100$  MPa and  $x_1 = 0.6333$ .

Another interesting property, which can be obtained from the measured values of the viscosity and density, is the excess activation energy of viscous flow  $\Delta E_a$ , which appears in:

$$\ln(V_{\text{mix}} \eta_{\text{mix}}) = \sum_{i=1}^2 x_i \ln(V_i \eta_i) + \frac{\Delta E_a}{RT} \quad (5)$$

where  $R$  is the universal gas constant. This relation is a modification of Eq. (4) based on Eyring's representation of the dynamic viscosity of a pure fluid [27]. Eq. (4) is the particular case of Eq. (5) in the case  $\Delta E_a = 0$  (ideal mixture, according to the Eyring's approach). Fig. 3a shows the variations of  $\Delta E_a(x)$  at  $T = 293.15$  K for different pressures and Fig. 3b shows the variations of  $\Delta E_a(x)$  at  $P = 60$  MPa for different temperatures. It can be seen that  $\Delta E_a$  is positive and increases with pressure and decreases with temperature. The very large values of the maximum of  $\Delta E_a$  show interactions between molecules of a strong attractive nature. A positive excess activation energy for viscous flow should correspond to the interlinking of molecules or the association of bonds within the ordered molecular structure [28].

### 3.2. The self-referencing method

The self-referencing method [9] has been originally developed to model the viscous behavior of petroleum cuts. For these kinds of fluids, it is not straightforward to use equations based on physical properties or scaling parameters such as molar mass, critical pressure, critical temperature or acentric factors, as it is the case for well-defined mixtures. The method does not involve molar mass neither any other physical properties nor scaling parameters, but it requires one ex-

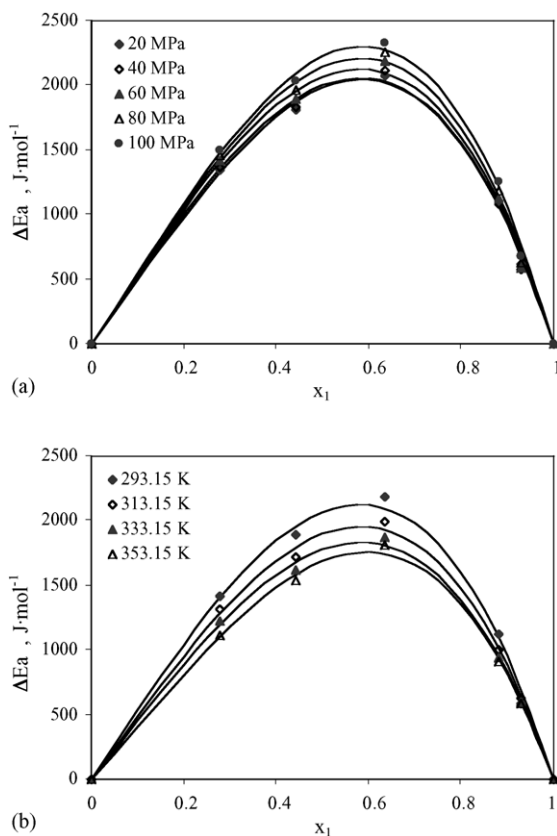


Fig. 3. (a) Excess activation energy of viscous flow  $\Delta E_a$  vs. composition for different pressures at  $T = 293.15$  K. (b) Excess activation energy of viscous flow  $\Delta E_a$  vs. composition for different temperatures at  $p = 60$  MPa.

perimental determination of viscosity  $\eta(p_0, T_0)$  at a reference pressure  $p_0$ , temperature  $T_0$  and the mixture composition. The method has afterwards been modified [29] and improved in order to be used with synthetic mixtures of known composition, requiring nine coefficients for each pure compound. The formulation of this method is:

$$\ln \left( \frac{\eta(p, T)}{\eta(p_0, T_0)} \right) = (ay^2 + by + c) \ln \left( 1 + \frac{(p - p_0)}{dy^2 + ey + f} \right) + (gy_0^2 + hy_0 + i) \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (6)$$

where  $y = y_0 + (gy_0^2 + hy_0 + i)(1/T - 1/T_0)$  and  $y_0 = \ln[\eta(p_0, T_0)]$ . This equation is used with  $p$  in MPa,  $T_0$  and  $T$  in K and  $\eta(p_0, T_0)$  in mPa·s.

The coefficients values for pure HFC-134a and pure TEGDME have been reported in a previous publication [5]. The viscosity of the pure compounds is described with an AAD of 0.80% a Bias of 0.10% and a MDev of 3.00% for HFC-134a and an ADD of 1.50%, a Bias of −0.70% and a MDev of 5.00% for TEGDME. In the present work the viscosity values of HFC-134a + TEGDME has been estimated



using the following mixing rules [29]:

$$\alpha_{\text{mix}} = \sum_{i=1}^n x_i \alpha_i \quad (7)$$

where, for a given compound ‘*i*’,  $\alpha_i$  represents any one of the pure compound parameters ( $a$ – $i$ ), and  $x_i$  is its molar composition. Excluding the reference points ( $p_0 = 20$  MPa and  $T_0 = 293.15$  K) the self-referencing method reproduces the viscosity of the HFC-134a + TEGDME with an ADD of 7.08%, a Bias of  $-3.67\%$  and a MDev of 36.11%, for a total of 195 points since one reference point has been subtracted for each mixture. The point of the maximum deviation is found at a  $T = 293.15$  K,  $p = 100$  MPa and  $x_1 = 0.6333$ .

### 3.3. The hard-sphere model

This model has been recently developed [30,31] for the simultaneous correlation of self-diffusion, viscosity and thermal conductivity of dense fluids. The transport coefficients of real dense fluids expressed in terms of  $V_r = V/V_0$ , with  $V_0$  the close-packed volume and  $V$  the molar volume, are assumed to be directly proportional to the values given by the exact hard-sphere theory. The proportionality factor, described as a roughness factor  $R_\eta$ , accounts for molecular roughness and departure from molecular sphericity. Universal curves for the viscosity were developed and expressed as:

$$\log \left( \frac{\eta_{\text{exp}}^*}{R_\eta} \right) = \sum_{i=1}^7 a_{\eta i} \left( \frac{1}{V_r} \right)^i \quad (8)$$

with

$$\eta_{\text{exp}}^* = 6.035 \times 10^8 \left( \frac{1}{MRT} \right)^{1/2} \eta_{\text{exp}} V^{2/3} \quad (9)$$

The coefficients  $a_{\eta i}$  are universal, independent of the chemical nature of the compound, and  $V_0$  and  $R_\eta$  are adjustable parameters. Assael et al. have given correlation formulas for  $V_0$  and  $R_\eta$  in the case of alkanes [10] and aromatics [12].  $R_\eta$  is independent of pressure and temperature, while  $V_0$  depends on temperature. This method can be applied to mixtures, knowing  $V_0$  and  $R_\eta$  parameters for each compound, and using the following mixing rules in order to determine these parameters for mixtures:

$$V_{0,\text{mix}}(T, x) = \sum_{i=1}^n x_i V_{0i}(T) \quad (10)$$

$$R_{\eta,\text{mix}} = \sum_{i=1}^n x_i R_{\eta i} \quad (11)$$

For this work calculations, the  $a_{\eta i}$  universal parameters reported by Assael et al. have been used [10] along with the previously published  $V_0$  and  $R_\eta$  values for pure [32]. The hard-sphere model predicts the viscosity of pure TEGDME with an ADD of 1.30%, a Bias of 0.20% and a MDev of

3.00%. Assael et al. [33] recommend a value of  $R_\eta = 1$  for pure HFC-134a, and the following expression for the close-packed volume has been proposed by Comuñas et al. [5]:

$$V_0 = 28.31 + 6.9383T_r + 8.675T_r^{-1} \quad (12)$$

where  $V_0$  is obtained in  $\text{cm}^3 \text{mol}^{-1}$ . The viscosity of pure HFC-134a is predicted with an ADD of 2.90%, a Bias of 0.20% and a MDev of 7.40%. Using the characteristic coefficients  $V_{0i}$  and  $R_{\eta i}$  for the pure components and the proposed mixing rules, Eqs. (10) and (11), the hard-sphere model predicts the viscosity of the mixtures with an ADD of 14.34%, a Bias of  $-14.34\%$  and a MDev of 29.66% at  $T = 293.15$  K,  $p = 90$  MPa and  $x_1 = 0.6333$ .

### 3.4. Friction theory

The friction theory (*f*-theory) [13,14] has also been applied. The *f*-theory in combination with simple cubic equations of state (EoS) has shown to deliver accurate viscosity estimation from low to high pressures. This model has been successfully applied to the accurate modeling of several types of fluids including complex systems such as reservoir fluids [34–36], among others.

In the *f*-theory the total viscosity,  $\eta$ , is separated into a dilute gas viscosity term  $\eta_0$  and a residual friction term  $\eta_f$ ,

$$\eta = \eta_0 + \eta_f \quad (13)$$

In the case of the HFC-134a dilute gas limit, the expression proposed by Chung et al. [37] has been used. In the case of the lubricant (TEGDME) the dilute gas term was neglected, due to the fact that the lubricant is consistently found in the dense liquid phase. Thus, for the mixture the dilute gas term contribution has been simply considered as linearly dependent on the mole fraction of the refrigerant. For the viscosity friction term, the quadratic friction model has been considered:

$$\eta_f = \kappa_r p_r + \kappa_a p_a + \kappa_{rr} p_r^2 \quad (14)$$

where  $\kappa_r$ ,  $\kappa_a$ , and  $\kappa_{rr}$  are temperature dependent friction coefficients;  $p_r$  and  $p_a$  are the repulsive and attractive terms of the EoS, which have been obtained from the Peng–Robinson (PR) EoS [38]. For the friction coefficients the following temperature parameterization has been applied:

$$\begin{aligned} \kappa_r &= \frac{a_0 + a_1(\exp(T_r^{-1} - 1) - 1) + a_2(\exp(2T_r^{-1} - 2) - 1)}{p_c} \\ \kappa_a &= \frac{b_0 + b_1(\exp(T_r^{-1} - 1) - 1) + b_2(\exp(2T_r^{-1} - 2) - 1)}{p_c} \\ \kappa_{rr} &= \frac{c_2(\exp(2T_r^{-1}) - 1)}{p_c} \end{aligned} \quad (15)$$

The parameters in Eq. (15) have been regressed against the HFC-134a viscosity data measured at the laboratory [26] (70 points). The performance of the model is satisfactory giving an AAD of 0.63% a Bias of  $-0.01\%$  and a MDev of 2.44%. In the case of the lubricant, viscosity values also measured in the laboratory [25] were used. For the pure lubricant the ADD,

Table 2

Parameters and deviations obtained with the friction theory model in combination with the PR EoS for pure compounds

Parameter	HFC-134a	TEGDME	Units
$a_0$	39.4278	679.0417	( $\mu\text{Poise}$ )
$a_1$	45.2898	−1041.7009	( $\mu\text{Poise}$ )
$a_2$	22.5327	182.7806	( $\mu\text{Poise}$ )
$b_0$	−28.4505	537.3642	( $\mu\text{Poise}$ )
$b_1$	162.4113	−865.1410	( $\mu\text{Poise}$ )
$b_2$	−48.2172	137.0217	( $\mu\text{Poise}$ )
$c_2$	0.020708	0.017587	
Pure fluid	Deviation		
	ADD (%)	Bias (%)	MDev (%)
HFC-134a	0.63	−0.01	2.44
TEGDME	1.46	−0.02	4.43

Bias and MDev are 1.46, −0.02 and 4.43%, respectively. The resulting numerical values for the  $f$ -theory model constants are reported in Table 2.

The mixture viscosity has been estimated using the following mixing rules:

$$\eta_{\text{mx}} = x_1 \eta_{0,1} + \kappa_{\text{r,mx}} p_{\text{r,mx}} + \kappa_{\text{a,mx}} p_{\text{a,mx}} + \kappa_{\text{rr,mx}} p_{\text{r,mx}}^2 \quad (16)$$

where  $p_{\text{a,mx}}$  and  $p_{\text{r,mx}}$  are the attractive and repulsive pressure contributions of the mixture and the  $\kappa_{\text{r,mx}}$ ,  $\kappa_{\text{a,mx}}$ , and  $\kappa_{\text{rr,mx}}$  are the viscous friction parameters for the mixture. The critical temperature, critical pressure and acentric factor values necessary in the PR EoS have been taken from the literature [32,39]. For the PR EoS the quadratic mixing rules have been used and the interaction binary parameter ( $k_{ij}$ ) has been set to zero. For the viscous friction parameters the following simple mixing rules, proposed in [13,14] have been used:

$$\begin{aligned} \kappa_{\text{r,mx}} &= \sum_{i=1}^n z_i \kappa_{\text{r},i} \\ \kappa_{\text{a,mx}} &= \sum_{i=1}^n z_i \kappa_{\text{a},i} \\ \kappa_{\text{rr,mx}} &= \sum_{i=1}^n z_i \kappa_{\text{rr},i} \end{aligned} \quad (17)$$

where

$$z_i = \frac{x_i}{M_i^\varepsilon M_m} \text{ with } M_m = \sum_{i=1}^n \frac{x_i}{M_i^\varepsilon} \quad (18)$$

where  $M_i$  is the molar mass of compound  $i$ . The exponent  $\varepsilon$  that appears in Eq. (18) has been correlated [14] against several compounds, giving the best results with  $\varepsilon = 0.3$ . The  $f$ -theory model predicts the viscosity of the mixtures with an ADD of 8.32%, a Bias of −5.51% and a MDev of 17.06% at  $T = 353.15 \text{ K}$ ,  $p = 100 \text{ MPa}$  and  $x_1 = 0.6333$ .

### 3.5. The free-volume viscosity model

Recently an approach in order to model the viscosity of Newtonian fluids (in the condensed phase) with small molecules has been proposed by Allal et al. [15]. This approach connects viscosity,  $\eta$ , to molecular structure via a representation of the free volume fraction. In its first version the model [15] could be only applied to dense fluids but a version valid for low density states has also been developed [16]. For pure fluids, this model delivers accurate viscosity estimations from very low to high pressures with only three adjustable parameters for each compound. In this last version, the viscosity has the following expression:

$$\eta = \eta_0 + \frac{\rho l \left( \alpha \rho + \frac{pM}{\rho} \right)}{(3RTM)^{1/2}} \exp \left[ B \left( \frac{\alpha \rho + \frac{pM}{\rho}}{RT} \right)^{3/2} \right] \quad (19)$$

where  $M$  is the molar mass,  $\rho$  the density and  $\eta_0$  the dilute gas viscosity term, for which the expression proposed by Chung et al. [37] has been used. In the case of the free-volume model,  $l$ ,  $\alpha$  and  $B$  are adjustable parameters for each pure fluid. This model can be also applied for mixtures using the following mixing rules [5]:

$$\alpha_{\text{mix}} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \alpha_{ij} \quad \text{with } \alpha_{ij} = (\alpha_i \alpha_j)^{1/2} \quad (20)$$

$$l_{\text{mix}} = \sum_{i=1}^n x_i l_i \quad (21)$$

$$\frac{1}{B_{\text{mix}}} = \sum_{i=1}^n \frac{x_i}{B_i} \quad (22)$$

The dilute gas term contribution of the mixture has been considered, as for the friction theory model, linearly dependent on the mole fraction of refrigerant. It seems that there is a typographical problem with the coefficients  $B$  given in [5] so, using a database of 70 points for pure HFC-134a [26] and 48 points for pure TEGDME [25] the parameter values for the pure compounds have been adjusted again. The viscosity of the pure compounds is described satisfactorily with an AAD of 1.35% a Bias of 0.20% and a MDev of 6.17% for HFC-134a and an ADD of 1.88%, a Bias of −0.55% and a MDev of 6.10% for TEGDME. The corrected parameters for pure HFC-134a and pure TEGDME are reported in Table 3. Taking into account these parameters and the mixing rules of Eqs. (19)–(21) the dynamic viscosity of (HFC-134a + TEGDME) can be predicted. The calculated free volume model values agree with the experimental values with an AAD of 27.51%, a Bias of −27.51% and a MDev of 55.21%. The point of maximum deviation is found at a  $T = 293.15 \text{ K}$ ,  $p = 100 \text{ MPa}$  and  $x_1 = 0.6333$ . These results are an indication for the limitations of the used mixing rules in correctly reproducing systems with strong attractive interactions. It is interesting to notice that for all the models the maximum deviation is ob-

Table 3

Parameters and deviations obtained with the free volume model for pure compounds

Pure fluid	$\alpha$ ( $\text{m}^5 \text{mol}^{-1} \text{s}^{-2}$ )	$B$	$l$ ( $\text{\AA}$ )
HFC-134a	25.1247	0.011418	0.958875
TEGDME	255.5527	0.002697	0.305256
Pure fluid	Deviation		
	ADD (%)	Bias (%)	MDev (%)
HFC-134a	1.35	0.20	6.17
TEGDME	1.88	−0.55	6.10

tained at  $x_1 = 0.6333$  where the quantity  $\Delta E_a$ , characteristic of the interactions, is also at a maximum.

#### 4. Conclusions

New viscosity data for the binary system 1,1,1,2-tetrafluoroethane (HFC-134a) + tetraethylene glycol dimethylether (TEGDME) are presented. The measurements (200 data points) have been obtained at various pressures (between 10 and 100 MPa) in the monophasic liquid state from  $T = 293.15$ – $373.15$  K. The measurements have been carried out with a falling body viscometer for four molar fractions  $x_1 = 0.28, 0.44, 0.63$  and  $0.88$ . The general uncertainty in the measurements is of the order of  $\pm 2\%$ , some additional uncertainty is found for the high pressure measurements at the 353.15 and 373.15 K isotherms due to lack of reference experimental data for the calibration of the apparatus. The data have been correlated using several viscosity models (mixing rules, self-referencing model, hard-sphere model, friction theory and free volume model). As it can be observed in Fig. 4, only two models are able to predict the viscosity with an average deviation less than 10%: the self-referencing model (AAD = 7.08% and MDev = 36.11%) and the friction theory (AAD = 8.32% and MDev = 17.07%). However, the self-referencing model needs one value at each composition for the pressure and temperature of reference. Additionally, the calculation of the excess activation energy of viscous flow

indicates that this system presents very important attractive interactions between its molecules. That could explain the not very good performance, even for the best models (the average absolute deviation is for each model several times higher than the experimental uncertainty). It can be concluded that the mixing rules, generally empirical, proposed for the calculation of the viscosity mixtures are probably not adapted to such strong interaction and in this sense some further study on this matter should be considered. In the case of the  $f$ -theory model the deviations may also be linked to the use of a cubic EoS, the PR EoS, as the core model for the thermodynamic description of a mixture of this type.

#### List of symbols

$M$	molar mass
$p$	pressure
$p_0$	reference pressure
$P_c$	critical pressure
$R$	gas constant
$T$	temperature
$T_0$	reference temperature
$T_r$	reduced temperature
$V$	molar volume
$x_i$	molar fraction of component $i$

#### Greek letters

$\eta$	viscosity
$\eta_0$	dilute gas viscosity
$\rho$	density
$\tau$	time

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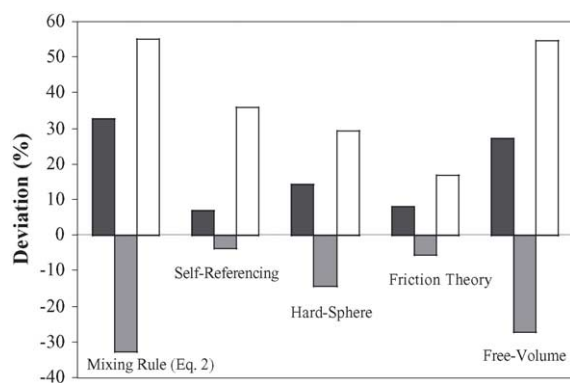


Fig. 4. Deviations between the experimental values and the predicted data for the analyzed models: ADD (black), Bias (grey) and MDev (white).

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