Compressed Liquid Viscosity of 1,1,1,3,3-Pentafluoropropane (R245fa) and 1,1,1,3,3,3-Hexafluoropropane (R236fa)

Xianyang Meng, Jianbo Zhang, and Jiangtao Wu*

Key Laboratory of Thermo-Fluid Science and Engineering of Ministry of Education (MOE), Xi'an Jiaotong University, Xi'an, 710049, China

ABSTRACT: The viscosity of compressed liquid 1,1,1,3,3-pentafluoropropane (R245fa) and 1,1,1,3,3,3-hexafluoropropane (R236fa) has been measured with a new vibrating-wire viscometer. Measurements for R245fa were carried out at 12 temperatures in the range from (263 to 373) K and at pressures from slightly above saturation up to 40 MPa, except for the isotherms at 373.14 K where the maximum pressure was 35 MPa. With regard to R236fa, measurements were performed at temperatures between (253 and 373) K and at pressures from slightly above saturation up to 40 MPa. The combined expanded uncertainty of these results with a level of confidence of 0.95 ($k = 2$) is about $\pm$ 2.8 %. The scheme based on a hard-spheres model was used to correlate the experimental results. The average absolute deviation of the experimental results from the correlations for R245fa and R236fa is 0.5 % and 0.43 %, respectively. Small extrapolations of the present correlation scheme to the saturation line were performed to enable a comparison with literature results at saturation pressure.

■ INTRODUCTION

The Montreal Protocol and its subsequent amendments have created a schedule to replace ozone depletion substances such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) with chlorine-free molecules in several industrial applications. The potential alternatives have been expanded to propane-derived hydrofluorocarbons, like 1,1,1,3,3-pentafluoropropane (R245fa) and 1,1,1,3,3,3-hexafluoropropane (R236fa). Despite the high global warming potential of these fluids especially for R236fa, they still have many practical and engineering applications at present. For example, R245fa and R236fa are excellent blowing agents to replace hydrochlorofluorocarbons for its desirable characteristics and could be used as working fluids in high-temperature heat pumps and power cycles.[1] R245fa is also used as one component of refrigerant mixtures in centrifugal chillers for its environmental safety and high thermodynamic efficiency.[2] In addition, these compounds may be suitable as cleaning solvents, release agents, and so on.

Although thermophysical properties for these substances should be required in practical applications, a literature survey shows that only a limited number of data sets of the viscosity of the saturated liquid of R245fa and R236fa have been published in the literature,[3-5] and no viscosity measurements in compressed liquid region of these two fluids could be found. The development of correlation schemes for the viscosity of these fluids requires accurate experimental data, covering modest ranges of thermodynamic conditions. For a more comprehensive study of their thermophysical properties, viscosity measurements of R245fa and R236fa were measured using a vibrating-wire instrument at temperatures from (253 to 373) K and at pressures up to 40 MPa. Viscosity models based on the hard-sphere scheme were developed for both R245fa and R236fa.

■ EXPERIMENTAL SECTION

Fluid Samples. The toluene was supplied by Tianjin Fuyu Industry of Fine Chemicals Co., Ltd., China. 1,1,1,2-Tetrafluoroethane (R134a) was manufactured by Sinochem Modern Environmental Protection Chemicals (Xi'an) Co., Ltd., China. 1,1,1,3,3-Pentafluoropropane and 1,1,1,3,3,3-hexafluoropropane were purchased from Zhejiang Lantian Environmental Protection Hi-Tech Co., Ltd., China. Completely specification of chemical samples is listed in Table 1. No further purification for toluene was done on the samples in the experiment. 1,1,1,2-Tetrafluoroethane, 1,1,1,3,3-pentafluoropropane, and 1,1,1, 3,3,3-hexafluoropropane were purified several times before use by freeze−pump−thaw cycles using liquid nitrogen and a high vacuum pump (< 0.01 Pa) to eliminate the effect of gaseous impurities.

Working Equations. Vibrating-wire sensors have been applied to measure the viscosity of various fluids over wide temperature and pressure ranges, because of the method's simplicity, rigorous mathematic description, well-established working equations, and simultaneous density measurement with a sinker as the tensioning mechanism.[6-8] In recent decades, many practical devices for the method have been developed.[9-16] In our laboratory, we have developed a vibrating-wire instrument used to simultaneously measure the viscosity and density of alternative fuels.[17] In this work, a new vibrating-wire viscometer with two clamps at both ends was designed to measure the viscosity of refrigerants at high pressure, such as R245fa and R236fa. In such a instrument, a tungsten wire was placed within a magnetic field perpendicular to its axes. When there is a constant current passing through the wire, the wire is driven in steady state transverse oscillations, which in turn induces complex voltage across the wire according to Faraday's law. The working equations that describe the motion of the wire within a fluid have been described previously.[6,7,14-16] The induced voltage V comprises two terms:[15]

$$V = V_1 + V_2 \qquad (1)$$

Table 1. Specification of Chemical Samples

chemical name	source	initial mass fraction purity	purification method
toluene	Fuyu Industry of Fine Chemicals Co., Ltd., China	0.995	none
R134a[a]	Sinochem Modern Environmental Protection Chemicals Co., Ltd., China	0.999	freeze−pump−thaw
R245fa[b]	Lantian Environmental Protection Hi-Tech Co., Ltd., China	0.999	freeze−pump−thaw
R236fa[c]	Lantian Environmental Protection Hi-Tech Co., Ltd., China	0.997	freeze−pump−thaw

[a] R134a = 1,1,1,2-tetrafluoroethane. [b] R245fa = 1,1,1,3,3-pentafluoropropane. [c] R236fa = 1,1,1,3,3,3-hexafluoropropane.

The first term, V_1, resulted from the intrinsic electrical impedance of the wire, is given by

$$V_1 = a + ib + icf \tag{2}$$

where a, b, and c are adjustable real constants, and i is an imaginary unit. The second term in eq 1, V_2, arises from the motion of the wire, given by

$$V_2 = \frac{\Lambda f i}{f_0^2 - (1 + \beta)f^2 + (\beta' + 2\Delta_0)f^2 i} \tag{3}$$

where Λ is the amplitude, f_0 is the resonance frequency of the wire in vacuum, the Δ_0 is internal damping of the wire, and the terms β and β' are respectively the added mass and the viscous damping of the fluids. Retsina et al.[6,7] analyzed the fluid mechanics of a wire and expressed β and β' by

$$\beta = k\frac{\rho}{\rho_s} \tag{4}$$

and

$$\beta' = k'\frac{\rho}{\rho_s} \tag{5}$$

The ρ and ρ_s are the density of a fluid and the wire, respectively, and k and k' are given by

$$k = -1 + 2\text{Im}(A) \tag{6}$$

and

$$k' = 2\text{Re}(A) \tag{7}$$

where A is a complex quantity given by

$$A = i\left(1 + \frac{2K_1(\sqrt{i\Omega})}{\sqrt{i\Omega}K_0(\sqrt{i\Omega})}\right) \tag{8}$$

where

$$\Omega = \frac{2\pi f \rho R^2}{\eta} \tag{9}$$

In eq 8, K_0 and K_1 are the modified Bessel functions of the zeroth and first order, and Ω is dimensionless frequency related to the Reynolds number of the flow around the wire with a radius of R. The fluid viscosity, η, when the density is known, can be calculated from the in-phase and quadrature voltages experimental determined over a certain frequency range covering the resonance frequency.

Apparatus. The vibrating sensor used in this work is a tungsten wire with a nominal radius of about 50 μm and a length of about 62 mm, obtained from Goodfellow (Cambridge, UK) with a mass fraction purity greater than 99.95 %. The wire is clamped at each end to two stainless steel pieces with screws. Concerning the operating conditions, the tension applied to the
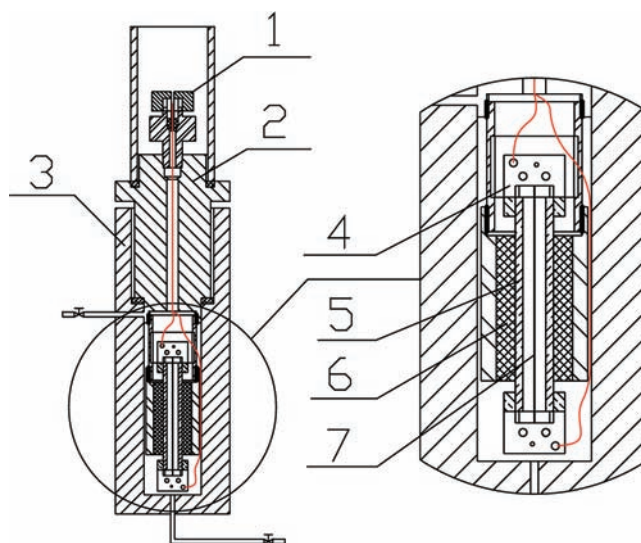

Figure 1. Schematic of the vibrating-wire apparatus: (1) feedthrough; (2) cap; (3) pressure vessel; (4) clamp; (5) ceramic tube; (6) magnets; (7) tungsten wire.

wire should lead to a resonance frequency on the order of 1 kHz. In the present work, the measured resonance frequency in ambient air at 298.15 K was about 1107.3 Hz. The two clamps were separated from each other by a machinable glass ceramic tube with an outer diameter of 10 mm and an inner diameter of 6 mm. A pair of samarium−cobalt magnets was mounted parallel onto a cage with a distance of 10 mm in the direction of the magnetic field, and the length of the rectangular magnets is about 38 mm. The magnetic field exerted on the wire was about 0.3 T. The cell was mounted inside a custom-made stainless steel vessel with a maximum operating pressure of 70 MPa. The electrical connections of the vibrating wire were commercially obtained from Conax Buffalo (model: MHC1), which can work at pressure below 55 MPa. The vibrating-wire assembly was shown in Figure 1.

The electrical drive is achieved by a function generator (model: 33220A, Agilent) providing a constant sinusoidal drive source. The in-phase and quadrature voltages of the signal were detected with the lock-in amplifier (model: SR830, Stanford Research Systems) over the frequency range ($f_r \pm 5g$), where g is half width of the resonant curve. The lock-in offset was set on at the beginning of acquiring to remove the majority contribution of V_1 in eq 1.

The apparatus was immersed completely in a thermostatic bath (model: 7037, Fluke). The temperature stability and uniformity of the bath were better than ± 3 mK. The temperature of the thermostatic bath was measured using a 100 Ω platinum resistance thermometer connected to a DMM (model: 3458A, Agilent). The thermometer has been calibrated over the experimental temperature range against a 25 Ω standard platinum-resistance
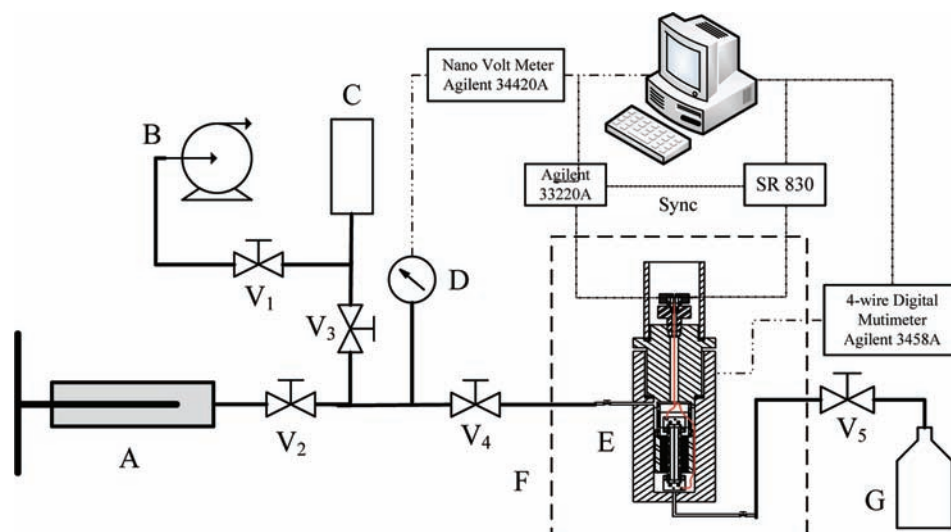
Figure 2. Schematic diagram of experimental system: (A) manual piston pump; (b) vacuum pump; (c) sample container; (d) pressure transducer; (e) vibrating-wire viscometer; (f) thermostatic bath; (g) wasting recycle; ($V_1 \sim V_5$) valves.

thermometer (model: WZPB, No. 92822, Yunnan Temperature Instruments Co., Ltd., China) certified by the National Institute of Metrology of China. The combined expanded uncertainty of temperature with level of confidence 0.95 ($k = 2$) is $U_c(T) = 12$ mK.

The pressure was generated with a manual piston pump (model: 50-6-15, HIP) and measured by a high pressure transducer (model: P3MB, HBM) with a pressure range up to 100 MPa. A 7 1/2 digits resolution nanovolt meter (model: 34420A, Agilent) was employed for the transformation of the pressure transducer measurement signal. The combined expanded uncertainty of pressure with the level of confidence 0.95 ($k = 2$) is $U_c(p) = 0.13$ MPa. A diagram of the experimental system is shown in Figure 2.

Calibration and Test. Though, as demonstrated by Goodwin and Marsh,[18] the vibrating wire viscometer can be operated as an absolute viscometer, the relative manner was preferred in present work. The density of the wire were taken from the literature ($\rho_s = 19300$ kg·m^{-3}). The resonance frequency in the absence of fluid, f_0, together with the internal damping of the wire, Δ_0, can be measured in vacuum, but the value of f_0 obviously varied with temperature and pressure because of the differences in properties between tungsten wire and ceramic tube. As mentioned by Kandil et al.,[15] we had to treat f_0 as an adjustable parameter in the regression analysis. The radius of the wire, R, was determined from the calibration experiment in toluene at $T_{ref} = 298.15$ K and $p_{ref} = 0.1$ MPa. The reference datum was taken to be $\rho_{ref} = 862.5$ kg·m^{-3} and $\eta_{ref} = 0.555$ mPa·s.[19] The final determined values of R and Δ_0 were 49.08 μm and $3.25 \cdot 10^{-5}$, respectively. The viscosity of the density known fluid can be obtained by fitting the experimental complex voltages to working equations.

This work carried out the viscosity measurement for toluene over the temperature range from (248 to 348) K and at pressures up to 40 MPa, listed in Table 2. When comparing the present results with the calculated results from the correlation of Assael et al.,[19] it is observed that the relative differences, shown in Figure 3, are within ± 1.0 %, except for two points at 248.16 K with values of 1.3 % at 20 MPa and 1.9 % at 30 MPa.

To test the performance of the present instrument on refrigerants, we also measured the viscosity of R134a at temperatures

Table 2. Experimental Values of Viscosity η of Toluene at Temperature T and Pressure p along with the Relative Deviations from Values Obtained with the Correlation of Assael et al.[19]

T	p	η	
K	MPa	mPa·s	$100\, \Delta\eta/\eta_{calcd}{}^a$
248.16	1	1.1901	0.77
	10	1.2846	0.99
	20	1.3969	1.30
	30	1.5211	1.88
273.15	1	0.7764	−0.20
	10	0.8352	0.02
	20	0.9052	0.47
	30	0.9742	0.48
	40	1.0453	0.31
298.14	1	0.5581	−0.29
	10	0.6005	0.03
	20	0.6440	−0.43
	30	0.6909	−0.55
	40	0.7419	−0.32
323.13	1	0.4252	0.10
	10	0.4563	−0.02
	20	0.4908	−0.27
	30	0.5267	−0.36
	40	0.5662	0.04
348.13	1	0.3356	0.67
	10	0.3616	0.62
	20	0.3907	0.59
	30	0.4198	0.49
	40	0.4497	0.47

$^a \Delta\eta = \eta_{exptl} - \eta_{calcd}$, where η_{exptl} is the experimental viscosity of toluene and η_{calcd} is obtained with the correlation of Assael et al.[19] The combined expanded uncertainty U_c is $U_c(T) = 12$ mK, $U_c(p) = 0.13$ MPa, and $U_c(\eta) = 0.028\eta$ (level of confidence = 0.95).

from (258 to 338) K and at pressures up to 40 MPa. The experimental results are listed in Table 3 along with the relative

4958

dx.doi.org/10.1021/je200854k |*J. Chem. Eng. Data* 2011, 56, 4956–4964
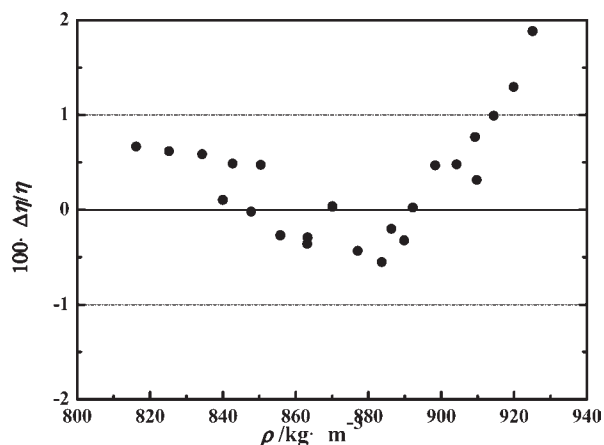
Figure 3. Fractional deviations $\Delta\eta/\eta = (\eta_{exptl} - \eta_{calcd})/\eta_{calcd}$ of the experimental viscosities η_{exptl} of toluene from values η_{calcd} obtained with the correlation of Assael et al.[19] as a function of density. ●, this work.

deviations from REFPROP 8.0,[20] shown in Figure 4. Figure 4 also shows the deviations of literature data from REFPROP 8.0. Our results deviate the equation of REFPROP 8.0 within ± 2.0 % except one point with a value of 2.43 % at 258.15 K and 40 MPa. The exact deviations between this work and literature data were not present; however, Figure 4 illustrates that our results are in good agreement with those from Okubo et al.[21] and Lavrenchenko et al.[22] and exhibit a reasonable agreement to the results of Assael et al.[23] and Oliveira and Wakeham.[24]

■ RESULTS AND CORRELATION

The viscosity of compressed liquid R245fa was measured along 12 isotherms at temperatures between (263 and 373) K, as shown in Table 4. The measurements were performed at pressures from slightly above saturation up to 40 MPa, except for the isotherms at 373.14 K where the maximum pressure was 35 MPa. The viscosity of R236fa was obtained at pressures up to the maximum pressure of 40 MPa and over the temperature range from (253 to 373) K along 13 isotherms, shown in Table 5. At each temperature and pressure, the experiment is measured three times at least, and the repeatability of the results is better than ± 0.5 % (the absolute difference less than 2 μPa·s). The density values, required to obtain the viscosity from the working equations, were calculated from REFPROP 8.0.[20] According to the author, the estimated uncertainty of density for R245fa is 0.1 % in the liquid phase below 400 K with pressures up to 30 MPa. Above 30 MPa, the uncertainties are 0.2 % at temperatures above 310 K and up to 1.0 % for lower temperatures. The uncertainties for R236fa are 1.0 % in density. The density data were verified by our previous results investigated in the temperature range from (293 to 373) K and at pressures up to 70 MPa.[1] Viscosities of R245fa and R236fa versus pressure or temperature plots are shown in Figures 5 and 6, respectively.

The viscosities of R245fa and R236fa were correlated with the hard-sphere model proposed by Assael and Dymond.[25,26] The experimental data were converted to reduced viscosities η^* according to

$$\eta^* = 6.035 \cdot 10^8 \frac{\eta V^{2/3}}{\sqrt{MRT}} \tag{10}$$

Table 3. Experimental Values of Viscosity η of R134a at Temperature T and Pressure p along with the Relative Deviations from Values Calculated with REFPROP 8.0[19]

T	p	η	
K	MPa	mPa·s	$100 \, \Delta\eta/\eta_{calcd}{}^a$
258.15	1	0.3251	−0.85
	5	0.3468	0.88
	10	0.3675	1.10
	15	0.3885	1.36
	20	0.4094	1.53
	25	0.4309	1.71
	30	0.4502	1.31
	35	0.4712	1.17
	40	0.4996	2.43
278.14	1	0.2536	0.44
	5	0.2678	0.36
	10	0.2859	0.57
	15	0.3033	0.62
	20	0.3209	0.80
	25	0.3381	0.80
	30	0.3543	0.50
	35	0.3712	0.33
	40	0.3885	0.21
298.14	1	0.1962	0.05
	5	0.2108	0.30
	10	0.2273	0.32
	15	0.2421	−0.09
	20	0.2567	−0.32
	25	0.2716	−0.37
	30	0.2876	0.02
	35	0.3017	−0.26
	40	0.3169	−0.23
318.13	2	0.1549	0.03
	5	0.1656	−0.16
	10	0.1828	0.25
	15	0.1970	−0.22
	20	0.2111	−0.28
	25	0.2254	−0.07
	30	0.2393	0.08
	35	0.2511	−0.56
	40	0.2647	−0.46
338.13	2	0.1152	−0.34
	5	0.1288	−0.21
	10	0.1466	−0.20
	15	0.1618	−0.19
	20	0.1754	−0.29
	25	0.1893	0.14
	30	0.2007	−0.51

$^a \Delta\eta = \eta_{exptl} - \eta_{calcd}$, where η_{exptl} is the experimental viscosity of R134a and η_{calcd} is the value calculated with REFPROP 8.0.[19] The combined expanded uncertainty U_c is $U_c(T) = 12$ mK, $U_c(p) = 0.13$ MPa, and $U_c(\eta) = 0.028\eta$ (level of confidence = 0.95).

where η is the experimental viscosity in Pa·s, V is the molar volume in m^3·mol^{-1}, M is the molar mass in kg·mol^{-1}, $R = 8.314510$ J·(mol·K)$^{-1}$ is the universal gas constant, and T is the
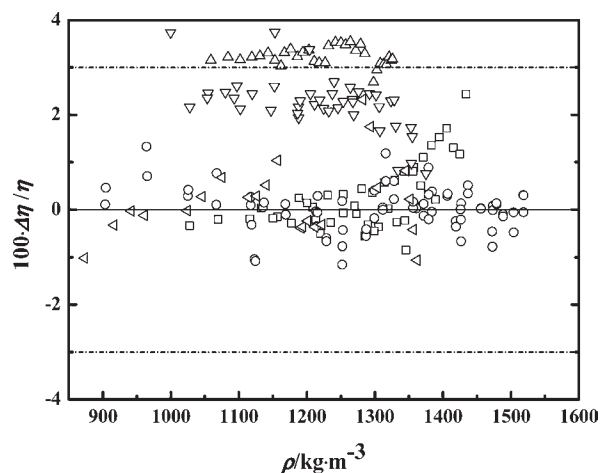
Figure 4. Fractional deviations $\Delta\eta/\eta = (\eta_{exptl} - \eta_{calcd})/\eta_{calcd}$ of the experimental viscosities η_{exptl} of R134a from values η_{calcd} calculated with REFPROP 8.0[20] as a function of density. □, this work; ○, Okubo et al.;[21] ◁, Lavrenchenko et al.;[22] △, Assael et al.;[23] ▽, Oliveira et al.[24]

Table 4. Experimental Values of Viscosity η of R245fa at Temperature T and Pressure p^a

T	p	η	T	p	η
K	MPa	mPa·s	K	MPa	mPa·s
263.15	1	0.6790	323.13	1	0.2952
	5	0.7113		5	0.3139
	10	0.7526		10	0.3372
	15	0.7951		15	0.3595
	20	0.8369		20	0.3816
	25	0.8778		25	0.4029
	30	0.9236		30	0.4250
	35	0.9686		35	0.4464
	40	1.0153		40	0.4694
273.14	1	0.5811	333.13	1	0.2601
	5	0.6083		5	0.2788
	10	0.6456		10	0.3009
	15	0.6801		15	0.3232
	20	0.7170		20	0.3433
	25	0.7534		25	0.3637
	30	0.7902		30	0.3837
	35	0.8293		35	0.4048
	40	0.8685		40	0.4241
283.14	1	0.4999	343.13	1	0.2301
	5	0.5252		5	0.2484
	10	0.5564		10	0.2698
	15	0.5887		15	0.2900
	20	0.6204		20	0.3100
	25	0.6519		25	0.3304
	30	0.6847		30	0.3488
	35	0.7184		35	0.3686
	40	0.7497		40	0.3872
293.14	1	0.4344	353.13	1	0.2053
	5	0.4571		5	0.2226
	10	0.4859		10	0.2428
	15	0.5143		15	0.2627

Table 4. Continued

T	p	η	T	p	η
K	MPa	mPa·s	K	MPa	mPa·s
	20	0.5433		20	0.2819
	25	0.5704		25	0.2999
	30	0.5998		30	0.3186
	35	0.6291		35	0.3361
	40	0.6589		40	0.3537
303.14	1	0.3799	363.14	2	0.1838
	5	0.4011		5	0.1972
	10	0.4282		10	0.2190
	15	0.4534		15	0.2389
	20	0.4796		20	0.2561
	25	0.5048		25	0.2746
	30	0.5306		30	0.2918
	35	0.5573		35	0.3084
	40	0.5829		40	0.3250
313.14	1	0.3343	373.14	2	0.1612
	5	0.3538		5	0.1758
	10	0.3790		10	0.1977
	15	0.4035		15	0.2165
	20	0.4270		20	0.2346
	25	0.4502		25	0.2518
	30	0.4745		30	0.2679
	35	0.4975		35	0.2839
	40	0.5211			

^{a} The combined expanded uncertainty U_c is $U_c(T)$ = 12 mK, $U_c(p)$ = 0.13 MPa, and $U_c(\eta) = 0.028\eta$ (level of confidence = 0.95).

absolute temperature in K. The reduced viscosity of a rough hard-sphere fluid is fitted to a universal curve of the reduced viscosity for a smooth hard-sphere fluid whose density dependence is represented by the correlation

$$\log_{10}\left[\frac{\eta^*}{R_\eta}\right] = 1.095 - \frac{9.26324}{V_r} + \frac{71.0385}{V_r^2} - \frac{301.9012}{V_r^3} + \frac{979.6900}{V_r^4} - \frac{1221.9770}{V_r^5} + \frac{987.5574}{V_r^6} - \frac{319.4636}{V_r^7} \quad (11)$$

The proportionality factor, R_η, accounts for molecular roughness and departure from molecular sphericity, independent of pressure and temperature. The reduced volume is defined as $V_r = V/V_0$, where V_0 is the temperature-dependent close-packed volume in $m^3 \cdot mol^{-1}$. The temperature dependence of V_0 were represented by the empirical relation,

$$V_0 \cdot 10^6/(m^3 \cdot mol^{-1}) = a + b(T/K) + c(T/K)^2 \quad (12)$$

The molar volume of R245fa and R236fa is calculated from equations suggested by Yin and Wu.[1] In that work, the density was measured over the temperature range from (293 to 373) K and at pressures up to 70 MPa, with a high-pressure vibrating tube densimeter. So, in this application, extrapolations were performed below 293 K, and the calculated results from that equation of state were compared with REFPROP 8.0. The density difference of the two equations for R245fa and R236fa is within ± 0.13 % and ± 0.5 %, respectively. The statistical values of fitting, the average absolute percentage deviation, AAD, the maximum absolute percentage deviation, MAD, and the

4960

dx.doi.org/10.1021/je200854k |*J. Chem. Eng. Data* 2011, 56, 4956–4964

Table 5. Experimental Values of Viscosity η of R236fa at Temperature T and Pressure p^a

T	p	η	T	p	η
K	MPa	mPa·s	K	MPa	mPa·s
253.15	1	0.5347	323.13	1	0.2100
	5	0.5621		5	0.2306
	10	0.5982		10	0.2530
	15	0.6363		15	0.2742
	20	0.6710		20	0.2950
	25	0.7092		25	0.3155
	30	0.7510		30	0.3353
	35	0.7898		35	0.3544
	40	0.8347		40	0.3744
263.16	1	0.4612	333.13	1	0.1844
	5	0.4857		5	0.2046
	10	0.5184		10	0.2274
	15	0.5511		15	0.2481
	20	0.5830		20	0.2683
	25	0.6154		25	0.2868
	30	0.6508		30	0.3059
	35	0.6835		35	0.3248
	40	0.7189		40	0.3434
273.14	1	0.3999	343.13	2	0.1669
	5	0.4237		5	0.1825
	10	0.4520		10	0.2044
	15	0.4821		15	0.2255
	20	0.5127		20	0.2447
	25	0.5412		25	0.2631
	30	0.5699		30	0.2805
	35	0.6012		35	0.2994
	40	0.6317		40	0.3154
283.14	1	0.3500	353.13	2	0.1456
	5	0.3722		5	0.1618
	10	0.3989		10	0.1858
	15	0.4259		15	0.2064
	20	0.4534		20	0.2239
	25	0.4798		25	0.2427
	30	0.5054		30	0.2591
	35	0.5325		35	0.2761
	40	0.5603		40	0.2925
293.14	1	0.3074	363.14	2	0.1248
	5	0.3281		5	0.1432
	10	0.3534		10	0.1663
	15	0.3789		15	0.1863
	20	0.4034		20	0.2051
	25	0.4271		25	0.2226
	30	0.4520		30	0.2395
	35	0.4757		35	0.2555
	40	0.5014		40	0.2713
303.14	1	0.2708	373.14	2	0.1074
	5	0.2906		5	0.1287
	10	0.3141		10	0.1531
	15	0.3383		15	0.1718
	20	0.3620		20	0.1886
	25	0.3838		25	0.2056

Table 5. Continued

T	p	η	T	p	η
K	MPa	mPa·s	K	MPa	mPa·s
	30	0.4053		30	0.2222
	35	0.4290		35	0.2366
	40	0.4513		40	0.2495
313.14	1	0.2385			
	5	0.2585			
	10	0.2817			
	15	0.3041			
	20	0.3268			
	25	0.3467			
	30	0.3678			
	35	0.3897			
	40	0.4100			

^{a} The combined expanded uncertainty U_c is $U_c(T)$ = 12 mK, $U_c(p)$ = 0.13 MPa, and $U_c(\eta) = 0.028\eta$ (level of confidence = 0.95).

average percentage deviation, Bias, are defined as follows

$$AAD = \frac{1}{N_b} \sum_{i=1}^{i=N_b} \left| \frac{\eta_{i,\exp} - \eta_{i,cal}}{\eta_{i,cal}} \right| \qquad (13)$$

$$MAD = \max\left(\left| \frac{\eta_{i,\exp} - \eta_{i,cal}}{\eta_{i,cal}} \right| \right) \qquad (14)$$

$$Bias = \frac{1}{N_b} \sum_{i=1}^{i=N_b} \frac{\eta_{i,\exp} - \eta_{i,cal}}{\eta_{i,cal}} \qquad (15)$$

The obtained R_η and parameters in eq 12, as well as the statistical values, are presented in Table 6.

■ DISCUSSION

Measurement Uncertainty. The main factors introducing errors to viscosity results include the uncertainties of temperature, pressure, fluid density, radius of tungsten wire, repeatability of measurement, and other sources which will cause relatively minor and neglectable errors. The uncertainty of temperature was ± 6 mK, which gave a maximum of ± 0.01 % in viscosity over the entire range of temperature and pressure for the two compounds. The pressure uncertainty of ± 0.0608 MPa gave the uncertainty in viscosity from ± 0.06 % to ± 0.45 %, the maximum of which occurred at a high temperature and low pressure state. The density uncertainty of the two compounds varies from 0.1 % to 1 %, which gave a variation of less than 0.9 % in measured viscosity over the whole range of measurements. The wire radius was a significant design parameter, adding about ± 0.8 % to the uncertainty in viscosity from a variation of ± 0.4 % in this work. The last factor considered in this work was the repeatability of measurement, which was estimated to be less than ± 0.5 %. By taking into account the uncertainties of temperature, pressure, repeatability of measurement, regression procedure, and the density of fluid, the combined expanded uncertainty of viscosity with a level of confidence 0.95 ($k = 2$) is better than ± 2.8 %.

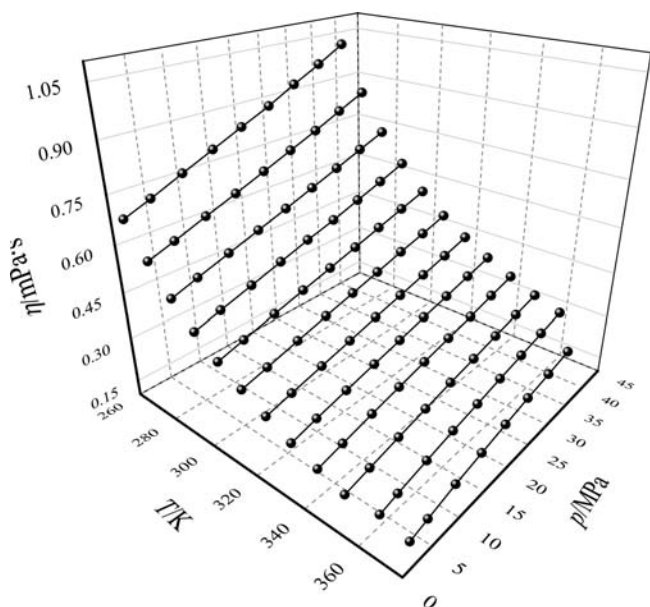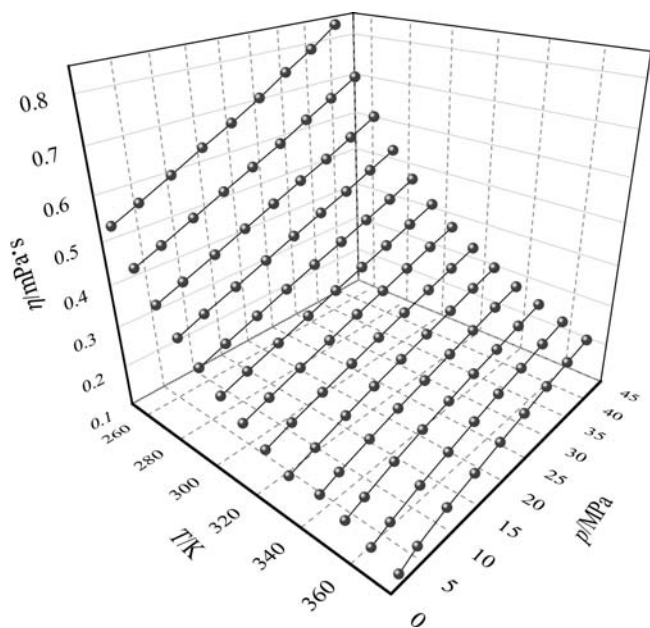**Figure 5.** Viscosities of R245fa at temperatures between (263 and 373) K and pressures between (1 and 40) MPa.

Figure 6. Viscosities of R236fa at temperatures between (253 and 373) K and pressures between (1 and 40) MPa.

Table 6. Coefficients and Deviations of Equations 10 to 12 for R245fa and R236fa

parameters	R245fa	R236fa
R_η	1.092	1.028
a	67.8148	70.1059
b	$-1.6264 \cdot 10^{-2}$	$-1.6815 \cdot 10^{-2}$
c	$-2.5180 \cdot 10^{-5}$	$-1.2080 \cdot 10^{-5}$
AAD/%	0.50	0.43
MAD/%	1.41	1.57
Bias/%	0.15	0.02

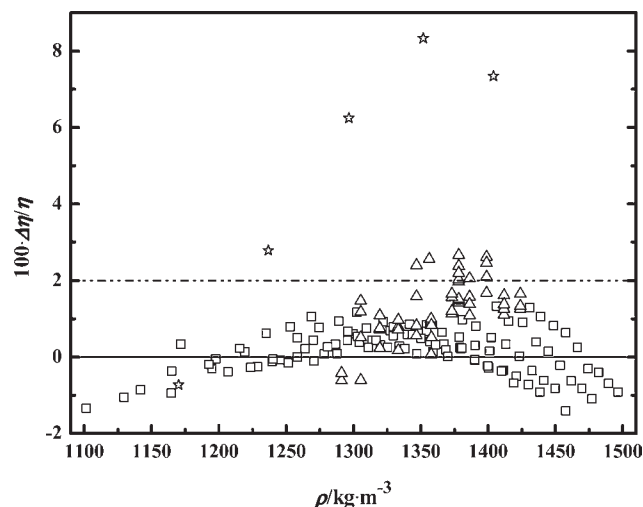**Figure 7.** Fractional deviations $\Delta\eta/\eta = (\eta_{exptl} - \eta_{calcd})/\eta_{calcd}$ of the experimental viscosities η_{exptl} of R245fa from values η_{calcd} obtained from eqs 10 to 12 as a function of density. □, this work; △, Laesecke and Hafer;[3] ☆, Geller et al.[4]

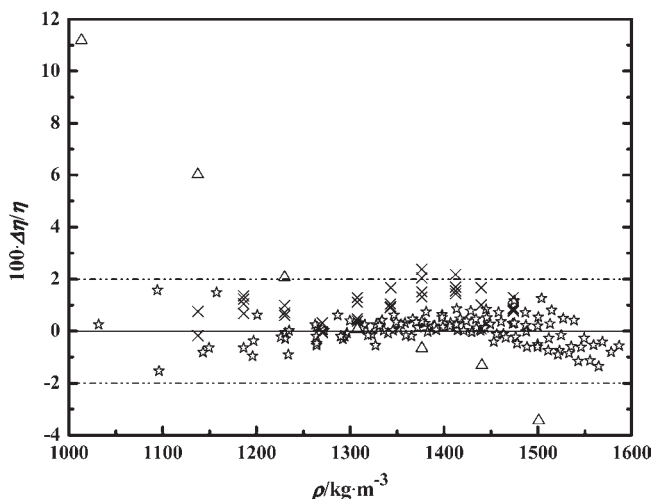**Figure 8.** Fractional deviations $\Delta\eta/\eta = (\eta_{exptl} - \eta_{calcd})/\eta_{calcd}$ of the experimental viscosities η_{exptl} of R236fa from values η_{calcd} obtained from eqs 10 to 12 as a function of density. ☆, this work; ×, Laesecke and Defibaugh;[5] △, Geller et al.[4]

R245fa. The relative deviations of our measurements from eqs 10 to 12 are shown in Figure 7. The maximum deviation does not exceed 1.5 %, and the average absolute deviation, AAD, of the experimental results from the fitting is 0.5 %. To the authors' knowledge, the only viscosity measurements on R245fa that could be found in the literature have been reported by Laesecke and Hafer[3] and Geller et al.,[4] both of which were obtained along the saturation line. In this work, the starting pressure of measurements is slightly above saturation, so for comparison purposes, extrapolations of the present correlation scheme to the saturation line were carried out. This correlation is able to represent the

results of Laesecke and Hafer[3] with the AAD of 1.7 %. As shown in Figure 7, the deviations between the data of Laesecke and

Hafer[3] and the present work are within ± 3.0 % at temperatures above 263 K, the lowest temperature of this work, while the deviations reach to 5.0 % at temperatures below that. The experimental data above 253.15 K of Geller[4] deviate from the correlation with greater deviations, especially at low temperatures, and the MAD is 8.33 % at 293.15 K.

R236fa. Figure 8 shows the relative deviations of this work and literature from eqs 10 to 12. The MAD is 1.57 %, and the AAD of the experimental results from the correlation is 0.43 %. As far as we are aware, the present results for R236fa at elevated pressures are also the first to be reported. Accordingly, we only show in Figure 8 a comparison with literature data of saturated liquid by extrapolating the present correlation to the saturation line similar to R245fa. The data of Laesecke and Defibaugh[5] agree well with our correlation with an AAD of 1.0 % and a MAD of 2.39 %. Geller[4] also reported the viscosity of R236fa along the saturation line, while obvious deviations were observed from Figure 8. Those data exhibit a systematic deviation with temperature increases, which reaches to 11.2 % at 373.15 K from −9.36 % at 233.15 K.

CONCLUSIONS

In this work, viscosity measurements of compressed liquids R245fa and R236fa in the temperature range (253 to 373) K and at pressures up to 40 MPa with a new developed vibrating-wire viscometer have been reported. To the knowledge of the authors, the present results are the first sets of viscosity data of compressed liquid region. The combined expanded uncertainty of results with a level of confidence of 0.95 ($k = 2$) is about ± 2.8 %. The results for both compounds were correlated successfully with a hard-sphere model for viscosity. The AAD of the experimental results from the correlations for R245fa and R236fa is 0.5 % and 0.43 %, respectively.

AUTHOR INFORMATION

Corresponding Author
*E-mail: jtwu@mail.xjtu.edu.cn. Fax: +86-29-82668789.

ACKNOWLEDGMENT

REFERENCES

(1) Yin, J. G.; Wu, J. T. Compressed liquid densities of 1,1,1,3,3-pentafluoropropane (HFC-245fa) and 1,1,1,3,3,3-hexafluoropropane (HFC-236fa). *Fluid Phase Equilib.* **2011**, *307*, 1–5.

(2) Park, K. J.; Kang, D. G.; Jung, D. J. Condensation heat transfer coefficients of HFC245fa on a horizontal plain tube. *Mech. Sci. Technol.* **2010**, *24*, 1911–1917.

(3) Laesecke, A.; Hafer, R. F. Viscosity of fluorinated propane isomers. 2. Measurements of three compounds and model comparisons. *J. Chem. Eng. Data* **1998**, *43*, 84–92.

(4) Geller, V.; Bivens, D. B.; Yokozeki, A. Transport properties and surface tension of hydrofluorocarbons HFC236fa and HFC 245fa. In *Proceedings of the 20th International Congress of Refrigeration IIR/IIF*, Sydney, Australia, 1999.

(5) Laesecke, A.; Defibaugh, D. R. Viscosity of 1,1,1,2,3,3-Hexafluoropropane and 1,1,1,3,3,3-Hexafluoropropane at Saturated-Liquid Conditions from 262 K to 353 K. *J. Chem. Eng. Data* **1996**, *41*, 59–62.

(6) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The theory of a vibrating-rod densimeter. *Appl. Sci. Res.* **1986**, *43*, 127–158.

(7) Retsina, T.; Richardson, S. M.; Wakeham, W. A. The theory of a vibrating-rod viscometer. *Appl. Sci. Res.* **1987**, *43*, 325–346.

(8) Padua, A. A. H.; Fareleira, J. M. N. A.; Calado, J. C. G.; Wakeham, W. A. Validation of an accurate vibrating-wire densimeter: density and viscosity of liquids over wide ranges of temperature and pressure. *Int. J. Thermophys.* **1996**, *17*, 781–802.

(9) Assael, M. J.; Papadaki, M.; Dix, M.; Richardson, S. M.; Wakeham, W. A. An absolute vibrating-wire viscometer for liquids at high pressures. *Int. J. Thermophys.* **1991**, *12*, 231–244.

(10) Dix, M.; Fareleira, J. M. N. A.; Takaishi, Y.; Wakeham, W. A. A Vibrating-Wire Densimeter for Measurements in Fluids at High Pressures. *Int. J. Thermophys.* **1991**, *12*, 357–370.

(11) Wilhelm, J.; Vogel, E.; Lehmann, J. K.; Wakeham, W. A. A vibrating-wire viscometer for dilute and dense gases. *Int. J. Thermophys.* **1998**, *19*, 391–401.

(12) Audonnet, F.; Padua, A. A. H. Simultaneous measurement of density and viscosity of n-pentane from 298 to 383 K and up to 100 MPa using a vibrating-wire instrument. *Fluid Phase Equilib.* **2001**, *181*, 147–161.

(13) Caudwell, D. R.; Trusler, J. P. M.; Vesovic, V; Wakeham, W. A. The viscosity and density of n-dodecane and n-octadecane at pressures up to 200 MPa and temperatures up to 473 K. *Int. J. Thermophys.* **2004**, *25*, 1339–1352.

(14) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. Validation of a vibrating-wire viscometer: Measurements in the range of 0.5 to 135 mPa·s. *J. Chem. Eng. Data* **2005**, *50*, 201–205.

(15) Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. Vibrating Wire Viscometer with Wire Diameters of (0.05 and 0.15) mm: Results for Methylbenzene and Two Fluids with Nominal Viscosities at *T* = 298 K and *p* = 0.01 MPa of (14 and 232) mPa·s at Temperatures between (298 and 373) K and Pressures below 40 MPa. *J. Chem. Eng. Data* **2005**, *50*, 647–655.

(16) Lundstrum, R.; Goodwin, A. R. H.; Hsu, K.; Frels, M.; Caudwell, D.; Trusler, J. P. M.; Marsh, K. N. Measurement of the viscosity and density of two reference fluids, with nominal viscosities at *T* = 298 K and *p* = 0.1 MPa of (16 and 29) mPa·s, at temperatures between (298 and 393) K and Pressures below 55 MPa. *J. Chem. Eng. Data* **2005**, *50*, 1377–1388.

(17) Meng, X. Y.; Zheng, P. J.; Wu, J. T.; Liu, Z. G. Density and Viscosity Measurements of Diethyl Adipate from (303 to 373) K and up to 20 MPa. *J. Chem. Eng. Data* **2008**, *53*, 1474–1478.

(18) Goodwin, A. R. H.; Marsh, K. N. An Absolute Viscometer for Liquids: Measurement of the Viscosity of Water at *T* = 298.15 K and *p* = 0.1 MPa. *J. Chem. Eng. Data* **2011**, *56*, 167–170.

(19) Assael, M. J.; Avelino, H. M. T.; Dalaouti, N. K.; Fareleira, J. M. N. A.; Harris, K. R. Reference Correlation for the Viscosity of Liquid Toluene from 213 to 373 K at Pressures to 250 MPa. *Int. J. Thermophys.* **2001**, *22*, 789–799.

(20) Lemmon, E. W.; McLinden, M. O.; Huber, M. L. NIST Standard Reference Database 23: *Reference Fluid Thermodynamic and Transport Properties* (REFPROP), version 8.0; National Institute of Standards and Technology: Boulder, CO, 2007.

(21) Okubo, T.; Hasuo, T.; Nagashima, A. Measurement of the viscosity of HFC 134a in the temperature range 213−423 K and at pressures up to 30 MPa. *Int. J. Thermophys.* **1992**, *13*, 931–942.

(22) Lavrenchenko, G. K.; Ruvinskij, G. Y.; Iljushenko, S. V.; Kanaev, V. V. Thermophysical properties of refrigerant R134a. *Int. J. Refrig.* **1992**, *15*, 386–392.

4963

dx.doi.org/10.1021/je200854k |*J. Chem. Eng. Data* 2011, 56, 4956–4964

(23) Assael, M. J.; Dymond, J. H.; Polimatidou, S. K. Measurements of the viscosity of R134a and R32 in the temperature range 270–340 K at pressures up to 20 MPa. *Int. J. Thermophys.* **1994**, *15*, 591–601.

(24) Oliveira, C. M. B. P.; Wakeham, W. A. The viscosity of liquid R134a. *Int. J. Thermophys.* **1993**, *14*, 33–44.

(25) Assael, M. J.; Dymond, J. H.; Papadaki, M.; Patterson, P. M. Correlation and prediction of dense fluid transport coefficients. I. n-alkanes. *Int. J. Thermophys.* **1992**, *13*, 269–281.

(26) Dymond, J. H.; Assael, M. J. Modified Hard-Spheres Scheme. In *Transport Properties of Fluids: Their Correlation, Prediction and Estimation*; Millat, J., Dymond, J. H., Nieto de Castro, C. A., Eds.; Cambridge University Press: Cambridge, U.K., 1996; pp 226–249.

4964

dx.doi.org/10.1021/je200854k |*J. Chem. Eng. Data* 2011, 56, 4956–4964