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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

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Viscosities are reported for two fluorinated propane isomers in the saturated-liquid state at temperatures from 262 K to 353 K. The compounds are 1,1,1,2,3,3-hexafluoropropane (R236ea) and 1,1,1,3,3,3-hexafluoropropane (R236fa). The measurements were performed in a capillary viscometer designed for fluids with vapor pressures above ambient. The estimated uncertainty of the viscosity measurements is ±3%. A free-volume model was used to correlate the experimental results, and they were also compared with predictions from an extended corresponding states model.

Introduction

The spectrum of alternative refrigerants is being expanded to include propane-derived hydrofluorocarbons (HFC). These compounds may be suitable working fluids for vapor compression systems at higher operating temperatures. Two such compounds have been proposed as replacements for R114 (1,2-dichloro-1,1,2,2-tetrafluoroethane). Their chemical names and ASHRAE designators (ANSI/ASHRAE, 1992) are 1,1,1,2,3,3-hexafluoropropane (R236ea) and 1,1,1,3,3,3-hexafluoropropane (R236fa). Their viscosity was measured as part of a more comprehensive study of their thermophysical properties.

Experimental Section

Chemicals. The purity of both the R236ea and the R236fa samples was stated by the manufacturers to be 99.9 mol %. Gas chromatographic analysis showed the samples to be less pure. The vapor of R236ea was 99.7 mol % pure and the liquid, 99.85 mol %. The R236fa sample had an actual purity of 99.6 mol % in the vapor and 99.9 mol % in the liquid. No attempts were made to characterize the impurities or to purify the samples further. Both fluids were used as received.

Apparatus and Procedure. The measurements were performed in a capillary flow viscometer which has been used previously with three fluorinated ethane derivatives (Ripple and Defibaugh, 1995). It consists of two stainless steel reservoirs with sapphire windows. The reservoirs are connected by a straight stainless steel capillary of length $l = 148$ mm and inner diameter $d = 0.236$ mm as well as by a stainless steel reflux tube. During a measurement, the position of the liquid−vapor interface is visually observed and manually timed as the liquid drains through the capillary from the upper to the lower reservoir. The rate of fall $\dot{h}$ of the interface is determined from the recordings. The working equation (Hardy, 1962) for the viscosity η is

$$\frac{\eta}{\rho_1 - \rho_v} = \frac{C}{\dot{h}} - m\,\frac{\rho_1}{\rho_1 - \rho_v}\,\frac{A}{8\pi l}\,\dot{h} \qquad (1)$$

where ρ_l and ρ_v are the density of saturated liquid and vapor, and the calibration constant $C = 6.415 \times 10^{-12}$ $m^3 \cdot s^{-2}$. The cross sectional area of the upper reservoir is $A = 1.20 \times 10^{-4}$ m^2.

The second term in eq 1 corrects for inertia and kinetic energy effects. The empirical correlation $m = 0.037(Re)^{1/2}$ was used for the Hagenbach−Couette correction factor (Cannon et al., 1960). The Reynolds number Re was approximated according to

$$Re = \frac{4A}{\pi d}\,\frac{\rho_1}{\rho_1 - \rho_v}\,\frac{\dot{h}^2}{C} \qquad (2)$$

and values ranged in the present experiments between 22 and 141 for R236ea and between 42 and 249 for R236fa.

The viscometer was immersed in a well-insulated, continuously stirred bath. The bath temperature was maintained constant with a circulator and an external precision temperature controller. The bath temperature was measured with a platinum resistance thermometer and an automatic ac bridge. The combined uncertainties in the temperature measurement and that due to temperature gradients and fluctuations amount to ±0.01 K. This introduces an uncertainty in the viscosity measurements of less than ±0.007%. The thermometer had been calibrated according to IPTS-68. The measured temperatures were converted to ITS-90 (Mangum, 1990) and are reported as such in Tables 1 and 2.

Saturated liquid and vapor density data are required to evaluate the viscosity from eqs 1 and 2. The experimental results of Defibaugh and Silva (1995) and Defibaugh and Weber (1995) were used for the saturated liquid density of both fluids. Their estimated uncertainty is ±0.1% which contributes to the uncertainty of the viscosity values by less than ±0.108%. Saturated vapor densities were calculated from measured vapor pressures assuming an ideal gas (Defibaugh and Silva, 1995; Defibaugh and Weber, 1995). Their uncertainty is estimated to be less than ±1%

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Table 1. Experimental Viscosities for Saturated Liquid R236ea

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
262.139	1534.49	3.320	0.6648
262.141	1534.48	3.320	0.6647
262.141	1534.48	3.320	0.6741
262.142	1534.48	3.320	0.6685
262.138	1534.49	3.320	0.6658
273.101	1502.60	5.226	0.5474
273.100	1502.61	5.226	0.5527
273.100	1502.61	5.226	0.5474
273.101	1502.60	5.226	0.5548
283.184	1472.48	7.642	0.4656
283.181	1472.49	7.641	0.4775
283.184	1472.48	7.642	0.4764
283.183	1472.48	7.642	0.4802
293.158	1441.83	10.77	0.4117
293.159	1441.82	10.77	0.4124
293.155	1441.84	10.76	0.4132
293.156	1441.83	10.76	0.4131
303.148	1409.88	14.75	0.3546
303.146	1409.88	14.75	0.3564
303.143	1409.89	14.75	0.3580
303.141	1409.90	14.75	0.3618
313.265	1376.37	19.78	0.3099
313.265	1376.37	19.78	0.3100
313.265	1376.37	19.78	0.3110
313.265	1376.37	19.78	0.3112
323.228	1341.50	25.84	0.2732
323.228	1341.50	25.84	0.2754
323.227	1341.51	25.84	0.2747
323.228	1341.50	25.84	0.2746
333.158	1305.02	33.08	0.2421
333.158	1305.02	33.08	0.2420
333.160	1305.01	33.09	0.2390
333.160	1305.01	33.09	0.2411
343.156	1265.64	41.73	0.2128
343.158	1265.63	41.73	0.2123
343.157	1265.63	41.73	0.2135
343.159	1265.62	41.73	0.2148

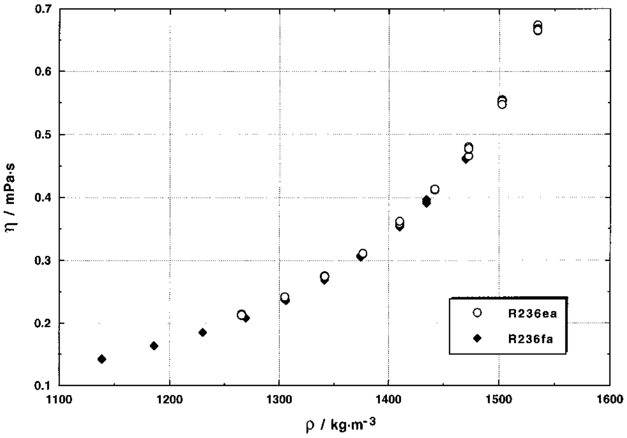

Figure 1. Experimental viscosity of saturated liquid R236ea and R236fa as a function of density.

Table 2. Experimental Viscosities for Saturated Liquid R236fa

T/K	ρ_l/(kg·m^{-3})	ρ_v/(kg·m^{-3})	η/(mPa·s)
262.139	1469.83	3.441	0.4600
262.139	1469.83	3.441	0.4598
262.142	1469.82	3.441	0.4603
262.139	1469.83	3.441	0.4622
273.383	1434.31	5.526	0.3902
273.383	1434.31	5.526	0.3938
273.384	1434.31	5.526	0.3964
273.385	1434.31	5.526	0.3964
282.100	1409.98	7.771	0.3529
282.099	1409.98	7.771	0.3520
282.095	1409.99	7.769	0.3524
282.095	1409.99	7.769	0.3546
293.191	1374.56	11.58	0.3070
293.193	1374.56	11.57	0.3080
293.187	1374.58	11.57	0.3054
293.186	1374.58	11.57	0.3048
303.116	1341.31	16.13	0.2681
303.109	1341.34	16.13	0.2685
303.098	1341.38	16.12	0.2702
303.089	1341.41	16.12	0.2683
313.201	1306.11	22.15	0.2377
313.202	1306.11	22.15	0.2358
313.197	1306.13	22.14	0.2356
313.205	1306.10	22.15	0.2373
323.111	1269.35	29.72	0.2078
323.111	1269.35	29.72	0.2078
323.122	1269.30	29.73	0.2077
323.112	1269.34	29.72	0.2085
333.148	1230.21	39.45	0.1849
333.150	1230.20	39.45	0.1854
333.149	1230.20	39.45	0.1847
333.150	1230.20	39.45	0.1849
343.145	1186.02	51.73	0.1638
343.147	1186.01	51.74	0.1640
343.148	1186.01	51.74	0.1635
343.148	1186.01	51.74	0.1629
353.162	1138.64	67.35	0.1430
353.154	1138.68	67.34	0.1417

since the temperature range of the measurements is sufficiently below the critical temperature of either fluid. If the uncertainty of the saturated vapor densities were ±1%, the associated uncertainty of the viscosities would be less than ±0.065%.

The uncertainty of measurements with this viscometer was estimated by Ripple and Defibaugh (1995) on the basis of applicable NIST guidelines (Taylor and Kuyatt, 1993). The analysis resulted in an expanded uncertainty of ±3% at the 95% confidence level.

Results and Discussion

The experimental results for the saturated liquid viscosity of R236ea and R236fa are presented in Tables 1 and 2. Both fluids were measured in the temperature range 262 K to 343 K at intervals of about 10 K. At least four measurements were taken at each temperature. Also, two measurements at 353 K could be performed with R236fa. Figure 1 shows the tabulated viscosities of both fluids versus saturated liquid density. The viscosity of R236ea is higher than that of R236fa in the temperature range explored in this study. This is illustrated in Figure 2 where the values have been plotted versus the reduced temperature T/T_c. The critical temperatures T_c of the fluids were also determined in this laboratory (Defibaugh and Silva, 1995; Defibaugh and Weber, 1995). They are $T_c = 412.44$ K for R236ea and $T_c = 398.07$ K for R236fa.

The results reveal the influence of molecular structure on the viscosity of the two isomers. The structural difference consists in the exchange of a fluorine and a hydrogen atom between the central and one end carbon atom. Since the fluorine atom is larger than the hydrogen atom, the exchange leads to a higher "roughness" of the R236ea molecule and to increased steric hindrance. Molecular roughness was introduced in the theoretical treatment of viscosity by Chandler (1975). More recently, the influence of molecular surfaces was investigated in the context of mixture viscosity (Mertsch and Wolf, 1994). Figure 2 shows that the viscosity difference between the two isomers increases with decreasing temperature. At the reduced temperature 0.83 the viscosity of R236ea is about 15% higher than that of R236fa while at the reduced temperature 0.66 the difference is 19%.

Instead of averaging repetitive measurements at individual temperatures, all experimental data were examined

Table 3. Parameter Values and Statistics of the Correlation, Eq 3, for Saturated Liquid R236ea and R236fa[a]

	R236ea	R236fa
$(\beta_1 \pm s)$/Pa·s	$0.383705 \times 10^{-7} \pm 0.157 \times 10^{-8}$	$0.354506 \times 10^{-7} \pm 0.102 \times 10^{-8}$
$(\rho_0 \pm s)$/kg·m^{-3}	1836.20 ± 39.1	1860.24 ± 31.7
$(\beta_6 \pm s)$/K^{-1}	$(0.347003 \pm 0.104) \times 10^{-3}$	$(0.469278 \pm 0.879) \times 10^{-4}$
AAD/%	0.573	0.598
RMS/%	0.716	0.735

[a] s = standard deviation; AAD = average absolute deviation; RMS = root mean square deviation.

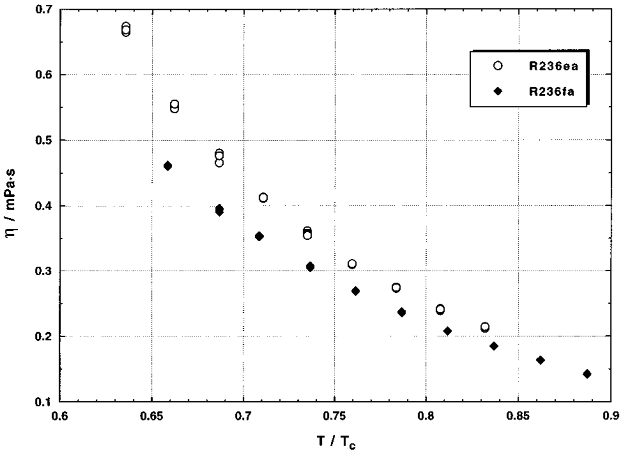

Figure 2. Experimental viscosity of saturated liquid R236ea and R236fa as a function of reduced temperature.

with the correlation described next. The model function was based on the free-volume expression originally proposed by Batschinski (1913). Additional temperature functions were included to form a "bank of terms". As before, exponential temperature functions were considered in the numerator while a linear temperature dependence was introduced in the second term of the denominator of the expression

$$\eta = \frac{\beta_1 \exp[\beta_2/T^{0.5} + \beta_3/T + \beta_4/T^{1.5} + \beta_5/T^2]}{\dfrac{1}{\rho} - \dfrac{1}{\rho_0}(1 + \beta_6 T)} \qquad (3)$$

The adjustable parameters β_1, ..., β_6 and ρ_0 were determined by nonlinear least squares minimization using the NIST package ODRPACK (Boggs et al., 1992). Eighteen of the possible term combinations were tested. For each fluid, the combination including β_1, β_6, and ρ_0 was the only one which represented the results within their estimated expanded uncertainty and where the standard deviation of each parameter was smaller than the parameter value. Considering the limited temperature range of the data as well as the physical and statistical significance of the parameters, this functional form was selected as a representative correlation of the experimental data. Parameter values and statistical measures are listed for both fluids in Table 3. Percent deviations of the results from the correlation are shown in Figure 3. The scatter of repetitive measurements at constant temperature indicates a precision of ±0.7%.

Previously measured viscosities for the two fluids could not be located in the literature. To provide an independent validation of the experimental results, a comparison with predicted viscosities was carried out. The predicted values were obtained from the extended corresponding states model which is implemented in NIST Standard Reference Database 23 (Gallagher et al., 1993). An internal development version of REFPROP (Version 4.17) was used where the shape factors for R236ea had been determined by regression of experimental density data (Defibaugh and Silva, 1995), but no viscosity data. No experimental information for R236fa had been incorporated. The viscosity calculation was therefore completely predictive for both fluids.

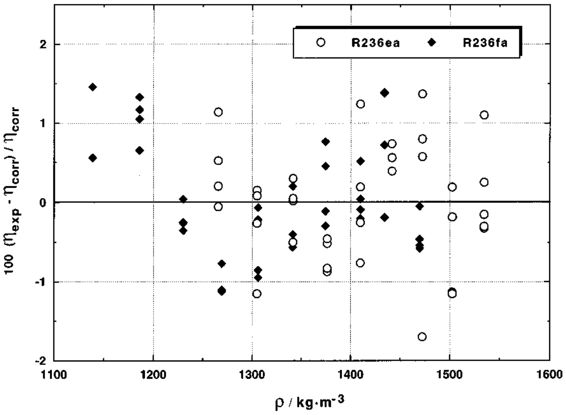

Figure 3. Percent deviations between experimental values and values calculated from the correlation, eq 3.

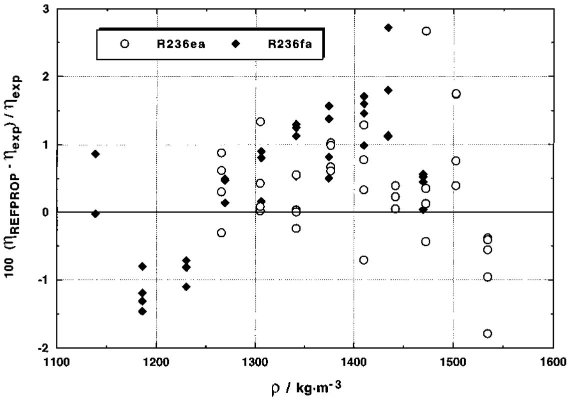

Figure 4. Percent deviations between viscosities estimated with an extended corresponding states model and experimental values.

Figure 4 illustrates the agreement between the predicted and measured viscosities. The majority of the deviations for R236ea range in the band ±1%. More systematic deviations are noted for R236fa, ranging between −1.5% and +2.8%. The deviations of the estimated viscosity values are related to the quality of the density estimation for the two fluids. For R236ea the estimated saturated liquid densities deviate on average by 0.006% from the experimental data while, for R236fa, an average deviation of 0.11% was observed.

The experimental viscosity values reported here have been used to improve the shape factors of R236ea and R236fa in REFPROP Version 4.24 and higher.

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