Viscosity of Fluorinated Propane Isomers. 2. Measurements of Three Compounds and Model Comparisons†

Arno Laesecke* and Richard F. Hafer

National Institute of Standards and Technology, Physical and Chemical Properties Division, 325 Broadway, Boulder, Colorado 80303-3328

Viscosity data are reported for three fluorinated propane isomers in the saturated-liquid state over a combined temperature range from 248 to 348 K. The compounds are 1,1,1,3,3-pentafluoropropane (R245fa), 1,1,2,2,3-pentafluoropropane (R245ca), and 1,1,1,2,3,3,3-heptafluoropropane (R227ea). The measurements were carried out in sealed gravitational capillary viscometers. The estimated uncertainty of the measurements is ±3.4%. Including earlier viscosity measurements on 1,1,1,3,3,3-hexafluoropropane (R236fa) and 1,1,1,2,3,3-hexafluoropropane (R236ea), the viscosity data of all five fluids were correlated within their experimental uncertainty in terms of the rough hard-sphere model. The experimental data were also compared with predictions of the extended corresponding-states method in NIST Standard Reference Database 23 (REFPROP). Deviations range between −20 and 15%.

Introduction

Fluorinated propane derivatives are being examined as chlorine-free alternatives for trichlorofluoromethane (R11) and 1,2-dichlorotetrafluoroethane (R114), which serve as working fluids in vapor-compression systems at higher operating temperatures such as chillers (Smith et al., 1993). Augmenting previous measurements on two R236-isomers (Laesecke and Defibaugh, 1996), the viscosity of three more fluorinated propane compounds was investigated in this work. Their chemical names and ASHRAE designators are 1,1,1,3,3-pentafluoropropane (R245fa), 1,1,2,2,3-pentafluoropropane (R245ca), and 1,1,1,2,3,3,3-heptafluoropropane (R227ea).

Experimental Section

Chemicals. The R245fa sample was purchased from PCR, Inc. in Gainesville, FL, with a stated purity of 97% by mole. (To ensure that the experiments can be repeated exactly, it is occasionally necessary to identify commercial products by manufacturers' names or labels. In no instance does such identification imply endorsement by the National Institute of Standards and Technology, nor does it imply that the particular product or equipment is necessarily the best available for the purpose.) Qualitative gas chromatography/mass spectrometry analysis of the R245fa sample revealed the presence of 1,1,1,2,3-pentafluoropropene (CF_3-$CF{=}CHF$), an unidentifiable R245fa-isomer, and of a small amount of methyl bromide. R245ca was an experimental sample synthesized at Allied Signal Corp. The volume of sample (∼4 mL) was just sufficient for measurements in the capillary viscometer. Therefore, qualitative gas chromatography/mass spectrometry analysis of the R245ca sample was carried out after the viscosity measurements by transferring the sample directly from the viscometer to the gas chromatograph. The analysis indicated 1,2-ethanediol as an impurity, possibly a residue from the bath, in which the viscometer was immersed during the measurements, that had formed in the high-pressure connection of the viscometer's filling valve. The R227ea sample was supplied by Great Lakes Chemical Corp. with a stated mass purity of 99.999%. Qualitative gas chromatography/mass spectrometry analysis confirmed the high purity as no impurities could be identified. The analyses were carried out qualitatively because some of the fluids were not included in the sample library for the calibration of the gas chromatograph. All fluids were used as received. They were condensed into the viscometers and degassed before the measurements.

Apparatus and Procedure. The normal boiling point temperatures of alternative refrigerants are below ambient temperature, which means that their vapor pressures at ambient temperature are higher than atmospheric pressure. Consequently, refrigerant viscometry requires sealed capillary viscometers to prevent the evaporation of the volatile samples during the measurements. The viscometers used in this work consist of two stainless steel reservoirs with sapphire windows. The reservoirs are connected in one viscometer by a straight vertical stainless steel capillary of length $l = 148$ mm and inner diameter $d = 0.236$ mm, while in the other viscometer a coiled capillary of length $l = 480$ mm and inner diameter $d = 0.508$ mm is used. The coiled capillary had an average coil diameter of $D = 150$ mm. The reservoirs of each viscometer are also connected by a stainless steel tube to return the liquid to the upper reservoir for a new measurement. The position h of the liquid−vapor interface in the upper reservoir is observed with a cathetometer and manually timed as the liquid drains through the capillary. The straight capillary viscometer has been used before with two fluorinated propane derivatives (Laesecke and Defibaugh, 1996) and three fluorinated ethane derivatives (Ripple and Defibaugh, 1997). The coiled capillary viscometer has been used before with six halogenated compounds and three mixtures (Ripple and Matar, 1993). The pentafluoropropane isomers were measured in the coiled capillary viscometer because

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* Corresponding author. Internet address: Arno.Laesecke@Boulder.NIST.gov.

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of their higher viscosity. R227ea has a much lower viscosity, and the efflux times in the coiled capillary viscometer became too short for accurate timing above 313 K. The liquid drained at this state in approximately 39 s over a level difference of 0.6 cm. Measurements with the straight capillary viscometer were therefore conducted with this fluid from 303 to 348 K.

The rate of fall of the interface, $\dot{h}$, is determined from the measurements. Together with the known cross sections of the upper reservoirs, $A = 1.20 \times 10^{-4}$ m^2 for the straight capillary and $A = 1.06 \times 10^{-4}$ m^2 for the coiled capillary viscometer, the volumetric flow rate of the liquid is obtained. The general working equation for both open and sealed gravitational capillary viscometers was derived by Wedlake (1979)

$$\eta = C_4\left[(\rho_l - \rho_v)\frac{C_1}{\dot{h}} - C_2\rho_l\dot{h}\right] + \sigma\frac{C_3}{\dot{h}} \qquad (1)$$

Here η is the viscosity of the liquid and σ is the surface tension. The first term on the right side of eq 1 is the Hagen–Poiseuille term. The pressure, which causes the liquid to flow through the capillary, is equal to the apparent driving head minus pressure losses due to the effects of vapor buoyancy at the lower and upper liquid interfaces. Consequently, this term includes the difference between the saturated liquid and saturated vapor density ρ_l and ρ_v. It should be noted that often quoted reviews on capillary viscometers discuss working equations that are applicable to open gravitational capillary viscometers when the vapor density is negligible. They do not mention the vapor buoyancy effect (Hardy, 1962; Kestin et al., 1973; Kawata et al., 1991), which can be appreciable. For example, the saturated-vapor density of R227ea at 348 K is 14% that of the liquid density. If that density is neglected, a 14% error in the measured viscosity would result.

Both viscometers were recalibrated because they had been completely disassembled for cleaning and for replacement of seals after being moved from their former location. The calibration fluid was a specially prepared toluene sample of 99.98% by mass purity, and the results of Kaiser et al. (1991) were used as reference data. Calibrations were carried out in the straight capillary viscometer at 323, 338, and 353 K, and from 250 to 340 K in the coiled capillary viscometer. The following values of the calibration constants C_1 in eq 1 were obtained

$$C_1 = (6.217 \pm 0.061) \times 10^{-12}\ \mathrm{m^3{\cdot}s^{-2}}\ \text{for the straight capillary viscometer}$$

$$C_1 = (2.430 \pm 0.031) \times 10^{-11}\ \mathrm{m^3{\cdot}s^{-2}}\ \text{for the coiled capillary viscometer}$$

Calibration measurements were also attempted with pentane because it has a lower viscosity and surface tension than toluene. However, the results were inconsistent with the toluene calibrations suggesting a lack of standard reference data for the viscosity of pentane. This *n*-alkane was not included in a recent data evaluation of calibration liquids (Dymond and Øye, 1994) because (i) the available saturated liquid viscosity data for pentane were considered not as extensive as for other hydrocarbons and (ii) because its low boiling point limits the useful temperature range for calibrations of open viscometers. In sealed viscometers, such as employed in this work, the low boiling point of pentane is of no concern. Besides, further measurements of high accuracy have recently been published (Oliveira and Wakeham, 1992; Abdulagatov and Rasulov, 1996). Combined with earlier measurements the body of available data appears sufficient to establish standard reference viscosity data of pentane for calibrations. This work is now underway.

The second term in eq 1 is the Hagenbach–Couette correction for inertia and kinetic energy effects. The correction parameter C_2 is given by

$$C_2 = \frac{m{\cdot}A}{8\pi l} \qquad (2)$$

where the kinetic energy coefficient m depends on the fluid flow according to the empirical correlation $m = 0.037(Re)^{1/2}$ (Cannon et al., 1960). The Reynolds number Re was approximated by

$$Re = \frac{4A}{\pi d}\frac{\rho_l}{(\rho_l - \rho_v)}\frac{\dot{h}^2}{C_1} \qquad (3)$$

Values of the Reynolds number in the coiled capillary ranged from 18 to 137 for R245fa, from 8 to 92 for R245ca, and from 66 to 275 for R227ea. The measurements with R227ea in the straight vertical capillary viscometer resulted in Reynolds numbers between 142 and 330. Kinetic energy corrections were small in the present measurements, contributing at most 0.5% to the viscosity of R227ea at 348 K.

The third term in eq 1 is an approximate correction for surface tension effects, which reduce the hydrostatic head driving the liquid flow. Their magnitude depends on the capillary radius, the contact angle of the liquid at the reservoir wall, and the ratio $\sigma{\cdot}(\rho_l - \rho_v)^{-1}$ (Wedlake et al., 1979). Using the surface tension correlation of Schmidt et al. (1996), the maximum of this ratio (15.3×10^{-6} m^3·s^{-2}) is found in the measurements for R245ca at 248 K. The associated relative reduction in the effective head is 0.4% according to Wedlake et al. R227ea exhibited a considerably lower surface tension than the two R245 isomers and the calibration fluid toluene. Hence, the surface tension difference between sample and calibration fluid is highest for R227ea, while the vapor pressure reduction due to the meniscus curvature is lowest. The opposite is true for the R245 isomers. Since these effects cancel each other and because of the small magnitude of the correction, it was not applied in the working eq 1 but included in the uncertainty estimate of the measurements.

The fourth correction in eq 1 is represented by parameter C_4. It accounts for the radial acceleration of the flowing liquid in viscometers with coiled capillaries. The correction is expressed in terms of the Dean number

$$De = Re\sqrt{\frac{d}{D}} \qquad (4)$$

by the empirical correlation

$$C_4 = 1 - \left[1 - \left(\frac{De_0}{De}\right)^{0.45}\right]^{(1/0.45)} \qquad (5)$$

as proposed by White (1929). Here, Re is the Reynolds number according to eq 3, d is the inner diameter of the capillary, and D is the diameter of the capillary coil. If the actual Dean number of a flow is less than the cutoff Dean number De_0, then $C_4 = 1$. Comparing measurements in straight and curved tubes, White concluded that no correction was needed for Dean numbers less than $De_0 =$

Table 1. Experimental Viscosities for Saturated Liquid R245fa[a]

T/K, measd	ρ_l/kg·m^{-3}, calcd	ρ_v/kg·m^{-3}, calcd	η/mPa·s, measd	T/K, measd	ρ_l/kg·m^{-3}, calcd	ρ_v/kg·m^{-3}, calcd	η/mPa·s, measd
250.092	1459.60	0.66	0.8615	283.193	1379.76	3.18	0.4986
250.089	1459.61	0.66	0.8566	283.194	1379.75	3.18	0.4994
250.089	1459.61	0.66	0.8574	285.139	1374.67	3.44	0.4828
250.091	1459.61	0.66	0.8581	285.141	1374.66	3.44	0.4832
255.095	1448.35	0.87	0.7889	285.136	1374.67	3.44	0.4808
255.096	1448.34	0.87	0.7936	285.137	1374.67	3.44	0.4811
255.094	1448.35	0.87	0.7902	290.965	1359.16	4.32	0.4387
255.096	1448.34	0.87	0.7629	290.970	1359.15	4.32	0.4426
260.116	1436.77	1.12	0.7094	290.954	1359.19	4.32	0.4407
260.117	1436.76	1.12	0.7068	290.967	1359.16	4.32	0.4423
260.116	1436.77	1.12	0.7060	290.971	1359.15	4.32	0.4425
260.116	1436.77	1.12	0.7159	291.486	1357.76	4.41	0.4464
265.120	1424.93	1.43	0.6522	290.975	1359.14	4.32	0.4427
265.119	1424.93	1.43	0.6497	290.956	1359.19	4.32	0.4421
265.118	1424.93	1.43	0.6502	295.054	1348.05	5.04	0.4247
270.018	1413.06	1.80	0.6038	295.042	1348.08	5.04	0.4214
270.016	1413.07	1.80	0.6008	295.055	1348.05	5.04	0.4171
270.014	1413.07	1.80	0.6017	295.086	1347.96	5.05	0.4180
270.015	1413.07	1.80	0.6024	300.045	1334.22	6.05	0.3913
275.106	1400.44	2.26	0.5615	300.044	1334.23	6.05	0.3920
275.107	1400.43	2.26	0.5592	300.042	1334.23	6.05	0.3910
275.109	1400.43	2.26	0.5643	300.043	1334.23	6.05	0.3889
275.103	1400.44	2.26	0.5635	305.051	1320.06	7.21	0.3678
280.074	1387.83	2.79	0.5192	305.064	1320.02	7.21	0.3664
280.075	1387.82	2.79	0.5167	305.050	1320.06	7.21	0.3647
280.081	1387.81	2.79	0.5216	305.051	1320.06	7.21	0.3666
280.075	1387.82	2.79	0.5182	310.095	1305.50	8.55	0.3463
283.194	1379.75	3.18	0.4956	310.098	1305.49	8.55	0.3453
283.192	1379.76	3.18	0.5017	310.099	1305.49	8.55	0.3430
283.193	1379.76	3.18	0.4959	310.101	1305.48	8.55	0.3392
283.193	1379.76	3.18	0.5003	315.043	1290.92	10.05	0.3189
283.193	1379.76	3.18	0.4983	315.049	1290.90	10.06	0.3195
283.193	1379.76	3.18	0.4961				

[a] The data of Tables 1−4 are available in electronic format via anonymous ftp from host "ftp.boulder.nist.gov" in directory "/pub/fluids/NIST_Data/Viscosity/Capillary".

11.6. Dawe (1973) summarized later investigations and suggested $De_0 = 6$, which leads to considerably higher corrections. The maximum Dean number in the present measurements is 16.0 for R227ea at 313 K. Under these conditions the difference between the correction of Dawe and the correction of White is 9%. A comparison between the R227ea measurements with both viscometers at the overlapping temperatures 303, 308, and 313 K shows that the data from the instrument with the coiled capillary tend to be up to 2.5% higher than those from the straight vertical viscometer if the correction according to White is applied. Apparently, this correction should become effective at a lower Dean number. Better agreement between the R227 results from the two instruments would be achieved with a cutoff Dean number of $De_0 = 9.3$, which is still considerably higher than $De_0 = 6$ as suggested by Dawe. Since the difference in the viscosity data stemming from a change of De_0 from 11.6 to 9.3 is within the estimated uncertainty of the measurements, the radial acceleration correction was applied as originally proposed by White. It affects only the R227ea measurements at 298 K and above.

Another error in the measured flow rate arises from a drainage film, which adheres to the inside walls and windows of the upper reservoir after inverting a viscometer to return the liquid for a new run. The lifting effect of such drainage films reduces the driving pressure head, thus increasing the efflux time (van Rossum, 1958). It depends on the density, viscosity, and surface tension of the liquid. A correction for this effect was not employed, but it was included in the uncertainty estimate below with a type B uncertainty margin of 1.5%.

The viscometers were immersed in a well-insulated, continuously stirred 75 L bath of ethylene glycol + water, whose temperature was maintained with a circulator and an external precision temperature controller. The temperature was measured with a platinum resistance thermometer (PRT) calibrated according to ITS-90 and accurate to ±0.01 K. The combined uncertainty of the thermometer and that due to temperature gradients and fluctuations in the thermostat is estimated at ±0.02 K. By analysis with the rough hard-sphere model discussed below, this introduces a maximum uncertainty of ±0.04% in the viscosity for R245ca at 248 K.

Saturated liquid and vapor density data are required to evaluate the viscosity from eqs 1−3. For the three fluids, the experimental results of Defibaugh et al. (1996) and Defibaugh and Moldover (1997) were interpolated for the saturated-liquid densities at the measurement temperature. The quoted experimental uncertainty of ±0.1% in the liquid-phase density introduces an uncertainty of ±1% in the R245ca viscosity results at 250 K. Saturated-vapor densities were calculated using the Carnahan−Starling−De Santis (CSD) model in NIST Standard Reference Database 23 (Huber et al., 1995). The CSD-model was compared with the extended corresponding-states (ECS) model to approximate the uncertainty in vapor density. A maximum deviation of 5% occurred for R227ea at 348 K. This introduces an uncertainty of ±0.8% in the viscosity at this temperature.

The total expanded uncertainty of the present measurements is estimated to be ±3.4% with a coverage factor $k = 2$ (Taylor and Kuyatt, 1994). This estimate includes a type A uncertainty of 1% representing the precision of the instruments. type B uncertainties include those due to pressure head variations (0.9%), drainage film effects (1.5%), calibration (2.4%), and kinetic energy correction (0.5%), as well as uncertainties of 1% and 0.8% due to the

Table 2. Experimental Viscosities for Saturated Liquid R245ca

T/K, measd	ρ_l/kg·m^{-3}, calcd	ρ_v/kg·m^{-3}, calcd	η/mPa·s, measd	T/K, measd	ρ_l/kg·m^{-3}, calcd	ρ_v/kg·m^{-3}, calcd	η/mPa·s, measd
248.544	1505.31	0.61	1.2756	288.178	1412.96	3.88	0.6235
248.545	1505.30	0.61	1.2868	288.179	1412.96	3.88	0.6232
248.545	1505.30	0.61	1.2881	288.179	1412.96	3.88	0.6238
248.547	1505.30	0.61	1.2842	288.178	1412.96	3.88	0.6206
248.554	1505.28	0.61	1.2802	293.114	1400.62	4.69	0.5813
248.555	1505.28	0.61	1.2897	293.115	1400.62	4.69	0.5790
248.560	1505.27	0.61	1.2872	293.114	1400.62	4.69	0.5780
248.562	1505.27	0.61	1.2891	293.114	1400.62	4.69	0.5808
253.128	1495.25	0.78	1.1691	298.286	1387.48	5.68	0.5350
253.129	1495.24	0.78	1.1667	298.285	1387.48	5.68	0.5385
253.129	1495.24	0.78	1.1665	298.286	1387.48	5.68	0.5355
253.130	1495.24	0.78	1.1701	298.286	1387.48	5.68	0.5366
258.175	1483.98	1.02	1.0478	303.151	1374.94	6.75	0.4999
258.175	1483.98	1.02	1.0576	303.148	1374.94	6.75	0.4997
258.175	1483.98	1.02	1.0490	303.148	1374.94	6.75	0.5031
258.175	1483.98	1.02	1.0599	303.148	1374.94	6.75	0.4995
258.175	1483.98	1.02	1.0348	308.342	1361.35	8.07	0.4689
258.174	1483.98	1.02	1.0486	308.345	1361.34	8.07	0.4695
258.124	1484.09	1.02	1.0553	308.343	1361.34	8.07	0.4723
258.124	1484.09	1.02	1.0569	308.344	1361.34	8.07	0.4704
258.124	1484.09	1.02	1.0578	313.112	1348.68	9.44	0.4374
258.125	1484.09	1.02	1.0585	313.113	1348.68	9.44	0.4376
263.243	1472.47	1.31	0.9559	313.114	1348.68	9.44	0.4346
263.242	1472.47	1.31	0.9580	313.113	1348.68	9.44	0.4392
263.242	1472.47	1.31	0.9565	318.092	1335.27	11.08	0.4122
263.243	1472.47	1.31	0.9576	318.093	1335.26	11.08	0.4113
268.076	1461.31	1.65	0.8720	318.093	1335.26	11.08	0.4101
268.076	1461.31	1.65	0.8723	318.093	1335.26	11.08	0.4099
268.076	1461.31	1.65	0.8741	323.194	1321.33	12.98	0.3846
268.076	1461.31	1.65	0.8678	323.196	1321.32	12.98	0.3843
273.159	1449.38	2.07	0.7951	323.195	1321.33	12.98	0.3861
273.160	1449.38	2.07	0.7999	323.194	1321.33	12.98	0.3831
273.159	1449.38	2.07	0.7983	323.194	1321.33	12.98	0.3861
273.159	1449.38	2.07	0.7966	328.095	1307.75	15.04	0.3633
278.406	1436.85	2.61	0.7342	328.100	1307.73	15.04	0.3647
278.406	1436.85	2.61	0.7302	328.097	1307.74	15.04	0.3635
278.406	1436.85	2.61	0.7320	328.100	1307.73	15.04	0.3651
278.406	1436.85	2.61	0.7309	333.228	1293.33	17.47	0.3414
283.146	1425.36	3.17	0.6759	333.232	1293.32	17.47	0.3424
283.146	1425.36	3.17	0.6769	333.227	1293.33	17.46	0.3422
283.146	1425.36	3.17	0.6806	333.230	1293.33	17.47	0.3404
283.146	1425.36	3.17	0.6800	333.228	1293.33	17.47	0.3428

saturated-liquid and saturated-vapor density data. The calibration and kinetic energy correction uncertainties are different from those of Ripple and Defibaugh (1997) because of a different cathetometer in the instrument setup and because of the different fluids that were measured in this work.

Results and Discussion

The experimental results for the saturated liquid viscosity of R245fa, R245ca, and R227ea are presented in Tables 1, 2, and 3, respectively. Figure 1 shows the measured viscosities of the three fluids in terms of reduced rather than absolute temperature because it is more suitable for comparison ($T_r = T/T_c$). Previously published results for the hexafluoropropane isomers R236ea and R236fa are also included (Laesecke and Defibaugh, 1996) as is the viscosity of the parent molecule propane. R245ca exhibits the highest viscosity among these five fluorinated propane derivatives, while R227ea and R236fa exhibit the lowest. All of them are considerably higher than the viscosity of propane. Experimental data by Schmidt et al. (1996) were used for the critical temperatures of four of the five fluids: 427.20 K for R245fa, 447.57 K for R245ca, 398.07 K for R236fa, and 412.45 K for R236ea. The critical temperature of R227ea (375.95 K) was measured by Beyerlein et al. (1993). No other experimental viscosity data for the fluorinated propane derivatives could be located in the literature.

Figure 1 shows also the saturated-liquid viscosity of chlorofluorcarbons R11 and R114, for which the fluorinated propanes are considered as substitute refrigerants. The experimental data by Kumagai and Takahashi (1991), corrected for the vapor buoyancy effect, are plotted. The viscosities of the fluorinated propanes are considerably higher than that of R11. On the other hand, the viscosity of R114 is closely matched by the viscosities of R236fa and R227ea.

Empirical correlations of saturated and compressed liquid viscosities of individual fluids are often formulated in terms of absolute or relative free volume (Batschinski, 1913; Hildebrand, 1971). Such correlations allow excellent data representation but have limited extrapolation capability.

In recent years, a number of successful correlations of dense-fluid transport properties has been based on the rough hard-sphere (RHS) model. Conceptually, this model is a refinement of the free-volume theories of Batschinski and Hildebrand since it is based on the application of kinetic theory of a dense fluid of smooth hard spheres to the van der Waals model of a liquid (Dymond, 1974). Further extending the model, Chandler (1975) showed that the transport coefficients of rough hard spheres are proportional to those of smooth hard spheres. The proportionality factor characterizes the degree of coupling between momentum transfer due to translational and rotational motions. For nonspherical molecules the pro-

Table 3. Experimental Viscosities for Saturated Liquid R227ea

T/K, measd	ρ_l/kg·m^{-3}, calcd	ρ_v/kg·m^{-3}, calcd	η/mPa·s, measd	T/K, measd	ρ_l/kg·m^{-3}, calcd	ρ_v/kg·m^{-3}, calcd	η/mPa·s, measd
Coiled Capillary Viscometer							
248.154	1545.11	5.91	0.4754	283.202	1439.29	22.83	0.2932
248.152	1545.12	5.91	0.4784	283.201	1439.30	22.83	0.2931
248.151	1545.12	5.91	0.4734	283.200	1439.30	22.83	0.2931
248.151	1545.12	5.91	0.4752	288.050	1423.33	26.84	0.2744
248.147	1545.13	5.91	0.4720	288.042	1423.35	26.83	0.2735
253.087	1530.78	7.32	0.4428	288.042	1423.35	26.83	0.2735
253.087	1530.78	7.32	0.4425	288.048	1423.33	26.84	0.2741
253.080	1530.80	7.32	0.4400	293.113	1405.60	31.60	0.2565
253.085	1530.79	7.32	0.4410	293.114	1405.60	31.60	0.2578
258.224	1516.33	9.07	0.4067	293.115	1405.60	31.60	0.2581
258.223	1516.33	9.07	0.4081	293.113	1405.60	31.60	0.2577
258.223	1516.33	9.07	0.4082	298.068	1387.73	36.93	0.2409
258.224	1516.33	9.07	0.4074	298.068	1387.73	36.93	0.2409
263.154	1502.54	11.04	0.3804	298.068	1387.73	36.93	0.2412
263.150	1502.55	11.04	0.3828	298.068	1387.73	36.93	0.2393
263.150	1502.55	11.04	0.3807	303.188	1368.34	43.18	0.2250
263.150	1502.55	11.04	0.3787	303.188	1368.34	43.18	0.2252
268.028	1487.92	13.30	0.3561	303.188	1368.34	43.18	0.2244
268.028	1487.92	13.30	0.3564	303.188	1368.34	43.18	0.2265
268.028	1487.92	13.30	0.3584	303.188	1368.34	43.18	0.2259
268.028	1487.92	13.30	0.3560	303.186	1368.35	43.18	0.2248
272.113	1474.66	15.48	0.3344	303.188	1368.34	43.18	0.2258
272.113	1474.66	15.48	0.3373	308.275	1348.90	50.30	0.2143
272.113	1474.66	15.48	0.3386	308.277	1348.89	50.30	0.2151
272.113	1474.66	15.48	0.3380	308.277	1348.89	50.30	0.2134
278.144	1456.00	19.20	0.3139	308.277	1348.89	50.30	0.2116
278.143	1456.00	19.20	0.3136	313.605	1326.58	58.80	0.1959
278.143	1456.00	19.20	0.3129	313.602	1326.59	58.80	0.1961
278.143	1456.00	19.20	0.3138	313.604	1326.58	58.80	0.1959
283.204	1439.29	22.83	0.2926	313.604	1326.58	58.80	0.1952
Straight Capillary Viscometer							
303.195	1366.60	42.80	0.2242	328.135	1243.88	86.66	0.1555
303.188	1366.63	42.79	0.2222	328.138	1243.86	86.66	0.1559
303.194	1366.60	42.80	0.2229	328.141	1243.84	86.67	0.1567
303.185	1366.64	42.79	0.2229	328.143	1243.83	86.67	0.1556
308.211	1344.08	49.60	0.2067	333.178	1215.31	99.32	0.1445
308.209	1344.09	49.60	0.2055	333.180	1215.30	99.33	0.1439
308.207	1344.10	49.59	0.2076	333.177	1215.31	99.32	0.1446
308.204	1344.11	49.59	0.2095	333.179	1215.30	99.32	0.1446
313.130	1321.01	57.15	0.1925	338.153	1185.72	113.47	0.1330
313.129	1321.02	57.15	0.1921	338.137	1185.82	113.43	0.1333
313.139	1320.97	57.16	0.1936	338.151	1185.73	113.47	0.1339
313.133	1321.00	57.16	0.1918	338.143	1185.78	113.44	0.1340
317.997	1297.19	65.54	0.1798	343.176	1154.26	129.86	0.1226
317.995	1297.20	65.54	0.1797	343.179	1154.24	129.87	0.1226
318.005	1297.15	65.56	0.1801	343.177	1154.25	129.86	0.1227
317.999	1297.18	65.55	0.1813	343.182	1154.22	129.88	0.1230
323.007	1271.47	75.34	0.1673	348.121	1121.72	148.20	0.1128
323.009	1271.46	75.34	0.1682	348.121	1121.72	148.19	0.1150
323.009	1271.46	75.34	0.1678	348.126	1121.69	148.21	0.1134
323.011	1271.45	75.35	0.1678	348.128	1121.67	148.22	0.1132

portionality factor is called the roughness factor and is considered a measure for the influence of nonspherical shape on the transport properties of such fluids. The modified rough hard-sphere model was applied by Assael et al. (1992a−e, 1994, 1995) to the transport properties of many different fluids such as paraffinic and aromatic hydrocarbons, alcohols, and methane- and ethane-derived refrigerants. Most recently, Bleazard and Teja (1996) presented parameter tables for the viscosity and thermal conductivity of 58 polar liquids.

In view of the successful application of the rough hard-sphere model, it was decided to use this method for the correlation of the present viscosity data for fluorinated propane derivatives. The experimental data were converted to reduced viscosities η^* according to

$$\eta^* = 6.0349 \times 10^8 \frac{\eta}{\rho^{2/3}\sqrt{MRT}} \tag{6}$$

where η is the experimental viscosity in Pa·s, ρ the density in mol·m^{-3}, M the molar mass in kg·mol^{-1}, $R = (8.314\,471 \pm 0.000\,014)$ J·(mol·K)$^{-1}$ the universal gas constant (Moldover et al., 1988), and T the absolute temperature in K. The constant on the right side of eq 6 carries the unit mol$^{-1/3}$. This reduced viscosity is considered that of a rough hard-sphere fluid and fitted to the reduced viscosity of a smooth hard-sphere fluid whose density dependence is represented by the empirical correlation

$$\log_{10}\left[\frac{\eta^*}{R_\eta}\right] = 1.095 - \frac{9.263\,24}{V_r} + \frac{71.0385}{V_r^2} - \frac{301.9012}{V_r^3} + \frac{797.6900}{V_r^4} - \frac{1221.9770}{V_r^5} + \frac{987.5574}{V_r^6} - \frac{319.4636}{V_r^7} \tag{7}$$

The reduced volume is defined as $V_r = \rho_0(T_r)/\rho$, where ρ_0 is the temperature-dependent close-packed density in kg·m^{-3}.

Adjustable parameters are the roughness factor R_η and those associated with the temperature dependence of the close-packed density $\rho_0(T_r)$. R_η was fitted as a constant,

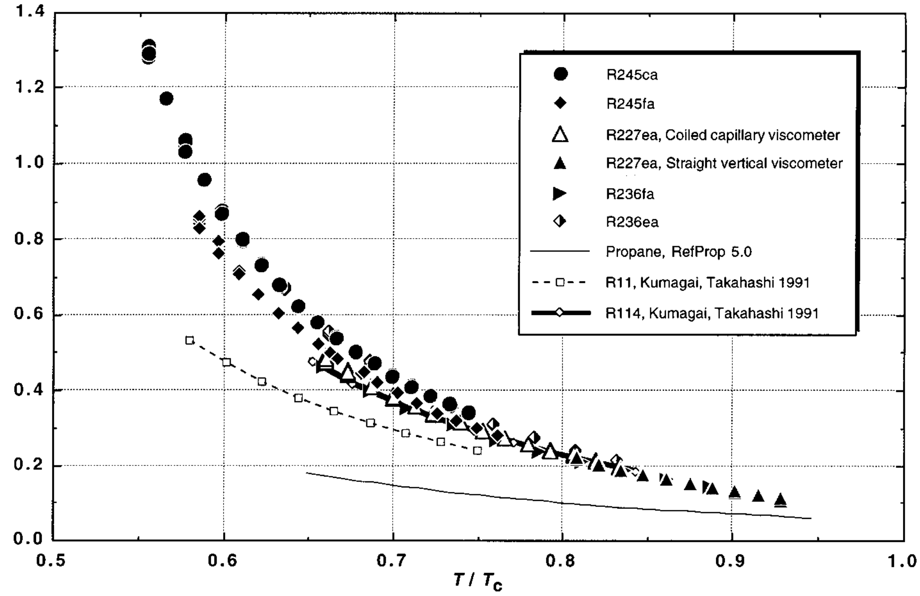

Figure 1. Experimental viscosity of saturated liquid R245fa, R245ca, R227ea, R236fa, and R236ea as a function of reduced temperature. The viscosities of R11, R114, and propane are shown for comparison. Data of Kumagai and Takahashi (1991) corrected for the vapor buoyancy effect.

Table 4. Parameter Values and Statistics of the Rough Hard-Sphere Correlation, Eq 6, for Saturated Liquid R245fa, R245ca, R227ea, R236fa, and R236ea (s = Standard Deviation)

fluid, formula	$(R_\eta \pm s)$	$(\beta_1 \pm s)$/kg·m^{-3}	$(\beta_2 \pm s)$/ kg·m^{-3}·K^{-1}
R245fa, $CF_3-CH_2-CHF_2$	1.131 ± 0.0437	1824 ± 30.0	571 ± 66.4
R245ca, $CHF_2-CF_2-CH_2F$	1.287 ± 0.0194	1775 ± 11.1	704 ± 25.5
R227ea, $CF_3-CHF-CF_3$	1.051 ± 0.0126	1995 ± 16.5	677 ± 31.4
R236fa, $CF_3-CH_2-CF_3$	0.909 ± 0.0347	2186 ± 36.2	154 ± 73.2
R236ea, $CF_3-CHF-CHF_2$	1.026 ± 0.0473	2082 ± 44.0	374 ± 89.5

and ρ_0 was fitted as a linear function of reduced temperature T_r

$$\rho_0 = \beta_1 + \beta_2 T_r \tag{8}$$

This functional form turned out sufficient to represent the experimental data, which cover a limited temperature range. Quartic polynomials may be necessary to represent high-pressure viscosities over wide temperature ranges (Assael et al., 1995). R_η was found to be sensitive to the functional form selected for ρ_0. The adjustable parameters R_η, β_1, and β_2 were determined for each fluid by nonlinear least-squares minimization using the NIST package ODRPACK (Boggs et al., 1992). The optimum parameter values and their standard deviations are listed in Table 4. Figure 2 shows how the experimental viscosities of all five fluids, reduced by the fitted roughness factors R_η, match the smooth hard-sphere viscosity correlation given by eq 7. Percent deviations between experimental and correlated values are shown in Figure 3 for the fluids that have been measured in this work, R245fa, R245ca, and R227ea. Figure 4 shows those for the previously measured hexafluoropropane isomers R236fa and R236ea. All experimental data are represented within their estimated experimental uncertainty.

There are advantages in applying the rough hard-sphere model to the data. First, the model can be safely extrapolated beyond the experimental conditions to pressures and temperatures in refrigeration cycles. This is of particular advantage with respect to the viscosity increase at lower temperatures and higher densities, which is usually underestimated when empirical correlations are extrapolated. Extrapolations of the model far beyond the data range will carry higher uncertainties due to the limited temperature range of the measurements. Extrapolations will also become incorrect below V_r = 1.1 because eq 6

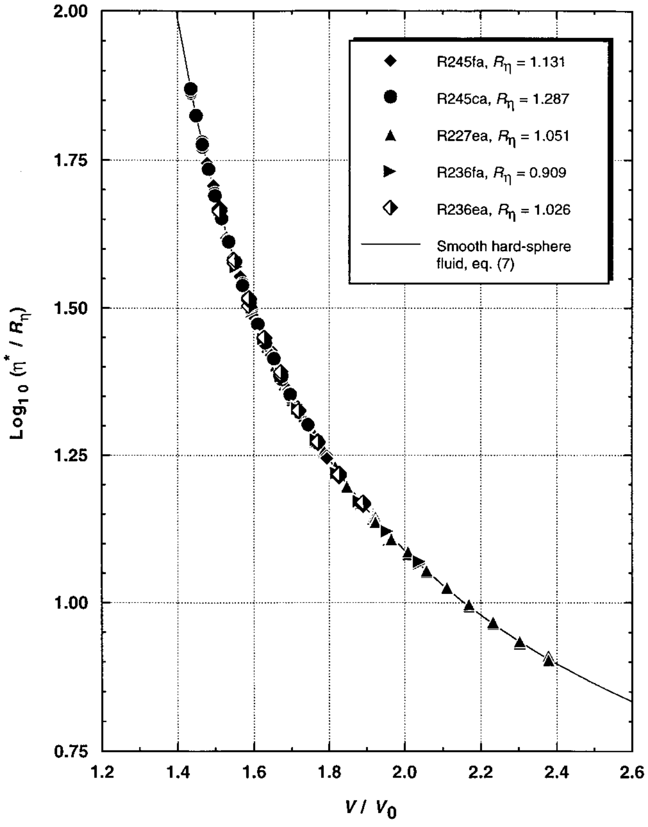

Figure 2. Rough hard-sphere model correlation for R245fa, R245ca, R227ea, R236fa, and R236ea.

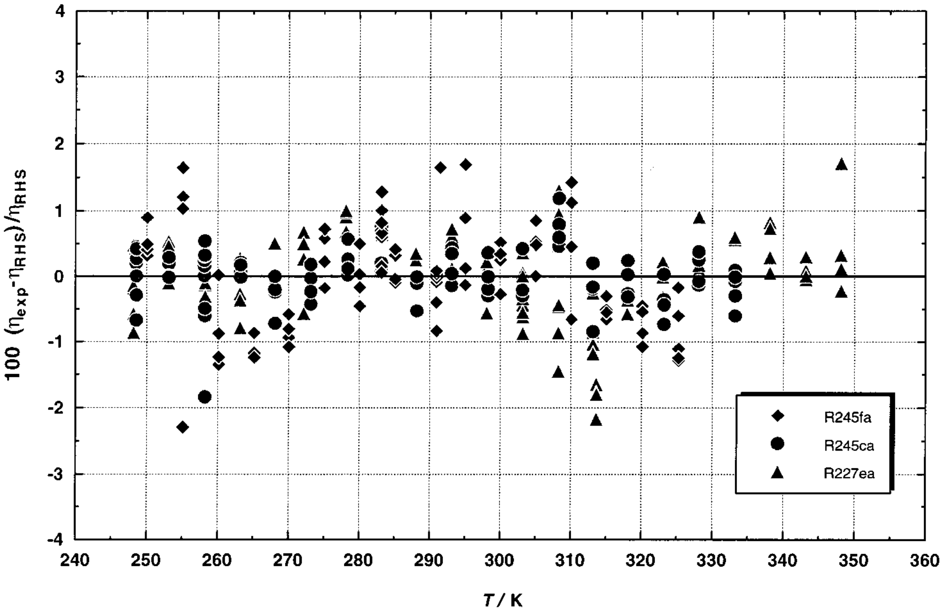

Figure 3. Percent deviations between experimental values and values calculated from the rough hard-sphere correlation for R245fa, R245ca, and R227ea.

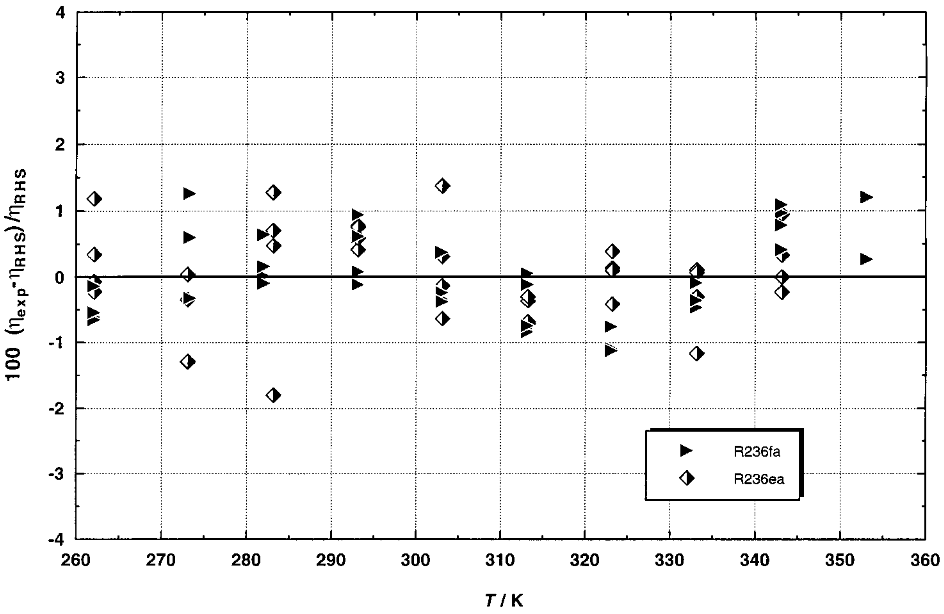

Figure 4. Percent deviations between experimental values (Laesecke and Defibaugh, 1996) and values calculated from the rough hard-sphere correlation for R236fa and R236ea.

exhibits a viscosity maximum in that density range (Bleazard and Teja, 1996). It has not been investigated what minimal amount of experimental data is necessary to establish the rough hard-sphere model for the entire fluid range of a substance. This would be useful to develop efficient measurement strategies.

The rough hard-sphere model should provide information about the degree of steric hindrance in a fluid, measured by the departure of the roughness factor R_η from 1. The fitted R_η-values in Table 4 suggest that R245ca ($R_\eta = 1.287$) and R245fa ($R_\eta = 1.131$) are the roughest molecules. This corresponds to their respective viscosities but does not compare with the viscosities and roughness factors of the other three compounds, Figure 1. Possibly this is due to the limited temperature range of the present data, which influences the correlation of the close-packed density ρ_0 and in turn that of the roughness factor R_η. Varying the temperature dependent-terms of the close-packed density $\rho_0(T_r)$ can significantly affect the roughness factor. However, the roughness factor of R236fa ($R_\eta = 0.909$) was found stable against such variations. R_η-values less than 1 were also reported by Assael et al. (1992e) and by Bleazard and Teja (1996), but the physical significance of such values is not conclusive.

The dominant method to predict transport properties of pure compounds and mixtures over wide ranges of fluid states is the extended corresponding-states (ECS) model as implemented in NIST Standard Reference Database 23 REFPROP (Huber et al., 1995). The ECS and the RHS model are similar procedures. Both require a reference fluid correlation and two structure-related parameters or shape factors. The ECS model gains its predictive capability for transport properties from the fact that the shape factors can be determined from thermodynamic data. On the other hand, the RHS model uses the smooth hard-sphere viscosity as reference that is accessible by measure-

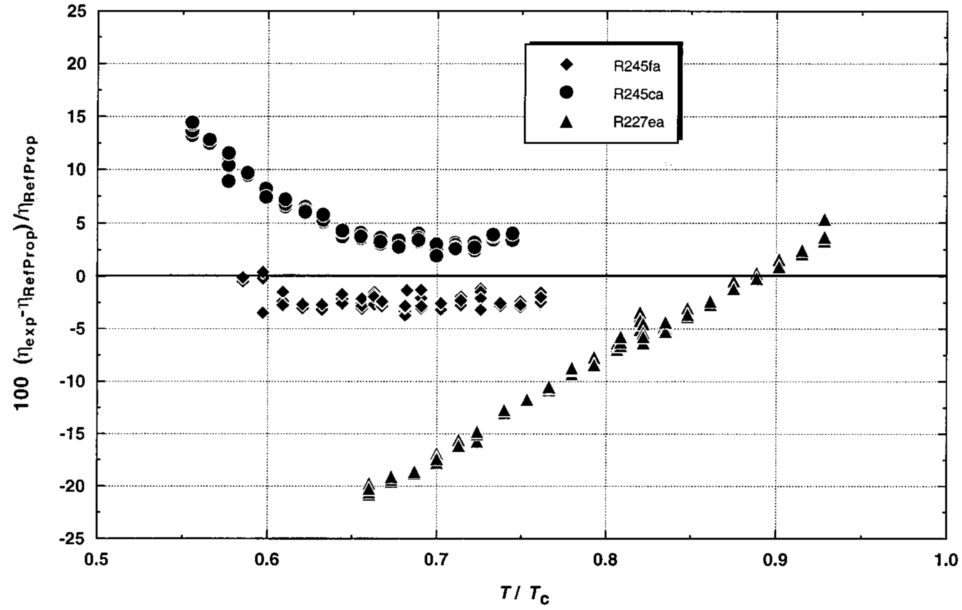

Figure 5. Comparison of experimental viscosities for R245fa, R245ca, and R277ea with predicted values from the extended corresponding-states model in REFPROP, version 5.05.

ments of simple fluids and computer simulations. The ECS model is based on different reference fluids for different classes of compounds. Reference fluid formulations for the ECS model require both extensive measurements and empirical viscosity surface correlations that can be reliably extrapolated.

First viscosity measurements of fluids such as those reported here allow reliability tests of predictions with the ECS model. The experimental viscosities for R236ea and R236fa were previously compared with ECS predictions, and very satisfactory agreement was found (Laesecke and Defibaugh, 1996). Such comparisons were also carried out for the new measurements of R245ca, R245fa, and R227ea using REFPROP version 5.05, in which the shape factors of the three fluids had been based only on thermodynamic property data (Defibaugh et al., 1996; Defibaugh and Moldover, 1997). Hence, the viscosity computations were completely predictive. This REFPROP version contained a revised viscosity formulation for the reference fluid R134a (Laesecke, 1997). Results of the comparison are shown in Figure 5 as percent deviations vs reduced temperature. The best agreement is found for R245fa, where the experimental viscosities are lower than the predicted values with an almost constant offset of −2.5%. In contrast, the deviations of the R245ca and R227ea viscosities are systematic and substantially higher than the estimated uncertainty of the measurements. Deviations of up to 15% occur for R245ca with decreasing temperature, whereas the deviations for R227ea vary with increasing temperature from −20% to 4%. The experimental data of this work can be used to improve the ECS predictions for the measured compounds.

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