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Viscosity Measurements of Ammonia, R32, and R134a. Vapor Buoyancy and Radial Acceleration in Capillary Viscometers

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The saturated liquid viscosity of ammonia (NH_3) and of the hydrofluorocarbons, difluoromethane (CH_2F_2, R32) and 1,1,1,2-tetrafluoroethane (CF_3-CH_2F, R134a), was measured in a sealed gravitational viscometer with a straight vertical capillary. The combined temperature range was from 250 to 350 K. The estimated uncertainty of the ammonia measurements is ±3.3 and ±2 to 2.4% for the hydrofluorocarbons with a coverage factor of two. The results are compared with literature data which have been measured with capillary viscometers of different design. Agreement within the combined experimental uncertainty is achieved when some of the literature data sets are corrected for the vapor buoyancy effect and when a revised radial acceleration correction is applied to data which were obtained in viscometers with coiled capillaries. An improved correction for the radial acceleration is proposed. It is necessary to extend international viscometry standards to sealed gravitational capillary instruments because the apparent inconsistencies between refrigerant viscosity data from different laboratories cannot be explained by contaminated samples.

KEY WORDS: ammonia; alternative refrigerants; capillary viscometer; R32; R134a; saturated liquid; radial acceleration correction; vapor buoyancy; viscosity.

1. INTRODUCTION

The measurements reported here were motivated by metrological interests concerning the viscometry of polar fluids and the use of sealed gravitational

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capillary instruments. Open gravitational viscometers are commercially available and routinely used in academia and industry for automated measurements of liquids whose vapor pressure is negligible relative to atmospheric pressure. They cannot be used for volatile liquids with higher than atmospheric vapor pressures simply because such liquids would evaporate during the experiments. Viscosity measurements of volatile liquids require sealed viscometers.

Sealed capillary instruments are state of the art for measurements over wide pressure and temperature ranges [1]. The fluid, liquid or gas, is pumped through a capillary *at a constant volumetric flow rate*, and the viscosity is deduced from the measured pressure drop across the length of the capillary. Achieving an unprecedented uncertainty of ±0.01%, the constant-flow rate capillary viscometer of van den Berg [2, 3] eclipsed previously developed instruments. Okubo *et al.* [4] measured the viscosity of R134a in a constant-flow rate viscometer in the temperature range 213 to 423 K at pressures up to 30 MPa. The uncertainty of the results was quoted as ±1.3%. The instrumentation and operation of such apparatus are rather sophisticated.

In conventional open capillary viscometers, liquids flow driven by gravity through straight vertical glass capillaries. The volumetric flow rate is measured by timing the efflux of the liquid through a graduated reservoir of known volume above the capillary. Such instruments are simple to operate. With proper calibration, their characteristic uncertainty is 0.2 to 0.3% [5].

Since open capillary viscometers were unsuitable for volatile compounds, their design was modified to investigate refrigerants, first chlorofluorocarbons (CFCs) and, predominantly since 1988, hydrofluorocarbons (HFCs). Refrigerants are necessarily volatile liquids because the vapor compression cycles in air conditioners and refrigerators operate typically between 253 and 333 K. Working fluids with high latent heats of vaporization at these temperatures are desired to achieve high volumetric cooling capacities. Sealed gravitational capillary viscometers were developed to measure the saturated liquid viscosity of refrigerants by employing the straightforward gravitational flow method, which has the advantage of simple instrumentation.

Phillips and Murphy [6] reported viscosity data for seven refrigerants, among them difluoromethane (R32). They used a thick-wall glass suspended-level instrument with an internal capillary diameter of 0.7 mm. The capillary tube was coiled to achieve measurable efflux times and to fit the necessary length of the tube into a thermostat. The diameter of the coil was not reported in the publication, nor was the number of coils. Neither the vapor buoyancy nor the radial acceleration correction for curved pipe flow were considered in the analysis of the efflux times. Large deviations of the results of Phillips and Murphy have been found regularly for all fluids which they measured [7, 8].

Shankland *et al.* [9] employed the instrument of Phillips and Murphy for the first measurements of the viscosity of 1,1,1,2-tetrafluoroethane (R134a) between 250 and 343 K. Subsequent R134a measurements by other investigators yielded viscosities more than 30% lower. Again, Shankland *et al.* did not report the diameter of the capillary coil or the number of coils of the instrument. The measurements were not corrected for the buoyancy of the vapor or for the radial acceleration of the fluid flow in the coil.

Ripple [7] developed novel sealed gravitational capillary viscometers for refrigerant measurements at NIST. To reach pressures higher than 2 MPa, a design different from thick-wall glass variants of suspended-level viscometers was chosen. Two compact stainless-steel instruments were built that can be used at vapor pressures up to approximately 3 MPa. The first viscometer has a one-coil capillary with an internal diameter of 0.508 mm and a coil diameter of approximately 151 mm [7]. It was used for measurements of six pure hydrofluorocarbons and three binary mixtures [10] up to about 310 K. R32, R125 (CF_3–CHF_2), and R134a were among the fluids studied. The second instrument has a 148-mm-long straight vertical capillary of 0.236 mm internal diameter. It was used for measurements of eight fluorinated hydrocarbons [11–13]. Comparative measurements of R227ea (1,1,1,2,3,3,3-heptafluoropropane; CF_3–CHF–CF_3) in both instruments indicated an inadequacy of the radial acceleration correction for the curved-pipe flow in the viscometer with the coiled capillary [13].

A major objective of the present work was to characterize the radial acceleration correction for coiled capillary viscometers. To investigate this issue, new measurements of R32 and R134a were carried out in the second viscometer with the straight vertical capillary. These fluids had been measured in the coiled capillary viscometer by Ripple and Matar [10]. The new results supplement the data for R125 [12] and R227ea [13], which had already been measured in both viscometers. With data for four fluids, the influence of the radial acceleration in coiled capillaries could be examined over a wider range of flow conditions.

The smaller internal diameter of the capillary in the straight vertical viscometer leads to longer efflux times, which make it possible to use the instrument to higher temperatures than the coiled capillary viscometer. The R32 measurements were conducted between 250 and 315 K, while R134a was measured between 242 and 350 K. The new data cover a temperature range which includes that of the R134a data of Shankland *et al.* [9]. Thus, the influence of the radial acceleration in the coiled capillary viscometer of

Phillips and Murphy and Shankland *et al.* could be investigated by comparison with the new data.

Another objective of the present work was to provide reference data for polar fluids for comparison with results from viscometers where fluids are exposed to electric and/or magnetic fields. Electroviscous and magnetoviscous coupling may occur in such instruments, resulting in increased apparent viscosities. Such coupling cannot occur in gravitational capillary viscometers because electric or magnetic fields are absent. Ammonia was included in the present work to compare with measurements with the NIST vibrating-wire viscometer. Magnetic fields in vibrating-wire instruments have strengths of 1 T [14]. Unusually high electrical conductivities of R32 samples were experienced in the NIST torsional-crystal viscometers and hot-wire thermal conductivity instruments. In these instruments, ac and dc electric fields are transmitted across the sample. Problems with R32 were also reported by Ripple and Matar [10] and by Barão *et al.* [15]. Thus, new measurements were warranted. Sample contaminations were suspected as a possible cause for the disparity in the reported viscosities of R134a [16]. Analyses of the different R134a samples which were used in this laboratory since 1990 revealed steadily increasing purities. The new viscosity measurements of R134a are therefore helpful to discern the influence of sample purity.

The final objective of the current measurements was to provide pure fluid reference data for a study of 10 binary and ternary alternative refrigerant mixtures of R32, R134a, R125, and propane which was conducted in the same instrument. These results will be published later.

This report continues with details of the characterization of the sample fluids, followed by a discussion of the viscometer, the experimental procedure, working equations, and experimental uncertainties. The results are presented in the third part and compared with literature data. The influence of the radial acceleration of the fluid flow in coiled capillary viscometers is examined. The, paper concludes with recommendations for future developments of sealed gravitational capillary viscometers for volatile fluids.

2. EXPERIMENTAL

2.1. Samples

Anhydrous ammonia was obtained from a commercial source. The purity was stated by the supplier as 99.99 mol %, with impurities of nitrogen, oxygen, carbon monoxide, and methane. The sample was analyzed in this laboratory by gas chromatography, and no detectable impurities were found.

Sample purities of the fluorinated hydrocarbons R32 and R134a were analyzed by a gas chromatographic–mass spectrometric method. No significant organic impurities were detected. A second gas chromatographic analysis revealed the presence of air in the samples. The R32 sample contained 0.072 ± 0.001 mol% air, while 0.060 ± 0.003 mol% air was found in the R134a sample. The amount of air was reduced during the condensation of the sample liquids into the evacuated viscometer and by pumping on the samples before the viscometer was sealed for the measurements. Other than that, the fluids were used as received without further purification.

Sample liquids were introduced into the viscometer after thorough evacuation of the instrument and transfer lines to 13 μPa (10^{-7} Torr). The lower reservoir was gently cooled with ice (in the case of ammonia) or over evaporating liquid nitrogen (in the case of the fluorinated hydrocarbons) to condense an average liquid volume of 2 to 3 cm^3 into the viscometer. This is about half the volume which is typically used in conventional open glass capillary viscometers. The sample transfer was initiated after the high vacuum had been maintained for at least 30 min.

2.2. Instrument and Procedures

Figure 1 shows all parts of the straight capillary viscometer including the sealing valve on the upper reservoir. The upper and the lower reservoirs are stainless-steel view cells with sapphire windows. Polytetrafluoroethylene O-rings seal the windows against 12.7 mm deep stainless-steel center pieces. The reservoirs are connected by a stainless steel reflux tube with a 3.9 mm internal diameter and by a straight vertical stainless-steel capillary of length $L = 148$ mm and inner diameter $d = 0.236$ mm. This capillary diameter is close to that of commercial Type 1 Ubbelohde viscometers. The arrangement of the reservoirs, capillary, and reflux tube establishes a unidirectional flow circuit for the sample liquid. The materials of the viscometer (stainless steel, sapphire, PTFE) are compatible with corrosive liquids.

The upper reservoir has a rectangular cross section which is nominally 12.7 mm deep and 9.4 mm wide ($A = 119.4 \times 10^{-6}\ \text{m}^2$). The height of the reservoir between the rounded corners is 7.87 mm. The flow rate of the liquid is determined by timing the downward movement of the liquid meniscus in that section of the upper reservoir at successive levels h with a stop watch and a cathetometer. The rate of fall of the liquid meniscus, $\dot{h}$, is obtained from a linear regression of the efflux times and the corresponding meniscus levels $h = h(t)$.

This flow rate measurement differs from the method used in conventional open glass capillary viscometers. These have graduated reservoirs of known volume above the capillaries, usually spherical glass bulbs with

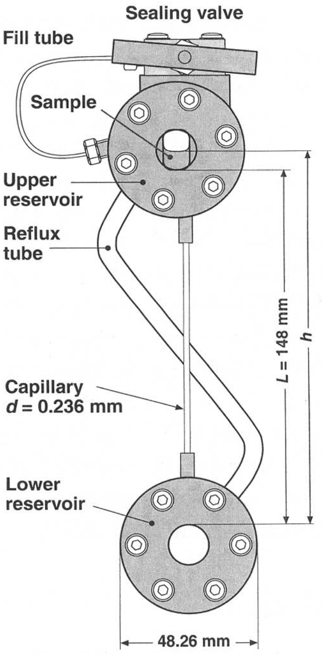

Fig. 1. Sealed gravitational viscometer with a straight vertical capillary.

circular cross section. The volumetric flow rate Q is obtained from the efflux time t of the liquid when it drains through the reservoir volume V. The viscosity η is evaluated from

$$\eta = c_0(\rho_1 - \rho_v)\, t - \frac{b\rho_1}{t} + c_1\sigma \tag{1}$$

where c_0, b, and c_1 are calibration constants, ρ_1 and ρ_v are the densities of saturated liquid and vapor, and σ is the surface tension between the two phases. This working equation for both open and sealed gravitational capillary viscometers was derived by Wedlake *et al.* [17]. Because the volume V is lumped into the calibration constant c_0, the viscosity is only a function of the efflux time t.

In the present viscometer the volumetric flow rate is determined via the rate of fall, $\dot{h}$. Equation (1) then reads in terms of $\dot{h}$,

$$\eta = \frac{C_1}{\dot{h}}(\rho_1 - \rho_v) - C_2\rho_1\dot{h} + \frac{C_3}{\dot{h}}\sigma \tag{2}$$

The cross-sectional area A of the upper reservoir appears in the calibration constant C_1 of the Hagen–Poiseuille term,

$$C_1 = \frac{\pi d^4 g h}{128 L A} \tag{3}$$

along with the inner diameter of the capillary $d = 0.236$ mm, the gravitational constant g, the driving pressure head h, and the length of the capillary $L = 148$ mm. Separate calibrations were carried out for the measurements of the fluorinated hydrocarbons, R32 and R134a, and for the ammonia series since new seals were installed for both. The calibration fluid was a specially prepared toluene sample of 99.98 mass% purity and the results of Kaiser *et al.* [18] were used as reference data. Calibrations were carried out at 320, 335, and 350 K. The following values of the calibration constant C_1 were obtained:

$C_1 = (6.184 \pm 0.015) \times 10^{-12}\ \mathrm{m}^3 \cdot \mathrm{s}^{-2}$ for R32 and R134a and

$C_1 = (6.060 \pm 0.015) \times 10^{-12}\ \mathrm{m}^3 \cdot \mathrm{s}^{-2}$ for ammonia.

The first value is 0.5% lower than the previously obtained result [13], which is commensurate with the uncertainty of the reference fluid viscosity. The value for the ammonia measurements is 2% lower than that for R32 and R134a. This difference may be due to thickness variations of the seals, although they were all machined in this laboratory to identical specifications in one batch. The 2% margin is entered below as a Type B contribution to the total uncertainty of the ammonia measurements.

The pressure difference, which drives the liquid flow, is equal to the apparent gravitational head minus the pressure head due to the buoyancy of the vapor column. The Hagen–Poiseuille term in Eq. (2), therefore, includes the difference between the saturated liquid and the saturated vapor densities $(\rho_1 - \rho_v)$. In many reviews of capillary viscometry, the vapor density is considered negligible [1, 19, 20] because the use of open instruments with nonvolatile liquids is assumed. An exception is the comprehensive work of Bauer and Meerlender [5], who addressed the vapor buoyancy effect. When volatile liquids are measured in sealed gravitational capillary viscometers, the vapor buoyancy must be accounted for because its effect is substantial. For example, the saturated vapor density of R134a at 350 K is 14.8% that of the saturated liquid. An error of that magnitude is introduced in the data analysis if the buoyancy of the vapor is neglected.

The second term in Eq. (2) is the Hagenbach–Couette correction for kinetic energy dissipation in the liquid at the inlet and outlet of the capillary. Instructions for commercial open capillary viscometers often advise to treat the correction parameter,

$$C_2 = \frac{mA}{8\pi L} \tag{4}$$

as a constant. However, experiments by Cannon *et al.* [21] revealed that the kinetic energy coefficient m depends on the flow conditions according to the empirical correlation,

$$m = 0.037\sqrt{Re} \tag{5}$$

For the present instrument, the Reynolds number Re can be approximated by

$$Re = \frac{4A}{\pi d} \frac{\rho_1}{(\rho_1 - \rho_v)} \frac{\dot{h}^2}{C_1} \tag{6}$$

Bauer and Meerlender [5] investigated the dependence of $m = f(Re)$ for Ubbelohde viscometers experimentally and found that Eq. (5) underestimates the kinetic energy dissipation. Better results were obtained with $m = 0.32$ for $Re < 50$. In the present work Reynolds numbers ranged from 18 to 142 for ammonia, from 130 to 332 for R32, and from 42 to 318 for R134a. Equation (5) was used throughout. The corresponding relative corrections ranged from 0.11% at 285 K to 0.31% at 335 K for ammonia, from 0.28% at 250 K to 1.14% at 315 K for R32, and from 0.05% at 240 K to 1.07% at 350 K for R134a. Following Bauer and Meerlender [5], the full kinetic energy corrections were entered as Type B uncertainties in the calculation of the total uncertainties below.

Interfacial effects influence the efflux of the liquid in the present viscometer more strongly than in conventional capillary viscometers. Their magnitude depends on the surface tension σ of the calibration and sample liquids, their contact angles at the reservoir wall, the internal diameter of the capillary, and the property ratio $\sigma(\rho_1 - \rho_v)^{-1}$, which will be called the *Laplace ratio.* The temperature dependence of the interfacial properties of the measured liquids is shown in Fig. 2 over the range of the measurements. Surface tension data for the calibration liquid toluene were compiled and correlated by Jasper [22]. Toluene densities were calculated from the equation of state of Goodwin [23]. The surface tension of ammonia, R32, and R134a was calculated from the correlations in NIST Standard Reference Database 23, REFPROP, Version 6, which are based on the most reliable literature data. Densities for these fluids were Calculated from the respective Tillner–Roth equations of state [24–26]. Figure 2 shows that toluene has the highest surface tension of the four liquids, followed by ammonia and the two HFCs. While the temperature dependence is approximately the same for toluene and the HFCs, the surface tension of ammonia decreases more rapidly with increasing temperature. Toluene and ammonia have the same surface tension at 282 K, while those of R32 and R134a are equal at 261 K. Figure 2 shows also the Laplace ratios $\sigma\,(\rho_l - \rho_v)^{-1}$, which characterize the vapor pressure depression over curved surfaces. Their order for toluene and ammonia and for the HFCs is reverse compared with the corresponding surface tension curves.

While conventional glass viscometers are shaped to minimize surface tension effects [27], the design of the present instrument could not be optimized to that end due to the requirement to hold pressures up to 3 MPa. This necessitated reservoirs with rectangular cross sections where the liquid is in contact with two stainless-steel and two sapphire walls. Due

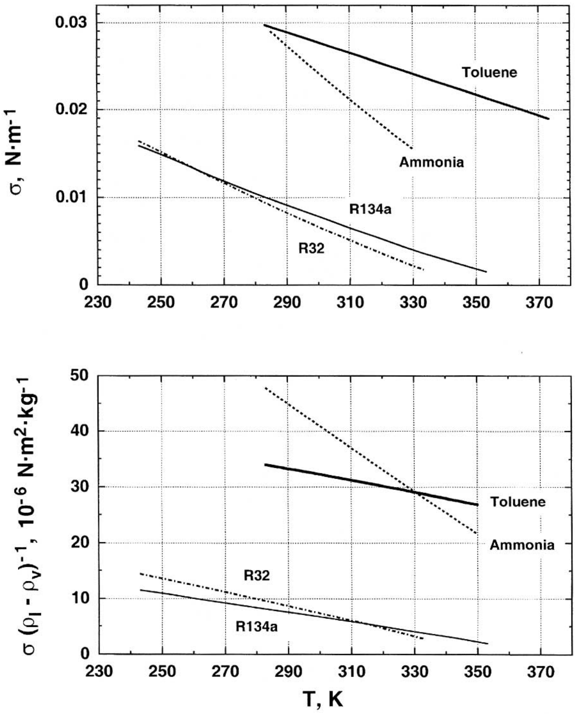

Fig. 2. Vapor–liquid surface tension (top) and the *Laplace* ratio (bottom) of the measured fluids as a function of temperature.

to the different wall potentials of these materials, they are wetted by the liquids with different contact angles. This difference is more pronounced for polar liquids such as those investigated here. The shape of the liquid meniscus in the present viscometer is illustrated schematically in Fig. 3a. A rise of the liquid occurs in the corners of the upper reservoir. The even more pronounced rise of liquid water in the corners of a microchannel with triangular cross section has been visualized by Lanzilotto *et al.* [28]. Figure 3b compares the size and shape of the liquid reservoir of the present

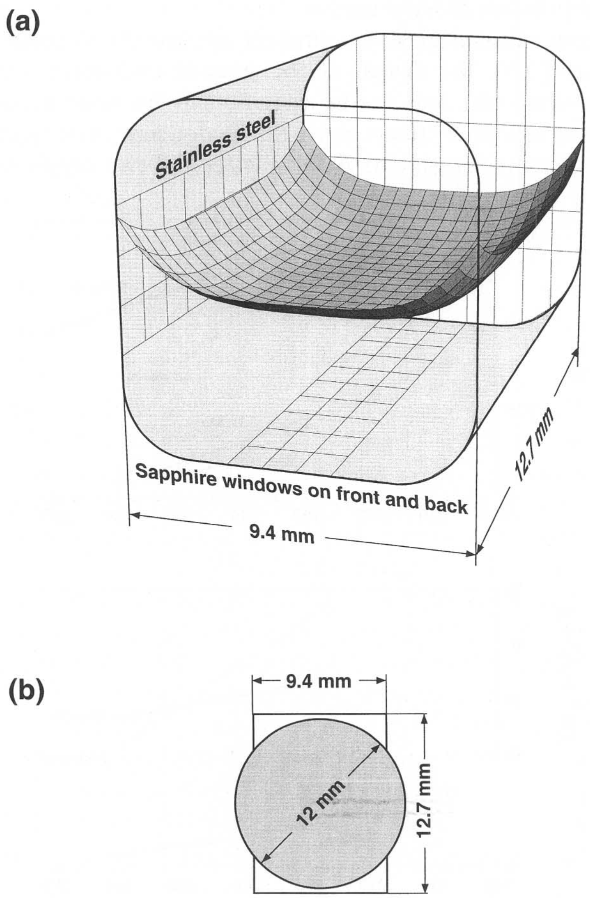

Fig. 3. (a) Liquid meniscus with corner rise in the upper reservoir of the viscometer. (b) Comparison of reservoir cross-section size and shape with that of an open Type 1 Ubbelohde viscometer.

viscometer with that of a Cannon[4] CUU viscometer of size 25 with a reservoir of 12 mm internal diameter.

The rise of the liquid in the corners of the rectangular upper reservoir creates an additional lift on the draining liquid which is not present in conventional capillary viscometers with circular measuring bulbs. Due to the difference in geometry, surface tension correction methods for conventional capillary viscometers are not quite adequate for the present instrument. The third term in Eq. (2) was introduced for suspended-level viscometers by Wedlake *et al.* [17] but was not evaluated in this work. Instead, three contributions due to surface tension effects were included in the evaluation of Type B experimental uncertainties (Table I). The uncertainty due to the surface tension difference between the calibration liquid and sample was neglected for ammonia. For R32 and R134a this contribution was included at 0.3%, which is the largest contribution of this effect in conventional viscometers as quoted by Bauer and Meerlender [5]. The analysis by Wedlake *et al.* [17] was followed to obtain an estimate for the contribution resulting from pressure head variations due to surface tension effects. The data in Table I of that reference were correlated by the equation,

$$\frac{h_\sigma}{h} = 0.1571 \left(\frac{\sigma}{\rho_l - \rho_v} \right)^{0.4208} \tag{7}$$

which gives the relative reduction in the effective head (h_σ/h) in percentage as a function of the Laplace ratio $\sigma(\rho_l - \rho_v)^{-1}$ in units of $10^{-6}\,\mathrm{N \cdot m^2 \cdot kg^{-1}}$. One hundred fifty percent of the margin obtained from this correlation was entered in the uncertainty evaluation. Third, contributions of 2% (ammonia) and 1.5% were estimated to account for wall drainage films and the corner rise in the upper reservoir.

The uncertainties of the saturated liquid and vapor densities were taken from the respective publications of the equations of state as quoted above. Since the thermodynamic properties of the three fluids are relatively well established, the maximum Type B uncertainty contribution for the densities is 0.2%, which is for the vapor density of R32.

The viscometer was 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 an ITS-90 calibrated platinum resistance

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[4] Identification of commercial products by manufacturer's names or labels does not 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.

Table I. Uncertainty Evaluation of the Present Measurements

	Uncertainty contribution					
	Ammonia		R32		R134a	
Limits of temperature range	285 K	335 K	250 K	315 K	240 K	350 K
Type A uncertainty (%)	1					
Type B uncertainty contributions (%)						
Kinetic energy correction (100% of the correction)	0.1	0.6	0.3	1.1	0.05	1.1
Calibration with toluene	2	2	0.5	0.5	0.5	0.5
Surface tension difference between calibration liquid and sample	0	0	0.3	0.3	0.3	0.3
Pressure head variations due to surface tension effects on curved interfaces [150% of the estimate according to Wedlake *et al.* [17], Eq. (7)]	1.2	0.9	0.75	0.9	0.8	0.4
Wall drainage films and corner rise in upper reservoir	2	2	1.5	1.5	1.5	1.5
Liquid density	0.1	0.1	0.05	0.05	0.05	0.05
Vapor density	0.1	0.1	0.2	0.2	0.1	0.1
Total Type B uncertainty	3.1	3.1	1.8	2.2	1.8	2.0
Total expanded uncertainty (%) (coverage factor of 2)	3.3	3.2	2.1	2.4	2.0	2.2

thermometer (PRT) accurate to ±0.01 K. The bath temperature was equilibrated for at least 30 min before a measurement series was initiated. The combined uncertainty of the thermometer and that due to temperature gradients and fluctuations in the thermostat is estimated as ±0.02 K. In the present measurements, this introduces a maximum uncertainty of ±0.03% in the viscosity for R134a at 240 K, which is negligible.

The uncertainty of the present measurements was evaluated following the guidelines of Taylor and Kuyatt [29]. These are summarized in Table I for the lowest and highest temperatures at which each fluid was measured. The total expanded uncertainty with a coverage factor of two for the ammonia measurements decreases slightly with temperature, from 3.3% at 285 K to 3.2% at 335 K. The uncertainty of the R32 and R134a measurements varies between 2% at the lowest and 2.2 and 2.4% at the highest temperatures, respectively. The lower overall uncertainty for the fluorinated hydrocarbons is due to smaller surface tension effects, while the increase with temperature is due to the growing contribution of the kinetic energy correction. These uncertainties are approximately one order of magnitude larger than those which are typical for conventional open capillary viscometers.

3. RESULTS AND DISCUSSION

The experimental results for the saturated liquid viscosity of ammonia, R32, and R134a are presented in Tables II to IV in the order of measurements. Usually, four runs were measured at each temperature. Due to the pressure limit of the viscometer, the ammonia measurements were confined to a maximum of 335 K and those of R32 to an upper temperature of 315 K, while those for R134a extended to 350 K. The temperature dependence of the measured viscosities is shown in Fig. 4 including the viscosities of toluene at the calibration points. Comparisons of the results are discussed in the following sections for each fluid individually.

Table II. Experimental Viscosities for Saturated Liquid Ammonia[a]

T (K)	ρ_l ($kg \cdot m^{-3}$)	ρ_v ($kg \cdot m^{-3}$)	η (mPa·s)
285.062	621.913	5.18360	0.1476
285.071	621.901	5.18514	0.1476
285.067	621.906	5.18445	0.1470
285.070	621.902	5.18497	0.1476
290.009	614.786	6.0758	0.1380
290.014	614.779	6.0767	0.1390
290.034	614.749	6.0806	0.1396
290.030	614.755	6.0798	0.1380
290.033	614.750	6.0804	0.1375
295.029	607.457	7.1014	0.1302
295.026	607.461	7.1007	0.1307
295.027	607.459	7.1009	0.1312
295.019	607.471	7.0992	0.1321
295.026	607.461	7.1007	0.1336
295.027	607.459	7.1009	0.1316
295.029	607.457	7.1014	0.1316
295.025	607.463	7.1005	0.1316

[a] The data are listed in the order of measurements. The densities are calculated, not measured.

Table II. *(Continued)*

T (K)	ρ_l (kg·m^{-3})	ρ_v (kg·m^{-3})	η (mPa·s)
300.022	599.967	8.2565	0.1247
300.016	599.976	8.2550	0.1252
299.972	600.042	8.2442	0.1252
299.977	600.035	8.2454	0.1248
304.998	592.303	9.5525	0.1187
304.998	592.303	9.5525	0.1179
304.991	592.314	9.5505	0.1183
304.990	592.316	9.5503	0.1199
310.006	584.490	11.022	0.1119
310.006	584.490	11.022	0.1134
310.001	584.498	11.020	0.1130
310.008	584.487	11.023	0.1137
315.041	576.334	12.675	0.1086
315.036	576.342	12.673	0.1075
315.048	576.323	12.677	0.1075
315.047	576.325	12.677	0.1075
320.106	568.020	14.552	0.1026
320.091	568.045	14.546	0.1027
320.090	568.047	14.546	0.1020
320.084	568.057	14.544	0.1023
320.099	568.032	14.550	0.1023
320.102	568.027	14.551	0.1020
325.034	559.642	16.595	0.0974
325.032	559.646	16.594	0.0977
325.033	559.644	16.595	0.0974
325.038	559.635	16.597	0.0974
330.039	550.830	18.910	0.0924
330.046	550.817	18.913	0.0929
330.044	550.821	18.912	0.0929
330.049	550.812	18.915	0.0934
335.070	541.674	21.529	0.0880
335.068	541.678	21.527	0.0888
335.062	541.688	21.524	0.0890
335.051	541.708	21.518	0.0888

Table III. Experimental Viscosities for Saturated Liquid R32[a]

T (K)	ρ_l (kg·m^{-3})	ρ_v (kg·m^{-3})	η (mPa·s)
290.084	993.441	37.29	0.1243
290.086	993.433	37.30	0.1237
290.083	993.445	37.29	0.1237
290.082	993.449	37.29	0.1237
295.052	973.740	43.22	0.1162
295.050	973.749	43.22	0.1153
295.054	973.732	43.22	0.1160
295.053	973.736	43.22	0.1162
300.077	952.893	50.09	0.1092
300.079	952.885	50.09	0.1095
300.079	952.885	50.09	0.1093
300.080	952.881	50.09	0.1100
310.135	907.701	67.11	0.0975
310.140	907.677	67.12	0.0974
310.141	907.673	67.12	0.0975
310.140	907.677	67.12	0.0976
251.621	1125.29	10.55	0.1921
251.623	1125.28	10.55	0.1922
251.618	1125.30	10.55	0.1927
251.617	1125.30	10.55	0.1920
255.071	1114.57	11.96	0.1836
255.067	1114.58	11.96	0.1844
255.065	1114.59	11.96	0.1841
255.066	1114.58	11.96	0.1853
260.071	1098.72	14.27	0.1747
260.065	1098.74	14.27	0.1747
260.070	1098.72	14.27	0.1745
260.065	1098.74	14.27	0.1753
265.051	1082.53	16.93	0.1650
265.053	1082.53	16.93	0.1652
265.050	1082.54	16.92	0.1648
265.053	1082.53	16.93	0.1646
270.073	1065.77	19.99	0.1552
270.072	1065.78	19.99	0.1557
270.071	1065.78	19.99	0.1558
270.070	1065.78	19.99	0.1560
275.059	1048.63	23.48	0.1463
275.061	1048.63	23.48	0.1467
275.060	1048.63	23.48	0.1465
275.061	1048.63	23.48	0.1477

[a] The data are listed in the order of measurements. The densities are calculated, not measured.

Table III. *(Continued)*

T (K)	ρ_l (kg · m^{-3})	ρ_v (kg · m^{-3})	η (mPa · s)
280.052	1030.93	27.48	0.1385
280.061	1030.90	27.48	0.1391
280.056	1030.92	27.48	0.1387
280.056	1030.92	27.48	0.1384
285.062	1012.56	32.05	0.1304
285.060	1012.57	32.05	0.1293
285.059	1012.57	32.05	0.1294
285.059	1012.57	32.05	0.1300
250.239	1129.54	10.02	0.1963
250.241	1129.53	10.02	0.1950
250.241	1129.53	10.02	0.1957
250.243	1129.53	10.02	0.1954
305.058	931.161	57.90	0.1045
305.060	931.152	57.91	0.1040
305.058	931.161	57.90	0.1037
305.057	931.165	57.90	0.1037
315.057	883.436	77.47	0.09201
315.059	883.426	77.48	0.09219
315.060	883.421	77.48	0.09138
315.059	883.426	77.48	0.09140

Table IV. Experimental Viscosities for Saturated Liquid R134a[a]

T (K)	ρ_l (kg · m^{-3})	ρ_v (kg · m^{-3})	η (mPa · s)
240.846	1395.20	3.9918	0.4215
240.965	1394.85	4.0136	0.4214
241.030	1394.66	4.0255	0.4193
245.493	1381.42	4.9120	0.3920
245.513	1381.36	4.9162	0.3902
245.529	1381.31	4.9196	0.3902
245.553	1381.24	4.9247	0.3884
250.009	1367.87	5.9573	0.3659
250.012	1367.86	5.9581	0.3691
250.013	1367.86	5.9584	0.3675
250.013	1367.86	5.9584	0.3675

[a] The data are listed in the order of measurements. The densities are calculated, not measured.

Table IV. *(Continued)*

T (K)	ρ_l (kg·m^{-3})	ρ_v (kg·m^{-3})	η (mPa·s)
255.316	1351.62	7.4106	0.3418
255.325	1351.59	7.4132	0.3418
255.337	1351.56	7.4168	0.3403
255.352	1351.51	7.4212	0.3432
260.043	1336.96	8.9202	0.3217
260.046	1336.96	8.9213	0.3205
260.047	1336.95	8.9217	0.3180
260.049	1336.95	8.9224	0.3192
265.026	1321.12	10.776	0.2997
265.027	1321.11	10.777	0.3020
265.029	1321.11	10.778	0.2986
265.030	1321.10	10.778	0.2975
270.044	1304.96	12.929	0.2780
270.046	1304.95	12.930	0.2770
270.046	1304.95	12.930	0.2770
270.048	1304.94	12.931	0.2770
275.756	1286.12	15.794	0.2632
275.756	1286.12	15.794	0.2614
275.758	1286.11	15.795	0.2623
275.760	1286.10	15.796	0.2588
280.060	1271.59	18.266	0.2471
280.062	1271.59	18.267	0.2463
280.063	1271.58	18.267	0.2463
280.063	1271.58	18.267	0.2471
285.042	1254.35	21.518	0.2326
285.044	1254.35	21.519	0.2319
285.045	1254.34	21.520	0.2326
285.046	1254.34	21.520	0.2305
290.118	1236.37	25.283	0.2165
290.118	1236.37	25.283	0.2184
290.119	1236.37	25.284	0.2165
290.120	1236.36	25.284	0.2178
295.087	1218.18	29.494	0.2024
295.089	1218.17	29.496	0.2036
295.089	1218.17	29.496	0.2041
295.090	1218.17	29.496	0.2013
300.095	1199.33	34.292	0.1915
300.098	1199.32	34.296	0.1909
300.099	1199.32	34.297	0.1894
300.099	1199.32	34.297	0.1909

Table IV. *(Continued)*

T (K)	ρ_l (kg·m^{-3})	ρ_v (kg·m^{-3})	η (mPa·s)
305.511	1178.13	40.231	0.1783
305.511	1178.13	40.231	0.1802
305.511	1178.13	40.231	0.1807
305.513	1178.12	40.233	0.1797
310.075	1159.59	45.887	0.1697
310.079	1159.57	45.892	0.1697
310.083	1159.56	45.898	0.1714
310.084	1159.55	45.899	0.1710
315.049	1138.59	52.867	0.1591
315.054	1138.57	52.874	0.1594
315.054	1138.57	52.874	0.1594
315.057	1138.55	52.878	0.1587
320.140	1116.16	60.958	0.1485
320.146	1116.13	60.969	0.1481
320.148	1116.12	60.972	0.1485
320.149	1116.11	60.974	0.1488
325.116	1093.00	70.007	0.1391
325.117	1092.99	70.009	0.1394
325.121	1092.98	70.017	0.1400
325.121	1092.98	70.017	0.1400
330.113	1068.52	80.351	0.1319
330.120	1068.49	80.367	0.1316
330.126	1068.46	80.381	0.1316
330.130	1068.44	80.390	0.1313
335.086	1042.54	92.231	0.1238
335.092	1042.50	92.246	0.1233
335.092	1042.50	92.246	0.1222
335.093	1042.50	92.249	0.1230
340.032	1014.91	105.83	0.1149
340.035	1014.89	105.84	0.1149
340.037	1014.88	105.84	0.1147
340.041	1014.86	105.86	0.1152
345.078	984.155	122.17	0.1058
345.082	984.129	122.19	0.1058
345.093	984.060	122.23	0.1058
345.106	983.977	122.27	0.1058
350.091	950.663	141.39	0.09709
350.099	950.605	141.42	0.09728
350.100	950.598	141.43	0.09748
350.102	950.584	141.44	0.09747

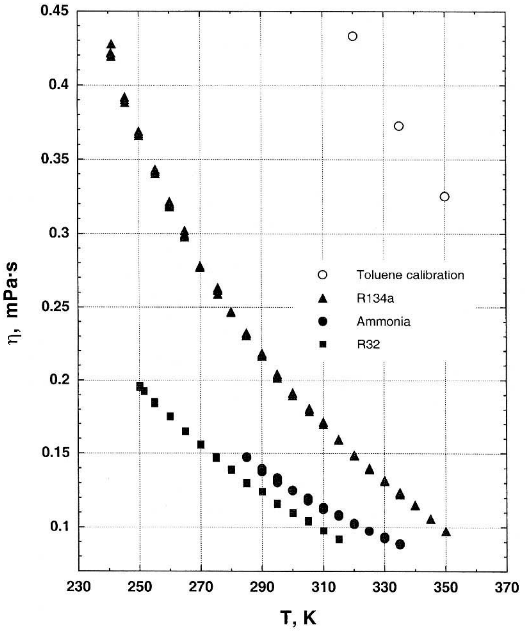

Fig. 4. Experimental viscosity of saturated liquid ammonia, R32, and R134a versus temperature. The viscosity of toluene at the calibration temperatures is shown for comparison.

3.1. Ammonia

Viscosity data for ammonia were recently compiled and correlated by Fenghour *et al.* [30]. The uncertainty of the correlation is quoted as ±2% for the liquid region between 270 and 400 K at pressures below 40 MPa. Figure 5 shows that the present results are between 2 and 4.5% lower than the reference values calculated from the correlation. These deviations are within the combined uncertainty range of experiment and correlation. The fact that the experimental results are lower than the correlation is noteworthy. Applying corrections for surface tension effects to the experimental data would have resulted in even lower viscosities. Among the previous data mentioned in the report by Fenghour *et al.* is a set of unpublished oscillating cylinder measurements by Wakao and Nagashima (1993), which appears to deviate from the correlation in a similar pattern as the present measurements. Clearly, more measurements are needed to reduce the existing uncertainty of the viscosity of ammonia.

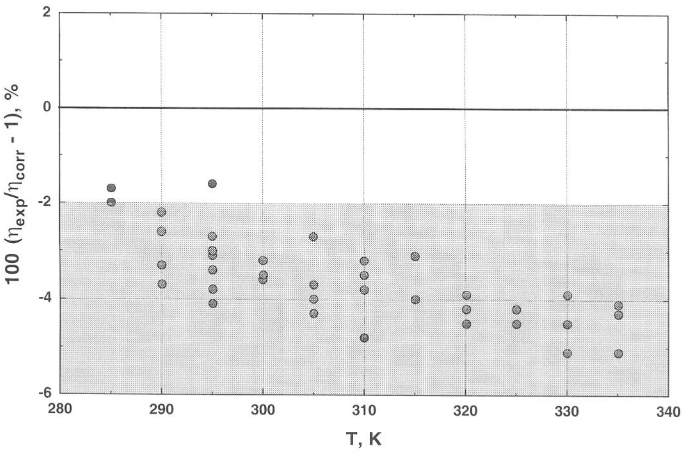

Fig. 5. Percentage deviations of the ammonia data relative to the correlation of Fenghour *et al.* [30]. The white area represents the ascribed uncertainty of the correlation.

3.2. R32

Difluoromethane (R32) is one of the two fluids which were measured in this work to supplement previous measurements by Ripple and Matar [10] with the sealed gravitational NIST viscometer with a *coiled* capillary. Since a correlation of the viscosity of R32 has yet to be developed, the extended corresponding states model of Klein *et al.* [31] was chosen as the reference to compare literature data and the experimental results of this work. Percentage deviations are shown as a function of density in Fig. 6. The Ψ-function of R32 in the ECS model was based on the data measured by Bivens *et al.* [32] in a forced-flow capillary viscometer with a mercury pump and on those measured by Assael *et al.* [33] in a vibrating-wire viscometer. Figure 6 illustrates the inconsistency between these two data sets. The data of Assael *et al.* are represented within their quoted experimental uncertainty of $\pm 0.5\%$, while the results of Bivens *et al.* are offset by -3 to -5% in the overlapping density range. This is outside their quoted uncertainty of $\pm 1.2\%$. The other data cluster around these two series. The previous measurements of Ripple and Matar agree with the results of Assael *et al.*, as does the correlation reported by Grebenkov *et al.* [34] for their falling-cylinder measurements with an uncertainty of $\pm 2.8\%$. However, at densities below $900\ \mathrm{kg \cdot m^{-3}}$ the deviations of this series increase systematically up to 8.8% at 333 K.

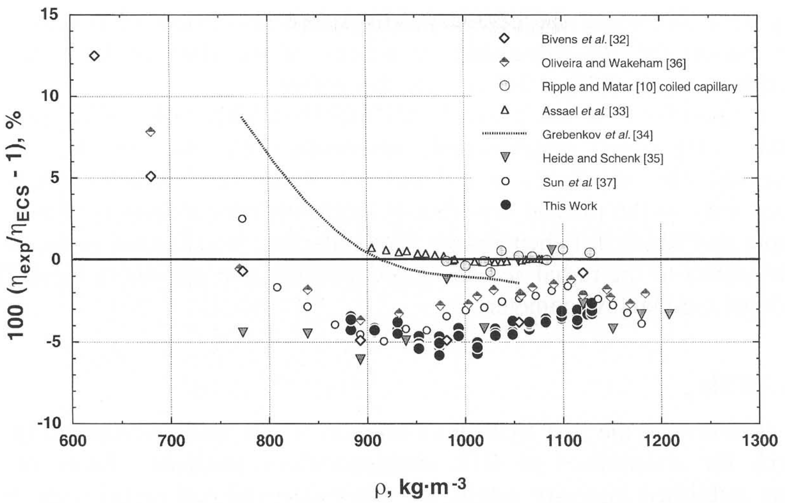

Fig. 6. Percentage deviations of viscosity data for R32 relative to values predicted with the extended corresponding states (ECS) model of Klein *et al.* [31].

The present measurements are 3 to 5% lower than the reference correlation. They agree with the results of Bivens *et al.* within the uncertainty quoted by these authors (±1.2%). They agree also with the data obtained by Heide and Schenk [35] in a rolling-ball viscometer at a quoted uncertainty of ±2%. However, the latter results scatter appreciably. The present results also agree with the vibrating-wire measurements of Oliveira and Wakeham [36] within the uncertainty as evaluated above. Based on the uncertainty of ±0.5 to 1% quoted by Oliveira and Wakeham, their results are inconsistent with the others except for those which Sun *et al.* [37] obtained in a sealed gravitational capillary viscometer. These results are considered unreliable for two reasons. Instead of the complete working equation of Wedlake *et al.* [17], which accounts explicitly for the vapor buoyancy effect, Sun *et al.* use a working equation for open capillary viscometers where the vapor buoyancy is neglected. They do mention, however, that their calibration constant A depends on the densities of the saturated liquid and vapor and employ a procedure to account for that effect. Unfortunately, that procedure remains incomplete as long as an inadequate working equation is used. The quoted uncertainty of ±3% appears doubtful, especially at liquid densities below 900 kg · m^{-3}. The deviations follow those of the data by Oliveira and Wakeham and of Bivens *et al.*, which are eventually 12.5% higher than the predicted viscosity at 347 K. This is within 4 K of the critical temperature of R32, where compressibility effects may have influenced the capillary flow in the instrument of Bivens *et al.* The reason for the increasing deviations of the data of Oliveira and Wakeham, up to 8% at 343 K, remains unclear.

Comparisons of the present measurements with those of Ripple and Matar [10] reveal systematically increasing differences as the density decreases. They reach 5% at a density of 980 $kg \cdot m^{-3}$, which exceeds the uncertainty of the present data but is within the uncertainty estimated by Ripple and Matar for their results. The difference is examined in Section 4 with respect to the radial acceleration correction that applies to liquid flow in coiled capillary viscometers.

3.3. R134a

R134a was the first hydrofluorocarbon which was investigated in the search for alternatives to R12 (dichlorodifluoromethane). Some of the many published viscosity results for this fluid exhibited inexplicably large deviations. The following discussion includes selected literature data which are of interest relative to the present measurements. The comparisons in Figs. 7a and 7b are based on a correlation which represents the data of Okubo *et al.* [4] within their quoted uncertainty of ±1.3%. These data were measured with a constant-flow rate capillary viscometer in the temperature range of 213 to 423 K at pressures from 1.58 to 30.19 MPa.

The deviations of the present results from this correlation are illustrated in Fig. 7a. Agreement is generally within the expanded uncertainty as evaluated in Table I. The higher deviations at lower densities (higher temperatures) may be due to the residual inadequacy of the kinetic energy correction as discussed above. Other data which agree with the correlation within their uncertainty are those measured by Bivens *et al.* [32] in a forced-flow capillary viscometer and the series by Heide and Schenk [35] measured in a rolling-ball viscometer. This level of agreement between the present results and those of Bivens *et al.* and Heide and Schenk is similar to that found for the R32 results (Fig. 6). Note, in Fig. 7a, that the R134a measurements of Ripple and Matar with the coiled capillary viscometer are between 2 and 4% higher than the present results from the viscometer with the straight vertical capillary.

Figure 7b shows percentage deviations of three literature data sets which were obtained with sealed gravitational capillary viscometers. The earliest R134a viscosity measurements were carried out by Shankland *et al.* [9] in a viscometer with a coiled capillary. These results deviate from the correlation systematically up to a maximum of 33% at 1000 $kg \cdot m^{-3}$ (343.15 K). As mentioned before, Shankland *et al.* accounted for neither the vapor buoyancy in their sealed instrument nor the radial acceleration

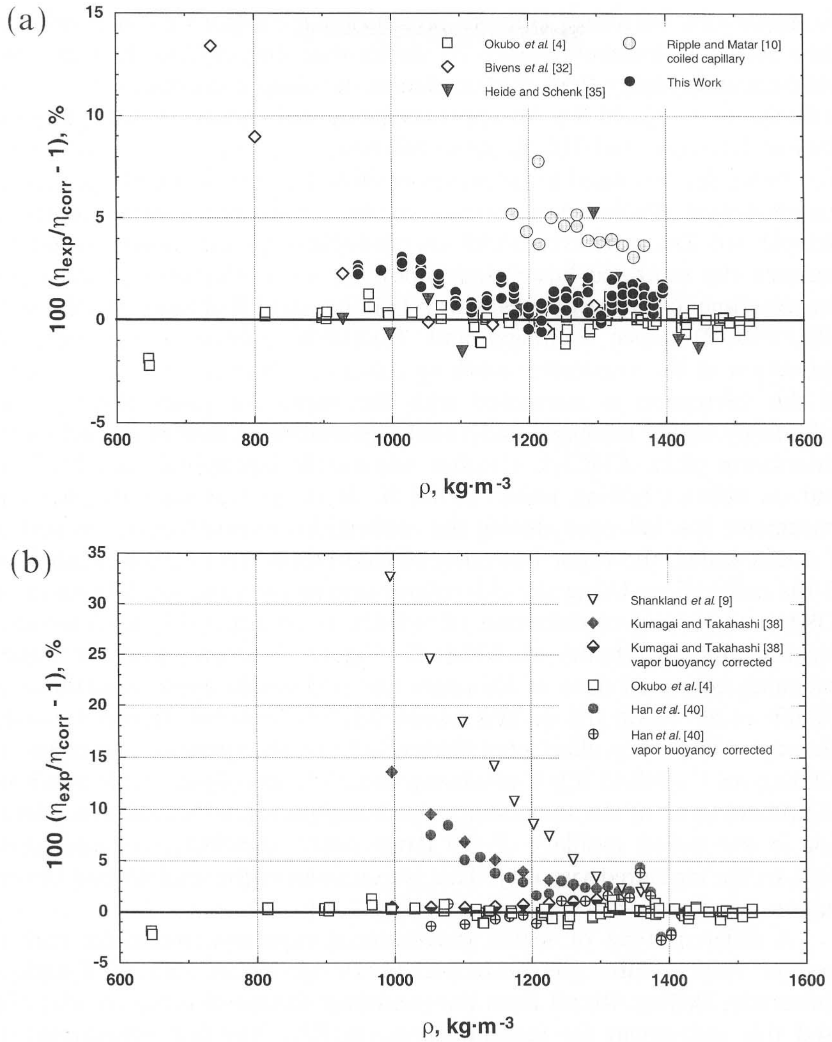

Fig. 7. (a) Percentage deviations of viscosity data for R134a relative to a correlation for the measurements of Okubo *et al.* [4]. (b) Percentage deviations of viscosity data for R134a relative to a correlation for the measurements of Okubo *et al.* [4].

of the liquid in the coiled capillary. The magnitudes of these two effects can be discerned by comparison with the data of Kumagai and Takahashi [38]. They were also obtained in a capillary viscometer but this instrument had a straight vertical tube. Ripple and Defibaugh [12] have already shown in the context of their measurements on R143a and R152a that

Kumagai and Takahashi failed to account for the vapor buoyancy effect in their sealed instrument. Figure 7b shows that their R134a data are also systematically higher than the correlation, reaching a maximum of 14% at 1000 kg · m^{-3} (343.15 K). An approximate correction can be applied to the data of Kumagai and Takahashi as follows.

First, the measured kinematic viscosities are reconstructed by dividing the published absolute viscosities η by the published liquid densities ρ_l. Second, the kinematic viscosities are multiplied by the density difference between the saturated liquid and vapor ($\rho_l - \rho_v$) which is calculated for the experimental temperatures with NIST Standard Reference Database 23 (REFPROP). Since Kumagai and Takahashi omitted the Hagenbach correction in the viscometer working equation, the remaining uncertainty of this correction is associated with the vapor buoyancy effect of the calibrating liquid. Kumagai and Takahashi calibrated their instrument with chloroform (R20, $CHCl_3$), a rather nonvolatile liquid, between 304.73 K and its normal boiling point, 334.41 K. It is not specified whether the viscometer was left open during the calibrations or whether it was sealed. If it was sealed, the vapor buoyancy of chloroform has to be accounted for in the calibration. Using the chloroform saturation tables of Altunin *et al.* [39], a maximum contribution of ±0.4% is obtained for the remaining experimental uncertainty at 334.41 K. Figure 7b shows that the vapor buoyancy-corrected data of Kumagai and Takahashi agree with those of Okubo *et al.* within the quoted uncertainty of the latter. In other words, the vapor buoyancy effect contributes 14% to the measured viscosity at 1000 kg · m^{-3} (343.15 K). Considering the 33% deviation of the result of Shankland *et al.* at the same temperature suggests that the radial acceleration in the coiled capillary of the latter study contributes an additional 19% to the measured viscosity. This is examined in the final section of this paper.

A different type of sealed gravitational capillary viscometer with a straight vertical tube was developed by the group of Zhu at Tsinghua University, Beijing. Recall from the preceding section that Sun *et al.* [37] used this instrument for measurements on R32. The first measurements with this instrument, however, were reported by Han *et al.* [40] for R134a in the range $233.15\ \mathrm{K} \leqslant T \leqslant 333.15\ \mathrm{K}$. In that paper the vapor buoyancy was not mentioned. The deviations of the R134a results in Fig. 7b suggest a lower precision, but the results agree with the previously discussed original data of Kumagai and Takahashi. The data of Han *et al.* were corrected here for vapor buoyancy as described above. Since the authors calibrated their instrument with water at 313.15 K and acetone at 303.15 K, the remaining uncertainty of the correction due to the vapor buoyancy of the calibration liquids is, at most, ±0.2% for acetone using the tables of

Vargaftik *et al.* [41]. The deviations of the corrected data of Han *et al.* from the correlation are also plotted in Fig. 7b. As with the data of Kumagai and Takahashi, application of the vapor buoyancy correction to the published values of Han *et al.* removes their systematic deviations and reconciles them with the correlation within the combined uncertainty.

Up to this point it could be shown that neglect of the vapor buoyancy effect in sealed gravitational capillary viscometers is one reason for the large deviations between the literature viscosity data for the hydrofluorocarbons, R32 and R134a. The results from such instruments with straight vertical tubes agree within their individual (not mutually combined) experimental uncertainty when this correction is applied properly. The remaining data sets which deviate outside of these margins were measured in sealed gravitational viscometers with *coiled* capillaries. These measurements are compared with those in straight vertical capillaries in the next section.

4. RADIAL ACCELERATION CORRECTION

Fluid flow in curved tubes of circular cross section was first studied analytically by Dean [42, 43]. His work motivated the subsequent extensive experiments of White [44]. In curved or coiled tubes, the flow resistance is increased by the radial acceleration which eventually induces secondary flow patterns. These are similar to Taylor vortices between concentric cylinders, one of which is rotating, or Görtler vortices, which occur along concave streamlines [45]. McConalogue and Srivastava [46] extended Dean's solution to flow rates where such vortices occur, and Bottaro [47] reviewed more recent experimental studies and computer simulations of that flow regime. As a result of his measurements, White proposed a correction which relates the increased friction in curved-pipe flow to the friction in straight-pipe flow. For the purpose of correcting viscosity measurements in coiled capillaries, this is written as

$$\eta_{\text{corrected}} = f(De)\,\eta_{\text{coiled}} \tag{8}$$

where $f(De)$ is White's empirical correction function,

$$f = 1 - \left[1 - \left(\frac{11.6}{De}\right)^{0.45}\right]^{1/0.45} \tag{9}$$

in terms of the Dean number

$$De = Re\sqrt{\frac{d}{D}} \tag{10}$$

As before, d denotes the internal diameter of the circular-tube cross section, and D denotes the diameter of the center line of the coiled tube. White concluded that Eq. (9) should be applied for Dean numbers $De \geqslant 11.6$. Despite further experimental and theoretical studies pursuant to that of White [48], this form of the radial acceleration correction remained unchanged. Dawe [49] summarized his extensive dilute gas measurements on helium, nitrogen, argon, krypton, and xenon in a brief paper in 1973 and concluded that the radial acceleration correction should be applied for $De \geqslant 6$. In the most recent review of capillary viscometry, instruments with coiled tubes and the radial acceleration correction are not mentioned [1].

White's expression of the radial acceleration correction, Eq. (9), was applied by Ripple and Matar [10]. Kumagai and Takahashi [38] applied it also to measurements in their coiled capillary viscometer. It should have been applied by Phillips and Murphy [6] and by Shankland *et al.* [9], who both used the same coiled capillary viscometer, although 18 years apart. This viscometer had a large internal diameter of the capillary tube (0.7 mm), so that the measurements were conducted at considerably higher flow rates than in other instruments. For example, the coiled-capillary viscometer of Ripple and Matar has an internal diameter of 0.508 mm. The straight-capillary viscometer used for the present measurements has an internal capillary diameter of 0.236 mm.

The following procedure was applied with the NIST data for four liquid hydrofluorocarbons to test White's correction. The ratios $\eta_{\text{coiled}}/\eta_{\text{straight}}$ and the corresponding Dean numbers were calculated for all experimental data obtained in coiled-capillary viscometers to examine the influence of the radial acceleration correction. The correction was reversed for the puplished experimental results for R32, R125, and R134a of Ripple and Matar [10] to obtain the uncorrected viscosity. Dean numbers were calculated via Eqs. (6) and (10) from the original rate-of-fall measurements. The viscosities η_{straight} were evaluated for R32 and R134a from temperature correlations of the present straight-capillary data and of the straight-capillary R125 data of Ripple and Defibaugh [12]. The results for R227ea were measured previously [13].

The results are plotted and compared with White's correction, Eq. (9), in Fig. 8. The ratios $\eta_{\text{coiled}}/\eta_{\text{straight}}$ for R32, R125, and R134a are consistent. The R134a data cover Dean numbers from 5 to 15, while the Dean numbers for the R32 and R125 data range from 9 to 22 because of the lower viscosity of these fluids. At $De = 5$ the data indicate a residual ratio of 1.02 instead of approaching the limiting case $\eta_{\text{coiled}}/\eta_{\text{straight}} = 1$ for $De \rightarrow 0$. This 2% offset may be due to the different samples which were used in the measurements of Ripple and Matar and in the present work. Figure 8 also shows an upturn in the ratio data at $De \sim 10$ reaching a maximum of about

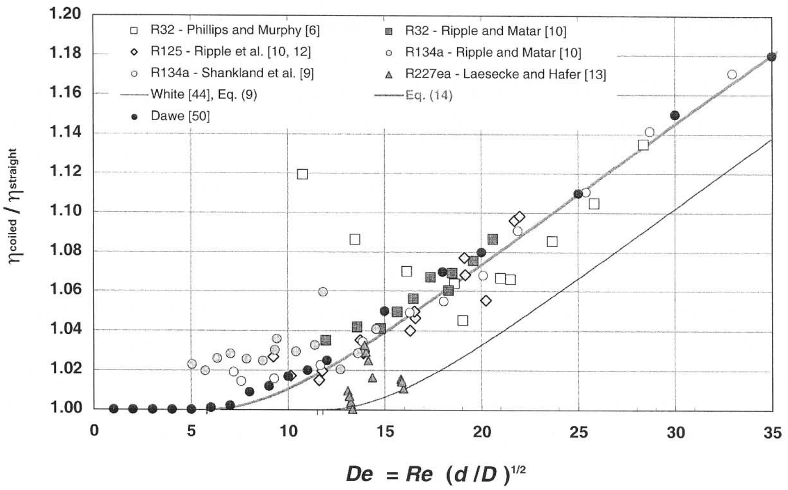

Fig. 8. Intercomparison of measurements with coiled-and straight-capillary viscometers in terms of the radial acceleration correction for curved-pipe flow.

1.10 at $De = 22$ for R125. This means that the flow resistance in the coiled-capillary viscometer was 10% higher than in the straight-vertical-capillary viscometer due to the radial acceleration. A comparison between this experimental value and the empirical correction of White reveals that the latter yields only a ratio of 1.05. In fact, the correlation seems systematically lower than the experimental data. A shift of White's correlation by a constant of six to lower Dean numbers gives a better agreement with the data. Among the three ratios $\eta_{\text{coiled}}/\eta_{\text{straight}}$ which were obtained for R227ea, only those at $De \sim 14$ appear consistent with the data for the other hydrofluorocarbons.

Testing the R32 data of Phillips and Murphy [6] and the R134a data of Shankland *et al.* [9] was not as straightforward because the vapor buoyancy correction had to be applied to obtain η_{coiled}. Since this correction and the radial acceleration correction are both multiplicative, they can be commutatively applied to the Poiseuille term in the viscometer working equation [Eq. (1)]. This was the only term used by Shankland *et al.*, while Phillips and Murphy also included the kinetic energy correction. It was not possible to separate this term in the following analysis because the respective calibration constant C_2 was not reported by Phillips and Murphy. Saturated liquid and vapor densities were calculated for the vapor buoyancy correction with NIST Standard Reference Database 23 (REFPROP) at the experimental temperatures of the R32 data of Phillips and Murphy and the R134a data of Shankland *et al.* The liquid densities reported by Phillips and

Murphy are 7.5 to 39% higher than the values calculated from REFPROP. This is one reason why these data deviate so drastically from others. The saturated liquid densities reported by Shankland *et al.* deviate only 0.1% from the recalculated values. Vapor buoyancy-corrected viscosities η_{coiled} were calculated via

$$\eta_{\text{coiled}} = \frac{\eta_{\text{lit}}}{\rho_{\text{lit}}} (\rho_{\text{l}} - \rho_{\text{v}})_{\text{REFPROP}} \tag{11}$$

where the subscript "lit" demotes the published data in the original papers. To obtain the ratios $\eta_{\text{coiled}}/\eta_{\text{straight}}$, viscosities at corresponding temperatures were calculated from fits of the present data reported in Tables III and IV. Kinematic viscosities reflecting only the gravitational flow in the capillary and the radial acceleration were obtained according to

$$\nu_{\text{vb}} = \frac{\eta_{\text{coiled}}}{\rho_{\text{lit}}} \tag{12}$$

They represent volumetric flow rates and are needed to calculate the Reynolds numbers at which the experiments were carried out:

$$\text{Re} = \frac{ghd^3}{32\pi nD\nu_{\text{vb}}^2} \tag{13}$$

The Reynolds numbers could not be evaluated directly from the information in the papers of Phillips and Murphy and of Shankland *et al.* because the coil diameter D and the number of coils of the capillary tube n were not reported. The driving pressure head was given in both papers as $h = 0.1$ m, and the instrument drawings show two coils of the capillary tube. Therefore, $n = 2$ was assumed in the analysis. The unknown coil diameter D in the Reynolds number, Eq. (13), and in the Dean number, Eq. (10), was varied simultaneously for both data sets. Results for a coil diameter of 0.195 m are shown in Fig. 8. This coil diameter appears to be in proportion with the other dimensions of the instrument drawings in the papers of Phillips and Murphy and of Shankland *et al.* With the exception of two points of Phillips and Murphy at $De = 10.4$ and 13, both data sets agree with the corresponding ratios of the NIST data within $\pm 2.5\%$ or less. Good agreement is also achieved with the shifted correlation of White for the radial acceleration correction,

$$f = 1 - \left[1 - \left(\frac{11.6}{De + 6}\right)^{0.45}\right]^{1/0.45} \tag{14}$$

applied for Dean numbers $De \geqslant 5$. Especially well represented are the ratios deduced from the R134a data of Shankland *et al.* This agreement is noteworthy because the coil diameter D affects only the horizontal shift of the ratios $\eta_{\text{coiled}}/\eta_{\text{straight}}$, and not their absolute value. This means that the data cannot be reconciled with White's original correction. The agreement between the ratios from the data of Shankland *et al.* and the shifted correction of White is consistent, while the ratios from Phillips and Murphy's data appear to be systematically lower. This is due to the fact that Shankland *et al.* used far more accurate densities in their analysis and because they employed only the Poiseuille term as the viscometer working equation. Consequently, the present analysis reveals the radial acceleration effect in the data of Shankland *et al.* with fewer uncertainties than in those of Phillips and Murphy, who also used the kinetic energy correction. Focusing on the ratios of Shankland *et al.* in the variation of the coil diameter D, its sensitivity can be assessed within rather narrow bounds. Based on variations of this parameter, it is estimated that the capillary coil in the viscometer of Phillips and Murphy and of Shankland *et al.* had a diameter of (0.195 ± 0.01) m. The narrow sensitivity lends further support to the modified radial acceleration correction, Eq. (14).

Of final interest is the magnitude of the radial acceleration as shown in Fig. 8. Shankland *et al.* conducted their R134a measurements up to 343.3 K, where the lowest viscosity occurred and, in turn, the highest flow rate. The coordinates of this point in Fig. 8 are a Dean number of 33 and a ratio $\eta_{\text{coiled}}/\eta_{\text{straight}} = 1.171$. Thus, the radial acceleration in the coiled capillary resulted in a 17% higher flow resistance of the fluid compared with the flow in a straight vertical tube under the same conditions. Recalling from the previous section and from Fig. 7b that the vapor buoyancy correction at this temperature accounts for about 14%, the total of both corrections is 31%. If corrected by this amount, the measurement by Shankland *et al.* agrees with the present result within the estimated uncertainty of this study. The same agreement is achieved when Eq. (14) is applied to all vapor buoyancy-corrected data of Shankland *et al.*, whereas a difference of about 5% would remain with White's original correlation, Eq. (9). These findings corroborate Eq. (14) further.

The liquid data of this work cover a similar range of Dean numbers as the gas measurements of Dawe [49]. It would be interesting to compare the results of the two studies to see if they agree. In his brief paper, Dawe [49] mentioned only that the radial acceleration correction should be applied for $De \geqslant 6$ rather than $De \geqslant 11.6$. He presented a graph similar to Fig. 8 but did not comment on other modifications of the correlation of White, Eq. (9). In order to find more detailed information, the original Ph.D. thesis of Dawe [50] was consulted. However, it was obtained only after the present work had progressed up to this point. It turned out that Dawe determined ratios $\eta_{\text{coiled}}/\eta_{\text{straight}}$ for numerous experimental data and derived from them curved-pipe flow correction factors in the range $1 \leqslant De \leqslant 60$ which are tabulated in the thesis. These values are included in Fig. 8. They agree very well with the modified White correlation, Eq. (14), as proposed in this work. Slight refinements of Eq. (14) still appear to be necessary because the largest deviation from Dawe's tabulated data is 1.2% at $De = 60$. Other than that, the deviations remain within −0.8%, which occurs at $De = 18$. Further investigations are necessary to reduce these uncertainties in the radial acceleration correction. Nevertheless, the proposed correlation, Eq. (14), constitutes substantial improvement over the previously used correlation, Eq. (9), of White [44].

5. CONCLUSIONS

New viscosity data are reported for saturated liquid ammonia, difluoromethane (R32), and 1,1,1,1-tetrafluoroethane (R134a). They were measured in a sealed gravitational viscometer with a straight vertical capillary. The uncertainty of the results is 3% for ammonia and ±(2 to 2.4)% for the hydrofluorocarbons. These estimates are derived by comparing the present viscometer, which is designed for volatile liquids, with the widely used and commercially available open capillary viscometers. Surface tension effects in the rectangular upper reservoir of the present viscometer contribute significantly to the uncertainty of the measurements. This warrants further analysis. These effects could be reduced by changing the shape of the upper reservoir to a circular cross section.

The ammonia results agree within combined uncertainty with the recent correlation of Fenghour *et al.* [30], although they are systematically lower. There is a great need for new viscosity measurements of ammonia because the existing data scatter widely and do not cover wide ranges. Ammonia is industrially important as 1 of the top 10 most produced chemicals. Since it is one of the most important polar fluids next to water, an accurate knowledge of its properties is key for the development of improved thermophysical models.

R32 and R134a were measured with the intent to clarify some of the large discrepancies among the literature data for these alternative refrigerants. The present results agree within their estimated uncertainty with data which were measured in rolling-ball and constant-flow rate capillary viscometers. Several other literature data were also measured in sealed gravitational capillary viscometers, but the vapor buoyancy effect was neglected in their analysis. It is demonstrated that deviations from the present data of up to 14% can be reconciled by properly accounting for the vapor buoyancy in sealed gravitational capillary viscometers.

The fact that the vapor buoyancy was systematically ignored by several researchers is indicative of the expansion of viscometry to a new application domain which is insufficiently understood. In the past, viscometry was limited to the predominant use of open instruments for nonvolatile liquids, while the recent search for alternative refrigerants required fast measurements of a new class of volatile fluids. Thus, sealed instruments were employed, but the working equations were obtained from handbooks, reviews, or other sources which pertained to open instruments. Consequently, there is a need to expand national and international standards (ASTM, DIN, ISO) for gravitational capillary viscometers to include sealed instruments. The temperature dependence of the viscosity of many volatile fluids and mixtures, in particular, has not been measured either because open capillary viscometers are unsuitable or because the instrumentation and operation of constant-flow rate viscometers are too complex. Expanded standards should promote measurements with sealed gravitational capillary viscometers to fill these data gaps.

Standard reference materials are important parts of any standardization. It is inadequate to calibrate sealed gravitational viscometers with nonvolatile liquids for subsequent measurements of volatile liquids. Hence, the standardization of sealed gravitational capillary viscometers involves the selection of volatile compounds as calibration fluids for such instruments. Normal pentane was proposed as a suitable calibration liquid in our previous work [13]. The properties of R134a are actually better known than those of *n*-pentane so that this hydrofluorocarbon also appears as a possible calibration liquid for measurements of volatile compounds. Other compounds with suitable thermophysical properties seem to be R143a (1,1,1-trifluoroethane) and sulfur hexafluoride (SF_6). They exhibit a high chemical stability, which is an important prerequisite for standard reference materials.

A major part of this study concerned the influence of radial acceleration on fluid flow in curved or coiled pipes. The correction of White [44] was compared with experimental viscosity data for four hydrofluorocarbons measured in similar NIST instruments with coiled and straight vertical capillaries. An improved correction is proposed which represents the radial acceleration effect within 1.2% for Dean numbers $De \leqslant 60$, while the correction of White is 5% lower. The modification was corroborated by an analysis of previous measurements of R32 and R134a in viscometers with coiled capillaries [6, 9] whose deviations could be reconciled in comparison with the experimental data of this work. An independent confirmation of the improved radial acceleration correction was found in the work of Dawe [49, 50]. The improved correction is applicable to many fluid dynamic problems involving curved-pipe flow such as chromatography, heat exchanger design, and blood flow in the cardiovascular system [51].

Perhaps the, most important result of this investigation is the reconciliation of systematic discrepancies that exist between the viscosity measurements of alternative refrigerants from different laboratories. This reconciliation is not limited to the fluids which were considered here, namely, R32 and R134a. It applies also to literature data for other refrigerants. It has been shown that these discrepancies resulted from incomplete metrology rather than from sample impurities. This should be kept in mind when the performance of other types of viscometers is assessed.

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NOTES ADDED TO PROOFS

The data of Tables II–IV are available in electronic format via anonymous FTP from host `FTP.Boulder.NIST.Gov` in directory /pub/`fluids/NIST_Data/Viscosity/Capillary`.

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