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Measurements of the Viscosity of New Refrigerants in the Temperature Range 270–340 K at Pressures up to 20 MPa[1]

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A recently modified vibrating-wire instrument was employed to measure the liquid viscosity of a wide selection of new refrigerants under pressure. Calibration of the viscometer with water over the range of measurements confirmed that the estimated uncertainty of the measurements is 0.5%, while the precision is 0.3%. With this instrument, the viscosity of chlorofluorocarbons (CFC's) and alternative refrigerants, R11, R12, R22, R32, R124, R125, R134a, R141b, and R152a, was measured over the temperature range from 270 to 340 K, from just above the saturation pressure up to 20 MPa. The experimental data, represented by polynomial functions of temperature and pressure, are used in a comparative examination of other recently reported experimental measurements of the viscosity of all these refrigerants, to investigate the uncertainty with which the viscosity is known.

KEY WORDS: high pressure; refrigerants; vibrating wire; viscosity.

1. INTRODUCTION

The introduction of new refrigerant fluids to reduce the harmful effects of chlorofluorocarbons in the upper atmosphere has prompted a worldwide program of measurements of the properties of such fluids. There have been a number of reports on the measurements of the viscosity of the new refrigerants, but as was clearly demonstrated at the 3rd Workshop on Alternative Refrigerants of the 13th European Conference on Thermophysical Properties in 1993 in Lisbon, there are discrepancies between the results of various authors that, in some extreme cases, exceed the estimated

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uncertainties by up to two orders of magnitude. This is attributed mostly to three factors: (a) impurities in the samples, (b) electrolytic effects in the instruments, and (c) the incapability of some instruments to be calibrated with water over the range of measurements.

For the last 3 years we have undertaken a program of research aiming to measure, as accurately as possible, the viscosity of the refrigerants R11, R12, R22, R32, R124, R125, R134a, R141b, and R152a. These measurements were employed in this paper, as a consistent baseline, to investigate in a comparative way the large discrepancies in the viscosity measurements reported in the literature.

2. MEASUREMENTS

2.1. The Viscometer

The vibrating-wire viscometer employed in the present measurements has been described in detail elsewhere [1-3]. It should, however, be pointed out that the entire instrument (including the electrical leads) was made out of stainless steel with the exception of the vibrating wire itself and the inner weight [1], which are made out of tungsten. Furthermore, all electrical connections were made by spot-welding. All these precautions were found to be necessary to eliminate the electrolytic effects present in the earlier version of the instrument. It was found [1, 3], during initial trials with water in the earlier version, that electrolytic action in the system caused particles of metal to be deposited preferentially on the tungsten wire. Typically, the particles found had a diameter of up to 20 μm, as revealed by scanning electron microscopy; energy-dispersive spectroscopy confirmed that they arose from the solders employed in the assembly of the previous instrument. The deposition of the particles, of course, had a very significant effect upon the damping characteristics of the wire, so that apparent higher time-dependent viscosities were observed as the extent of deposition increased [1].

Following the introduction of the assembly described, it was found that the reproducibility of the viscosity of water measurements under repeated cycling of temperature and pressure was one of ±0.1% over several weeks and was therefore approximately equal to the precision of measurements. Indeed, even if the vibrating-wire sample was exchanged with another sample from the same roll, the reproducibility remained of the same order. This is taken to be conclusive evidence that the wire remained uncontaminated during the measurements.

The liquid refrigerant's purity was also checked before and after the measurements. A stainless-steel microfilter in the inlet of the viscometer ensured that no solid particles from the sample bottles could enter. The R134a sample was from a high-purity sample that was specially prepared and circulated to selected laboratories [3] for comparison purposes.

Finally, the working equations [1] of the viscometer demonstrate that absolute measurements of the viscosity of a fluid require a knowledge of the wire radius and the density of the wire material. Because these two quantities are inaccessible to sufficiently accurate direct measurement for the small sample of wire employed (100-μm diameter, 5-cm length), it was preferable to perform relative measurements in which these quantities were determined [1] from standard reference values for the viscosity of water. The measurement of the viscosity of water performed at a pressure of 0.1 MPa and a temperature of 293.15 K, for which an accurate reference value is available [4], confirmed the values obtained for these two quantities. Furthermore, following this calibration, the viscosity of water was measured over the whole range of interest (down to 280 K) and was compared with the values recommended by the IAPS [5]. Taking all the aforementioned results into consideration, the uncertainty of the present measurements is believed to be $\pm 0.5\%$. As a further check of the continuing good operation of the instrument, after the completion of the viscosity measurements of each liquid, repeated runs over the whole range were retaken and the viscosity of water was measured before and after every refrigerant.

Hence, in relation to the three possible causes of discrepancies among the various investigators, it can be emphasized that the present viscometer has been calibrated with water, no electrolytic effects are present during measurements, and the purity of all samples was checked.

2.2. Fluids

The nominal purity and the supplier of the refrigerants considered are as follows: R11, R12, R22 (99.95%; SICNG Chemical Industries of Northern Greece S.A.), R32 (99.98%; ICI Chemicals and Polymers Ltd.), R124 (99.95%; Du Pont de Nemours International S.A.), R125 (99.95%; Du Pont de Nemours International S.A.), R134a (99.91%; ICI Chemicals and Polymers Ltd.), R141b (99.9%; Elf Atochem S.A.), and R152a (99.9%; Du Pont de Nemours International S.A.). Gas chromatography analysis was employed to check the purity before and after the measurements.

3. RESULTS

The measurements of the viscosity of the nine refrigerants were performed along four isotherms, 273.15, 293.15, 313.15, and 333.15 K (except

R32 and R125, which were restricted to 313.15 K), from saturation pressure up to 20 MPa. About eight measurements of the viscosity were obtained for each isotherm. The measurements themselves are reported elsewhere (R134a and R32 [3]; R11, R12, R141b, and R152a [6]; R22, R124, and R125 [7]). All measurements of the viscosity, η, of each refrigerant, have been correlated as a function of the reduced temperature, T_r ($=T/T_c$, where T_c is the critical temperature), and reduced pressure, P_r ($=P/P_c$, where P_c is the critical pressure), for the purpose of interpolation only, by an equation of the form

$$\eta = \sum_{i=0}^{2} \sum_{j=0}^{3} C_{ij} P_r^i T_r^j \tag{1}$$

The values of all constants and the critical parameters used are shown in Table I. In the same table the maximum deviation and the standard deviation of each fit are also shown. It can be seen that the maximum deviation of all measurements from the fitted equations is 0.16%, while the worst standard deviation is 0.07%. In Table II the viscosity, η_s, calculated from Eq. (1), and the corresponding density, ρ_s, at the saturation pressure, P_s, for four temperatures are shown. Values employed for the saturation density and pressure are discussed in detail elsewhere [3, 6, 7].

The present measurements and Eq. (1) can be used as a consistent baseline to allow a comparative examination of previous measurements reported in the literature. Such a baseline has the advantage that deviations between instruments in various laboratories, for the nine refrigerants, can be seen. The scatter of experimental viscosity data reported in the literature extends in some cases up to 25%. It was hence preferred to examine measurements performed the last 4 years where the scatter is no more than ±10%.

In Figs. 1–3 the deviations of other investigators' experimental values of the viscosity of the nine refrigerants at saturation from the values calculated by Eq. (1) are shown. Note that our own measurements are, in essence, represented by the baseline itself, since the maximum deviation of all our points from the baseline is 0.15% (see Table I). In some cases, where measurements near saturation were reported, these were converted to saturation values. This correction never ammounted more than 0.5%.

The measurements of Oliveira and Wakeham [8, 9] and van der Gulik [10] were all performed in a calibrated vibrating-wire instrument, with quoted uncertainties of ±0.6 and ±1.1%, respectively. Although for R134a the measurements of Oliveira and Wakeham agree fully with the present values, in the case of R32 and R125 the measurements deviate by about 2.5 and 5%, respectively, from the present values. This quite alarming

Table I. Coefficients and Critical Constants of Eq. (1)

	R11	R12	R22	R32	R124	R125	R134a	R141b	R152a
C_{00} (μPa · s)	10148.6	3162.34	1136.26	953.43	7339.90	1730.45	4084.68	12673.8	2817.96
C_{01} (μPa · s)	−37890.8	−8729.07	−1720.76	−1446.38	−23181.8	−2838.64	−11376.4	−49402.6	−7662.37
C_{02} (μPa · s)	49761.7	8717.06	631.85	539.67	25690.6	1165.34	11408.0	67183.0	7401.25
C_{03} (μPa · s)	−22489.2	−3102.53	0	0	−9829.60	0	−4078.83	−31283.9	−2504.58
C_{10} (μPa · s)	160.22	119.18	327.56	246.20	140.01	213.31	266.99	205.64	125.52
C_{11} (μPa · s)	−389.49	−280.89	−805.02	−595.08	−319.52	−482.26	−635.66	−529.35	−302.45
C_{12} (μPa · s)	261.29	188.02	514.28	375.96	205.83	296.92	401.22	366.56	199.69
C_{13} (μPa · s)	0	0	0	0	0	0	0	0	0
C_{20} (μPa · s)	0	−16.25	−81.57	−65.63	−3.79	−29.92	−30.40	0	−16.82
C_{21} (μPa · s)	0	44.01	204.99	160.73	12.38	73.01	78.44	0	46.49
C_{22} (μPa · s)	0	−30.44	−129.28	−99.17	−10.21	−45.49	−51.20	0	−32.46
C_{23} (μPa · s)	0	0	0	0	0	0	0	0	0
P_c (MPa)	4.403	4.129	4.99	5.793	3.66	3.631	4.064	4.230	4.517
T_c (K)	471.15	384.981	369.30	351.36	395.40	229.4	374.18	477.26	386.41
Max. dev. (%)	0.11	0.11	0.12	0.07	0.11	0.16	0.15	0.08	0.12
σ (%)	±0.03	±0.03	±0.05	±0.03	±0.04	±0.07	±0.06	±0.04	±0.05

Table II. Viscosity, η_s, Pressure, P_s, and Density, ρ_s, at Four Temperatures at Saturation

	R11	R12	R22	R32	R124	R125	R134a	R141b	R152a
				273.15 K					
P_s (MPa)	0.040	0.311	0.498	0.813	0.163	0.671	0.294	0.028	0.264
ρ_s ($\mathrm{kg \cdot m^{-3}}$)	1533	1396	1281	1056	1436	1320	1295	1280	959
η_s ($\mu\mathrm{Pa \cdot s}$)	524.8	250.1	210.5	156.7	346.7	203.9	273.7	541.0	215.9
				293.15 K					
P_s (MPa)	0.089	0.570	0.910	1.475	0.327	1.206	0.572	0.065	0.512
ρ_s ($\mathrm{kg \cdot m^{-3}}$)	1487	1329	1210	936	1371	1219	1225	1243	912
η_s ($\mu\mathrm{Pa \cdot s}$)	420.7	202.0	170.8	125.2	270.6	154.0	214.7	426.6	172.3
				313.15 K					
P_s (MPa)	0.175	0.963	1.532	2.478	0.593	2.014	1.016	0.133	0.910
ρ_s ($\mathrm{kg \cdot m^{-3}}$)	1438	1254	1128	893	1301	1090	1147	1205	860
η_s ($\mu\mathrm{Pa \cdot s}$)	344.7	163.3	135.9	99.0	214.5	114.7	167.1	345.8	138.4
				333.15 K					
P_s (MPa)	0.314	1.526	2.425		0.996		1.680	0.246	1.502
ρ_s ($\mathrm{kg \cdot m^{-3}}$)	1387	1168	1030		1222		1053	1164	800
η_s ($\mu\mathrm{Pa \cdot s}$)	286.6	131.9	107.4		171.3		127.9	284.7	112.5

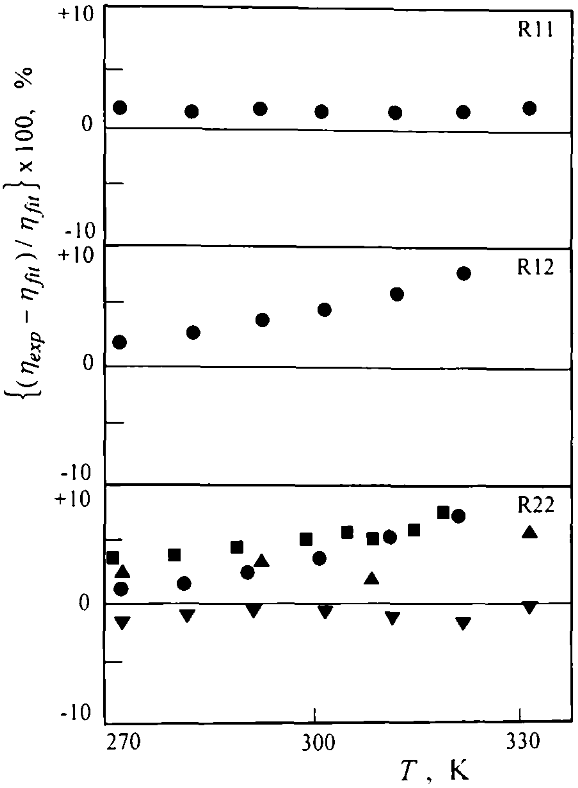

Fig. 1. Percentage deviations of the viscosity measurements of R11, R12, and R22 along the saturation line, from Eq. (1): (●) Kumagai and Takahashi [12]; (▼) Bivens et al. [15]; (■) Diller et al. [19]; (▲) Arnemann and Kruse [20].

difference is probably attributed to the fact that for those measurements some of the first samples ever produced were employed. Hence their purity is suspected. The measurements of the viscosity of R152a performed by van der Gulik [10] agree well with the present set.

Okubo et al. [11] employed a calibrated capillary viscometer for the measurement of the viscosity of R134a. This set of measurements, with a quoted uncertainty of 1.3%, agrees well with the present values.

A capillary viscometer calibrated with water and chloroform, with a quoted uncertainty of about 1%, was also employed by Kumagai and Takahashi [12, 13] for the measurement of the viscosity of R11, R12, R22, R134a, R152a [12], and R141b [13]. Although the measurements of R11, R141b, and R152a agree well with the present values, the measurements of

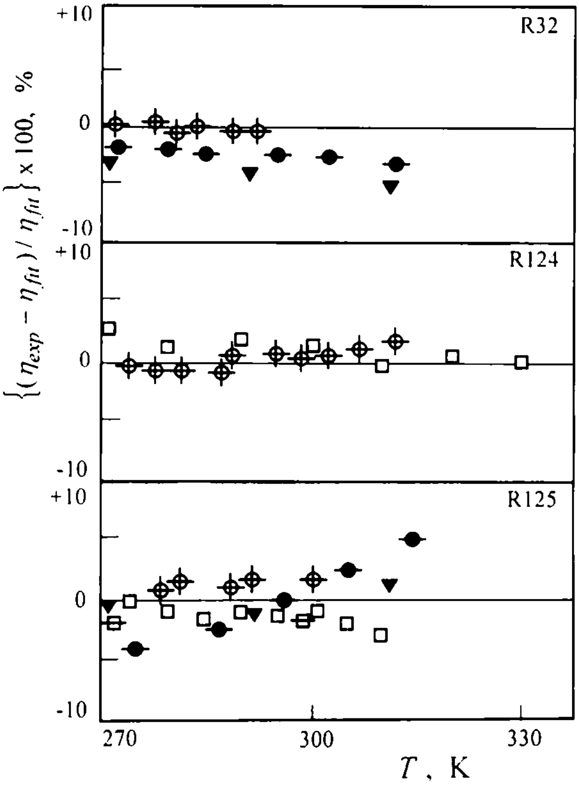

Fig. 2. Percentage deviations of the viscosity measurements of R32, R124, and R125 along the saturation line, from Eq. (1): (-●-) Oliveira and Wakeham [9]; (-⊕-) Ripple and Matar [14]; (▼) Bivens et al. [15]; (-⊟-) Wilson et al. [16]; (□) Diller and Peterson [18].

R12, R22, and R134a show a distinctively different temperature slope, with deviations rising up to 8%.

Finally, a calibrated capillary viscometer was also employed by Ripple and Matar [14] for measurements on R32, R124, R125, and R134a, by Bivens et al. [15] for R22, R32, R125, and R134a, and by Wilson et al. [16] for R125 (near saturation), with quoted uncertainties of ±4, ±1.2, and ±2%, respectively. All the measurements of Ripple and Matar [14] fully agree with the present values (maximum deviation about 2%). The measurements of Bivens et al. [15] also agree well with the present values, with the exception of the measurements of the viscosity of R32, where deviations rise to 5%. The measurements of Wilson et al. [16] agree well with the present values.

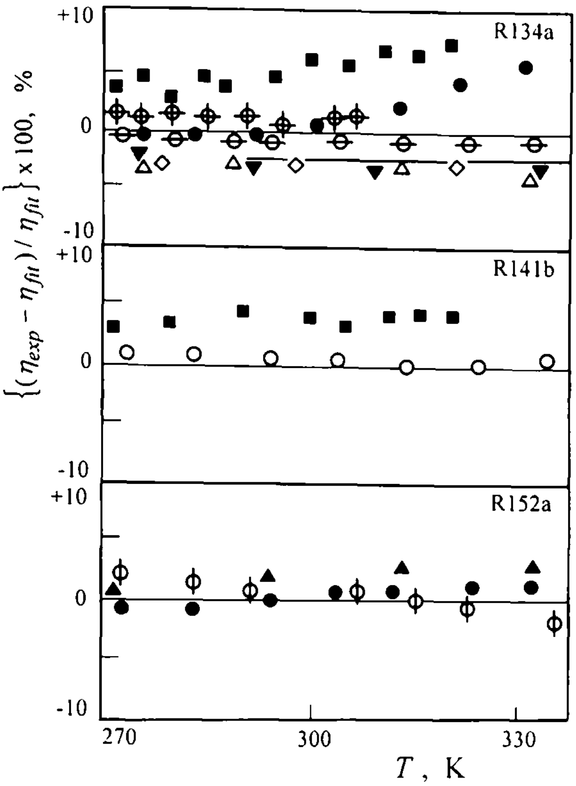

Fig. 3. Percentage deviations of the viscosity measurements of R134a, R141b, and R152a along the saturation line, from Eq. (1): (-⊖-) Oliveira and Wakeham [8]; (ϕ) van der Gulik [10]; (◇) Okubo et al. [11]; (●) Kumagai and Takahashi [12]; (○) Kumagai and Takahashi [13]; (-⊕-) Ripple and Matar [14]; (▼) Bivens et al. [15]; (■) Diller et al. [17]; (▲) Arnemann and Kruse [20]; (△) Arnemann [21]; (——) Krauss et al. [22].

A torsional-crystal viscometer, whose reproducibility was checked by means of ethane to be ±2%, was employed by Diller et al. [17–19] for measurements on R22, R124, R125, R134a, and R141b. Although the measurements of R124 and R125 agree very well with the present values, the measurements of R22, R134a, and R141b show a distinctively different temperature slope with deviations increasing to a maximum of 8%.

A falling-body viscometer calibrated with oils and water was employed by Arnemann and Kruse [20, 21] for the measurement of the viscosity of R22, R134a, and R152a. The uncertainty of the measurements is not quoted. These measurements deviate from the present values by up to 7% in the case of R22.

Krauss et al. [22] have recently published a correlation, with a quoted uncertainty of ±5%, for the viscosity of R134a based on a large collection of experimental data. In Fig. 3 it can be seen that this correlation agrees with the present values to 2.5%.

Only four of the aforementioned studies have performed measurements under pressure: those by Oliveira and Wakeham [8] on R134a, van der Gulik [10] on R152a, Okubo et al. [11] on R134a, and Diller et al. [17–19] on R22, R124, R125, R134a, and R141b. The comparison of these measurements with the present values follows the pattern discussed at saturation conditions.

4. CONCLUSION

The discussion of the comparison of the experimental values of the viscosity at saturation of other investigators with the present values as the baseline, in our opinion, shows clearly the following.

(a) Although the measurements considered were all performed during the last 4 years, the discrepancies among the various sets are much larger than the quoted uncertainties.

(b) Although the situation is improving, it still seems that the viscosity of these refrigerants is not known more accurately than ±5%.

(c) Very few measurements at higher pressures exist. More are required.

(d) To be able to know the viscosity in the liquid phase better, more accurate measurements for all these refrigerants are still required.

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