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Measurements of the Viscosity of R134a and R32 in the Temperature Range 270–340 K at Pressures up to 20 MPa

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This paper reports new measurements of the liquid viscosity of R134a and R32 in the temperature range 270 to 340 K and pressures up to 20 MPa. The measurements have been carried out in a vibrating-wire instrument calibrated with respect to the standard reference value of the viscosity of water. It is estimated that the uncertainty of the present viscosity data is one of 0.5%. The experimental data have been represented by polynomial functions of temperature and pressure for the purposes of interpolation.

KEY WORDS: high pressure; refrigerants; R134a; R32; vibrating-wire technique; viscosity.

1. INTRODUCTION

Among the fluids considered as substitutes for the environmentally harmful refrigerants, R134a (1,1,1,2-tetrafluoroethane) has been considered the most suitable for domestic refrigeration applications. Indeed R134a is already commercially available and its use is spreading fast. However, for other applications, several other fluids or their mixtures are considered more suitable, and among them R32 (difluoromethane) has been identified as a very promising one.

In the case of R134a, there have been some measurements of the viscosity. A recent collection and subsequent correlation of viscosity measurements published by Krauss et al. [1] in early 1993 showed discrepancies of 10 to 30%. Since then two more sets of viscosity

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measurements [2, 3] appeared in the literature. Moreover, the lack of accurate transport property data for R134a prompted an international collaborative venture of measurements. Hence, ICI Chemicals and Polymers Ltd., upon request, prepared a certified specially pure sample and supplied, from this sample, eight laboratories to measure its properties. The people involved in this project are Professor William Wakeham (Imperial College, U.K.), Dr. Ian McLure (Sheffield University, U.K.), Dr. Rich Perkins (NIST, USA), Professor Akira Nagashima (Keio University, Japan), Professor Carlos Nieto de Castro (University of Lisbon, Portugal), Professor Johannes Straub (Technical University of Munich, Germany), Professor Eckhard Vogel (University of Rostock, Germany), and Professor Marc Assael (Aristotle University, Greece). In this way, the main problem of sample impurities or contamination is controlled. The measurements of the viscosity of R134a presented in this paper have been performed with the aforementioned sample.

In the case of R32, very few measurements of the viscosity at saturation exist and none to our knowledge, at higher pressures. Even along the saturation line experimental measurements show a 5% scatter, with one case rising to 20%.

The large discrepancies observed in the measurement of the viscosity of liquid refrigerants are attributed mostly to three main effects: impurities in the samples, electrolytic effects in the instruments, and incapability of some instruments to be calibrated with water. The measurements presented in this paper are believed, as is shown, to be free of all these effects.

2. EXPERIMENTS

The vibrating-wire viscometer employed for the present measurements has been described in detail elsewhere [4–6] and thus is presented only briefly here. It consists of a 100-μm-diameter straight tungsten wire, suspended from the top plate of a pressure vessel, and carrying tensioning weights on its lower end. Except for the wire itself and the inner weight [4, 5], which are made out of tungsten, all other components and electrical leads are made out of stainless steel, spot-welded together where necessary. This arrangement was found to be necessary to eliminate electrolytic effects [6] due to the dissimilar metals present in the earlier version of the instrument. The wire is set into transverse vibration electromagnetically and the subsequent motion of the wire within the liquid is observed by electromagnetic induction. The magnetic field is provided by two samarium–cobalt magnets, plated with an impervious gold layer to guard against chemical atack and linked by a yoke made of magnetic stainless steel. The decay of the transverse vibrations, which conform to a damped sinusoidal oscillation, is related to the viscosity and the density of the liquid by the working equation

$$\Delta = \frac{(\rho/\rho_w)k' + 2\Delta_0}{2[1 + (\rho/\rho_w)k]} \tag{1}$$

In this equation, Δ is the logarithmic decrement of the oscillation in the liquid, Δ_0 the logarithmic decrement in vacuo, ρ the fluid density, and ρ_w the density of the wire material. In addition, k and k' are quantities that depend [4] upon the viscosity of the fluid through the equations

$$k = -1 + 2\,\mathrm{Im}(A) \tag{2}$$

$$k' = 2\,\mathrm{Re}(A) + 2\Delta\,\mathrm{Im}(A) \tag{3}$$

where

$$A = (i - \Delta_0)\left\{1 + \frac{2K_0(s)}{sK_1(s)}\right\} \tag{4}$$

and

$$s = [(i - \Delta)\Omega]^{1/2} \tag{5}$$

$$\Omega = \rho\omega R^2/\eta \tag{6}$$

in which R is the radius of the vibrating wire and ω the frequency of the oscillation. K_0 and K_1 are modified Bessel functions [4].

From the above equations the viscosity η can be obtained as a function of the density from the measurements of the frequency of oscillation in the liquid and the decrement in the liquid and in vacuo provided the radius of the wire and its density are known. Since, however, these last two quantities cannot be measured with sufficient accuracy, they can be obtained by the measurement of the viscosity of liquids of known viscosity in the fashion described elsewhere [4]. The modifications described earlier allow the use of water as a calibrant. Hence, water whose viscosity is very accurately known was used for the calibration of the viscometer. Taking all parameters into account, the uncertainty of the instrument is thus estimated to be ±0.5% while the precision and the reproducibility of the measurements are about ±0.1%. The use of water in the instrument served also as a check that no electrolytic effects are taking place [6].

The sample of R134a, as mentioned before, was part of a specially prepared certified sample by ICI Chemicals and Polymers Ltd. The purity was 99.91% (R134, 850 ppm; R114, 36 ppm; R114a, 35 ppm; R124, 13 ppm; R1122, 3 ppm; and water, 6 ppm). The sample of R32 was also supplied by ICI Chemicals and Polymers Ltd. at a nominal purity of 99.98%. Chromatographic analysis before and after the measurements ensured that no contamination of the samples took place. Furthermore, the use of a stainless-steel 20-30-μm microfilter in the inlet of the instrument, ensured that no solid particles can enter.

3. RESULTS

The measurements of the viscosity of R134a were carried out along four isotherms, 273.15, 293.15, 313.15, and 333.15 K, from above saturation pressure up to 20 MPa. The density values employed in the calculation of the viscosity were obtained by an equation of state published by Tillner-Roth and Baehr in 1993 [7], based on their density measurements. The uncertainty quoted for the density values is 0.02% for the whole range of our measurements.

The measurements of the viscosity of R32 were carried out along three isotherms, 273.15, 293.15, and 313.15 K, from above saturation pressure up to 20 MPa. The density values employed in the calculation of the viscosity were obtained by an equation submitted by Defibaugh et al. [8] in 1993. This is based on their measurements, which extend up to 7 MPa. The uncertainty quoted for the density values is less than 0.02%. Furthermore, the extrapolated values of the proposed equation to 20 MPa agree within the mutual uncertainties with the older values of McLinden in 1990 [9] and of Malbrunot et al. in 1968 [10].

Tables I and II show the experimental measurements of the viscosity of R134a and R32. All measurements 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 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

$$\eta = \sum_{i=0}^{2} \sum_{j=0}^{3} C_{ij} P_R^i T_R^j \qquad (7)$$

The values of all constants are shown in Table III. In the same table the maximum deviation and the standard deviation of each fit are also shown. It can be seen that in the case of R134a the maximum deviation from the fit is 0.15% and the standard deviation is ±0.06%, while in the case of R32 the maximum deviation is 0.07% and the standard deviation is ±0.03%. It should also be pointed out that the above equation was employed to calculate the values at nominal temperatures shown in Tables I and II, together with the experimental values.

Table I. Measurements of the Viscosity of R134a

Pressure P (MPa)	Temperature T (K)	Viscosity $\eta(T, P)$ (μPa·s)	Density $\rho(T_{nom}, P)$ (kg·m^{-3})	Viscosity $\eta(T_{nom}, P)$ (μPa·s)
$T_{nom} = 273.15$ K				
0.95	273.151	276.2	1298	276.4
2.40	273.176	282.3	1303	282.3
3.70	273.197	287.5	1308	287.4
5.10	273.164	292.8	1313	292.9
6.35	273.245	297.1	1317	297.7
7.75	273.197	302.9	1321	302.9
8.70	273.194	306.2	1324	306.5
9.10	273.203	307.7	1326	307.9
$T_{nom} = 293.15$ K				
1.75	293.201	218.8	1232	219.1
3.80	293.208	226.4	1242	226.5
5.50	293.208	232.4	1250	232.5
7.20	293.208	238.2	1257	238.4
8.70	293.194	243.5	1264	243.5
10.80	293.194	250.1	1272	250.5
12.85	293.201	257.2	1279	257.1
14.30	293.176	261.5	1285	261.6
$T_{nom} = 313.15$ K				
3.60	313.155	176.8	1167	176.8
5.10	313.239	182.2	1176	182.2
6.70	313.187	187.6	1186	187.8
8.05	313.253	192.2	1194	192.4
9.70	313.219	197.8	1203	197.8
11.35	313.230	202.6	1211	203.0
12.70	313.219	206.8	1218	207.2
14.60	313.198	212.7	1227	212.7
$T_{nom} = 333.15$ K				
2.10	333.182	129.5	1059	129.8
4.20	333.184	138.9	1084	138.8
6.00	333.138	146.0	1102	145.9
8.00	333.260	153.1	1119	153.4
9.60	333.205	158.7	1131	158.9
11.20	333.212	164.0	1143	164.1
12.75	333.161	168.7	1153	168.8
14.30	333.173	173.2	1162	173.2

In Table IV, the viscosity at saturation conditions is shown for both refrigerants. These values have been obtained by the use of Eq. (7), while values for the saturation pressure, P_s, and saturation density, ρ_s, are obtained from the respective density references discussed previously.

In Fig. 1 the deviations of other investigators' experimental values of the viscosity of R134a at saturation, from the values calculated by Eq. (7) are shown. It is interesting to note that although all investigators considered measured the viscosity of R134a during the last 5 years, the

Table II. Measurements of the Viscosity of R32

Pressure P (MPa)	Temperature T (K)	Viscosity $\eta(T, P)$ (μPa · s)	Density $\rho(T_{\mathrm{nom}}, P)$ (kg · m^{-3})	Viscosity $\eta(T_{\mathrm{nom}}, P)$ (μPa · s)
		$T_{\mathrm{nom}} = 273.15$ K		
1.60	273.238	157.9	1058	158.1
2.75	273.142	160.2	1063	160.2
3.70	273.128	161.9	1066	161.2
4.65	273.135	163.5	1069	163.4
5.80	273.146	165.4	1073	165.4
6.70	273.139	166.9	1076	166.8
7.70	273.194	168.4	1079	168.4
8.80	273.286	169.9	1082	170.2
		$T_{\mathrm{nom}} = 293.15$ K		
2.10	292.738	127.0	987	126.4
2.70	293.203	127.5	988	127.5
3.00	293.242	128.1	990	128.1
4.90	293.148	131.5	1000	131.6
7.20	293.228	135.6	1010	135.7
9.00	293.226	138.6	1018	138.7
10.55	293.199	141.3	1024	141.3
12.20	293.187	143.8	1031	143.9
13.90	293.073	146.6	1038	146.5
15.55	293.102	149.1	1043	148.9
		$T_{\mathrm{nom}} = 313.15$ K		
3.70	313.130	101.8	905	101.8
5.50	313.205	105.7	920	105.7
7.25	313.168	109.3	933	109.3
8.50	313.203	111.8	941	111.8
10.30	313.169	115.0	952	115.1
11.80	313.214	117.6	960	117.7
13.65	313.217	120.6	970	120.7
15.45	313.125	123.5	979	123.4

Table III. Coefficients and Constants of Eq. (7)

Coefficients C_{ij} (μPa·s)	R134a	R32
C_{00}	4,084.68	953.43
C_{01}	−11,376.40	−1,446.38
C_{02}	11,408.00	539.67
C_{03}	−4,078.83	0
C_{10}	266.99	246.20
C_{11}	−635.66	−595.08
C_{12}	401.22	375.96
C_{13}	0	0
C_{20}	−30.40	−65.63
C_{21}	78.44	160.73
C_{22}	−51.20	−99.17
C_{23}	0	0
P_c (MPa)	4.064	5.793
T_c (K)	374.18	351.36
Max. dev. (%)	0.15	0.07
σ (%)	±0.06	±0.03

scattering on average is 10%, rising in an extreme case to 20%. The measurements of Oliveira and Wakeham [3] were performed in a similar vibrating-wire instrument calibrated using many hydrocarbons, with a quoted uncertainty of ±0.6%. This set of measurements agree very well with the present measurements. A calibrated capillary viscometer was

Table IV. The Viscosity of R134a and R32 at Saturation

Fluid	Temperature T_s (K)	Pressure P_s (MPa)	Density ρ_s (kg·m^{-3})	Viscosity $\eta(T_s, P_s)$ (μPa·s)
R134a	273.15	0.294	1295	273.7
	283.15	0.415	1261	242.6
	293.15	0.572	1225	214.7
	303.15	0.770	1188	189.7
	313.15	1.016	1147	167.1
	323.15	1.317	1102	146.6
	333.15	1.680	1053	127.9
R32	273.15	0.813	1056	156.7
	283.15	1.107	1020	140.4
	293.15	1.475	936	125.2
	303.15	1.927	940	111.4
	313.15	2.478	894	99.0

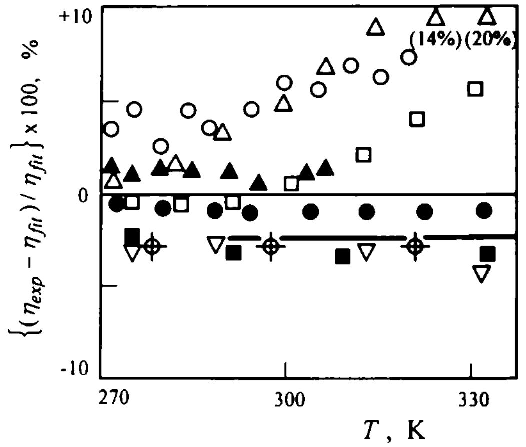

Fig. 1. Percentage deviations of the viscosity measurements of R134a along the saturation line, from Eq. (7). (—) Ref. 1; (▲) Ref. 2; (●) Ref. 3; (□) Ref. 11; (⊕) Ref. 12; (○) Ref. 13; (△) Ref. 14; (■) Ref. 15; (▽) Ref. 16.

employed for the measurements by Kumagai and Takahashi [11], Okubo et al. [12], and Ripple and Matar [2] with quoted uncertainties of ±0.5, ±1.3, and ±4%, respectively. The maximum deviations of these three sets of measurements from the values of Eq. (7) are 6, 3.5, and 2%, which except in the latter case exceed the mutual uncertainty of the instruments. The measurements of Diller et al. [13], performed in a torsional-crystal viscometer with a 2% reproducibility, show deviations of up to 8%. Higher up than all other measurements, the values of Shankland et al. [14] performed in an Ostwald viscometer, show a maximum deviation from the present set of 20%. Finally, the measurements of Geller [15] and Arnemann [16] show a maximum deviation of 4% approximately, from the values calculated by Eq. (7). In the same figure, values from the recently proposed correlation by Krauss et al. [1] are also included. The values of the correlation, quoted with a 5% uncertainty, agree very well with the present set of measurements.

In Fig. 2 the deviations of other investigators' experimental values of the viscosity of R32 at saturation, from the values calculated by Eq. (7) are shown. In the case of R32, to our knowledge, only four other sets of measurements of its viscosity at saturation conditions have been reported. The measurements of Oliveira and Wakeham [17] were performed in a similar vibrating-wire instrument calibrated using many hydrocarbons, with a quoted uncertainty of ±1%. Although in the case of R134a, an excellent agreement with the present measurements was noticed, for R32 an

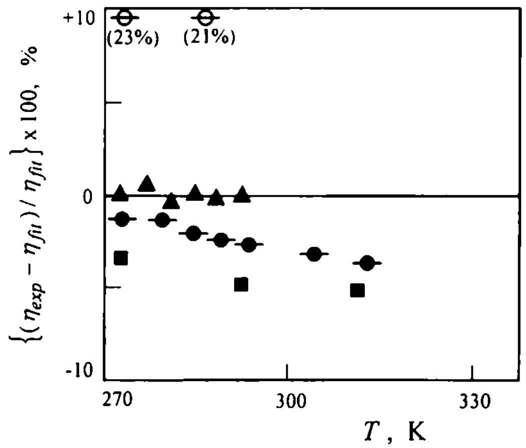

Fig. 2. Percentage deviations of the viscosity measurements of R32 along the saturation line, from Eq. (7). (▲) Ref. 2; (■) Ref. 15; (-●-) Ref. 17; (-⊖-) Ref. 18.

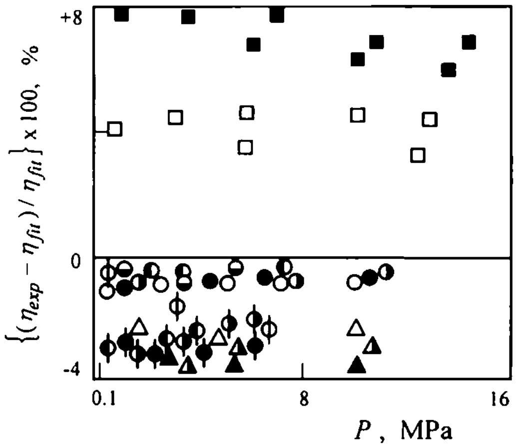

Fig. 3. Percentage deviations of the high-pressure viscosity measurements of R134a, from Eq. (7). Ref. 3: (○) 293.35 K; (●) 303.14 K; (◑) 313.15 K; (◐) 323.15 K; (◒) 333.15 K. Ref. 12: (△) 273 K; (▲) 298 K; (◭) 324 K. Ref. 13: (□) 270 K; (■) 330 K. Ref. 19: (ф) 277.38 K; (Ф) 302.27 K; (◑) 320.72 K; (◐) 339.98 K.

unexplainable maximum deviation of 4% from the present set is apparent. The measurements of Ripple and Matar [2] performed in a calibrated capillary viscometer with a quoted uncertainty of ±4%, as in the case of R134a, agree very well with the present measurements. The measurements of Geller [15] show a maximum deviation of 5.5%. Finally, the measurements of Phillips and Murphy [18], performed in 1970 with a Ubbelohde suspended level-type viscometer calibrated with diethyl ether, are clearly much higher than all other measurements, showing a maximum deviation of 23%, probably attributed to inaccurate calibration, unavailable accurate density values, and impurities in the sample.

In the case of high-pressure measurements, only four other sets have been reported for the viscosity of R134a, while none for R32. In Fig. 3 the deviations of the high-pressure measurements of the viscosity of R134a of other investigators from the values of Eq. (7) are shown as a function of pressure. The values of Oliveira and Wakeham [3], Okubo et al. [12], and Diller et al. [13] follow the analysis presented in the discussion of the saturation values. It is noteworthy that in the case of the measurements by Oliveira and Wakeham [3], the agreement is excellent, 1.3%, over the whole range. In the case of Okubo et al. [12] the pressure gradient agrees with that of the present set and a shift of only about 3% is noticed. The much higher deviations of Diller et al. [13], discussed already, rise to 8% in the case of the high-pressure measurements. Finally, the high-pressure values reported by Lavrenchenko et al. [19], performed in a capillary viscometer with an uncertainty of 2–3%, show a maximum deviation from the present set of 3.5%.

4. CONCLUSION

New measurements of the viscosity of R134a and R32 have been presented. The measurements were performed in a recently modified vibrating-wire instrument and cover a temperature range from 270 to 340 K at pressures up to 20 MPa. The overall uncertainty in the reported data is ±0.5%, an estimate confirmed by the measurement of the viscosity of water.

From the discussion of the results, it is apparent that more careful and more accurate work is still necessary. Although in the case of the viscosity measurements of R134a the general picture is getting better, for R32 much more work is required.

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