Measurements of the Viscosity of Refrigerants in the Vapor Phase[1]

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Measurements of the viscosity of refrigerants R124, R125, R134a, and R152a in the vapor phase are presented. The measurements, performed in a new vibrating-wire instrument, cover a temperature range from 273 to 333 K from about atmospheric pressure up to below the saturation pressure. The uncertainty of the reported values is estimated to be better than ±1 %. Comparison with measurements of other investigators reveals a lack of reliable data in the vapor region for these compounds.

KEY WORDS: refrigerants; R124; R125; R134a; R152a; vapor phase; vibrating-wire viscometer.

1. INTRODUCTION

Ever since the discovery of the destructive impact of chlorine on the ozone layer in the stratosphere, a world wide effort has been focused on the elimination of the sources that generate and release chlorine atoms. Being such a source, the old generation of refrigerants had to be replaced. The Montreal Protocol was the first step in the transition from CFCs to alternative environmentally acceptable refrigerants. Among the candidates, 1-chloro-1,2,2,2-tetrafluoroethane (R124) and pentafluoroethane (R125) are possible replacements for R114 and R502, respectively. 1,1,1,2-Tetrafluoroethane (R134a) is already employed as a replacement of R12, while 1,1-difluoroethane (R152a) is considered a potential substitute for R22. The properties of these new compounds are urgently needed, and viscosity is one of them. It is worthwhile to point out, however, that

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although there are a number of literature reports on the viscosity of these substances in the liquid phase, only a limited number refers to the vapor phase.

This paper describes a new vibrating-wire instrument developed to measure the viscosity of the above-mentioned four refrigerants in the vapor phase in the temperature range 273 to 333 K from around atmospheric pressure up to below the saturation pressure.

2. EXPERIMENTS

The gas-phase viscometer constructed operates according to the vibrating-wire technique. The basic characteristics of the instrument are similar to those of the liquid-phase apparatus [1] but the construction differs due to the much lower viscosity value of gases. The viscometer, shown in Fig. 1, consists of a tungsten wire with a diameter of 7.36 μm and a length of 102 mm. The upper end of the wire is kept in place by a chuck, insulated from the support plate by PTFE washers. A 1.5 g weight attached
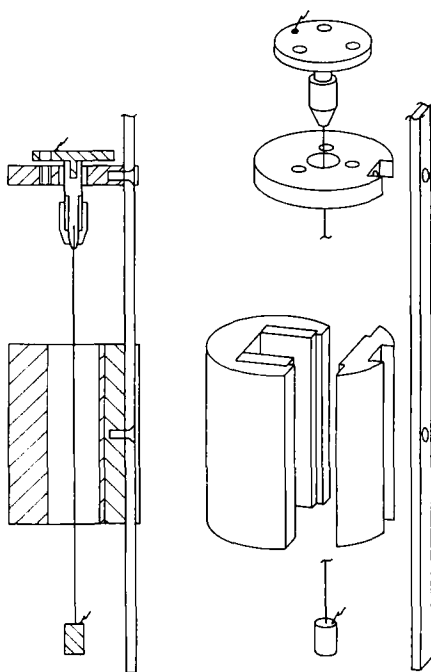

Fig. 1.   Schematic diagram of the vapor-phase
vibrating-wire viscometer.

to its lower end keeps the wire under constant tension in the vertical position. In contrast to the liquid-phase viscometer [1], no buoyancy-compensation mechanism is required for obvious reasons. Two samarium–cobalt magnets, placed in a magnetic-steel shell, provide the homogeneous magnetic field of 1 T, in which the wire vibrates. Electrical connections to the wire are made through the upper chuck and the bottom weight.

Similarly to the liquid-phase viscometer, a viscosity measurement consists of the initiation of a transverse vibration of the wire followed by observation of the decay of the subsequent motion. The oscillation is initiated by applying two consecutive DC pulses, of opposite sign to the wire. This was found to induce a symmetric oscillation of the wire. The voltage produced by the oscillation of the wire, about $110\,\mu V$, is amplified about 62,000 times to approach the level of 5–10 V that is easily detectable by the A/D converter. The frequency of sampling is 50 kHz, with a resolution of 1 part in 2×10^4. The observed voltages, V, are fitted as a function of time to an equation of the form

$$V = Ce^{-\varDelta\omega t} \sin(\omega t + \phi) \tag{1}$$

where $\varDelta$ and ω are the logarithmic decrement and the frequency of oscillation.

To perform the pressure measurements the viscometer is placed in a stainless-steel pressure vessel. Temperature stability is achieved by immersing the pressure vessel in a 110-liter ethylene–glycol bath. The bath temperature is regulated by a PID controller and registered by two calibrated platinum-resistance thermometers with an uncertainty of about ± 20 mK. The pressure is measured with a pressure transmitter with an uncertainty of ± 0.005 MPa.

2.1. Working Equations and Error Analysis

According to the vibrating-wire technique, the characteristic parameters of the oscillation, that is, the logarithmic decrement $\varDelta$ and the frequency of oscillation ω, are related to the viscosity by the following expressions [1]:

$$\varDelta = \frac{(\rho/\rho_s) k' + 2\varDelta_0}{2[1 + (\rho/\rho_s) k]} \tag{2}$$

where

$$k = -1 + 2\,\text{Im}(A) \qquad \text{and} \qquad k' = 2\,\text{Re}(A) + 2\,\text{Im}(A) \tag{3}$$

and

$$A = (i - \Delta) \left\{ 1 + \frac{2K_1(s)}{sK_0(s)} \right\} \quad \text{with} \quad s = [(i - \Delta)\, \Omega]^{1/2} \quad \text{and} \quad \Omega = \frac{\rho \omega R^2}{\eta}$$

(4)

In the above expressions, Δ_0 and ω_0 are the logarithmic decrement and the frequency of oscillation of the motion in vacuum, ρ and ρ_s are the density of the vapor and the wire, respectively, and K_0 and K_1 are the zero- and first-order modified Bessel functions.

With the sampling rates and resolution mentioned above, repeated measurements under nominal identical conditions confirmed the reproducibility and precision of the decrement Δ and the frequency ω to be better than ± 0.1 and $\pm 0.01\%$, respectively. The logarithmic decrement in vacuum Δ_0 was directly measured with the vibrating-wire viscometer and found to be equal to 0.00068 with a fluctuation of ± 0.00001 in its value, resulting in an error of no more than $\pm 0.04\%$ in the viscosity.

The uncertainty in the value of the wire density employed [2] is estimated to be $\pm 0.2\%$, which, in turn, introduced an error of $\pm 0.2\%$ in the viscosity calculations. To determine the diameter of the wire, scanning electron microscopy was employed. The photographs indicated a value of $7.36\,\mu m$ with an uncertainty of $\pm 0.3\%$. This uncertainty affected the viscosity by as much as $\pm 0.5\%$.

To conclude the analysis, the uncertainty involved in the measurement of the temperature, the pressure, and the value of the vapor density employed must be considered. The effect in the viscosity from the uncertainty in the measurement of the temperature is negligible, as an error of 20 mK produces an uncertainty in the viscosity of about 0.04%. The pressure was measured with an uncertainty of ± 0.005 MPa. This uncertainty enters the calculations through the density of the vapors, resulting in an uncertainty in the value of the viscosity of about $\pm 0.3\%$. This value, however, is increased at very low pressures. Finally, the vapor densities employed in this work are accurate to within $\pm 0.05\%$, which results in a maximum error of $\pm 0.02\%$ in viscosity.

In conclusion, it is believed that the uncertainty of the current measurements is about $\pm 1\%$, while the precision of these measurements is much better. To test this value as well as the reproducibility of the apparatus, the viscosity of argon was repeatedly measured. The results were compared with those produced by Kestin and Leidenfrost [3]. The deviations never exceeded $\pm 0.5\%$, while the reproducibility, checked over long periods of time, was always better than $\pm 0.3\%$.

The refrigerant samples of R124, R125, and R152a were supplied by Du Pont de Nemours International S.A. at purities (by weight) of better

than 99.95 % for the first two fluids and 99.9 % for R152a. The R134a sample was provided by ICI Chemicals & Polymers Ltd. with a purity of better than 99.9 %. All purity values were confirmed by chromatographic analysis. It should also be pointed out that the R134a sample was part of an international round-robin project [4] currently taking place under the auspices of the Subcommittee on Transport Properties of Commission I.2 on Thermodynamics of IUPAC.

3. RESULTS

The viscosity measurements performed cover the temperature range from 273 to 333 K with the exception of the R125 measurements, whose

Table I. Viscosity of Vapor R124

P (MPa)	T (K)	$\eta(T, P)$ (μPa $\cdot$ s)	$\rho(T_n, P)$ (kg $\cdot$ m^{-3})	$\eta(T_n, P)$ (μPa $\cdot$ s)
		$T_n = 273.15$ K		
0.121	273.51	10.54	7.558	10.52
		$T_n = 283.15$ K		
0.125	283.16	10.87	7.503	10.87
		$T_n = 293.15$ K		
0.251	293.17	11.37	15.08	11.37
		$T_n = 303.15$ K		
0.132	303.18	11.62	7.358	11.62
0.353	303.17	11.75	20.98	11.75
		$T_n = 313.15$ K		
0.134	313.18	11.96	7.212	11.96
0.367	313.17	12.12	20.92	12.12
		$T_n = 323.15$ K		
0.142	323.12	12.39	7.399	12.39
0.377	323.06	12.53	20.66	12.53
0.574	323.11	12.61	33.16	12.61
		$T_n = 333.15$ K		
0.171	333.19	12.82	8.666	12.82
0.402	333.15	12.98	21.29	12.98
0.704	333.14	13.06	40.09	13.06
0.922	333.17	13.12	56.31	13.12

maximum temperature was restricted to 313 K, due to the comparatively low critical point of this refrigerant (339 K). The pressure range extended from almost atmospheric up to about 1 atm below the saturation pressure. To check the continuing smooth operation of the instrument, the viscosity of argon was measured before and after each refrigerant. The reproducibility of the results was always better than $\pm 0.5\%$.

Table II. Viscosity of Vapor R125

P (MPa)	T (K)	$\eta(T, P)$ (μPa·s)	$\rho(T_n, P)$ (kg·m^{-3})	$\eta(T_n, P)$ (μPa·s)
		$T_n = 273.15$ K		
0.128	274.47	11.75	6.949	11.68
0.293	274.48	11.90	16.52	11.83
0.583	274.46	11.97	35.57	11.90
		$T_n = 283.15$ K		
0.246	283.16	12.23	13.14	12.23
0.391	283.17	12.31	21.54	12.31
0.603	283.29	12.35	34.93	12.35
0.810	283.15	12.41	49.70	12.41
		$T_n = 293.15$ K		
0.139	293.17	12.50	7.002	12.50
0.434	293.18	12.72	23.06	12.72
0.629	293.17	12.80	34.79	12.80
0.830	293.18	12.85	48.09	12.85
1.056	293.17	12.96	65.05	12.96
		$T_n = 303.15$ K		
0.199	303.16	12.98	9.758	12.98
0.429	303.20	13.13	21.83	13.13
0.635	303.19	13.22	33.50	13.22
0.848	303.19	13.31	46.63	13.31
1.060	303.18	13.41	61.07	13.41
1.279	303.19	13.54	77.95	13.54
		$T_n = 313.15$ K		
0.188	313.18	13.35	8.883	13.35
0.434	313.19	13.54	21.23	13.54
0.653	313.17	13.64	33.04	13.64
0.864	313.11	13.76	45.28	13.76
1.074	313.13	13.87	58.50	13.87
1.285	313.16	14.00	73.11	14.00

To calculate the viscosity of R124 the density measurements of
Kubota et al. [5] were employed. These values cover the temperature
range from 298 to 423 K. Since no other density measurements of vapor
R124 that cover a wider temperature range could be found in the literature,
the equation proposed by Kubota was extrapolated to 273 K. No density
measurements could be found in the literature for R125 corresponding to

Table III.   Viscosity of Vapor R134a

P (MPa)	T (K)	$\eta(T, P)$ (μPa·s)	$\rho(T_n, P)$ (kg·m^{-3})	$\eta(T_n, P)$ (μPa·s)
		$T_n = 273.15$ K		
0.186	273.94	10.77	8.830	10.74
		$T_n = 283.15$ K		
0.191	283.15	11.20	8.692	11.20
		$T_n = 293.15$ K		
0.199	293.19	11.53	8.709	11.53
0.400	293.18	11.61	18.44	11.61
0.500	293.21	11.63	23.73	11.63
		$T_n = 303.15$ K		
0.200	303.20	11.88	8.419	11.88
0.555	303.18	12.02	25.38	12.02
		$T_n = 313.15$ K		
0.138	313.21	12.25	5.537	12.25
0.304	313.19	12.37	12.57	12.37
0.517	313.18	12.44	22.33	12.44
0.619	313.14	12.49	27.35	12.49
0.929	313.14	12.53	44.52	12.53
		$T_n = 323.15$ K		
0.147	323.15	12.51	5.708	12.51
0.466	323.15	12.68	19.09	12.68
0.760	323.17	12.79	32.99	12.79
1.230	323.18	12.91	60.12	12.91
		$T_n = 333.15$ K		
0.143	333.15	12.82	5.371	12.82
0.404	333.16	13.02	15.76	13.02
0.633	333.13	13.11	25.63	13.11
0.837	333.17	13.19	35.14	13.19
1.100	333.17	13.26	48.70	13.26
1.473	333.19	13.38	71.57	13.38

the temperature and pressure ranges of the present work, and thus the densities were calculated from the equation of state proposed by Outcalt and McLinden [6]. Tillner-Roth and Baehr [7] measured the density of R134a and R152a with an uncertainty of about $\pm0.03\%$ and within a temperature range of 293–453 K. Their equations were extrapolated to cover the temperature range of the viscosity measurements.

Table IV.   Viscosity of Vapor R152a

P (MPa)	T (K)	$\eta(T, P)$ (μPa · s)	$\rho(T_n, P)$ (kg · m^{-3})	$\eta(T_n, P)$ (μPa · s)
		$T_n = 273.15$ K		
0.206	275.19	9.29	6.399	9.21
		$T_n = 283.15$ K		
0.211	283.19	9.60	6.271	9.60
		$T_n = 293.15$ K		
0.219	293.13	9.93	6.251	9.93
0.417	293.14	9.95	12.57	9.95
		$T_n = 303.15$ K		
0.193	303.18	10.36	5.262	10.36
0.396	303.15	10.37	11.315	10.37
0.596	303.21	10.37	17.97	10.37
		$T_n = 313.15$ K		
0.215	313.16	10.69	5.671	10.69
0.381	313.14	10.69	10.39	10.69
0.605	313.16	10.72	17.35	10.72
0.811	313.18	10.73	24.54	10.73
		$T_n = 323.15$ K		
0.204	323.15	11.01	5.182	11.01
0.481	323.24	11.08	12.84	11.08
0.664	323.13	11.11	18.39	11.11
0.802	323.17	11.13	22.89	11.13
		$T_n = 333.15$ K		
0.211	333.14	11.33	5.186	11.33
0.405	333.15	11.40	10.26	11.40
0.627	333.18	11.47	16.49	11.47
0.814	333.19	11.47	22.16	11.47
0.997	333.12	11.48	28.17	11.48
1.242	333.20	11.51	37.17	11.51

The viscosity measurements of the four refrigerants are shown in Tables I to IV. Values corrected to nominal temperatures are also shown.

4. DISCUSSION

4.1. Saturation Values

Employing the pressure values shown in Tables I to IV, viscosity values were determined by simple extrapolation. The resulting values are shown in Table V. For comparison purposes, these saturation values were fitted to a simple equation of the form

$$\frac{\eta_s}{\eta_s(298.15)} = a_0 + a_1 \left(\frac{T}{298.15}\right) \tag{5}$$

The required constants are shown in Table VI. In the same table, the standard deviation of the four fits is also shown. The maximum standard deviation is $\pm 0.03\%$.

Equation (5) made possible the comparison among various authors that had measured the viscosity of refrigerants along the saturation line. This comparison is presented in Fig. 2. It should be noted that, due to the lack of experimental viscosity data for R124, no comparison could be made and so R124 is not included in this figure.

Oliveira and Wakeham [8] measured the viscosity of vapor R125 along the saturation line with a vibrating-wire viscometer calibrated with nitrogen and helium and with a stated accuracy of $\pm 1\%$. The deviations that arise when comparing their data with those presented in this work vary from 4 to 9%, which far exceeds the mutual uncertainty of the instruments. A discussion between the two groups resulted in the conclusion [16] that this difference can be attributed to the fact that the R125 sample employed by Oliveira and Wakeham [8] was among the first ever produced and consequently of questionable purity. Nabizadeh and Mayinger [9] measured the viscosity of vapor R134a using an oscillating-disk apparatus calibrated with nitrogen with an accuracy of $\pm 0.5\%$. Their measurements were performed very close to saturation pressure and agree very well with the present ones at 303.15 K. However, at 333.15 K an unexplainable difference of 7% arises. Pasekov and Ustyuzhanin [10] employed a variation of the capillary technique in an instrument calibrated with nitrogen to perform measurements accurate to $\pm 0.9\%$, which agree very well with the set presented here. Krauss et al. [11] presented a correlation for the viscosity of R134a with an accuracy of $\pm 4\%$. The

Table V.   Viscosity of Vapor R124, R125, R134a, and R152a at Saturation

T_s (K)	P_s (MPa)	$\rho(T_s, P_s)$ (kg·m^{-3})	$\eta(T_s, P_s)$ (μPa·s)
		R124	
273.15	0.163	10.36	10.53
283.15	0.234	14.64	10.96
293.15	0.327	20.24	11.39
303.15	0.445	27.41	11.82
313.15	0.593	36.56	12.25
323.15	0.775	48.11	12.69
333.15	0.996	62.66	13.12
		R125	
273.15	0.671	41.74	11.91
283.15	0.909	57.24	12.46
293.15	1.206	77.58	13.00
303.15	1.571	104.5	13.56
313.15	2.014	141.3	14.10
		R134a	
273.15	0.293	14.43	10.78
283.15	0.415	20.23	11.22
293.15	0.572	27.77	11.66
303.15	0.770	37.49	12.10
313.15	1.016	50.02	12.54
323.15	1.317	66.19	12.98
333.15	1.680	87.23	13.42
		R152a	
273.15	0.264	8.377	9.23
283.15	0.372	11.65	9.61
293.15	0.512	15.91	9.99
303.15	0.691	21.44	10.37
313.15	0.910	28.36	10.76
323.15	1.178	37.15	11.14
333.15	1.502	48.39	11.52

Table VI.   Coefficients of Eq. (5)

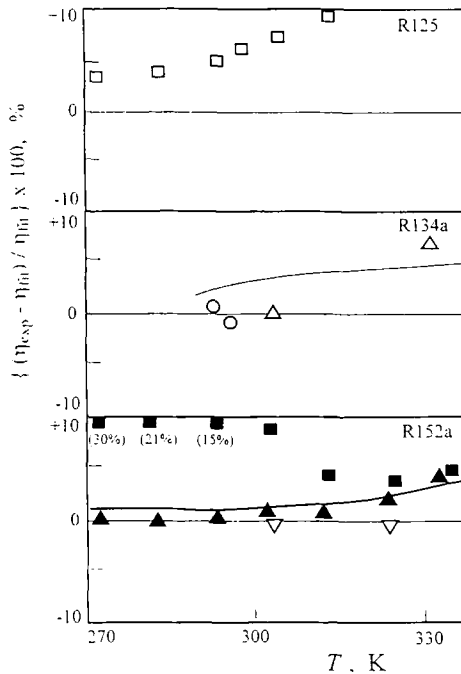| Fluid	$\eta_s(298.15)$ (μPa·s)	a_0	a_1	σ (%)
R124	11.61	−0.1095	1.109	±0.030
R125	13.28	−0.2311	1.231	±0.021
R134a	11.88	−0.1050	1.105	±0.004
R142a	10.18	−0.1186	1.119	±0.021

Fig. 2. Percentage deviations of the viscosity measurements of R125, R134a, and R152a along the saturation line, from Eq. (5). (□) Oliveira and Wakeham [8]; (△) Nabizadeh and Mayinger [9]; (○) Pasekov and Ustyuzhanin [10]; (———) Krauss et al. [11]; (▲) Mayinger [12]; (▽) Takahashi et al. [13]; (—) Krauss et al. [14]; (■) van der Gulik [15].

deviation between the present data and the values derived from this correlation fall within mutual uncertainty.

The viscosity of vapor R152a was measured along the saturation line by Mayinger [12] with an oscillating-disk instrument. Their values, reported with an uncertainty of ±0.5%, are obtained relative to the viscosity of nitrogen. The average deviation between them and the values presented in this paper is within mutual uncertainty. However, a maximum deviation of 3.9% appears at 333.15 K. Takahashi et al. [13] also employed an oscillating-disk instrument calibrated with nitrogen to measure the viscosity of vapor R152a. Their measurements cover a wide pressure range from 0.1 MPa up to almost saturation pressure and therefore an expansion to

saturation conditions is allowable. The values obtained in this way agree with the present set within $\pm 0.4\%$. Krauss and Stephan [14] also produced a correlation for the viscosity of R152a along the saturation boundary, accurate to $\pm 4\%$. These data agree with the values here presented, within mutual uncertainty. van der Gulik [15] performed viscosity measurements of vapor R152a employing a vibrating-wire apparatus accurate to $\pm 2\%$. These measurements, however, exhibit large deviations that rise up to $\pm 30\%$ at lower temperatures, decreasing to 4% with rising temperature. These deviations, according to the author, are attributed to a poor estimation of the decrement in vacuum.

In conclusion, the general picture along the saturation line shown in the figure is a rather distressing one, with deviations of various investigators far exceeding the mutual uncertainties of the instruments.

It should be noted here that equations for the saturation values of the four refrigerants have also been presented elsewhere [18]. However, in the case of R125 the coefficients of Eq. (5) are slightly different from the ones presented here. The maximum deviation between the two equations is 1%. The reason for this difference lies in a misprint in the original density equation [19], which was consequently corrected [6].

4.2. Vapor-Phase Values

Since there are very few viscosity measurements in the vapor phase, a different approach was adopted. To correlate a wider range of conditions, Krauss et al. produced a correlation for R134a [11] and another for R152a [14]. Both these correlations, based on a collection of critically assessed viscosity measurements, cover the whole fluid region with an estimated uncertainty of about $\pm 4\%$. The work of Krauss et al. is based on the residual concept according to which the viscosity is expressed as the sum of three contributions, as

$$\eta(\rho, T) = \eta_0(T) + \Delta\eta_R(\rho) + \Delta\eta_c(\rho, T) \tag{6}$$

where $\eta_0(T)$ is the dilute-gas contribution based only on temperature, $\Delta\eta_R(\rho)$ accounts for the density dependence, and $\Delta\eta_c(\rho, T)$ represents the critical enhancement.

In Fig. 3 a comparison of the present measurements with the Krauss correlations is shown. In the same figure the deviation of our previous viscosity measurements in the liquid phase [16, 17] is also included. It should be noted that in optimizing these correlations, the liquid-phase data were included but not the vapor-phase data, since they were not available.
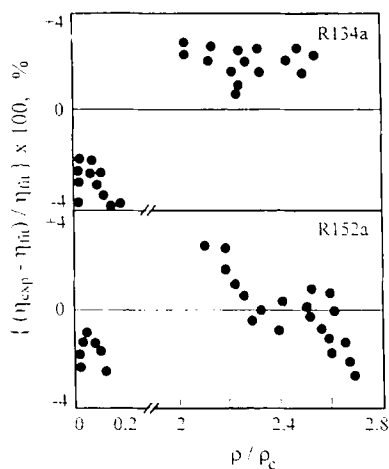
The comparison is good, although there is a systematic trend of deviations in the vapor phase.

5. CONCLUSION

A new viscometer has been constructed to measure the viscosity of gases in the temperature range 273–333 K. The instrument was successfully employed to measure the viscosity of four refrigerants with an accuracy of $\pm 1\%$ and a reproducibility of better than $\pm 0.3\%$. The results that refer to the saturation boundary fitted to simple polynomials, indicated a lack of good vapor-phase viscosity values.

ACKNOWLEDGMENTS

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