The Viscosity of the Refrigerant 1,1-Difluoroethane Along the Saturation Line[1]

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The viscosity coefficient of the refrigerant R152a (1,1-difluoroethane) has been measured along the saturation line both in the saturated liquid and in the saturated vapor. The data have been obtained every 10 K from 243 up to 393 K by means of a vibrating-wire viscometer using the free damped oscillation method. The density along the saturation line was calculated from the equation of state given by Tamatsu et al. with application of the saturated vapor-pressure correlation given by Higashi et al. An interesting result is that in the neighborhood of the critical point, the kinematic viscosity of the saturated liquid seems to coincide with that of the saturated vapor. The results for the saturated liquid are in satisfying agreement with those of Kumagai and Takahashi and of Phillips and Murphy. A comparison of the saturated-vaport data with the unsaturated-vapor data of Takahashi et al. shows some discrepancies.

1. INTRODUCTION

The refrigerant R152a (1,1-difluoroethane) is regarded as one of the attractive working fluids for refrigerators and heat-pump systems, since it does not contain toxicogenic chlorine atoms which deplete the ozone layer and it is nontoxic. On the other hand, it is inflammable, and therefore, it is preferably applied as one of the components of a refrigerant mixture or in isolated industrial applications. For both purposes the knowledge of the viscosity coefficient along the saturation line, both in the saturated liquid and in the saturated vapor, is demanded for the design of efficient

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apparatuses. The present investigation was contracted for industrial application.

For measurements of the viscosity coefficient along the saturation line, the vibrating-wire viscometer is extremely suited, since it is simple and small, it does not disturb the system, and it does not use pressure differences. With the latter it is impossible to create a state exactly on the saturation line, whereas disturbances make it difficult to maintain such a state. More involved apparatuses will function less well when a transition surface is present. A small vibrating-wire viscometer mounted in the lower half of a relatively long vessel makes it possible to investigate the viscosity of the boiling liquid, while the transition surface is located in the upper half of the vessel, whereas the investigation of the viscosity of the saturated vapor is possible in the situation upside down.

Such a formation has been applied for the present measurements; the details are given in the next section. The results are presented in Section 3, whereas in Section 4 a comparison is made with literature data and some correlations are discussed.

2. METHOD

As mentioned above, the measurements were performed by means of a vibrating-wire viscometer, described previously [1–4]. It consists of a thin tungsten wire with a length of 15 mm and a radius of about 25 μm, mounted in an insulating support. This set was placed in a relatively long beryllium bronze pressure vessel suited for pressures up to 100 MPa and installed between the poles of an electromagnet. For the measurements in the boiling liquid the bessel was mounted vertically with the viscometer wire also vertically in the bottom part of the vessel, and for the measurements in the saturated vapor the vessel was mounted upside down with the viscometer vertically in its top part. The temperature of the vessel was measured within 0.1 K by means of a platinum resistance thermometer with use of a resistance table according to DIN 43760. The temperature was regulated by means of a proportionally integrating regulation system with a second platinum resistance thermometer as sensor.

The vessel was connected with the storage vessel via a small filling system provided with a simple Bourdon manometer used as pressure indicator, range 0–5 MPa, a small extra vessel offering the possibility of thermal compression, a connection to a vacuum pump, and several valves. The material to be investigated was obtained from Du Pont (USA) via the Dutch Company HoekLoos. It was stated by the supplier to be pure within 99.90 wt%, containing, at most, 10 wt ppm water, 1.50 vol% nonabsorbable gases in the vapor phase, 0.01 vol% residue, 0.1 wt ppm acid, free as

HCl, 10 wt ppm acetylene, and 100 wt ppm CFC-12. The material was not further purified but used as delivered by the supplier.

At the start of the investigation the complete filling system and the vessel containing the viscometer were evacuated, with the vessel at a temperature of 30°C. The system was made free of leakage before. The pumping was continued until the damping df of the wire did not change anymore. At this vacuum the residual damping of the wire was measured to be 0.329 Hz at a frequency f of 3571.00 Hz, so that $(df/f)_0$ is equal to 0.9213×10^{-4}. Consequently, the system was filled with vapor up to about 0.4 MPa, the filling pressure in the storage vessel. After a few days the system was pumped again to the same vacuum pressure and then filled definitely. This procedure was repeated when the vessel had to be mounted upside down. Several times during the investigation delay of boiling was observed, confirming purity of the material.

For a measurement of the viscosity, first the temperature was measured and also the pressure was read from the manometer. Then the wire was set into vibration by the combined action of the magnetic field and a sinusoidal electric current with a frequency close to the resonance frequency of the wire. After the current was stopped, the voltage, induced by the decaying vibration, was amplified, sampled, and stored as a series of 2048 digital numbers in a personal computer. In order to get rid of noise this sampling procedure was repeated 100 times and the resulting numbers were added. After Fourier transformation, the width and frequency of the resonance line were computed. This determination was repeated a few times with different sampling times. So one measurement resulted in four or five values of the width and frequency with a spread in df/f of about 0.3% for measurements on the liquid to about 1% for those on the vapor at low temperature. These values were averaged afterwards.

In order to obtain measurements taken on the saturation line, the following procedure was adopted. After the temperature was set at the desired value a series of measurements was taken, passing through the coexistence range. After each measurement the amount of sample material in the vessel was changed by adding or removing material by means of the extra vessel. Between the measurements at least 1 h was spent for equilibration. From the series obtained in this way, those two or three successive measurements were taken which were most constant with respect both to the observed pressure and to the measured width of the resonance line, and these were calculated and are presented in the tables. Measurements outside the saturation range differ in pressure, whereas measurements with constant pressure but different widths are measurements with the transition surface at the level of the wire. Only measurements where the transition surface is situated in the other half of the vessel, shifting a bit for the

different measurements due to the different amounts of material, can be expected to result in the same values for resonance width and observed pressure.

For the computation of the viscosity, the density at the measured temperatures and, in this case, also the pressure on the saturation line are determined from literature data. The viscosity coefficient of the fluid is then computed according to the working equations for the damped vibrating-wire viscometer given in Refs. 3 and 4.

When the low-temperature vapor measurements were started, the wire was heated in between the measurements in order to avoid precipitation of sample fluid on the wire. Test measurements without heating showed that precipitation did not occur, but the analysis of the data afterward indicated that the system was severely disturbed by this extra heat source in the vessel in boiling circumstances. Therefore, these results had to be discarded and the measurements had to be repeated without heating.

3. RESULTS

For the computation of the viscosity the density on the saturation line at the measured temperatures had to be determined from literature data. Three sets of data were available: the NIST Standard Reference Database No. 23, December 1989, provided by the contractor, measurements and a correlation of the saturated-vapor pressure and densities in the gas phase by Tillner-Roth and Baehr [5, 6] for temperatures above room temperature, and results obtained by Watanabe and co-workers [7 9]. The results for the vapor densities at the high temperatures near the critical temperature obtained from the NIST data base deviate considerably from those of the other two sets. The Tillner–Roth and Baehr data have to be extrapolated to the lower temperatures for the vapor densities and supplemented with the data of Sato et al. [7] for the saturated liquid. Therefore, the not yet published equation of state of Tamatsu et al. [8], which is based on measurements and is valid over the whole measuring range, has been chosen. To be able to calculate the densities, first the saturated vapor pressure had to be determined, and to this aim the correlation of Higashi et al. [9] has been taken for consistency. The differences from the Tillner Roth and Baehr results are negligible for the present case, however.

The resonance frequency of the wire, f, varied from 2900 Hz at 373 K to 4200 Hz at 243 K for the present measurement series, whereas the width of the resonance peak, df, varied from 1.54 Hz for the saturated vapor to 90 Hz for the saturated liquid at 243 K. The damping factor df/f varied

from 0.00027 for the vapor at 243 K up to 0.002 at 373 K and for the liquid from 0.009 at 373 K up to 0.022 at 243 K. The residual damping factor $(df/f)_0$, which amounted to 0.00009 as mentioned above, has to be subtracted from df/f and is, therefore, not negligible, especially not for the low-temperature measurements on the vapor. Accordingly, the accuracy of the measurements is estimated to vary from 0.5% for the low-temperature liquid data to 2% for the low-temperature vapor data.

The parameter m, introduced by Stokes [10], has been determined from the corrected df/f values and the calculated densities. Its value, which is a measure of the reliability of the measurements, ranges from 3.5 at 243 K to 5.4 at 373 K for the liquid and from 0.97 at 243 K up to 5.35 at 373 K for the vapor, while it should lie between 0.14 and 6.25 for the present configuration [3] so that the boundary conditions are amply satisfied.

The value of m is inversely proportional to the density for values of the density small compared to the density of the wire, which is taken to be $19,300 \text{ kg} \cdot \text{m}^{-3}$. The value of the viscosity coefficient is equal to an apparatus constant multiplied by the frequency and the density and divided by m^2 [3, 4] and is, therefore, in first approximation also inversely proportional to the density. The effect on the value of the viscosity coefficient of future corrections in the density can be calculated according to this rule.

The results of the present measurements are presented in Tables I and II and in Figs. 1–6. The tables give the temperatures T, the pressures p calculated according to Ref. [9], the densities ρ calculated from T and p according to Ref. [8], the viscosity coefficients η computed from ρ and the measured values of df/f, and the kinematic viscosity coefficients $v = \eta/\rho$ for the saturated liquid and for the saturated vapor, respectively. The measurements are not presented in the order they were taken. For each temperature two or three values are given, obtained in the way described above.

Figure 1 shows the experimentally determined viscosity coefficient plotted as a function of the temperature, together with the saturated-liquid data of Kumagai and Takahashi [11] and those of Phillips and Murphy [12]. Also, the critical temperature is indicated, as well as some extrapolated values of the viscosity coefficient of the saturated vapor. The latter are based on measurements of the viscosity coefficient of the unsaturated vapor by Takahashi et al. [13] and are calculated by means of a correlation formula provided by the authors. The solid lines are only polynomial fitting curves meant as guides for the eye. An enlargement of this plot is given as Fig. 2, showing the vapor data separately. The axis of ordination is now only 1.5% of that in Fig. 1. The values of η measured in the unsaturated vapor by Takahashi et al. [13] are indicated with small

crosses, whereas the extrapolated data for the saturated vapor are plotted as circles. The results are discussed in the following section.

The same data are shown as a function of density in Figs. 3 and 4. In Fig. 4 the same enlargement of the axis of ordination is applied as in Fig. 2, but now, naturally, the density range differs from that in Fig. 3. The

Table I.   Viscosity of R152a in the Saturated-Liquid Phase

Temperature (K)	Pressure (MPa)	Density (kg·m⁻³)	Viscosity (μPa·s)	Kinematic visc. (10⁻⁶ m²·s⁻¹)
243.15	0.0778	1021.5	338.3	0.3312
243.16	0.0778	1021.5	339.5	0.3323
243.17	0.0778	1021.5	339.0	0.3319
253.25	0.1216	1001.0	283.4	0.2831
253.25	0.1216	1001.0	283.9	0.2836
262.98	0.1805	980.6	247.3	0.2522
263.05	0.181	980.5	246.8	0.2518
263.05	0.181	980.5	247.1	0.2520
273.21	0.264	958.4	219.5	0.2291
273.24	0.265	958.3	219.8	0.2294
283.21	0.373	935.6	195.0	0.2085
283.25	0.374	935.5	195.0	0.2085
283.25	0.374	935.5	194.9	0.2084
293.18	0.513	911.7	173.1	0.1899
293.19	0.513	911.7	173.3	0.1900
293.20	0.513	911.7	174.0	0.1909
303.23	0.691	886.3	155.1	0.1750
303.23	0.691	886.3	154.4	0.1742
313.16	0.909	859.5	138.5	0.1612
313.16	0.909	859.5	138.3	0.1609
323.19	1.178	830.4	124.0	0.1493
323.19	1.178	830.4	123.9	0.1492
333.23	1.503	798.8	109.5	0.1371
333.24	1.504	798.7	109.1	0.1365
343.17	1.887	764.3	96.58	0.1264
343.18	1.887	764.2	96.52	0.1263
353.15	2.342	725.1	84.66	0.1168
353.15	2.342	725.1	84.58	0.1167
353.16	2.342	725.0	84.62	0.1167
363.17	2.879	678.5	73.40	0.1082
363.18	2.880	678.5	73.31	0.1081
363.19	2.880	678.4	73.22	0.1079
372.89	3.489	620.4	60.68	0.0978
372.92	3.490	620.2	61.78	0.0996
372.92	3.490	620.2	61.69	0.0995
372.95	3.492	620.0	61.37	0.0990

fluidity, the reciprocal of the viscosity, of the saturated liquid is not a strict linear function of the molar volume in this case, as can be expected since the data are not isothermal. As a function of the pressure the data show qualitatively the same behavior as in the preceding figures.

Figures 5 and 6 show the results for the kinematic viscosity as a function of the temperature and of the pressure, respectively. In both cases the kinematic viscosity of the saturated vapor, which is the largest, seems to

Table II. Viscosity of R152a in the Saturated-Vapor Phase

| Temperature (K)	Pressure (MPa)	Density (kg·m^{-3})	Viscosity (μPa·s)	Kinematic visc. (10^{-6} m^2·s^{-1})
243.25	0.0781	2.641	12.02	4.554
243.28	0.0782	2.644	12.09	4.572
253.12	0.1209	3.974	11.92	2.999
253.12	0.1209	3.974	11.83	2.977
263.16	0.1818	5.833	11.94	2.046
263.20	0.1820	5.841	11.97	2.048
273.22	0.2645	8.329	12.00	1.441
273.22	0.2645	8.330	11.09	1.440
273.22	0.2645	8.330	12.02	1.443
283.18	0.3729	11.583	11.62	1.003
283.18	0.3729	11.583	11.64	1.005
283.19	0.3729	11.584	11.61	1.002
293.21	0.5135	15.824	11.51	0.7273
293.21	0.5135	15.824	11.41	0.7212
303.23	0.6909	21.26	11.31	0.5320
303.23	0.6910	21.26	11.38	0.5352
313.19	0.9097	28.14	11.37	0.4040
313.19	0.9098	28.14	11.23	0.3991
313.19	0.9098	28.14	11.35	0.4031
323.19	1.178	36.94	11.69	0.3165
323.19	1.178	36.94	11.53	0.3120
333.16	1.501	48.15	12.10	0.2514
333.18	1.501	48.17	12.08	0.2508
343.20	1.888	62.75	12.87	0.2051
343.20	1.888	62.75	12.86	0.2049
343.20	1.888	62.76	12.96	0.2065
353.19	2.344	82.00	13.14	0.1603
353.19	2.343	82.00	13.26	0.1617
353.19	2.344	82.00	13.14	0.1602
363.16	2.879	108.57	14.30	0.1317
363.16	2.879	108.58	14.35	0.1322
373.07	3.500	148.67	15.26	0.1026
373.07	3.501	148.69	15.21	0.1023
373.08	3.501	148.72	15.22	0.1024
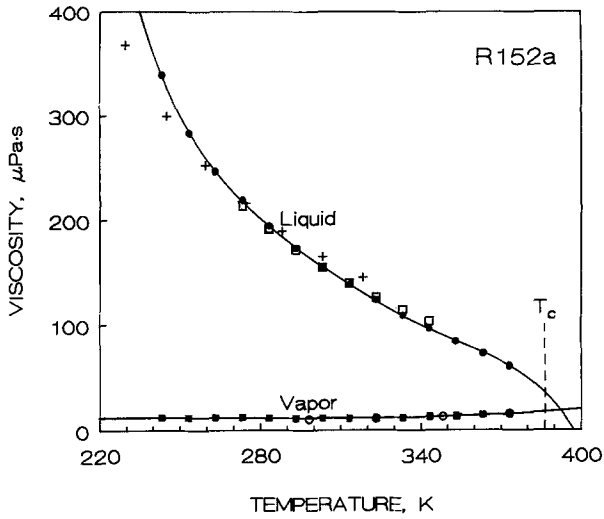
Fig. 1. The viscosity coefficient of the saturated liquid (●) and of the saturated vapor (■) as a function of the temperature, compared with literature data: ⊡, Kumagai and Takahashi [11]; +, Phillips and Murphy [12]; ○, extrapolated values of Takahashi et al. [13]. The solid lines are polynomial fitting curves as guides for the eye.
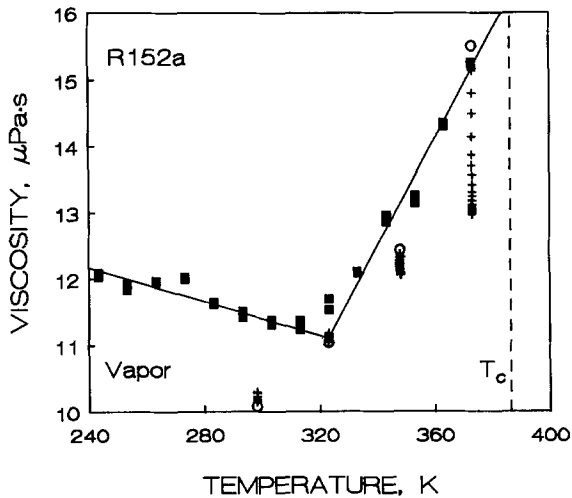

Fig. 2. The viscosity coefficient of the saturated vapor (■) as a function of the temperature, compared with data of Takahashi et al. [13]: +, unsaturated-vapor values; ○, extrapolated values according to their correlation. The solid lines are linear curves as guides for the eye.
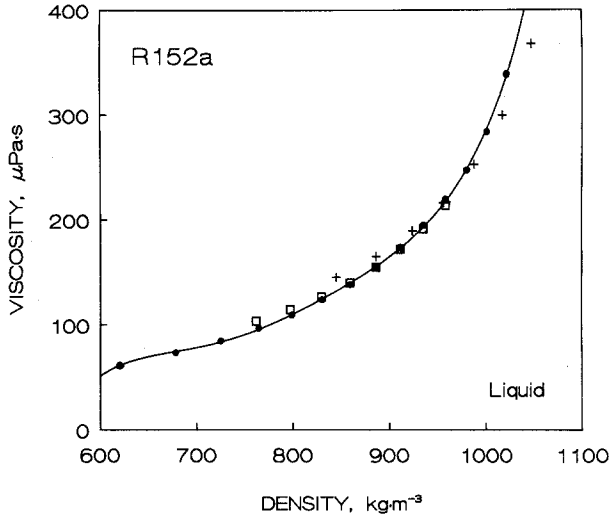
Fig. 3. The viscosity coefficient of the saturated liquid (●) as a function of the density, compared with literature data: □, Kumagai and Takahashi [11]; +, Phillips and Murphy [12]. The solid line is a polynomial fitting curve as guide for the eye.
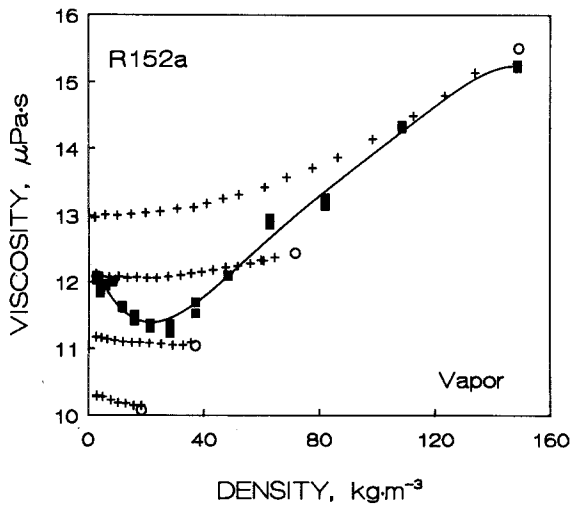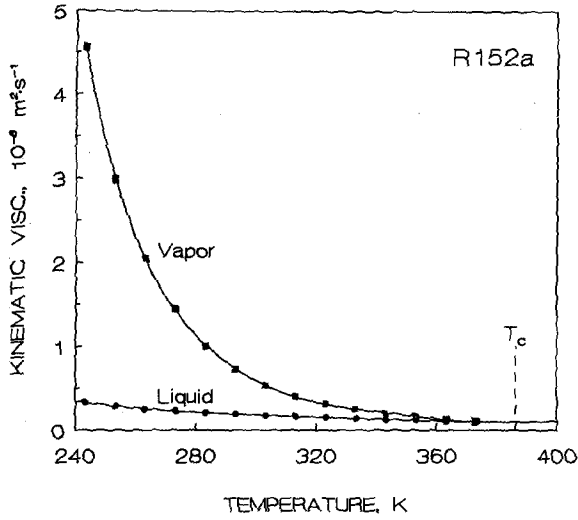

Fig. 4. The viscosity coefficient of the saturated vapor (■) as a function of the density, compared with data of Takahashi et al. [13]: +, unsaturated-vapor values; ○, extrapolated values according to their correlation. The solid line is a polynomial fitting curve as guide for the eye.

Fig. 5. The kinematic viscosity coefficient $v = \eta/\rho$ of the saturated liquid (●) and of the saturated vapor (■) as a function of the temperature. The solid lines are polynomial fitting curves as guides for the eye.
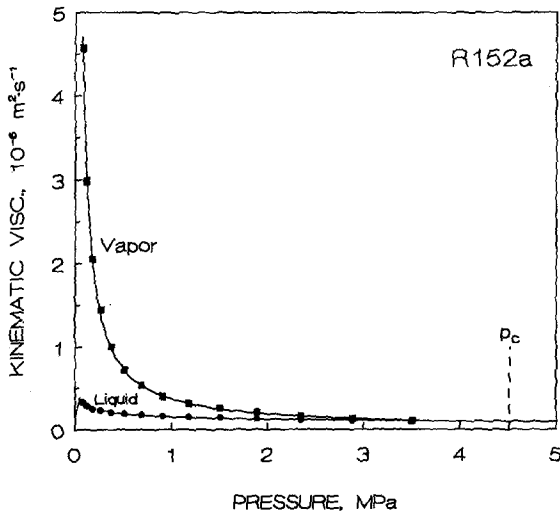

Fig. 6. The kinematic viscosity coefficient $v = \eta/\rho$ of the saturated liquid (●) and of the saturated vapor (■) as a function of the pressure. The solid lines are fitting curves as guides for the eye.

approach asymptotically that of the saturated liquid in the direction of the critical point. This phenomenon offers the possibility to obtain a good estimate of the viscosity in the critical region by a small extrapolation.

4. DISCUSSION

Figures 1 and 3 show a comparison of the present data for the saturated liquid with those of Kumagai and Takahashi [11]. Although the temperatures at which the data are taken are nearly the same, it is clearly seen that the densities deviate from ours from 0 % at 273 K up to −0.5 % at 343 K. This is, however, not enough to explain the differences in viscosity, which extend from −2.7 % at 273 K up to +7.3 % at 343 K. The measurements of Kumagai and Takahashi have been performed by means of a capillary viscometer not driven by a pressure difference but by gravity and surface tension. The latter had to be estimated from a correlation so that the differences originate probably from this estimation. The data of Phillips and Murphy [12] are part of a survey study of many refrigerants, published in 1970. They also used such a capillary viscometer but they do not give details. These data gave a tremendous improvement compared to the data of Mears et al. [14], published in 1955, which were in general 1.5 times too high, but still they have to be considered as only guide data. Within these limitations the agreement between our data and those mentioned is satisfying.

There are no experimental data for the viscosity of the saturated vapor at our disposal, only the unsaturated vapor data of Takahashi et al. [13] and a correlation given by the authors, which makes it possible to calculate the saturated-vapor data by extrapolation. A comparison is shown in Figs. 2 and 4. The unsaturated-vapor data of Takahashi are indicated by crosses and the extrapolated values by circles. For the high temperatures the agreement is reasonable but at room temperature the behavior is different. Our data clearly show a slow decrease as function of the temperature and of the density with a minimum at a temperature of around 310 K and at a density of around 25 kg · m^{-3} and then a fast increase up to the critical temperature. The extrapolated data of Takahashi et al. [13] show, on the contrary, only an increase toward the critical temperature. On the other hand, their unsaturated-vapor data show, as a function of density, a change in the sign of the slope more or less at the same temperature where our results show the minimum. An explanation may be found in the difference in method, vibrating wire and oscillating disk, possibly combined with effects of the high dipole moment of R152a [15], but also impurities can play a role: both samples were not purified further and are from different suppliers, and finally, the extrapolation method can be not permitted.

Figures 5 and 6 show that at low temperatures and pressures, fluctuations in temperature and pressure due to the temperature regulation and other external sources have a large influence on the saturated-vapor measurements, since in this range the kinematic viscosity changes rapidly with temperature and pressure. This is an extra source of inaccuracy.

In the literature many prediction methods or correlations can be found for the dynamic viscosity of a saturated liquid. A well-known method is based on the idea of Andrade [16] that the viscosity of a liquid is an exponential function of the temperature. This may be true for dense fluids far from the critical region, but for data along the saturation line it does not work. Therefore, the formula is extended with correction terms to

$$\ln \eta = A + B/T + CT + DT^2 \tag{1}$$

as applied by both Kumagai and Takahashi [11] and Phillips and Murphy [12]. This formula works quite well; it represents our experimental values mostly within 0.5 %. The values of the coefficients in Eq. (1) are given in Table III. However, the contributions of the four terms are of the same order of magnitude and alternating in sign, so that the third and fourth terms are by no means correction terms. The various terms therefore have no scientific meaning, and so it is not amazing that the values of the coefficients, obtained by the various authors, lie far apart.

Another correlation method is based on the representation of Batschinski [17] and Hildebrand [18], which considers the reciprocal of the viscosity, the fluidity, as a function of the molar volume. For isotherms this function is mostly linear [2, 19, 20], but for the present case, as mentioned above, this cannot be expected. Latini et al. [21] proposed a variant by substituting a direct empirical relationship between the density and the temperature. For the present measurements no linear relation between $1/\eta$ and $1/(1.4 - T_r)$ can be found, however, so that their method cannot be applied. Here, T_r is the reduced temperature T/T_c, where T_c is the critical temperature.

Table III. Coefficients in Eqs. (1) and (2)

$$A = -48.42838$$
$$B = 4303.0185$$
$$C = 0.1320925$$
$$D = -0.0001586461$$
$$a_0 = -24.047751$$
$$a_1 = 0.48068275$$
$$a_2 = -0.0009574647$$

The simplest representation in this spirit for our data is

$$1/\eta = a_0 + a_1 V + a_2 V^2 \tag{2}$$

Besides the three lowest temperatures, it gives the viscosity data within 0.5% of the experimental values. At 243 K the deviation is -2.75%; at 253 K, $+0.7\%$; and at 363 K, $+1.5\%$. The coefficients are also given in Table III. In this case the contribution of the third term is an order of magnitude smaller than those of the first two terms.

Finally, the value of the viscosity at the critical point is estimated by extrapolation of the kinematic viscosity v as mentioned above: $v_{cr} = 85 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, $\eta_{cr} = 31 \mu\text{Pa} \cdot \text{s}$, roughly half of the saturated-liquid value at 373 K, the nearest temperature, and roughly double the saturated-vapor value at the same temperature.

ACKNOWLEDGMENTS

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