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Vapor Pressure and Liquid and Gas Densities of 2,2,2-Trifluoroethanol[1]

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Forty-three vapor pressures were measured for temperatures from the normal boiling point to the critical point. These data were obtained with a phase-equilibrium cell designed for precise static measurements at pressures up to 20 MPa. The cell is located within an oil-operated thermostatic bath which provides a homogeneous temperature field with variations less than ±1 mK. The vapor pressure data were fitted to a Wagner-type equation. Sixty-two liquid densities were measured on seven isotherms between 20 and 140°C for pressures up to 16 MPa. These measurements were carried out with a precision density meter operating on a vibrational technique. Sixty-nine gas-*PVT* triples were determined from Burnett expansion series on five isotherms between 140 and 200°C for pressures up to the saturation line. In all experiments, temperature measurements were made with platinum resistance thermometers. Precise pressure measurements were performed using a mercury column of 6-m height and a standard deadweight gauge for the higher pressures.

KEY WORDS: Compressibility factor; critical data; gas density; isothermal compressibility; liquid density; *PVT*- data; 2,2,2-trifluoroethanol; vapor pressure.

1. INTRODUCTION

2,2,2-Trifluoroethanol (TFE) has gained significance as a working fluid for energy transformation processes. Because of its suitable thermodynamic properties and a thermal stability limit above 320°C, TFE has been tested in various applications. In mixtures with tetraethylenglucoldimethylether

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(E181), it has been proposed as an alternative refrigerant to ammonia for absorption heat pumps. For heat transformers, this mixture was found to be superior to other binary working fluids [1]. In Rankine cycle plants with organic working fluids for the purpose of low-temperature heat recovery (ORC technology), TFE is used in mixtures with water (fluorinol). Comparative studies in the field of ORC technology show fluorinol to yield the best process efficiency [2].

Up to now, only a few experimental thermophysical data of trifluoroethanol are available in the literature. Some authors give single values of the vapor pressure or short pieces of the vapor pressure curve [3–7] and others present values for the liquid density at low pressures and temperatures [8–10]. In recent studies [11, 12] more extensive experiments have been performed, but the results presented there cannot be regarded as precision measurements.

In this study, the vapor pressure and the density of the gaseous and liquid TFE have been measured over wide ranges of temperature and pressure. Based on the experimental data obtained, equations for both the vapor pressure and the density of the saturated liquid are given.

2. EXPERIMENTAL

The experiments were performed with three apparatuses using different methods. The vapor pressure of trifluoroethanol was measured in a high-pressure phase-equilibrium cell within a precision thermostat. The density of gaseous TFE was determined by Burnett-expansion experiments. Measurements of this kind were performed for temperatures up to 200°C; later they will be extended to 320°C. A density meter working on a vibrational principle was employed to determine liquid densities. Unfortunately, density meters using this very precise technique are not available for temperatures higher than 140°C. Due to this restriction we end up with an experimental gap between the liquid and the gas *PVT* data.

2.1. Sample

The sample used in the experiments was produced by Kali Chemie, Hannover, Germany. In order to minimize the major impurity, which is water, the TFE was synthesized under a nitrogen atmosphere. The resulting purity specified by the manufacturer is better than 99.96% of the total mass, with water being the remaining impurity. We have degassed the sample at normal boiling temperature using an ultrasonic bath. The success of the degassing procedure was proved by gas chromatography. The prepared fluid sample was stored in a special stainless-steel siphon vessel.

From this vessel the liquid TFE was injected into the measuring cells of the different experimental setups by compression of the siphon. By this procedure contact between TFE and the moist air of the environment was avoided, which otherwise would have led to an increased water content of the sample.

2.2. Vapor Pressure Measurements

The vapor pressure experiments were performed with a high-pressure phase-equilibrium apparatus which essentially is designed for the study of vapor–liquid equilibria in mixtures. This device permits measurements at temperatures from 300 to 620 K with pressures up to 20 MPa. Much effort was put into the design of the thermostat with a toroidal oil flow concept. Temperature was measured by three platinum resistance thermometers (PT 10) which were arranged in the oil bath arround the measuring cell. Local temperature differences as well as temperature changes in time were observed to be less than ±1 mK. The thermometers were calibrated by the Physikalisch-Technische Bundesanstalt in Braunschweig, Germany, according to IPTS-68. The total uncertainty of the temperature measurement is estimated to be less than ±5 mK.

Pressure measurements were performed with a mercury column of 6-m height for pressures up to 800 kPa. Higher pressures were measured by an oil-operated standard deadweight gauge made by Ruska (Houston, Tex.). The fluid sample is separated from the pressure transmission fluid (nitrogen) by a precision differential pressure null indicator also made by Ruska. The total uncertainty of the pressure p is estimated to be less than $0.3 \times 10^{-3}\,p$ or 0.2 kPa, whichever is greater. These values include corrections due to different hydrostatic levels. The correct function of the temperature and pressure measurement devices was proved by vapor pressure experiments with pure water substance which showed excellent agreement with established correlations [13].

2.3. *PVT* Measurements of the Superheated Vapor

The density of gaseous trifluoroethanol was determined from Burnett-expansion experiments. For each isotherm, this classical method [14] results in a series of decreasing pressures which are the basis for the evaluation of the density without any measurements of mass or volume.

A particular advantage of our Burnett apparatus is given by the special design of the measuring cells. They are arranged as helicoidal coiled tubes in the center of the toroidal oil flow thermostat of this apparatus. This design secures fast heat transfer toward the next state of thermal equilibrium after an expansion. A turbo molecular pump provides fast evacuation during the expansion series. To measure pressure we used a precision standard deadweight gauge and a mercury column of 6-m height. For temperature measurements platinum resistance thermometers (PT10) were arranged inside the thermostatic bath. A detailed description of the whole Burnett apparatus is given by Klobasa [15].

2.4. *PVT* Measurements of the Liquid

The measurements of the liquid *PVT* relation were performed with a density meter made by Paar (Graz, Austria) which operates on a vibrational technique. In this method a U-formed tube with various fillings of fluid samples is vibrating like a cantilever beam. The tube is stimulated by magnetic coils, and the periodic time of the resulting free oscillation is measured electronically.

From a one-dimensional model for the vibrating tube the functional relation between the measured periodic time τ and the density ρ of the fluid in the tube is found to be

$$\rho = K(\tau^2 - \tau_0^2) \tag{1}$$

where τ_0 is the periodic time of the evacuated tube and K is a coefficient which is a function of pressure p and temperature T. The surface of K over p and T can be determined from measurements with a reference fluid with known density ρ_r and periodic time τ_r. Instead of developing a complicated $K(p, T)$ surface, we directly determine the liquid density from

$$\rho(p, T) = \rho_r(p, T)\frac{\tau^2(p, T) - \tau_0^2(T)}{\tau_r^2(p, T) - \tau_0^2(T)} \tag{2}$$

Therefore, both τ and τ_r are measured for each value of T and p. The vacuum periodic time τ_0 has to be measured for each isotherm. The reference fluid with the known density ρ_r was pure water substance.

A schematic diagram of the setup employed for the measurement of the liquid density is given in Fig. 1. The measuring cell of the density meter (1) is placed inside a thermostated container (2). Moreover, the meter itself is thermostated by the oil flow. Temperature is measured inside the meter between the legs of the vibrating tube by a PT100 platinuum resistance thermometer. The meter is rinsed by nitrogen and evacuated with a turbo molecular pump (3). The sample of liquid TFE is stored in a siphon vessel (4). The reference fluid demineralized water also is carefully degassed and stored in another siphon vessel (5). A spring inside the siphon produces a pressure difference against the ambient to secure that no impurities will

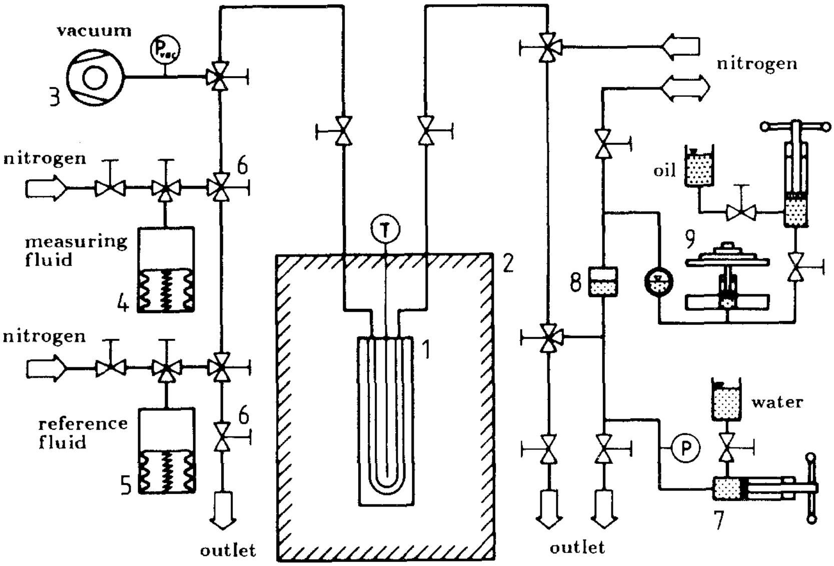

Fig. 1. Setup for the liquid density measurements: (1) measuring cell of the vibrational density meter, (2) thermostated container, (3) turbo molecular pump, (4) siphon vessel with measuring fluid, (5) siphon vessel with reference fluid, (6) junction valve, (7) hand pump, (8) differential pressure null indicator, and (9) standard deadweight gauge.

soak in. From the siphon vessels the desired fluid samples are filled into the measuring cell through junction valves (6). Then the sample is pressurized with a water-operated hand pump (7). Long tubes prevent mixing of the water with the substances of the sample. The water used for pressure generation is separated from the pressure transmission fluid (nitrogen) by a differential pressure null indicator (8). As in all our measurements, an oil-operated standard deadweight gauge (9) made by Ruska is used for the pressure measurements.

3. RESULTS

3.1. Critical Properties

Different values for the critical temperature T_c are reported in the literature [1, 2, 4, 7, 11, 16–18]. Unfortunately, most of the authors do not indicate the source of their values. Only one T_c value has been obtained by observation of the vanishing meniscus [7]. This value is used for further analysis. The critical pressure was found by inserting this T_c value into a

Table I. Experimental Vapor Pressure of 2,2,2-Trifluoroethanol

T (K)	p (kPa)
353.15	128.96
353.15	128.98
363.15	186.09
363.15	186.07
373.15	261.82
383.15	360.01
383.15	360.16
393.15	484.95
393.15	485.02
403.15	641.16
403.15	641.26
413.15	833.19
413.15	833.34
423.15	1066.57
423.15	1066.60
433.15	1345.75
433.15	1345.77
443.15	1676.63
443.15	1676.84
453.15	2065.92
453.15	2066.09
463.15	2520.35
463.15	2520.51
473.15	3047.8
473.15	3047.6
478.15	3341.6
478.15	3341.6
483.15	3657.6
483.15	3657.7
488.15	3998.0
488.15	3998.1
493.15	4365.2
493.15	4365.4
495.15	4521.7
495.15	4520.9
495.15	4520.8
497.15	4681.4
497.15	4681.6
497.15	4681.2
498.15	4764.1
498.15	4764.5
499.15	4849.1
499.15	4849.1

vapor pressure equation fitted to the vapor pressure data obtained in this work. Volumetric measurements at the siphon vessel were used to determine an approximate value for the critical density.

Based on these considerations, the following critical data were selected.

$$T_c = (499.29 \pm 0.1)\ \mathrm{K}$$

$$p_c = (4860.6 \pm 0.1)\ \mathrm{kPa}$$

$$\rho_c = (487 \pm 12)\ \mathrm{kg \cdot m^{-3}}$$

3.2. Vapor Pressure

Forty-three experimental values of the vapor pressure are given in Table I. The data were fitted to a vapor pressure equation with four coefficients using the technique described by Wagner [19]. The resulting equation was found to have the structure

$$\ln \frac{p}{p_c} = \frac{T_c}{T} \sum_{i=1}^{4} a_i \left(1 - \frac{T}{T_c}\right)^{v_i} \tag{3}$$

Coefficients a_i and exponents v_i found by this regression analysis are given in Table II. The average and maximum of the relative deviations are 0.077×10^{-3} and 0.240×10^{-3}, respectively. These very small deviations of the measured vapor pressures from the vapor pressure equation with only four coefficients exhibit the high degree of precision obtained in the measurements with our apparatus. Vapor pressures at temperatures between 373 and 473 K reported by Girsberger [5] are, on average, 0.8% lower than the values from Eq. (3). Girsberger used TFE samples with a

Table II. Numerical Constants of Eq. (3) for the Vapor Pressure and Eq. (4) for the Saturated Liquid Density

i	v_i	a_i
1	1.0	−8.895557585
2	1.5	2.762807991
3	2.0	−3.310311526
4	3.0	−4.676431484
i	μ_i	b_i
1	1/3	2.072244026
2	2/3	0.565915839

Table III. Density of Liquid 2,2,2-Trifluoroethanol

p (MPa)	ρ ($kg \cdot m^{-3}$)
293.15 K	
0.4933	1391.2
2.1024	1393.7
4.0656	1396.7
6.0298	1399.7
7.9950	1402.6
9.9612	1405.4
11.9284	1408.1
13.8966	1410.8
15.8659	1413.4
313.15 K	
0.4927	1356.7
2.1018	1359.6
4.0650	1362.9
6.0292	1366.3
7.9945	1369.5
9.9607	1372.7
11.9279	1375.9
13.8962	1378.9
15.8654	1381.9
333.14 K	
0.4926	1319.6
2.1017	1323.1
4.0650	1327.1
6.0292	1330.9
7.9944	1334.7
9.9605	1338.3
11.9278	1341.9
13.8960	1345.3
15.8653	1348.6
353.15 K	
0.4920	1279.8
2.1011	1283.8
4.0643	1288.5
6.0285	1293.1
7.9937	1297.5
9.9600	1301.7
11.9272	1305.8
13.8954	1309.8
15.8647	1313.7

Table III. *(Continued)*

p (MPa)	ρ ($kg \cdot m^{-3}$)
373.15 K	
0.4926	1235.4
2.1017	1240.3
4.0649	1246.0
6.0292	1251.5
7.9944	1256.8
9.9607	1261.8
11.9279	1266.6
13.8962	1271.3
15.8655	1275.8
393.15 K	
0.8854	1188.0
2.1021	1192.7
4.0653	1200.1
6.0296	1207.0
7.9948	1213.4
9.9611	1219.6
11.9284	1225.4
13.8966	1231.0
15.8659	1236.2
413.16 K	
2.1024	1140.4
4.0657	1150.0
6.0300	1158.7
7.9952	1166.9
9.9615	1174.4
11.9288	1181.6
13.8971	1188.3
15.8664	1194.7

water content of 0.5% of the total mass. Vapor–liquid equilibrium (VLE) measurements in the binary system of water and TFE conducted in our laboratory show that vapor pressure differences between liquid mixtures with 0.04% water (TFE sample in this work) and those with 0.5% water (Girsbergers TFE sample) are in the range of 0.5% of the vapor pressure. The VLE measurements mentioned above will be reported elsewhere.

Table IV. Density of Gaseous 2,2,2-Trifluoroethanol

p (kPa)	ρ ($kg \cdot m^{-3}$)
413.15 K	
125.4	3.714
151.6	4.507
182.9	5.467
220.4	6.633
265.0	8.046
318.5	9.762
381.6	11.843
455.8	14.367
542.2	17.429
641.4	21.144
753.4	25.651
423.15 K	
146.3	4.257
176.7	5.163
213.1	6.265
256.7	7.599
308.9	9.220
370.6	11.184
443.8	13.568
529.7	16.461
629.8	19.969
744.7	24.226
874.4	29.390
443.15 K	
124.1	3.420
150.0	4.150
181.4	5.035
218.9	6.107
264.1	7.410
318.2	8.989
382.8	10.905
459.5	13.229
550.3	16.049
657.0	19.471
781.3	23.621
925.1	28.656
1088.2	34.764
1270.0	42.175
1466.9	51.164

Table IV. *(Continued)*

p (kPa)	ρ ($kg \cdot m^{-3}$)
453.15 K	
124.5	3.356
150.8	4.073
182.3	4.940
220.5	5.993
265.8	7.271
320.2	8.821
385.6	10.701
463.6	12.982
556.1	15.749
665.2	19.107
792.4	23.178
941.4	28.119
1111.5	34.114
1303.6	41.385
1515.7	50.201
1743.1	60.908
473.15 K	
131.2	3.377
158.8	4.098
192.1	4.971
232.1	6.030
280.2	7.315
338.1	8.875
407.6	10.766
490.4	13.061
588.9	15.845
705.9	19.223
843.6	23.320
1004.9	28.291
1191.8	34.322
1406.0	41.638
1647.5	50.513
1914.6	61.281

3.3. Liquid Density

Experimental 2,2,2-trifluoroethanol liquid density data are listed in Table III. The uncertainty of the density is estimated to be $\pm 0.12\ kg \cdot m^{-3}$. The liquid density on each of the isotherms was correlated as a function of pressure with second-order polynomials. Saturated liquid densities ρ' were calculated by introducing the vapor pressure into these polynomials. To the extrapolated density data the coefficients of the equation

$$\frac{\rho'}{\rho_c} = 1 + \sum_{i=1}^{2} b_i \left(1 - \frac{T}{T_c}\right)^{\mu_i} \tag{4}$$

were fitted. The coefficients b_i and the exponents μ_i of Eq. (4) are given in Table II. The average and maximum of the relative deviations from this equation are 0.329×10^{-3} and -0.696×10^{-3}, respectively.

3.4. Gas Density

The results of the Burnett experiments are given in Table IV. The compressibility factor

$$Z = \frac{p}{\rho RT} \tag{5}$$

was determined for five temperatures. The gaseous density of trifluoroethanol was calculated with the gas constant $R = 83.112\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. The uncertainty of the compressibility factor was estimated as ± 0.0025 at pressures close to ambient pressure and ± 0.0005 at higher pressures.

Unfortunetly, technical problems occurred with the measurements at 160 and 190°C. Therefore, no results can be reported for these isotherms. The measurements will later be extended to temperatures up to 320°C (593.15 K). The missing isotherms of 160 and 190°C will then also be measured to complete the experimental data.

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