Int J Thermophys (2010) 31:2078–2085
DOI 10.1007/s10765-010-0886-6

Density of Vapor and Liquid Pentafluorobenzene Along the Saturation Line

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Received: 26 April 2010 / Accepted: 11 November 2010 / Published online: 30 November 2010

Abstract The density of vapor and liquid pentafluorobenzene along the liquid–vapor coexistence curve has been studied by a gamma-ray attenuation technique over the temperature range from 293.5 K to 530.9 K. According to measurements, the coordinates of the critical point are $T_C = (531.04 \pm 0.05)$ K and $\rho_C = (518.8 \pm 2)\ \text{kg}\cdot\text{m}^{-3}$. The critical exponent β of the coexistence curve equals 0.345 ± 0.005. The results of our measurements were compared with data available in the literature. The height dependence of the density of a two-phase sample was investigated in relation to the temperature and time. These experiments made it possible to determine the isothermal compressibility of liquid and vapor phases near the critical point.

Keywords Critical exponent · Critical point · Density · Gamma densimeter · Gravitational effect · Isothermal compressibility · Liquid and vapor phases · Pentafluorobenzene

1 Introduction

Pentafluorobenzene is used as a solvent and raw material for organofluoric synthesis. A knowledge of its properties is necessary for optimization of technological processes and carrying out of scientific calculations. Data on pentafluorobenzene density in a wide temperature range were obtained previously only for the liquid phase up to

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490 K [1,2]. The critical density was defined by an extrapolation of the fitting equation for the saturated liquid density to the critical temperature. The purpose of this study is to obtain precise experimental data on the density of both liquid and vapor pentafluorobenzene along the saturation line from room temperature to the critical point.

2 Experimental

Measurements of the density of pentafluorobenzene (C_6HF_5) were carried out on a gamma-densimeter of the Institute of Thermophysics SB RAS described in detail in [3]. For the gamma-ray source, we use ^{137}Cs isotope having an activity of 50 GBq and a photon energy of 662 keV. The narrow beam of gamma quanta penetrates through the cell containing the two-phase system. The intensity of transmitted radiation is measured with a scintillation counter. The experimental cell is a thick-walled stainless steel cylinder, 40 mm in internal diameter and 140 mm in length. The face planes of the cylinder are closed with stainless-steel caps. The volume is connected with a filling vessel, a liquid level regulation system, and a vacuum pump by means of an arrangement of valves. The cell is placed in a dry thermostat. The temperature in the thermostat is held to within ±5 mK throughout the measurements. The lifting gear allows for vertical movement of the installation with respect to the beam and, thus, for measurements of the gamma-ray attenuation in the sample in relation to the distance from the cell bottom (h). This makes it possible for concurrent measurements of the densities of two equilibrium phases along the coexistence curve. The temperature of the samples is measured on ITS-90 with a 50 Ω platinum resistance thermometer calibrated at the Siberian Scientific Research Institute of Metrology, Novosibirsk. The uncertainty of the temperature, including the uncertainty of the calibration and the temperature gradients, does not exceed 0.05 K. The experimental errors of the liquid and vapor densities fail within (1 to 1.5) $\text{kg} \cdot \text{m}^{-3}$ over the temperature range from 293 K to 530 K.

3 Results and Discussion

The pentafluorobenzene sample was supplied by the Novosibirsk Institute of Organic Chemistry SB RAS with a stated minimum purity of 99.8 mol%. Before the experiments, the initial product was purified further by boiling for the purpose of removing dissolved gases and volatile components.

The density (ρ) was measured along the liquid–vapor coexistence curve. The value of the liquid density at room temperature was measured by the indirect Archimedean method with an uncertainty better than 0.03 %. In Table 1 and Fig. 1 are given the temperature dependencies of the present experimental densities of liquid and vapor pentafluorobenzene along the coexistence curve.

The hydrostatic (or gravitational) effect connected with the high compressibility of the sample near the critical point manifests itself in that densities of the phases become height-dependent when the temperature is close to the critical value (Fig. 2). This phenomenon was observed at temperatures above 529 K. To determine the

Table 1 Present experimental orthobaric liquid and vapor densities of pentafluorobenzene

T (K)	ρ_l (kg · m^{-3})	ρ_v (kg · m^{-3})
293.47	1525.2	–
314.00	1483.8	1.13
334.00	1441.8	–
353.98	1399.8	–
374.24	1353.6	–
393.95	1307.6	15.9
413.94	1257.5	24.8
413.94	–	24.9
413.95	–	24.7
433.98	1203.0	38.6
454.02	1142.5	58.3
473.98	1072.2	87.1
493.99	986.7	131.1
504.08	933.6	163.1
514.20	866.1	208.7
524.52	764.6	287.7
529.16	675.1[a]	366.3[a]
530.65	608.0[a]	432.1[a]
530.92	576.8[a]	458.1[a]

[a] Value was obtained by extrapolation (see text)

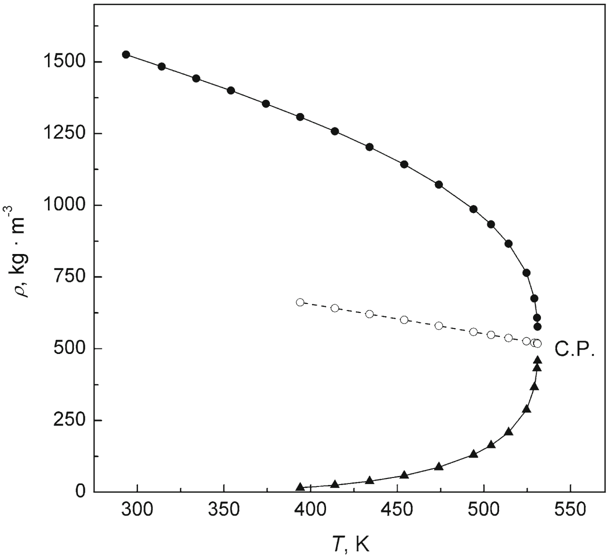

Fig. 1 Orthobaric densities of pentafluorobenzene along the liquid–vapor equilibrium line. *Solid circles* and *triangles* are the experimental points for liquid and vapor phases, respectively. *Open circles* are the midpoints of the coexistence curve

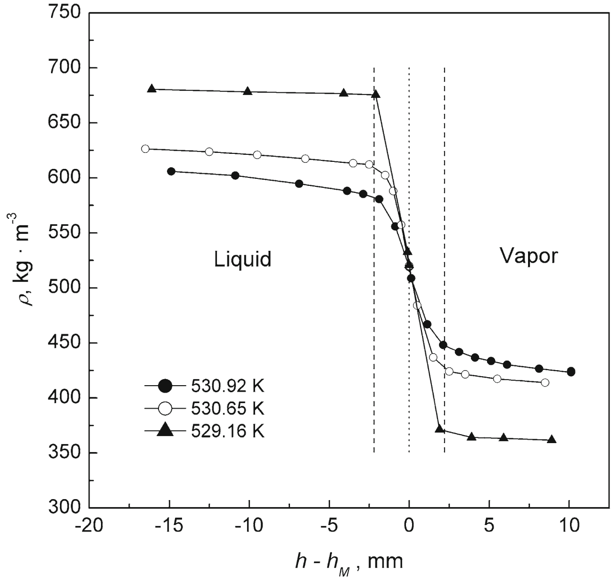

Fig. 2 Height dependence of the density of two-phase sample of pentafluorobenzene near the critical point. *Dotted line* is meniscus location, *dashed lines* show the boundaries of gamma-ray beam (see text)

densities of the liquid and vapor in equilibrium with each other, we must extrapolate to the two-phase interface. On the other hand, since the diameter of the gamma-ray beam is 4.4 mm, the stepwise density change occurring in passing through the interface appears as a continuous transition taking place in the height interval equal to the beam width (Fig. 2). The following procedure was used for determination of the meniscus location, h_M, and the densities of the equilibrium phases. The observed density profile over the region of it drastic change was fitted with a polynomial. It can be easily shown that the $\mathrm{d}\rho/\mathrm{d}h$ derivative has a maximum value when the axis of the gamma-ray beam passes through the phase boundary. This distance was taken as the meniscus location, h_M. The densities of the liquid (ρ_l) and vapor (ρ_v) phases in equilibrium with each other were determined by extrapolation of the approximate height dependencies of the liquid $\rho_\mathrm{l}(h)$ and vapor $\rho_\mathrm{v}(h)$ densities to h_M.

According to a theory of critical phenomena [4], the asymptotic behavior of the liquid–vapor coexistence curve in the vicinity of the critical point is described by

$$(\rho_\mathrm{l} - \rho_\mathrm{v}) = A\varepsilon^{\beta} \quad (1)$$

Here, $\varepsilon = 1 - T/T_\mathrm{C}$, T_C is the critical temperature, A is a constant, and β is the critical exponent of the coexistence curve. To determine β and T_C, data for the density (Table 1) over the range of ε from 2.23×10^{-4} to 0.107 were fitted by Eq. 1, where $A = 2150.86$, $T_\mathrm{C} = (531.042 \pm 0.050)$ K, and $\beta = 0.345 \pm 0.005$ (Fig. 3). A total error is listed for the critical temperature and critical exponent. Random errors of T_C and β are ±0.009 K and ±0.0035, respectively. The obtained value of the critical temperature agrees with the recommended value of $T_\mathrm{C} = (530.9 \pm 0.1)$ K [2], to

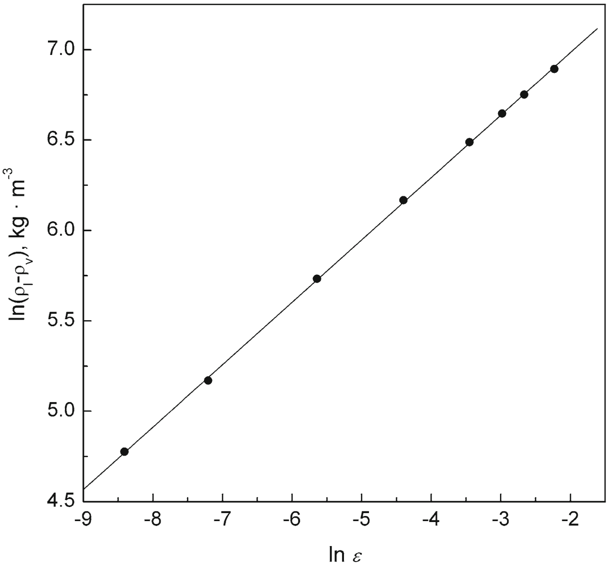

Fig. 3 Dependence of $\ln(\rho_l - \rho_v)$ on $\ln(\varepsilon)$ along the coexistence curve. The *circles* are experimental points. The *line* represents Eq. 1

within the estimated uncertainties. The present critical exponent value is practically equal to the β value of perfluorobenzene 0.343 ± 0.005 [3].

To determine the critical density (ρ_C), experimental data over the same temperature range were fitted by the equation [4],

$$(\rho_l + \rho_v)/2 = \rho_C + B\varepsilon,$$

where $B = 571.025\ \mathrm{kg \cdot m^{-3}}$, and $\rho_C = 518.83 \pm 2.0\ \mathrm{kg \cdot m^{-3}}$. A random error of ρ_C is $\pm 0.4\ \mathrm{kg \cdot m^{-3}}$. The present critical density value is in good agreement with the result of Hales and Townsend [1] ($\rho_C = 517.6\ \mathrm{kg \cdot m^{-3}}$). The data for the density of the liquid and vapor phases along the coexistence curve were fitted by the equation [5],

$$\rho_{l,v} = 518.83 \left(1 + C_1\varepsilon^{0.345} + C_2\varepsilon^{2/3} + C_3\varepsilon + C_4\varepsilon^{4/3}\right) \tag{2}$$

where $C_1 = -2.06335$, $C_2 = -0.19922$, $C_3 = 1.56677$, and $C_4 = 0$ for the vapor phase and $C_1 = 1.98732$, $C_2 = 0.84031$, $C_3 = -0.86740$, and $C_4 = 0.96259$ for the liquid phase.

Equation 2 describes the experimental data with standard deviations of $\pm 1\ \mathrm{kg \cdot m^{-3}}$ for the vapor (394 K to 530.9 K) and $\pm 0.55\ \mathrm{kg \cdot m^{-3}}$ for the liquid (293 K to 530.9 K). Figure 4 shows the results of our measurements in comparison with literature data [1]. The data for the densities of the saturated vapor and liquid make it possible to calculate the enthalpy of vaporization (ΔH_{vap}) using the Clausius–Clapeyron equation. For this purpose, the literature data for the saturated vapor pressure [6,7] in the range from 321.9 K to 528.18 K were approximated by the empirical equation,

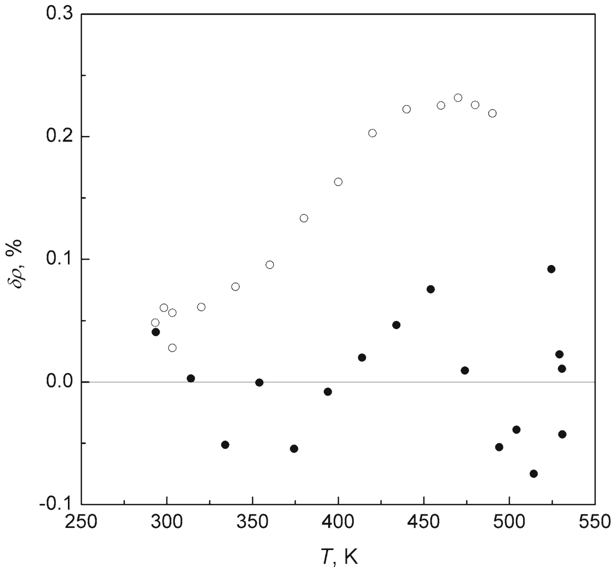

Fig. 4 Deviations (in %) of our data (*solid circles*) and data from [1] (*open circles*) for the density of liquid pentafluorobenzene along the coexistence curve from Eq. 2; $\delta\rho = 100[\rho_i/\rho_l(\text{Eq. 2}) - 1]$

Table 2 Calculated values of thermodynamic properties of pentafluorobenzene along the coexistence curve

T (K)	P_S (kPa)	ρ_l (kg · m^{-3})	ρ_v (kg · m^{-3})	ΔH_{vap} (J · mol^{-1})
400.00	319.47	1292.9	18.16	28731
420.00	509.40	1241.2	28.48	27249
440.00	775.28	1184.9	43.70	25237
460.00	1135.1	1121.9	65.73	22891
480.00	1609.6	1048.6	98.11	20108
500.00	2223.7	956.64	148.85	16542
510.00	2593.1	896.94	187.55	14199
520.00	3011.8	816.30	246.54	11039
530.00	3491.2	644.95	394.17	4574
531.04	3546.4	518.83	518.83	0

$$\ln(P_S) = \left(D_1\varepsilon + D_2\varepsilon^{1.25} + D_3\varepsilon^3 + D_4\varepsilon^7\right)\frac{T_C}{T} + D_5, \tag{3}$$

where P_S is in kPa, $D_1 = -8.32322$, $D_2 = 1.65886$, $D_3 = -3.13882$, $D_4 = -9.30177$, and $D_5 = 8.17369$. Equation 3 describes the data [6,7] with a standard deviation of ±0.04 %. A summary of the calculated thermodynamic properties for pentafluorobenzene along the coexistence curve is given in Table 2.

Figure 2 shows the results of our measurements of the sample density near the critical point in relation to the distance from the meniscus. These data make it possible

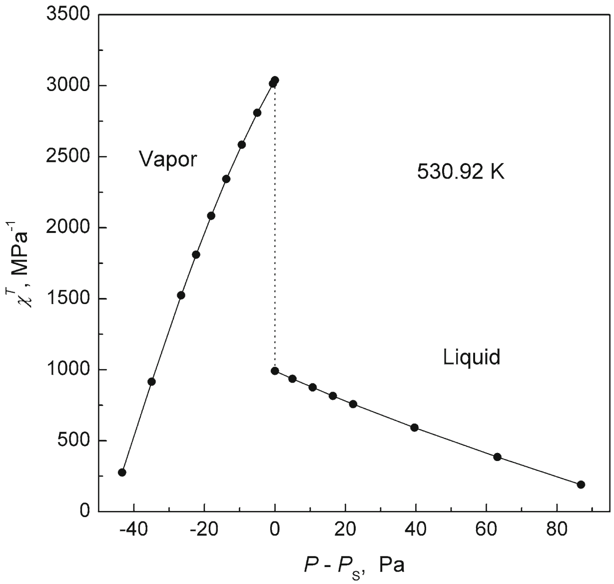

Fig. 5 Isothermal compressibility of pentafluorobenzene as a function of the pressure at 530.92 K

Table 3 Estimated isothermal compressibility of pentafluorobenzene along the coexistence curve

T (K)	P_S (kPa)	χ_l^T (MPa^{-1})	χ_v^T (MPa^{-1})
529.16	3447.8	71	387
530.65	3525.3	465	1984
530.92	3540.0	992	3039

to estimate an isothermal compressibility, $\chi_{v,l}^T$, of pentafluorobenzene in the liquid and vapor phases [3]. The approximated dependencies of $\rho_{v,l}(h)$, which have been obtained for the determination of the vapor and liquid densities on the saturation line, were used as initial data. Figure 5 and Table 3 show the results of the calculations. The uncertainty in $\chi_{v,l}^T$ is (15 to 35) %, and it is mainly determined by the error in $d\rho/dh$.

The asymptotic behavior of the isothermal compressibility on the liquid–vapor coexistence curve is described by [8]

$$\chi^T = A\varepsilon^{-\gamma}$$

where γ is the critical exponent for the compressibility. The treatment of Table 3 data gives the following values of the critical exponents: $\gamma_v = 0.75 \pm 0.20$, $\gamma_l = 0.95 \pm 0.16$ (the uncertainties of both values denote the random errors of approximation). The γ_v and γ_l values coincide with each other, as the theory predicted. However, their absolute value is much less than the most reliable experimental results, $\gamma = 1.2$ to 1.3 [4]. It seems likely that it is due to more sharp changes of the phase's density in the immediate vicinity of the liquid–vapor interface, which is not taken into account for an extrapolation of $\rho_{l,v}(h)$ dependencies to the meniscus.

4 Conclusion

The density of vapor and liquid pentafluorobenzene along the liquid–vapor coexistence curve has been studied by a gamma-ray attenuation technique over the temperature range from 293.5 K to 530.9 K. The purity of the samples used throughout the measurements was 99.8 mol%. The experimental uncertainties of the temperature and density measurements were estimated to be within 0.05 K and (1 to 1.5) $\text{kg} \cdot \text{m}^{-3}$, respectively. The critical temperature, critical density, critical exponent of the coexistence curve, and the temperature dependencies of the liquid and vapor density along the saturation line were determined. On the basis of the results from this study and literature data, the enthalpy of vaporization of pentafluorobenzene was calculated. The height dependence of the density of the two-phase sample was investigated in relation to the temperature and time. These experiments made it possible to determine the isothermal compressibility of the liquid and vapor phases near the critical point.

Acknowledgment We gratefully acknowledge the partial financial support for this research from the Russian Federal Agency for Education (Reg. No. 2.2.1.1/1269).

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