(P, ρ, T) Behavior of 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) at Temperatures between 253 K and 403 K and Pressures up to 20 MPa

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Pressure−density−temperature data (10 655 data points) in the gas and liquid homogeneous phases and in the bulk zone are reported for 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea). The measurements have been performed with a vibrating tube densimeter over 12 isotherms at temperatures between 253 K and 403 K and pressures up to 20 MPa. The uncertainties of temperature and density measurements are less than 0.02 K and 0.1 kg m^{-3}, respectively. The uncertainty on the pressure values is less than 2×10^2 Pa in the vapor phase and less than 2×10^3 Pa in the compressed liquid phase. A correlation for saturated liquid density has been developed from the present data. Furthermore, a comparison is made between experimental data and a semipredictive density model.

Introduction

The fluid 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) is a new generation refrigerant which is proposed as a promising substitute refrigerant for compression cycles and in particular for high-temperature heat pump applications. Over the past few years, a moderate amount of experimental density data have been published for this compound. The present work aims at increasing the amount of experimental data available, in the whole range of interest for this fluid. Notably, the present work is up to now the only source of density data in the compressed liquid region between 315 K and the critical temperature.

Experimental Section

Apparatus and Procedure. The density of R227ea was measured with an Anton Paar digital vibrating stainless steel tube densimeter (DMA 512, Graz, Austria) at temperatures from 253 K to 403 K and pressures up to 20 MPa.

A schematic diagram of the experimental cell and its peripheral equipment is given in refs 1 and 2.

The current method is designed for isothermal runs for both the calibrations of the vibrating tube and the density measurements. Pressure increases or decreases are obtained through mass transfers from a high-pressure-loading cell inside the measurement circuit.

As an indirect synthetic method, the vibrating tube densimeter is based on the application of the relation between the vibrating period of a one-dimensional resonator and its vibrating mass. The general principle has been reported by various authors.[3−8]

In a recent paper Bouchot and Richon[2] have shown that it is possible to generate accurate experimental P, ρ, T data over the whole state surface of pure compounds or mixtures in the regions of superheated vapor, compressed liquid, and bulk and along the coexistence curves, in the range of accessible temperatures.

Periods (τ) are converted into density (ρ) values through a calibration formula valid for both liquid and gas densities over the whole pressure and temperature operating ranges.

The development of this formula and the calibration procedure is fully described by Bouchot and Richon.[2] The parameters of the calibration formula are obtained by means of the densities of a single reference fluid, HFC R134a, for which an accurate equation of state is available,[9] vacuum being the second reference.

The DMA 512 cell can be modeled by means of a linear hollow vibrating system whose internal volume is

$$V_i = V_i(T,P) \tag{1}$$

The total vibrating mass of the system is

$$M = M_0 + \rho V_i \tag{2}$$

M_0 is the mass of the evacuated tube, and ρ is the fluid density to be determined. This system has a natural transversal stiffness:

$$K = K(T,P) \tag{3}$$

and is vibrating with a period (τ) in an undamped harmonic way under the effect of a mechanical excitation.

The relation between these quantities can be written in the following general form

$$\rho = (M_0/V_i)[(K/K_0)(\tau^2/\tau_0^{\,2}) - 1] \tag{4}$$

where K_0 and τ_0 are respectively the transversal stiffness and the vibrating period of the evacuated tube.

To ensure equilibrium through quasi-static transformations, the corresponding flow rates have been set sufficiently low. They usually cause a speed of pressure decrease below 5×10^3 Pa s^{-1}.

Thermal regulation was performed through a regulated thermal liquid bath. Temperature stability is achieved within 0.005 K inside the branches of the vibrating tube during at least 15 min using a P.I.D. regulator (Hallikainen, GEC Elliott, London, U.K.). The ITS-90 tempera-

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ture inside the tube was measured by means of a four-wires 100 Ω/0 °C Pt resistance probe, which was calibrated against a 25 Ω reference probe (5187SA-Tinsley- “Les automatismes appliqués”, France).

The uncertainty on temperature measurements is estimated to be 0.02 K. For pressure measurements, two pressure transducers (Druck PTX611) are used to work respectively up to 0.25 and 4 MPa; a third one (Sedeme) is used for pressure measurements up to 25 MPa. In this work, the pressure transducers were calibrated against a dead weight balance (Desgranges & Huot model 5202S CP, Aubervilliers, France) in the range 3×10^5 to 25×10^6 Pa. In the range from 10 Pa to 4×10^5 Pa, the pressure transducers were calibrated against a numerical pressure standard (Desgranges & Huot model 24610).

The apparatus allows measurements up to 423 K and 40×10^6 Pa. An on-line data acquisition system connected to a computer through a GP-IB port enables the recording of the temperature−pressure−period data during an isothermal run. A detailed description of the experimental procedure is reported by Bouchot.[1]

The uncertainties on pressure measurements are estimated to be less than 2×10^2 Pa in the vapor phase and less than 2×10^3 Pa in the compressed liquid phase, because of the fact that three pressure transducers are used. The maximum uncertainty on densities, resulting from the propagation of vibrating period, temperature, and pressure errors, is estimated to be ± 0.1 kg·m^{-3} on any value from low-pressure vapor densities to high-pressure compressed liquid densities.

Materials. The C_3F_7H, 1,1,1,2,3,3,3-heptafluoropropane (R227ea), was supplied by Solvay Fluor und Derivate (Hannover, Germany) as a material of stated purity better than 99.99%. It was then degassed and distilled under vacuum.

Results

The experimental (P, ρ, T) data for R227ea, along twelve isotherms (253, 267, 280, 294, 308, 322, 335, 349, 363, 377, 389, and 403) K and at pressures up to 20 MPa, are all tabulated and reported in files in the Supporting Information.

The files contain respectively compressed liquid, superheated vapor, and bulk zone data. For the compressed liquid, superheated vapor, and bulk zone, 6888, 956, and 2811 points were respectively measured for a total of 10 655 data points.

The present experimental data are represented in Figure 1.

Discussion and Conclusions

Saturated Liquid Density. Compressed liquid density data have been fitted against pressure for each isotherm. Each correlation was then extrapolated to the saturation pressure, calculated from a literature correlation.[10] The extrapolated saturation density data are reported in Table 1.

These saturated liquid density data have then been regressed as a function of temperature assuming the following expression:

$$\rho^{\mathrm{sl}} = \rho_{\mathrm{c}}\left(1 + \sum_{i=1}^{4} a_i x^i\right) \qquad (5)$$

where

$$x = [(T_{\mathrm{c}} - T)/T_{\mathrm{c}}]^{1/3} \qquad (6)$$

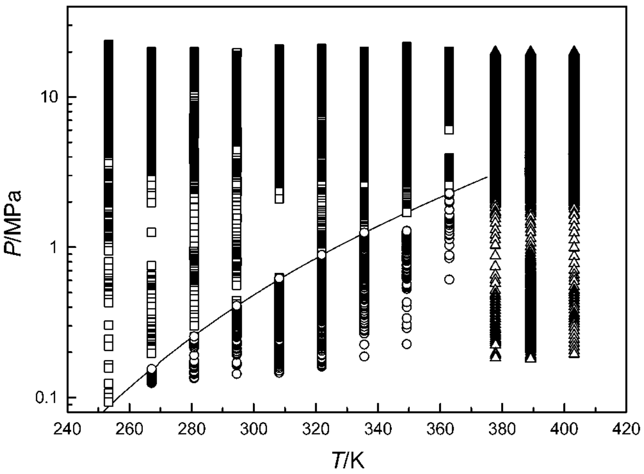

Figure 1. Present density data for R227ea: □, liquid; ○, vapor; △, supercritical fluid; —, saturation line.

Table 1. Saturated Liquid Density

T/K	ρ/kg·m^{-3}	T/K	ρ/kg·m^{-3}
253.37	1555.08	321.90	1279.08
267.09	1506.28	335.59	1201.28
280.81	1456.72	349.27	1111.65
294.55	1402.31	362.95	983.95
308.20	1341.23		

Table 2. Coefficients for Eq 5

i	a_i
1	1.752 869 7
2	1.647 689 9
3	−1.862 025 4
4	1.339 730 1

Table 3. Critical Constants of R227ea

T_c/K	375.95
P_c/kPa	2934.6
ρ_c/kg·m^{-3}	580

The coefficients of eq 5 are given in Table 2. The critical constants adopted were privately communicated by D. Defibaugh and J. Schmidt to the authors and are reported in Table 3.

This equation has been validated against saturated liquid sources available in the literature.[11−13] The results of the validation are presented in Table 4, together with the claimed experimental uncertainties, and in Figure 2.

Compressed Liquid, Superheated Vapor, and Bulk Zone Densities. The following sources of density data have been found in the literature for R227ea: ref 14 for the liquid phase, ref 15 for the vapor phase, and ref 16 for the bulk zone. These data are represented in Figure 3.

The first aim was to check previous literature data against the density model of Scalabrin et al.[17,18] This is a semipredictive model that requires an initial density value in the liquid phase, either at saturated or compressed conditions. It is able to represent the whole (P, ρ, T) surface, except for the zone just above the critical isotherm. The initial data were the saturated liquid density at $T_{\mathrm{r}} = 0.7$, calculated through the correlation presented in the preceding section. As reference fluids in the cited model, the fluids R12 and R134a were chosen. Dedicated equations of state for both these fluids were assumed from the literature.[9,19]

The only quantities needed to establish the density model are the critical constants which are reported in Table 3, together with the following data: saturated liquid density at $T_{\mathrm{r}} = 0.7$ ($T = 263.16$ K), $\rho_{\mathrm{sl}} = 1520.94$ kg·m^{-3}, and molar mass = 170.03 g·mol^{-1}.

Table 4. Validation of Saturated Liquid Density Correlation against Literature Data[1]

ref	year	AAD (%)	BIAS (%)	max. (%)	NPT	uncertainty (%)		
						ρ	T	P
this work		0.046	0.000	−0.12	9	1×10^{-2}	7×10^{-3}	7×10^{-2}
11	1992	2.720	2.414	7.80	8		3×10^{-3}	10^{-2}
12	1993	2.059	−2.059	−2.42	7	2	3×10^{-2}	3
13	1997	0.064	0.051	0.24	26	5×10^{-2}	3×10^{-3}	0.5

[1] NPT = number of experimental points.

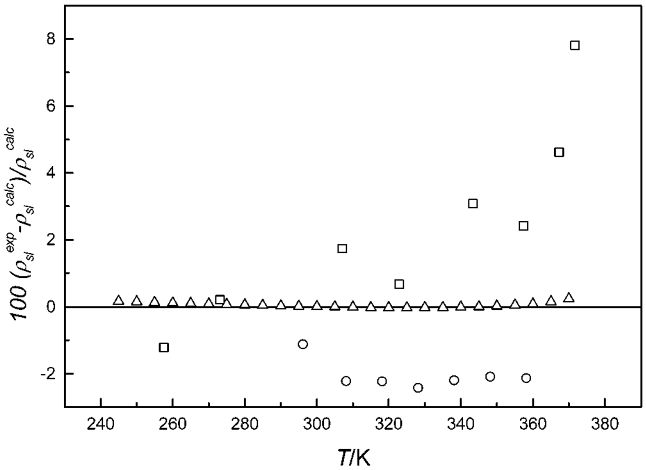

Figure 2. Relative percent deviations between saturated liquid density correlation and literature data: □, ref 11; ○, ref 12; △, ref 13.

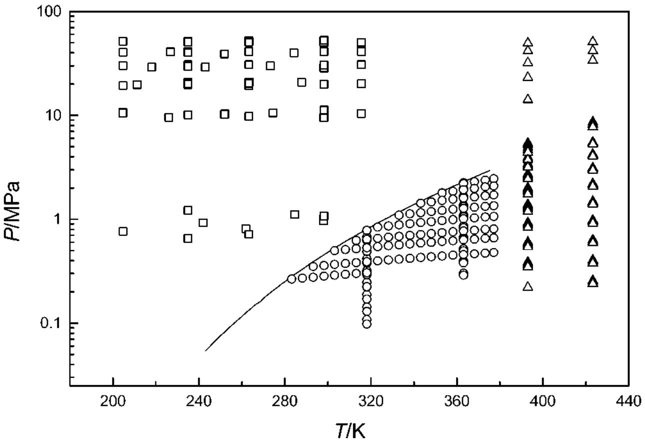

Figure 3. Literature density data for R227ea: □, ref 14; ○, ref 15; △, ref 16; —, saturation line.

Table 5. Validation of Density Model against Literature Data[1]

ref	year	phase	AAD (%)	BIAS (%)	max. (%)	NPT
14	1994	liq	1.083	−1.071	−2.01	83
15	1999	vap	0.247	−0.092	−1.56	141

Table 6. Validation of Our Data against the Density Model[18]

phase	AAD (%)	BIAS (%)	max. (%)	NPT
liq	0.828	−0.819	−1.85	6888
vap	0.424	−0.346	−2.41	952

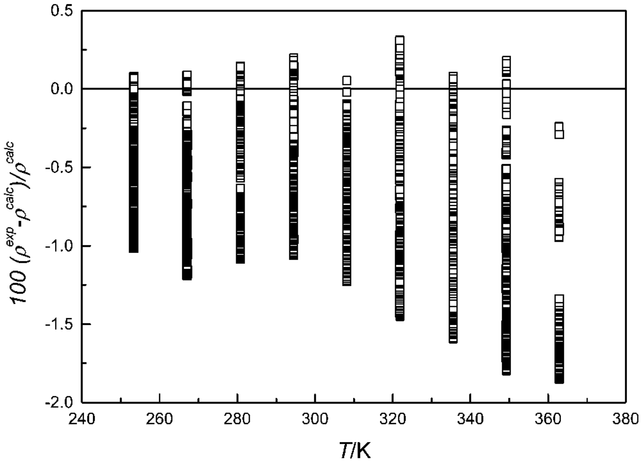

Figure 4. Relative percent deviations between present liquid-phase data and the density model.

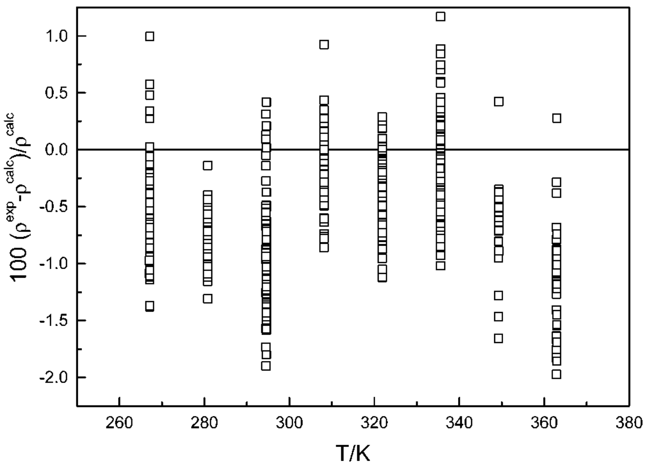

Figure 5. Relative percent deviations between present vapor-phase density data and the density model.

Validation results for the literature data are reported in Table 5. We did not take into consideration the bulk zone data near the critical isotherm, such as for instance the data reported in ref 16, since the density model is not reliable in this zone. We verified then the present experimental data against the same model, and the results are presented in Table 6.

Both literature data and present data are in good agreement with the density model. In fact, its uncertainty, in terms of AAD, is reported to be about ±0.5%.[17,18] The results for the vapor phase are below this value, both for literature data and for present data. The results for the liquid phase report an AAD which is roughly twice as large as that for vapor, but this is due mainly to the high-pressure limit, where it is known that the model accuracy slightly decreases.

In Figures 4 and 5 relative percent deviations between our data and the density model are shown, for the liquid and vapor phases, respectively.

Supporting Information Available:

Measured thermodynamic quantities tabulated for the various isotherms and reported in ASCII format. This material is available free of charge via the Internet at http://pubs.acs.org.

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