



Compressed liquid densities of binary mixtures of difluoromethane (R32) and 2,3,3,3-tetrafluoroprop-1-Ene (R1234yf) at temperatures from (283 to 363) K and pressures up to 100 MPa

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ABSTRACT

The compressed liquid densities of binary mixtures difluoromethane (R32) and 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) were measured using a high pressure vibrating-tube densimeter over the temperatures from (283 to 363) K and pressures up to 100 MPa at five different compositions, $x_{R32} = (0.189, 0.268, 0.500, 0.723, 0.904)$ in the present work. The combined expanded uncertainties of the temperature, pressure, mole fraction and the density with a level of confidence of 0.95 ($k = 2$) is estimated to be 16 mK, 0.062 MPa ($p \leq 60$ MPa), 0.192 MPa (60 MPa $< p < 100$ MPa), 0.01 and up to $0.6 \text{ kg} \cdot \text{m}^{-3}$ depending on the temperature and pressure ranges, respectively. The experimental data were correlated using the modified Tait equation. The isothermal compressibility, κ_T , and the isobaric thermal expansivity, α_p , were determined using liquid densities of mixtures and modified-Tait equation. Furthermore, the relative deviations of the experimental data with the equation of state (EOS) from Akasaka were lower than 1% from (283 to 363) K with the pressure up to 40 MPa.

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1. Introduction

Chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are three categories of refrigerants which have been used in the air conditioning, the heating and ventilating. CFCs and HCFCs have been phased out with relatively high global warming potential (GWP) values and high ozone depletion potential (ODP). The phase-out process of R22 has already been accomplished while the US will stop using R22 in 2020. In developing countries such as China, India and Vietnam, the phase out has started in 2015 and will be finished in 2030 according to the Montreal Protocol [1].

As an alternative refrigerant for R22, R32 has ODP of zero, GWP of 675 that applied in the domestic air conditioner, heat pump and refrigeration equipment [2–4]. The enthalpy of vaporization of R32 is greater than R22 and its air conditioning charge is two-thirds of R22 under the same cooling capacity. In China, the refrigeration and air conditioning industry are one of major consumer industries of HCFCs and at least 16 production lines used R32 as an alternative for R22 to produce air conditioning. However, the main disadvantages of pure R32 are that its high saturated vapor pressure,

high GWP and the high temperature are generated at the outlet of the compressor.

In order to find ways to improve the properties of pure R32, it is believed that the refrigerant mixture of R32 and new refrigerant can balance both the environment and performance requirements to get a high system coefficient of performance for refrigeration equipment [5]. As an alternative refrigerant to 1,1,1,2-tetrafluoroethane (R134a), 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) has a low GWP of 4 and ODP of zero. Also, the life cycle climate performance (LCCP) of R1234yf is lower than that of R134a, and the atmospheric decomposition products are the same as R134a. The important is that R1234yf has low saturated vapor pressure, and is considered to be a new generation of automotive alternate refrigerant with potential, and has been accepted by automobile manufacturers in Western Europe.

The study of R32/R1234yf mixture mainly focused on the flow and heat transfer performance in the tube were reported [6,7]. Kojima et al. [8] measured the COPs of R32/R1234yf with GWP of approximately 190 with a vapor compression cycle under two heating modes, where the heat sink water change temperature 10 K and 25 K. At a temperature change of 10 K, the COPs of mixtures are significantly lower than that of R410A. These studies have shown that the mixture of R32 and R1234yf is an alternative refrigerant. The thermophysical properties of mixtures of R32 and R1234yf were summarized in Table 1. Table 1 shows that only

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Table 1
Thermodynamics properties of R32 + R1234yf.

Property	T/K	P/MPa	Method	Author	AAD(%) ^a
VLE	273–333	–	Static method	Kamiaka et al. [11]	3.63
VLE	283–323	–	Molecular simulation	Hu et al. [12]	0.57
Surface tension	293 - T_c	–	Surface light scattering	Cui et al. [13]	4.37
Liquid viscosity	293 - T_c	–	Surface light scattering	Cui et al. [13]	0.86
Liquid viscosity	283–323	1.58–2.74	Moving piston digital viscometer	Dang et al. [14]	2.0
Vapor viscosity	278–338	atmospheric	Falling-ball-type viscometer	Dang et al. [15]	0.555
Liquid density	283–323	1.58–2.74	densimeter	Dang et al. [14]	–
Liquid density	273–373	up to 10	Anton Paar U shape	Li et al. [16]	–
Gaseous PvTx	279–347	0.10–2.66	Single-sinker magnetic suspension densimeter	Cai et al. [17]	0.23

^a Average absolute deviation for properties in the literatures.

one literature presents experimental liquid densities with limited temperature and pressure ranges. Additionally, Akasaka et al. [9] measured the critical point of R32 + R1234yf by a visual observation of meniscus disappearance. Also, Akasaka et al. [10] established the state of equation in the Helmholtz energy within the temperature range from (263 to 373) K and pressure range of (2 to 40) MPa.

In this work, the compressed liquid densities of binary mixtures of R32 and R1234yf were measured over the temperature range from (283 to 363) K and at pressures up to 100 MPa using a high pressure vibrating-tube densimeter covering the whole mole fraction of $x_{R32} = (0.189, 0.268, 0.500, 0.723, 0.904)$. The experimental data were correlated using the modified Tait equation and compared with the equation of state (EOS). Furthermore, the isothermal compressibility, κ_T , and the isobaric thermal expansivity, α_p , were calculated.

2. Experimental

2.1. Samples

R1234yf was manufactured by Honeywell International Inc. with a stated mass fraction purity greater than 0.999. R32 was supplied by Zhejiang Lantian Environmental Protection Fluoro Material Co., Ltd. with a declared purity of 0.998 mass fraction. R1234yf and R32 were degassed with a freeze/pump/thaw process three times. The specifications of chemical samples are summarized in Table 2.

2.2. Measurements

The compressed liquid densities of binary mixtures of R32 and R1234yf were measured using the Anton Paar vibrating-tube densimeter (DMA HPM) at temperatures from 283 K to 363 K and pressures up to 100 MPa. The vibrating-tube densimeter was calibrated with water and vacuum over the entire temperature and pressure ranges. A detailed description of the instrument, calibration procedure, and uncertainty determination can be found in our previous works [18–25]. The combined expanded uncertainties U_c , with a confidence level of 0.95 ($k=2$), are $U_c(T) = 16$ mK, $U_c(p) = 0.062$ MPa ($p \leq 60$ MPa), $U_c(p) = 0.192$ MPa ($60 < p < 140$ MPa), $U_c(x) = 0.01$, and $U_c(\rho) = 0.6$ kg·m⁻³, respectively.

Table 2
Specification of samples.

Chemical name	CAS Reg.No.	Molecular formula	Source	Initial mass fraction purity ^a	Purification method
Difluoromethane	75-10-5	CH ₂ F ₂	Zhejiang Lantian	0.998	Freeze/pump/thaw
2,3,3,3-Tetrafluoroprop-1-Ene	754-12-1	CF ₃ CFCH ₂	Honeywell International Inc	0.999	Freeze/pump/thaw

^a All the stated purities of the samples listed above were obtained by the certificates of suppliers, and no purity measurement was performed after purification.

In our previous work, Yang et al. [25] measured the high pressure densities of R134a in the temperature range of (283 to 363) K and at the pressure range of (3 to 80) MPa in order to confirm the reliability of the experimental system. The maximum relative deviation is 0.18% and the average relative deviation is 0.01% of the experimental density data and the calculated values, which are in good agreement with the standard equation. Therefore, the experimental system is reliable and the accuracy of the measurement results is reasonably acceptable.

3. Results and discussion

3.1. Experimental data

The experimental densities of the binary mixtures of $\{(x) \text{ R32} + (1-x) \text{ R1234yf}\}$ with mole fraction $x_{R32} = (0.189, 0.268, 0.500, 0.723, 0.904)$ along isotherms between (283 and 363) K at pressures up to 100 MPa are given in Table 3. The experimental data of the binary mixtures of R32/R1234yf with the mole fraction $x = 0.189$ versus pressure and temperature are plotted in Figs. 1 and 2, respectively. As shown in Figs. 1 and 2, the measured densities smoothly increase with pressure increasing for each measured isotherm and decrease with temperature increasing for each measured isobar. The experimental data of R32/R1234yf binary mixtures at the temperature of 283 K are plotted in Fig. 3 shown the densities decrease with the mole fraction of R32.

3.2. Correlation

In order to facilitate the application of the experimental results in practical engineering, the density experimental data were correlated using the modified Tait equation for each mixture, which has been used in our previous works: [26–29]

$$\rho(T, p) = \frac{\rho_0(T)}{1 - C \ln((B(T) + D(p))/(B(T) + 0.1 \text{ MPa}))} \quad (1)$$

where $\rho_0(T)$ represents the density of fluid at reference pressure $p_0 = 0.1$ MPa, which is the function of temperature only. $B(T)$, C and $D(p)$ are adjusted parameters. It is assumed that $B(T)$ is dependent on temperature, C is independent on temperature and $D(p)$ is dependent on pressure. Therefore, the optimal structure of the temperature function $\rho_0(T)$, $B(T)$ and $D(p)$ are described by the polynomial

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