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Thermodynamic properties of (R1234yf + R290): Isochoric $p\rho Tx$ and specific heat capacity c_v measurements and an equation of state

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ABSTRACT

In this paper, isochoric $p\rho Tx$ and specific heat capacity c_v for (R1234yf + R290) binary mixtures were measured using an adiabatic batch calorimeter with intermittent heating. A total of 42 $p\rho Tx$ data points over temperatures from (254.28 to 348.30) K and 89 isochoric specific heat capacity data points over temperatures from (255.48 to 347.55) K were obtained for liquid (R1234yf + R290) with mole fractions of R1234yf at (0.825, 0.607, 0.521 and 0.285). The standard uncertainties were estimated to be 10 mK for temperature, 5 kPa for pressure, 0.3% for density and 1.0% for isochoric specific heat capacity. The experimental $p\rho Tx$ data were correlated by an empirical Tait equation with average absolute relative deviation of 0.19%. A Helmholtz energy equation of state based on the multi-fluid approximations model was developed for (R1234yf + R290) using the present and available experimental data. Eleven mixture rules are employed and the optimal Helmholtz energy equation of state calculates the density, VLE and isochoric specific heat capacity properties with sufficient accuracy. The compressed liquid density and isochoric specific heat capacity data in this work are well represented with average absolute relative deviation of 0.21% and 0.66%, respectively.

1. Introduction

In recent years, with global warming and ozone depletion, looking for alternative refrigerants that are efficient and environmentally friendly is of much significance. The positive azeotrope (R1234yf + R290) mixtures [1] is a potential alternative refrigerant for its zero ozone depletion potential, ultra-low global warming potential, lower flammability than pure R290 and much better volumetric refrigeration capacity than pure R1234yf. Knowledge of reliable thermophysical property of refrigerant is essential for evaluating the performance in the refrigeration cycle. In our previous work, we measured the gaseous pressure-density-temperature-mole fraction ($p\rho Tx$) property from (265.546 to 300.268) K [2] and saturated liquid $p\rho Tx$ property from (255.048 to 300.135) K [3] for (R1234yf + R290) mixtures using a compact single-sinker densimeter. Additional, we studied the vapour–liquid equilibrium (VLE) property [1] from (253.150 to 293.150) K using an apparatus based on the recirculation method. Brown et al. [4] obtained its gaseous density at temperatures from (268.15 to 363.15) K by the constant-volume method.

Among the above studies, truncated virial equation of state (EOS), PR-VDW model (Peng-Robinson EOS [5] combined Van der Waals [6] mixing rule) and PT-VDW (Patel-Teja EOS [7] model combined Van der Waals mixing rule) were used to correlate the gaseous density data [2,4], empirical VDNS [8] and modified Rackett [9,10] equations were applied to fit the liquid density data [3], and PR-VDW model and PR-HV-NRTL model (PR EOS with non-random two liquids [11] activity coefficient model involving Huron–Vidal [12] mixing rule) were used to present the VLE data [1]. However, these equations are not accurate enough to present the experimental data of many different properties simultaneously. The virial EOS is only suitable for gaseous state and the cubic EOSs are hard to describe liquid properties.

This work measured the isochoric $p\rho Tx$ and specific heat capacity c_v of compressed liquid (R1234yf + R290) mixtures. The $p\rho Tx$ data were obtained at temperatures from (254.28 to 348.30) K and the c_v data were obtained at temperatures from (255.48 to 347.55) K with mole fractions of R1234yf at (0.825, 0.607, 0.521 and 0.285). What's more, a Helmholtz energy EOS based on the multi-fluid approximations model was developed for (R1234yf

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+ R290) using the present and available experimental data. The Helmholtz energy EOS calculates the density, VLE and isochoric specific heat capacity properties with sufficient accuracy for technical applications.

2. Experimental

2.1. Chemicals

Table 1 contains the critical temperatures, critical pressures, critical densities and acentric factors for the measured samples of R1234yf [13] and R290 [14]. R1234yf was supplied by Honeywell with a stated mole fraction purity of no less than 0.999, while R290 was supplied by Beijing AP BAIF Gases Industry Co. Ltd. with a claimed mole fraction purity of no less than 0.999. All the samples were used without further purification.

2.2. Experimental apparatus and uncertainty

As shown in Fig. 1, the adiabatic batch calorimeter that was used for these measurements has been described in our previous work [15] and the accuracy was verified by measuring the liquid c_v of propane at temperatures from (236.31 to 339.76) K, it is only briefly introduced here. The sample heat capacity is decided by:

$$c_v = (Q - Q_0 - W_{pv})/(m\Delta T) \tag{1}$$

where Q is the electric energy supplied to the sample bomb, Q_0 is the heat applied to the empty bomb, W_{pv} is the change-of-volume work due to the slight dilation of the cell, m is the mass of sample, and ΔT is the temperature rise during a heating process. In this work, the compressed liquid density is obtained by:

$$\rho = m/V_{\mathrm{bomb}} \tag{2}$$

where m is the mass of sample, V_{bomb} is the bomb volume and calibrated as a function of both temperature and pressure with the uncertainty of 0.1 cm^3 in our previous work [15]:

$$V_{\mathrm{bomb}} = \left[1.53 \times 10^{-3}(T - 273.15) + 71.80\right] \times (1 + (2.80 \times 10^{-4})p) \tag{3}$$

The temperature was measured by a 25 Ω standard platinum resistance thermometer (SPRT) with an uncertainty of 4 mK. An $8^1/_2$ multimeter (KEITHLEY 2002) was used to acquire the temperature and the overall standard uncertainty of temperature was estimated to be 10 mK. A Mensor CPT6010 digital pressure transducer (DPT) with a stated accuracy of 0.02% was used to measure the pressure, and the range of 20 MPa was used in this experiment. The overall standard uncertainty of pressure was estimated to be 5 kPa. The tested samples were filled by gravimetrically with a 10 mg resolution and the standard uncertainties in mole fraction were estimated to be less than 0.002. Considering the uncertainties from the mass, calibrated volume and mole fraction, the standard uncertainty for the density was estimated to be 0.30%.

As for the specific heat capacity, the heat applied to the bomb was supplied by a KEITHLEY 2230G-30-1 DC Power Supply and the uncertainty in heat energy was estimated to be less than 0.15%. An empirical compressed liquid density equation was developed according the density measured above and the mass m in Eq. (1) was calculated by the calibrated volume and the density values derived by the empirical equation. The uncertainty for the m was estimated to be less than 0.40%, including the uncertainties from the calculated density and the volume. The derivative quantity in W_{pv} calculation was also derived by the developed compressed liquid density equation. The uncertainty was estimated to be less than 0.40% as a consequence of the deviation of the calculated pressure derivative and the uncertainty of the volume change. By combining the various sources of experimental uncertainty, the standard uncertainty in heat capacity is calculated to be less than 1.0%.

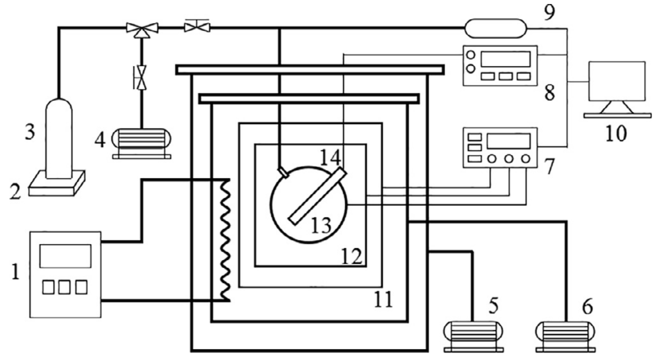

Fig. 1. Schematic diagram of the experimental system: 1, refrigerating machine; 2, scale; 3, gas cylinder; 4–6, vacuum pump; 7, DC power system; 8, multimeter; 9, pressure transducer; 10, computer; 11, outer adiabatic shield; 12, inner adiabatic shield; 13, bomb; 14, thermometer.

3. Experimental results and discussion

3.1. Compressed liquid density and isochoric specific heat capacity results

Compressed liquid density data for (R1234yf + R290) binary mixtures are presented at temperatures ranging from (254.28 to 348.30) K with mole fractions of R1234yf from (0.285 to 0.825). The experimental results are listed in Table 2.

The Tait equation [16] was used to correlated the density data, it has the following form:

$$\rho^{-1} = \rho_s^{-1}\left[1 - C\ln\left(\frac{B + p}{B + p_s}\right)\right] \tag{4}$$

with B given by Eq. (5). The saturation pressure p_s and saturation density ρ_s were calculated from the developed PR-vdW model and modified Rackett equation for (R1234yf + R290) mixtures in reference [3], respectively.

$$B = p_c[-1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3}] \tag{5}$$

$$T_r = T/T_{cm} \tag{6}$$

Table 1
Information of the two samples used in this work.[a]

Materials	CAS no.	Mole fraction[b]	T_c/K	p_c/MPa	ρ/kg·m^{-3}	ω
R1234yf[c]	754-12-1	>0.999	367.85	3.382	475.55	0.276
R290[d]	74-98-6	>0.999	369.89	4.251	220.48	0.152

[a] T_c, p_c and ω were taken from reference [13] for R1234yf and reference [14] for R290.
[b] As stated by the supplier, and used without further purification.
[c] 2,3,3,3-tetrafluoroprop-1-ene, supplied by Honeywell.
[d] Propane, supplied by Beijing AP BAIF Gases Industry Co. Ltd.