

Gas phase *PVTx* properties for binary mixtures of HFC-161 and HFC-134a

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ABSTRACT

An experimental study of the pressure–volume–temperature–composition (*PVTx*) properties in the gas phase for binary mixtures of ethyl fluoride (HFC-161) and 1,1,1,2-tetrafluoroethane (HFC-134a) was conducted in the range of temperatures from 318.22 to 403.20 K, pressures from 1120.6 to 5767.0 kPa, densities from 0.494 to 3.974 mol dm^{−3}, and compositions from 0.3203 to 0.9474 HFC-161 mole fractions. The measurements were performed with an isochoric cell apparatus. The uncertainties in the present work were estimated to be ±1.5 kPa for pressure and ±6 mK for temperature. On the basis of the experimental *PVTx* property data, a truncated virial equation of state was developed for the HFC-161/134a binary system. This equation reproduces the experimental data in the gas phase within ±0.18% in pressure and within ±0.32% in density.

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1. Introduction

With the increasing recognition of environment protection, a great deal of attention has been devoted to the negative environmental effect of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). It is strongly recommended to replace remaining CFCs and HCFCs with zero ozone depletion potential (ODP) refrigerants such as hydrofluorocarbons (HFCs). Ethyl fluoride or HFC-161 has a boiling point 235.85 K and critical temperature 375.31 K that are desirable for an HCFC-22 alternative. However, the flammability of HFC-161 lowers its potential as a refrigerant. 1,1,1,2-Tetrafluoroethane (HFC-134a) is nonflammable for it to serve as a replacement for CFCs and HCFCs in refrigeration application. Reliable information about the thermodynamic properties of HFC-161/134a is essential for its application as a working fluid in the refrigeration system. The vapor–liquid equilibrium properties of the mixtures as refrigerant containing HFC-161 are also discussed by Beyerlein, Kul et al. [1–3]. However, for the HFC-161/134a binary system, there are no published reports on its gas phase *PVTx* properties.

PVTx data are required as one of the most important types of information in evaluating the performance of refrigeration cycles and determining their optimal compositions. In the present study, we aim to measure a first set of *PVTx* properties in the gas phase of this important binary blend. A total of 111 gaseous *PVTx* data for the HFC-161/134a binary system were measured using an isochoric method in a wide range of temperatures from

318.22 to 403.20 K and corresponding pressures from 1120.6 to 5767.0 kPa.

2. Experimental

The experimental apparatus includes a sample cell, a high-accuracy thermostatic bath, a pressure measurement system, a temperature measurement system, and a vacuum system. It is the same as the one described previously [4].

The temperature in the thermostatic bath can be varied from 230.15 to 453.15 K. The bath fluid is alcohol, distilled water, or silicon oil, depending on temperature range. Its temperature fluctuations are determined to be less than ±3 mK in 30 min. The temperature measurements are made with a four-lead 25 Ω platinum resistance thermometer and a Keithley 2010 data acquisition/switch unit. The overall temperature uncertainty is ±6 mK.

The pressure measurement system includes a pressure transducer, a diaphragm differential pressure detector, an oil-piston type dead-weight pressure gauge, and an atmospheric pressure gauge. The whole pressure measurement system has an uncertainty of ±1.5 kPa in the pressure range of 0.1–6.0 MPa.

For the isochoric method, the vessel was filled with a known sample mass using a precision chemical balance. The accuracy of the balance is ±0.5 mg, and its maximum allowable mass is 1.5 kg. The uncertainty in density values is estimated to be within ±0.15% in present work. Considering all the possible effects on the composition determination, the uncertainty of the sample compositions determined in the present measurements was estimated to be ±0.1 mol%.

The samples of the HFC-161 and HFC-134a, provided by Zhejiang Chemical Industry Research Institute, have a purity of 99.74 mass%

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for the HFC-161 with the principal impurities of ethylene and isobutane, and 99.99 mass% for the HFC-134a. They were used without further purification.

3. Results and discussion

In this study, a total of 111 PVTx data were obtained at temperatures from 318.22 to 403.20 K along 9 independent isopleths: 0.3203, 0.4301, 0.5191, 0.5217, 0.5472, 0.7135, 0.8840, 0.9206 and 0.9474 HFC-161 mole fractions. A temperature correction to the densities was made to compensate for the thermal expansion of the sample cell. Results of the isochoric measurements are given in Table 1.

Table 1
Experimental PVTx properties of HFC-161/134a system.

T/K	P/kPa	$\rho/\text{mol dm}^{-3}$	x^*	T/K	P/kPa	$\rho/\text{mol dm}^{-3}$	x^*
373.17	4684.5	3.974	0.9474	378.18	2582.4	1.094	0.3203
378.21	5039.5	3.973	0.9474	383.17	2645.9	1.094	0.3203
383.17	5339.6	3.972	0.9474	388.23	2709.2	1.094	0.3203
388.24	5637.0	3.971	0.9474	393.22	2773.3	1.094	0.3203
373.17	4489.8	3.035	0.9206	398.20	2835.5	1.093	0.3203
378.22	4717.5	3.034	0.9206	403.19	2896.0	1.093	0.3203
383.25	4935.0	3.033	0.9206	343.17	1908.6	0.895	0.7135
388.23	5145.4	3.033	0.9206	348.25	1962.3	0.895	0.7135
393.21	5355.3	3.032	0.9206	353.21	2013.6	0.894	0.7135
398.23	5563.9	3.031	0.9206	358.21	2064.2	0.894	0.7135
403.20	5767.0	3.030	0.9206	363.20	2115.2	0.894	0.7135
363.21	3609.0	2.096	0.8840	368.18	2165.4	0.894	0.7135
368.19	3755.7	2.095	0.8840	373.18	2213.5	0.893	0.7135
373.17	3897.1	2.095	0.8840	378.18	2263.6	0.893	0.7135
378.15	4034.3	2.094	0.8840	383.19	2311.7	0.893	0.7135
383.16	4169.9	2.094	0.8840	388.23	2359.0	0.893	0.7135
388.24	4304.7	2.093	0.8840	393.21	2407.7	0.893	0.7135
393.17	4434.6	2.093	0.8840	398.19	2454.1	0.892	0.7135
398.22	4565.6	2.092	0.8840	403.19	2501.8	0.892	0.7135
403.20	4693.6	2.092	0.8840	338.16	1696.7	0.805	0.5217
343.20	2100.6	1.096	0.3203	343.19	1744.2	0.805	0.5217
348.24	2178.0	1.096	0.3203	348.21	1792.4	0.805	0.5217
353.19	2248.2	1.096	0.3203	353.19	1838.2	0.805	0.5217
358.22	2317.7	1.096	0.3203	358.22	1884.1	0.804	0.5217
363.22	2385.6	1.095	0.3203	363.21	1929.0	0.804	0.5217
368.19	2451.4	1.095	0.3203	368.18	1973.2	0.804	0.5217
373.17	2517.6	1.095	0.3203	373.17	2016.7	0.804	0.5217
378.17	2061.3	0.804	0.5217	338.20	1298.0	0.560	0.5472
383.22	2104.0	0.803	0.5217	343.17	1328.9	0.560	0.5472
388.24	2147.1	0.803	0.5217	348.19	1358.9	0.560	0.5472
393.14	2189.5	0.803	0.5217	353.24	1389.1	0.559	0.5472
398.20	2232.3	0.803	0.5217	358.22	1418.4	0.559	0.5472
403.19	2273.4	0.803	0.5217	363.22	1447.3	0.559	0.5472
323.21	1308.3	0.636	0.4301	368.18	1476.1	0.559	0.5472
328.21	1349.4	0.636	0.4301	373.15	1504.1	0.559	0.5472
333.17	1386.8	0.636	0.4301	378.16	1532.6	0.559	0.5472
338.16	1423.5	0.636	0.4301	383.17	1561.1	0.559	0.5472
343.23	1460.1	0.635	0.4301	388.21	1589.2	0.558	0.5472
348.17	1495.0	0.635	0.4301	393.20	1617.0	0.558	0.5472
353.17	1529.8	0.635	0.4301	398.14	1645.2	0.558	0.5472
358.22	1564.2	0.635	0.4301	403.18	1672.2	0.558	0.5472
363.20	1598.9	0.635	0.4301	328.22	1120.6	0.496	0.5191
368.18	1632.7	0.635	0.4301	333.20	1147.9	0.496	0.5191
373.17	1666.4	0.634	0.4301	338.20	1174.4	0.496	0.5191
378.19	1699.2	0.634	0.4301	343.26	1200.9	0.496	0.5191
383.22	1732.3	0.634	0.4301	348.24	1227.2	0.496	0.5191
388.20	1764.6	0.634	0.4301	353.26	1252.5	0.496	0.5191
393.13	1796.4	0.634	0.4301	358.22	1277.9	0.495	0.5191
398.20	1829.2	0.634	0.4301	363.20	1302.7	0.495	0.5191
403.18	1861.2	0.633	0.4301	368.20	1327.7	0.495	0.5191
318.22	1168.1	0.560	0.5472	373.21	1353.5	0.495	0.5191
323.20	1203.0	0.560	0.5472	378.19	1377.8	0.495	0.5191
328.19	1235.5	0.560	0.5472	383.25	1402.5	0.495	0.5191
333.17	1267.6	0.560	0.5472	388.22	1427.6	0.495	0.5191
393.21	1450.8	0.495	0.5191	403.18	1499.4	0.494	0.5191
398.20	1475.2	0.494	0.5191				

x^* denotes the mole fraction of HFC-161.

To represent the experimental PVTx data in the gas phase of the HFC-161/134a binary system, a truncated virial equation of state was developed. The virial-type equation of state consists of two terms [5,6]:

$$Z = \frac{P}{\rho RT} = 1 + B_m \rho + C_m \rho^2 \quad (1)$$

where Z , P , T , and ρ denote the compressibility factor, pressure, temperature and molar density, respectively; R is the universal gas constant; and the second and third virial coefficients of the HFC-161/134a binary mixture, B_m and C_m , are calculated with the following mixing rules:

$$B_m = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j B_{ij} \quad (2)$$

and

$$C_m = \sum_{i=1}^2 \sum_{j=1}^2 \sum_{k=1}^2 x_i x_j x_k C_{ijk} \quad (3)$$

B_{ij} in Eq. (2) and C_{ijk} in Eq. (3) are expressed as follows:

$$B_{11} = b_1 + b_2 T_{r,1}^{-1} + b_3 \exp(T_{r,1}^{-1}) \quad (4)$$

$$B_{22} = b_4 + b_5 T_{r,2}^{-1} + b_6 \exp(T_{r,2}^{-1}) \quad (5)$$

$$B_{12} = B_{21} = b_7 + b_8 T_{r,12}^{-1} + b_9 \exp(T_{r,12}^{-1}) \quad (6)$$

$$C_{111} = c_1 + c_2 T_{r,1}^{-3} + c_3 T_{r,1}^{-13} \quad (7)$$

$$C_{222} = c_4 + c_5 T_{r,2}^{-5} + c_6 T_{r,2}^{-12} \quad (8)$$

$$C_{112} = C_{211} = C_{121} = c_7 + c_8 T_{r,1}^{-5} + c_9 T_{r,12}^{-7} \quad (9)$$

$$C_{221} = C_{122} = C_{212} = c_{10} + c_{11} T_{r,221}^{-5} + c_{12} T_{r,221}^{-6} \quad (10)$$

and

$$T_{r,i} = \frac{T}{T_{c,i}} \quad (11)$$

$$T_{r,ij} = \frac{T}{T_{c,ij}} \quad (12)$$

$$T_{r,ijk} = \frac{T}{T_{c,ijk}} \quad (13)$$

with

$$T_{c,ij} = (T_{c,i} T_{c,j})^{1/2} \quad (14)$$

$$T_{c,ijk} = (T_{c,i} T_{c,j} T_{c,k})^{1/3} \quad (15)$$

where T_r is the reduced temperature; and the critical temperatures, $T_{c,1} = 375.31$ K for HFC-161 and $T_{c,2} = 374.21$ K for HFC-134a, were reported by Booth and Swinehart [7] and Tillner-Roth and Baehr [8], respectively. Note that $T_{c,ij}$ and $T_{c,ijk}$ are not real critical temperature but parameters used in the present model. The values of numerical coefficients b_i , and c_i in Eqs. (4)–(10) for HFC-161/134a were determined by fitting the present PVTx data into the EOS. The numerical constants are listed in Table 2.

Fig. 1 represents the density deviations of the present PVTx data from the virial EOS in the gas phase of the HFC-161/134a binary system. The maximum and average absolute density deviations from Eq. (1) are 0.32% and 0.09%, respectively. Fig. 2 shows the pressure deviations of the measured PVTx data from Eq. (1). The maximum and average absolute pressure deviations from Eq. (1) are 0.18% and 0.06%, respectively. The suitable range of Eq. (1) is from 1120.6 to 5767.0 kPa in pressure, from 318.22 to 403.20 K in temperature and from 0.494 to 3.974 mol dm⁻³ in density.

Table 2
Numerical coefficients in Eqs. (4)–(10) for HFC-161/134a system.

<i>i</i>	$b_i/\text{dm}^3 \text{ mol}^{-1}$	$c_i/\text{dm}^6 \text{ mol}^{-2}$
1	−0.024199	−0.021097
2	−5.888963	0.049167
3	2.094633	−0.01261
4	0.257398	0.024965
5	−1.360808	0.154719
6	0.317713	−0.111789
7	0.885459	−0.071521
8	5.385239	0.455915
9	−2.399197	−0.352268
10		0.127102
11		−1.77253
12		1.598464

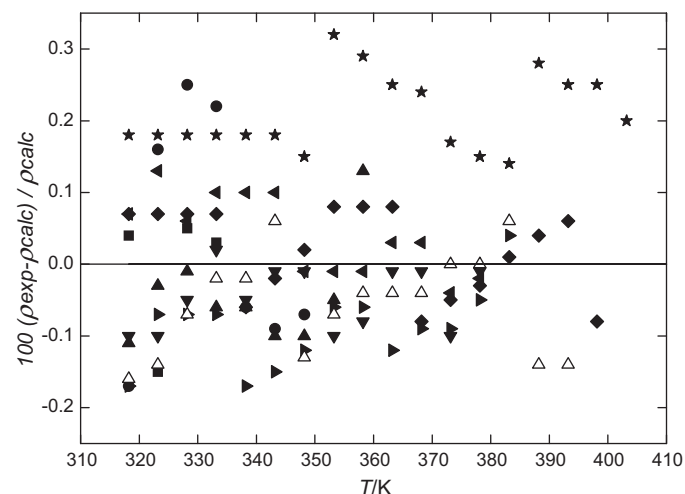


Fig. 1. Density deviations of measured *PVTx* data from values calculated from Eq. (1) for HFC-161/134a system 0.3203 (▼); 0.4301 (◆); 0.5191 (△); 0.5217 (▸); 0.5472 (□); 0.7135 (◀); 0.8840 (▲); 0.9206 (●); 0.9474 (■) HFC-161 mole fractions.

4. Conclusions

In this work, the *PVTx* properties in the gas phase for the HFC-161/134a binary system have been measured using the isochoric method. The maximum uncertainties were estimated to be ± 1.5 kPa, ± 6 mK and $\pm 0.15\%$ for pressure, temperature, and density, respectively. A total of 111 *PVTx* data were obtained along nine independent isopleths: 0.3203, 0.4301, 0.5191, 0.5217, 0.5472, 0.7135, 0.8840, 0.9206 and 0.9474 HFC-161 mole fractions.

By using the experimental values, a virial-type equation of state for the HFC-161/134a system has been developed. The developed

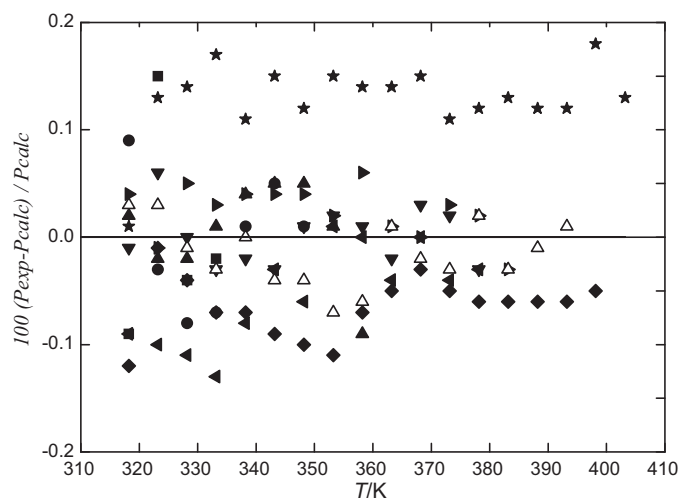


Fig. 2. Pressure deviations of measured *PVTx* data from values calculated from Eq. (1) for HFC-161/134a system 0.3203 (▼); 0.4301 (◆); 0.5191 (△); 0.5217 (▸); 0.5472 (□); 0.7135 (◀); 0.8840 (▲); 0.9206 (●); 0.9474 (■) HFC-161 mole fractions.

model represents the experimental gas phase *PVTx* data within $\pm 0.18\%$ in pressure and within $\pm 0.32\%$ in density for the range of temperatures from 318.22 to 403.20 K and pressures up to 5767.0 kPa. The present model for the HFC-161/134a binary system is valid for the entire range of compositions.

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