PρT Property Measurements for *trans*-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) in the Gaseous Phase

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Measurements of the *PρT* properties for *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) in the gaseous phase were carried out using metal bellows volumometer. A total of 204 *PρT* property values was obtained in the range of temperatures from (310 to 360) K, pressures from (657 to 2300) kPa, and densities from (34 to 146) kg·m^{-3}. The sample purity was better than 99.96 % in mole fraction. The present data were compared with the existing data and equations of state. The Benedict−Webb−Rubin−Starling (BWRS) and Martin−Hou equations of state were used to correlate the present data.

Introduction

Because *trans*-1,3,3,3-tetrafluoropropene (HFO-1234ze(E)) has a zero value of ODP (ozone depletion potential) and a low value of GWP (global warming potential), it is expected to be a next generation refrigerant. To design applications in the refrigeration cycle, the thermophysical properties of refrigerants are required. These properties are calculated from the equation of state. To develop the equation of state, measurements of thermophysical properties are needed.

For HFO-1234ze(E), measurements of the thermophysical properties such as critical parameters,[1] vapor pressure,[2] the isobaric specific heat capacity of liquid,[3] and *PρT* properties of liquids[2] have been reported in our group. Grebenkov et al. recently reported the measurements of these properties.[4] On basis of these measurements, the equation of state using the ECS (extended corresponding state) model was developed by Akasaka.[5]

In this work, *PρT* property measurements for HFO-1234ze(E) in the gaseous phase are carried out using a metal bellows volumometer to complement the existing data and help to modify the existing equation of state. The present data are compared with the existing data and equations of state. The parameters for the Benedict−Webb−Rubin−Starling (BWRS) and Martin−Hou equations of state for HFO-1234ze(E) are provided.

Experimental Section

The metal bellows volumometer was used for density measurements. The apparatus and procedure were reported in detail in our previous publication.[2]

The density of the sample is obtained by dividing the mass of sample by the inner volume of the volumometer. A sample of known mass is loaded inside the metal bellows volumometer, and nitrogen gas as a pressure medium is filled outside the metal bellows. The mass of the sample is measured by a precision analytical balance with the uncertainty of 4 mg. The pressure of nitrogen gas is measured by a digital pressure gauge (Paroscientific, 43K) with the uncertainty of 1 kPa. The pressure of the sample is determined by substituting the differential pressure due to the elastic force of a metal bellows from the pressure of nitrogen gas. The differential pressure was calibrated as functions of the metal bellows displacement and temperature in advance.[2] The uncertainty of the sample pressure measurement is estimated to be no greater than 2 kPa. The inner volume of the metal bellows is determined from the measurement of the metal bellows displacement. The displacement of the metal bellows is detected by a linear variable differential transformer. The uncertainty of the sample pressure measurement is estimated to be 1 μm. The standard deviation of the calibration data is 0.028 cm^3. The uncertainty of the density measurement U_ρ is estimated from eq 1.

$$U_\rho = 2\sqrt{\left(\frac{1}{V}\right)^2 u_m{}^2 + \left(-\frac{m}{V^2}\right)^2 u_V{}^2} \qquad (1)$$

where u_m and u_V are the uncertainties of the sample mass and the inner volume of volumometer. The values of u_m and u_V are 4 mg and 0.028 cm^3, respectively. The metal bellows volumometer is immersed in a thermostatted silicone oil bath to keep the temperature constant. The temperature of silicone oil is measured by a 25 Ω standard platinum resistance thermometer (Chino, R800-2) and precise thermometer bridge (Tinsley 5840) with the uncertainty of 10 mK including the temperature fluctuation in the oil bath.

The sample of HFO-1234ze(E) is manufactured by Central Glass Co. Ltd., Japan, and its purity was better than 99.96 %.

Results and Discussion

Comparison with the Existing Equations of State. *PρT* properties for HFO-1234ze(E) were measured on six isotherms in the temperature range of (310 to 360) K at pressures up to near-saturation pressure with different sample masses of (1.504 to 5.522) g. The experimental data are listed in Table 1. The experimental data distribution is shown on a pressure−temperature plane in Figure 1.

The experimental data were compared with Peng−Robinson equation of state[6] (PR equation) and the equation of state developed by Akasaka.[5] The PR equation is used widely because it can calculate the thermophysical properties using a few parameters such as critical parameters and the acentric factor.

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Table 1. Experimental $P\rho T$ Properties for HFO-1234ze(E)

T/K	P/kPa	ρ/kg·m^{-3}	U_ρ/kg·m^{-3}	T/K	P/kPa	ρ/kg·m^{-3}	U_ρ/kg·m^{-3}
			$m = 1.504$ g				
310.00	657	34.36	0.19	340.00	810	37.63	0.21
310.00	669	35.06	0.19	340.00	827	38.54	0.21
310.00	681	35.86	0.20	340.00	845	39.55	0.22
310.00	695	36.78	0.20	340.00	864	40.55	0.23
320.00	691	34.42	0.19	340.00	882	41.66	0.23
320.00	701	35.05	0.19	340.00	903	42.85	0.24
320.00	716	35.92	0.20	340.00	921	43.82	0.24
320.00	730	36.80	0.20	350.00	777	34.25	0.19
320.00	743	37.60	0.21	350.00	794	35.10	0.19
320.00	759	38.61	0.21	350.00	809	35.85	0.20
320.00	775	39.62	0.22	350.00	824	36.66	0.20
320.00	791	40.64	0.23	350.00	841	37.55	0.21
320.00	808	41.76	0.23	350.00	861	38.60	0.21
320.00	823	42.77	0.24	350.00	880	39.57	0.22
320.00	837	43.67	0.24	350.00	899	40.59	0.23
330.00	718	34.26	0.19	350.00	921	41.80	0.23
330.00	731	34.99	0.19	350.00	943	42.97	0.24
330.00	746	35.85	0.20	360.00	806	34.26	0.19
330.00	762	36.76	0.20	360.00	822	35.02	0.19
330.00	778	37.66	0.21	360.00	838	35.83	0.20
330.00	792	38.48	0.21	360.00	858	36.81	0.20
330.00	810	39.52	0.22	360.00	872	37.50	0.21
330.00	828	40.65	0.23	360.00	893	38.54	0.21
330.00	844	41.61	0.23	360.00	914	39.59	0.22
330.00	866	42.95	0.24	360.00	934	40.62	0.23
340.00	747	34.24	0.19	360.00	957	41.79	0.23
340.00	762	35.03	0.19	360.00	980	42.97	0.24
340.00	778	35.89	0.20	360.00	996	43.76	0.24
340.00	794	36.75	0.20				
			$m = 1.948$ g				
320.00	851	44.36	0.19	340.00	1134	56.71	0.25
320.00	866	45.45	0.20	350.00	974	44.44	0.19
320.00	881	46.49	0.20	350.00	992	45.42	0.20
320.00	899	47.75	0.21	350.00	1009	46.40	0.20
320.00	910	48.63	0.21	350.00	1033	47.69	0.21
330.00	893	44.43	0.19	350.00	1050	48.68	0.21
330.00	908	45.39	0.20	350.00	1073	49.96	0.22
330.00	927	46.54	0.20	350.00	1081	50.42	0.22
330.00	943	47.55	0.21	350.00	1097	51.34	0.22
330.00	961	48.73	0.21	350.00	1118	52.57	0.23
330.00	981	50.03	0.22	350.00	1146	54.28	0.24
330.00	1001	51.36	0.22	350.00	1166	55.47	0.24
330.00	1020	52.67	0.23	350.00	1184	56.54	0.25
330.00	1041	54.12	0.24	360.00	1013	44.41	0.19
330.00	1063	55.64	0.24	360.00	1032	45.38	0.20
330.00	1075	56.44	0.25	360.00	1053	46.47	0.20
340.00	933	44.41	0.19	360.00	1076	47.64	0.21
340.00	953	45.51	0.20	360.00	1093	48.62	0.21
340.00	971	46.56	0.20	360.00	1123	50.21	0.22
340.00	989	47.62	0.21	360.00	1142	51.25	0.22
340.00	1008	48.82	0.21	360.00	1164	52.52	0.23
340.00	1030	50.12	0.22	360.00	1190	53.97	0.23
340.00	1049	51.33	0.22	360.00	1217	55.45	0.24
340.00	1069	52.63	0.23	360.00	1246	56.97	0.25
340.00	1090	53.99	0.23	360.00	1249	57.15	0.25
340.00	1117	55.66	0.24				
			$m = 2.548$ g				
330.00	1097	57.98	0.19	350.00	1299	63.70	0.21
330.00	1113	59.21	0.20	350.00	1325	65.31	0.22
330.00	1139	61.03	0.21	350.00	1352	67.13	0.23
330.00	1165	63.02	0.21	350.00	1374	68.68	0.23
340.00	1154	58.04	0.19	350.00	1403	70.69	0.24
340.00	1175	59.40	0.20	350.00	1434	72.82	0.25
340.00	1196	60.76	0.20	350.00	1460	74.47	0.25
340.00	1218	62.25	0.21	360.00	1263	57.94	0.19
340.00	1238	63.68	0.21	360.00	1285	59.28	0.20
340.00	1262	65.39	0.22	360.00	1310	60.71	0.20
340.00	1284	67.01	0.23	360.00	1335	62.17	0.21
340.00	1305	68.59	0.23	360.00	1359	63.66	0.21
340.00	1331	70.60	0.24	360.00	1386	65.23	0.22
340.00	1356	72.51	0.25	360.00	1414	66.98	0.23
340.00	1384	74.55	0.25	360.00	1438	68.45	0.23
350.00	1212	58.14	0.20	360.00	1466	70.29	0.24
350.00	1228	59.18	0.20	360.00	1502	72.60	0.25
350.00	1253	60.74	0.20	360.00	1535	74.54	0.25
350.00	1281	62.46	0.21				

Table 1. Continued

T/K	P/kPa	ρ/kg·m^{-3}	U_ρ/kg·m^{-3}	T/K	P/kPa	ρ/kg·m^{-3}	U_ρ/kg·m^{-3}
			$m = 3.023$ g				
340.00	1308	68.83	0.20	350.00	1526	79.54	0.23
340.00	1331	70.59	0.20	350.00	1552	81.57	0.24
340.00	1354	72.27	0.21	350.00	1580	83.73	0.25
340.00	1378	74.19	0.21	350.00	1611	86.28	0.25
340.00	1398	75.77	0.22	360.00	1441	68.77	0.20
340.00	1420	77.51	0.23	360.00	1466	70.30	0.20
340.00	1441	79.28	0.23	360.00	1493	72.04	0.21
340.00	1465	81.46	0.24	360.00	1523	73.94	0.21
340.00	1482	83.02	0.24	360.00	1545	75.43	0.22
340.00	1490	83.71	0.25	360.00	1580	77.76	0.23
350.00	1376	68.87	0.20	360.00	1607	79.57	0.23
350.00	1400	70.45	0.20	360.00	1634	81.53	0.24
350.00	1422	72.01	0.21	360.00	1665	83.71	0.25
350.00	1451	74.02	0.21	360.00	1695	85.89	0.25
350.00	1474	75.65	0.22	360.00	1725	87.95	0.26
350.00	1499	77.45	0.22				
			$m = 3.888$ g				
350.00	1645	88.62	0.20	360.00	1737	88.54	0.20
350.00	1667	90.44	0.21	360.00	1760	90.28	0.21
350.00	1692	92.58	0.21	360.00	1787	92.36	0.21
350.00	1722	95.16	0.22	360.00	1815	94.55	0.22
350.00	1748	97.50	0.23	360.00	1850	97.28	0.23
350.00	1773	99.83	0.23	360.00	1886	100.24	0.24
350.00	1798	102.24	0.24	360.00	1926	103.58	0.25
350.00	1822	104.65	0.25	360.00	1936	104.54	0.25
350.00	1850	107.61	0.26	360.00	1964	107.10	0.25
350.00	1869	109.92	0.26	360.00	1999	110.25	0.26
			$m = 5.522$ g				
360.00	2157	125.99	0.22	360.00	2247	136.47	0.24
360.00	2180	128.50	0.23	360.00	2279	140.52	0.25
360.00	2212	132.17	0.23	360.00	2287	141.76	0.26
360.00	2224	133.70	0.24	360.00	2300	143.52	0.26

The acentric factor and critical parameters for the PR equation were adapted for the values reported by Higashi et al.[1] The equation of state developed by Akasaka adopted the ECS model. No equation except for that by Akasaka exists presently using several experimental data. Figure 2 shows the deviation of the experimental data including the data by Grebenkov from the PR equation. In the same manner, deviations from the equations of state by ECS model were shown in Figure 3. As shown in Figure 2, it is found that the PR equation can calculate the density for HFO-1234ze(E) in the gaseous phase within 1 % even though the PR equation uses only a few parameters. As shown in Figure 3, the deviation of the present data from the ECS model increases at a higher pressure range or at a higher density range. The relative standard deviation and the mean bias error of the present data from the ECS model are 0.5 % and −1.1 %, respectively. It is considered that no data of $P\rho T$ properties in the gaseous phase were used to fit the ECS model. The data by Grebenkov are scattering and are far from the present data and both equations of state. The relative standard deviation and the mean bias error of the data by Grebenkov from the PR equation are 1.8 % and +2.6 %, respectively. The relative standard deviation and the mean bias error of the data by Grebenkov from the ECS model are 1.4 % and +2.4 %, respectively.

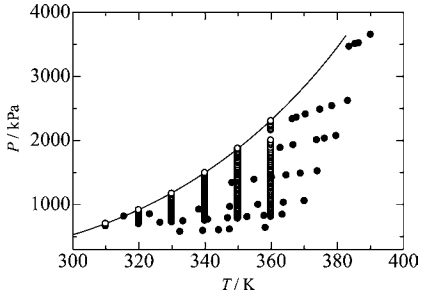

Figure 1. Distribution of the $P\rho T$ property measurements for HFO-1234ze(E). The solid line is a saturation curve calculated from the correlation formulated by Tanaka et al.[2] ○, this work; ●, Grebenkov et al.[4]

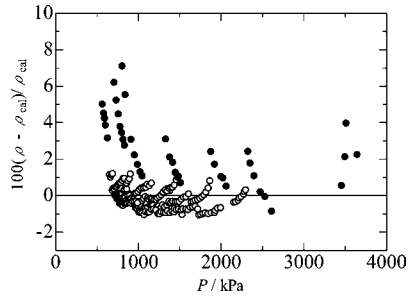

Figure 2. Deviation of the density of the present data from PR equation. ○, this work; ●, Grebenkov et al.[4]

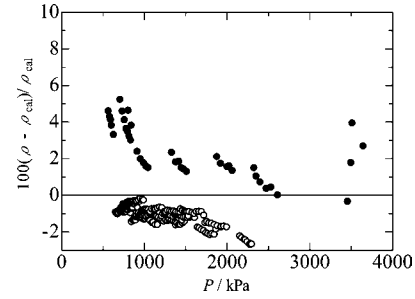

Figure 3. Deviation of the density of the present data from the equation of state using the ECS model developed by Akasaka. ○, this work; ●, Grebenkov et al.[4]

Table 2. Parameters for the BWRS Equation of State for HFO-1234ze(E)

A_0	$8.1201 \cdot 10^{2}$
B_0	$1.3614 \cdot 10^{-1}$
C_0	$9.4168 \cdot 10^{7}$
D_0	$3.5038 \cdot 10^{9}$
E_0	$6.9071 \cdot 10^{10}$
a	$9.4752 \cdot 10^{1}$
b	$1.0304 \cdot 10^{-1}$
c	$2.2963 \cdot 10^{7}$
d	$7.2297 \cdot 10^{3}$
α	$-2.2931 \cdot 10^{0}$
γ	$5.9655 \cdot 10^{-2}$
R	8.3145
P	kPa
T	K
ρ	$\text{kmol} \cdot \text{m}^{-3}$

Table 3. Parameters for the Martin−Hou Equation of State for HFO-1234ze(E)

A_2	$-4.0533 \cdot 10^{2}$
B_2	$-1.3848 \cdot 10^{0}$
C_2	$-5.1375 \cdot 10^{4}$
A_3	$-1.2647 \cdot 10^{2}$
B_3	$8.9313 \cdot 10^{-1}$
C_3	$-1.4403 \cdot 10^{1}$
A_4	$1.2880 \cdot 10^{1}$
B_5	$-4.0922 \cdot 10^{-2}$
R	8.3145
P_c	3632 kPa
T_c	382.51 K
V_c	$0.2347\ \text{m}^3 \cdot \text{kmol}^{-1}$
P	kPa
T	K
v	$\text{m}^3 \cdot \text{kmol}^{-1}$

Correlation. On the basis of the present data, the parameters for the BWRS equation of state[7] and Martin−Hou equation of state[8] were determined. The functional form is given in eq 2 for the BWRS equation and in eqs 3 to 6 for the Martin−Hou equation. The BWRS equation can correlate the data without the critical parameters and acentric factor. Although the Martin−Hou equation requires critical parameters, it uses only 8 parameters to correlate the data, while the BWRS equation uses 11 parameters. The parameters for HFO-1234ze(E) are given in Table 2 for the BWRS equation of state and in Table 3 for the Martin−Hou equation of state.

$$P = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} + \frac{E_0}{T^4}\right)\rho^2 + \left(bRT - a - \frac{d}{T}\right)\rho^3 + \alpha\left(a + \frac{d}{T}\right)\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2) \times \exp(-\gamma\rho^2) \quad (2)$$

$$P = \frac{RT}{(v - b')} + \frac{A_2 + B_2 T + C_2 e^{-5.475T/T_c}}{(v - b')^2} + \frac{A_3 + B_3 T + C_3 e^{-5.475T/T_c}}{(v - b')^3} + \frac{A_4}{(v - b')^4} + \frac{B_5}{(v - b')^5} \quad (3)$$

$$b' = V_c - \frac{\beta V_c}{15 Z_c} \quad (4)$$

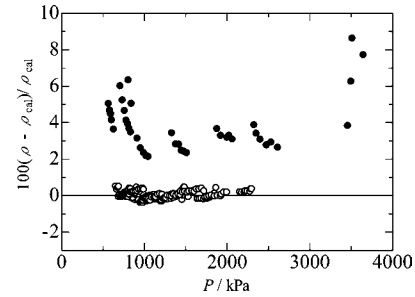

Figure 4. Deviation of the density of the present data from the equation of state using the BWRS equation of state. ○, this work; ●, Grebenkov et al.[4]

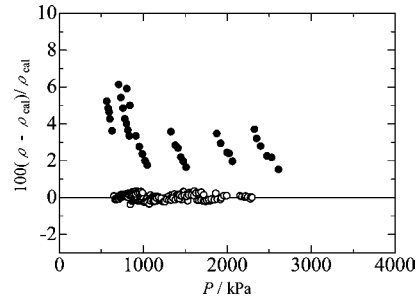

Figure 5. Deviation of the density of the present data from the equation of state using the Martin−Hou equation of state. ○, this work; ●, Grebenkov et al.[4]

$$Z_c = \frac{P_c V_c}{RT_c} \quad (5)$$

$$\beta = 20.533 Z_c - 31.883 Z_c^{\,2} \quad (6)$$

where ρ and v in these equations are the molar density and molar volume, respectively. The deviations of the present data from the equations of state are shown in Figure 4 for the BWRS equation of state and in Figure 5 for the Martin−Hou equation of state. The BWRS and Martin−Hou equations of state represent the present data very well. The relative standard deviations of the present data are 0.17 % from the BWRS equation of state and 0.16 % from the Martin−Hou equation of state. The data by Grebenkov are far from both equations of state. The relative standard deviation and the mean bias error of the data by Grebenkov from the BWRS equation are 2.2 % and +4.1 %, respectively. Even though the data by Grebenkov over the critical temperature was excepted due to the lack of solution for density, the relative standard deviation and the mean bias error from the ECS model are 1.2 % and +3.4 %, respectively.

Conclusion

PρT properties for HFO-1234ze(E) in the gaseous phase have been measured using a metal bellows volumometer. A total of 204 *PρT* values was obtained. The measured data were compared with the existing equations of state; it is found that the PR equation can be represented within 1 %, and it is better for the ECS model developed by Akasaka, which is improved by using the present data in fitting the equation. The present data were correlated by BWRS and Martin−Hou equations of state, and these parameters were determined. The BWRS and

Martin−Hou equations can represent the present data with relative standard deviations of 0.17 % and 0.16 %, respectively.

Acknowledgment

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