Vapor Pressures of 1,1,1,3,3-Pentafluoropropane (HFC-245fa) and 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea)

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The vapor pressures of 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) and 1,1,1,3,3-pentafluoropropane (HFC-245fa), two ozone-friendly fluorinated propane derivatives, were measured with a modified Burnett apparatus. The vapor pressures were measured at temperatures from (253 to 373) K and pressures from (87 to 2824) kPa for HFC-227ea and at temperatures from (255 to 393) K and pressures from (21 to 1950) kPa for HFC-245fa. The measurement uncertainties were estimated to be within ±10 mK and within ±1 kPa. The Wagner-type vapor pressure equations were used to correlate the experimental data for HFC-227ea and HFC-245fa, respectively. The results were also compared with available literature data.

Introduction

In the search for alternative refrigerants, fluorinated propane derivatives with zero ozone depletion potential (ODP) and lower global warming potential (GWP) have been considered to be promising replacements for chlorine containing compounds.

1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) and 1,1,1,3,3-petafluoropropane (HFC-245fa), two partially fluorinated hydrocarbons, have both zero ODP and low GWP. HFC-227ea can be used as an alternative to halon, and blends containing HFC-227ea are potential alternatives to chlorodifluoromethane (HCFC-22) and R-502. HFC-245fa is currently being evaluated as a promising replacement for 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114) in high temperature heat pumps and chemical blowing agents. Vapor pressure is one of the most fundamental thermodynamic properties that affect cycle analyses and the measurements of other properties. Some measurements of the vapor pressure of HFC-227ea have been reported previously,[1−8] but only two sets of experimental vapor pressure data have been published[9,10] for HFC-245fa. Bobbo et al.[11,12] also reported several vapor pressure data points of HFC-245fa in their vapor−liquid equilibrium measurements.

This paper reports the measurements of vapor pressures for HFC-227ea and HFC-245fa. The results are compared with previously reported experimental data. The data were also used to develop correlations for the vapor pressure of HFC-227ea and HFC-245fa.

Experimental Section

Materials. The samples of HFC-245fa and HFC-227ea were purchased from Zhejiang Fluoro-Chemical Technology Research Institute. The manufacturer stated that the purities were more than 99.9% for HFC-227ea and more than 99.8% for HFC-245fa. Before use, the HFC-245fa and HFC-227ea samples in the sample bottles were frozen with liquefied nitrogen and the vapor space was evacuated by a vacuum pump (KYKY FD110) to remove possible air impurities. The deaerated samples' purities were checked by gas chromatographic analysis (Lunan SP-6800A) and were found to be more than 99.91% for HFC-227ea and more than 99.93% for HFC-245fa, based on the area responses of a thermal conductivity detector.

Apparatus and Procedure. The Burnett apparatus described by Fu et al.[13] was used for the measurements. The modified apparatus shown in Figure 1 was used in this work. The system includes a thermostatic bath, a temperature measurement system, a pressure measurement system, a vacuum system, and a sample cell.

The thermostat bath temperature could be varied from (223 to 453) K. The temperature instability was less than ±2 mK in 1 h and less than ±5 mK in 8 h. Silicone oil, distilled deionized water, or alcohol was used as the bath fluid depending on the temperature range. The temperature measurement system included platinum-resistance thermometers (Tinsley, 5187SA) with an uncertainty of ±2 mK, a precision thermometer bridge (Tinsley, 5840D) with an accuracy of ±1 mK, a select switch (Tinsley, 5840CS/6T) and a personal computer. The overall temperature uncertainty for the bath and the temperature measurement system was less than ±10 mK. The temperatures were determined based on the international temperature scale of 1990 (ITS-90).

The pressure measurement system, which could measure pressures up to 6 MPa, included a piston-type pressure gauge, a pressure transducer, and two digital manometers. A very sensitive diaphragm pressure transducer (Xi'an Instrument, 1151DP) separated the sample in the thermostat bath from nitrogen which transmitted the pressure outside the bath. The transducer uncertainty was 0.2%, the measurable pressure difference range was (0 to 15) kPa, the available temperature range was (233−393) K, and the maximum allowable pressure was 14 MPa. An absolute pressure digital manometer (Yokogawa, MT210, 767367) was used to measure the atmospheric pressure. The accuracy of the digital manometer was 0.015%, and the pressure range was (0.001 to 130) kPa. At pressures below

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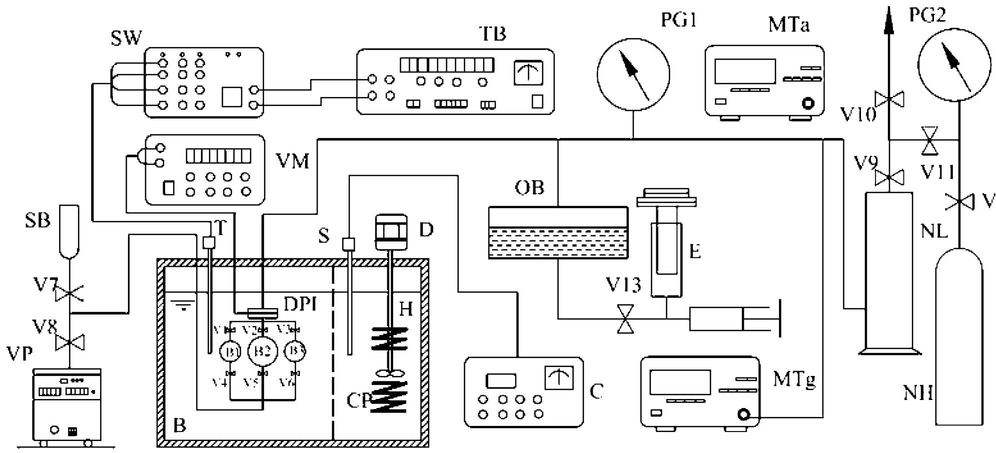

Figure 1. Burnett experimental apparatus: B, thermostatic bath; B1, sample cell (600 mL); B2, sample cell (1000 mL); B3, sample cell (200 mL); C, temperature controller; CP, cooler; D, stirrer; DPI, differential pressure detector; E, oil piston type pressure gauge; H, heater; NH, N_2 bottle; NL, pressure damper; OB, oil-gas separator; PG1, PG2, pressure gauge; T, platinum resistance thermometer; S, temperature sensor; SB, sample bottle; SW, selector switch; TB, thermometer bridge; V1−V13, valves; VM, digital multimeter; VP, vacuum pump; MTa, absolute pressure digital manometer; MTg, gauge pressure digital manometer.

130 kPa, the nitrogen transmits the sample pressure directly to the absolute pressure digital manometer, so the pressure measurement system has a maximum uncertainty of ±100 Pa. Pressure above 130 kPa was measured with a piston-type pressure gauge having an accuracy of 0.005% in the pressure range of (0.04−6) MPa, with the atmospheric pressure measured by the digital manometer, so the overall pressure uncertainty was estimated to be less than ±400Pa. For pressures below 3 MPa, a gauge pressure digital manometer (Yokogawa, MT210, 767366) was used to measure the pressure in parallel with the piston type pressure gauge to avoid operator error. The accuracy of the gauge pressure digital manometer was 0.015% for a pressure range of −80 kPa to 3 MPa gauge pressure. In this work, although the results measured by the gauge pressure digital manometer showed very good agreement with the data measured by the piston-type pressure gauge, only the piston-type pressure gauge results were published because of the smaller uncertainty.

The highest vacuum provided by the vacuum pump (KYKY FD110) was about 1×10^{-6} Pa.

Before the experiment, the platinum-resistance thermometers, the thermometer bridge with the select switch, the piston-type pressure gauge, and the digital manometers were calibrated by NIM (National Institute of Metrology, China) in 2003. Before and after use, the sensitive diaphragm pressure transducer was tested by the authors using the digital manometers.

The Burnett apparatus included three sample cells made of 1Cr18Ni9Ti stainless steel. The sample cell with 200 mL interior volume was used in this work. Before the experiment, the sample cell was rinsed with acetone to remove any residue from previous experiments.

After the sample cell was filled, the thermostat bath temperature was controlled at the experimental temperature. After thermal equilibrium was established between the sample and the heat transfer fluid in the bath and the pressure remained constant, the temperature and the pressure of the sample were measured.

Results and Discussions

HFC-227ea. The experimental vapor pressures of HFC-227ea were measured in a temperature range from (253 to 373) K which gave vapor pressures from (87 to 2824) kPa. All the measurement results are listed in Table 1.

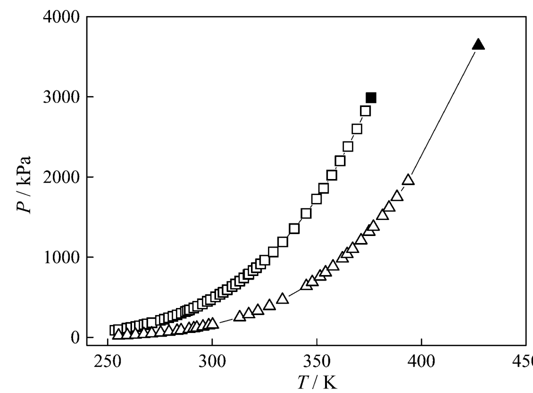

Figure 2. Present experimental vapor pressure data for HFC-227ea and HFC-245fa. HFC-227ea: □, experimental data; ■, critical point. HFC-245fa: △, experimental data; ▲, critical point.

Table 1. Experimental Vapor Pressure Data of HFC-227ea

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
253.308	86.81	285.181	299.49	309.512	634.38
253.316	86.83	285.192	299.62	311.160	664.23
253.333	86.86	287.137	319.89	313.130	701.36
255.212	94.46	289.069	340.97	315.109	740.37
257.257	103.23	289.104	341.37	317.152	781.99
257.263	103.26	291.060	363.71	317.497	789.45
259.592	114.05	291.160	365.01	319.507	832.46
261.280	122.37	293.041	387.68	321.160	869.25
263.260	132.72	293.150	388.98	323.135	914.73
265.171	143.42	293.230	390.05	323.173	915.90
267.151	155.12	285.181	299.49	325.108	962.18
267.155	155.14	285.192	299.62	329.166	1065.42
269.187	167.93	287.137	319.89	333.692	1190.13
271.142	181.01	289.069	340.97	339.169	1355.77
273.131	195.16	295.218	415.24	344.870	1545.33
273.144	195.21	295.324	416.61	349.816	1725.80
273.158	195.29	297.212	441.61	353.217	1859.33
275.154	210.31	297.220	441.76	357.129	2022.59
275.166	210.44	299.068	467.46	361.124	2201.09
275.176	210.49	299.162	468.90	364.880	2380.95
276.994	224.91	301.537	503.72	369.164	2600.04
279.185	243.27	303.663	536.19	373.218	2825.10
281.143	260.66	305.189	560.59	373.220	2825.21
283.177	279.74	307.191	593.83	373.222	2825.26

Figure 2 shows the variation of the vapor pressure with the temperature. The accuracy of the measured vapor pressure data was affected not only by the pressure measurement but also by the temperature instabilities. The

Table 2. Deviations of Experimental Vapor Pressure Data of HFC-227ea from Eq 2

author	no. points	exp range T/K	exp range P/kPa	absolute deviation (kPa) max	absolute deviation (kPa) RMS	relative deviation (%) max	relative deviation (%) RMS
Present work	68	253−373	87−2825	0.82	0.32	−0.223	0.062
Turk et al.[1]	43	203−375	5−2928	7.18	1.83	0.440	0.224
Shi et al.[2]	84	243−375	54−2936	2.88	0.45	0.555	0.211
Di Nicola[3]	27	235−365	36−2402	1.50	0.71	−0.853	0.217
Hu et al.[4]	145	233−375	32−2937	2.58	0.63	0.527	0.179
Weber[5]	31	298−354	451−1906	4.47	2.46	0.241	0.177
Salvi-Narkhede et al.[6]	21	238−373	41−2831	9.11	5.28	1.606	0.593
Gruzdev et al.[7]	32	273−373	192−2818	4.47	1.88	1.378	0.472
Horstmann et al.[8]	15	296−374	421−2850	12.64	4.78	−0.494	0.241

overall pressure uncertainties of the vapor pressure data were estimated with the expression

$$\Delta P = \Delta P_f + \left(\frac{dP}{dT}\right)_s \Delta T \qquad (1)$$

where ΔP is the vapor pressure data uncertainty, ΔP_f is the pressure uncertainty caused by the pressure measurement system, $(dP/dT)_s$ is the first derivation of the vapor pressure with temperature and ΔT is the temperature uncertainty. For the apparatus used in the experiments, $\Delta T \le 10$ mK, $\Delta P_f < 100$ Pa when $P < 130$ kPa and $\Delta P_f < 400$ Pa when $P \ge 130$ kPa. $(dP/dT)_s$ was determined from the experimental data or a vapor pressure equation. In this work, the maximum total pressure uncertainty was estimated to be not more than ±1 kPa for HFC-227ea.

The eight previously published sets of HFC-227ea vapor pressure data are summarized in Table 2. Some investigators also gave vapor pressure correlations for HFC-227ea. All of the available data, as well as the present results listed in Table 1, were compared with a vapor pressure equation given by Duan et al.,[14] which was based on experimental vapor pressure data from several authors. The comparison showed that the data measured by Turk et al.,[1] Shi et al.,[2] Di Nicola,[3] and in the present work were very consistent with most of the absolute deviations of these data sets from the selected vapor pressure equation of not more than ±2 kPa except the data for temperatures near the critical point. Therefore, these data were selected to develop a new vapor pressure equation for HFC-227ea. A Wagner-type analytical correlation for the vapor pressure of HFC-227ea was developed by using a weighted least-squares fit, and the equation

$$\ln(P/P_c) = (A_1\tau + A_2\tau^{1.25} + A_3\tau^3 + A_4\tau^7)T_c/T \qquad (2)$$

where $\tau = 1 - T/T_c$, $T_c = 375.95$ K[15] is the critical temperature, $A_1 = -8.16642$, $A_2 = 1.62516$, $A_3 = -3.43328$, and $A_4 = -2.12985$. The critical pressure $P_c = 2989.16$ kPa was determined by extrapolating the experimental vapor pressure data to the critical temperature. The equation is valid for temperatures from 202 K to the critical point. The normal boiling-point temperature and the acentric factor of HFC-227ea were calculated from eq 2 to be $T_b = 256.797$ K and $\omega = 0.3539$.

Parts a and b of Figure 3 showed the absolute deviations of the experimental vapor pressure data of HFC-227ea from eq 2 for selected data sets, which were used to develop eq 2, and other data sets, respectively. Parts a and b of Figure 4 showed the corresponding relative deviations, respectively. Table 2 summarizes the deviations of the available data from eq 2 for HFC-227ea. The present data agrees well with eq 2 over the whole temperature range. The maximum and root-mean-square (RMS) absolute deviations of our data from eq 2 are 0.82 kPa and 0.32 kPa, respectively. Di Nicola's[3] data can be represented within

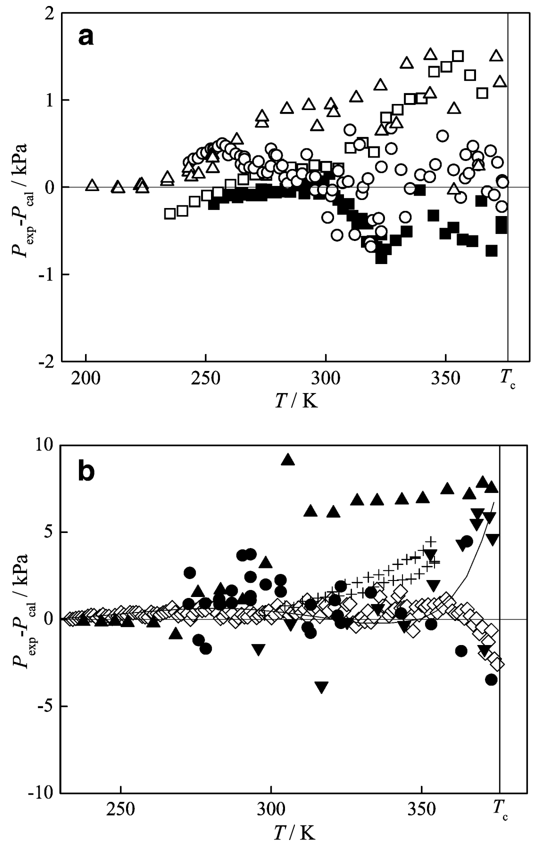

Figure 3. Absolute deviations of experimental vapor pressure data of HFC-227ea from eq 2. (a) Symbol descriptions: ■, present work; △, Turk[1] (six points were outside of the scale); ○, Shi[2] (one point was outside the scale); □, Di Nicola.[3] (b) Symbol descriptions: ◇, Hu;[4] +, Weber;[5] ▲, Salvi-Narkhede;[6] ●, Gruzdev;[7] ▼, Horstmann[8] (one point was outside of the scale); solid line, NIST.[16]

±1.5 kPa, although a slight systematic offset of about 0.07% was observed above 270 K with increasing negative deviations observed for temperatures below 270 K. Equation 2 agrees well with the experimental data of Shi et al.[2] and Hu et al.[4] Increasing deviations for temperatures above 240 K were observed in the measurements of Turk et al.,[1] but most of the absolute deviations of the experimental data from eq 2 are less than 2 kPa except for temperatures above 373 K. Figure 4b shows that Weber's[5] results are systematically 0.2% higher than eq 2. The maximum and RMS deviations of Weber's results from eq 2 were 0.24% and 0.18%, respectively. The experimental data of Salvi-Narkhede et al.,[6] Gruzdev et al.,[7] and Horstmann et al.[8] show relatively large uncertainties.

HFC-245fa. The vapor pressures of HFC-245fa were measured in a temperature range from (255 to 393) K with vapor pressures from (21 to 1950) kPa. The experimental results for the vapor pressure of HFC-245fa are listed in Table 3. According to an error analysis that was the same

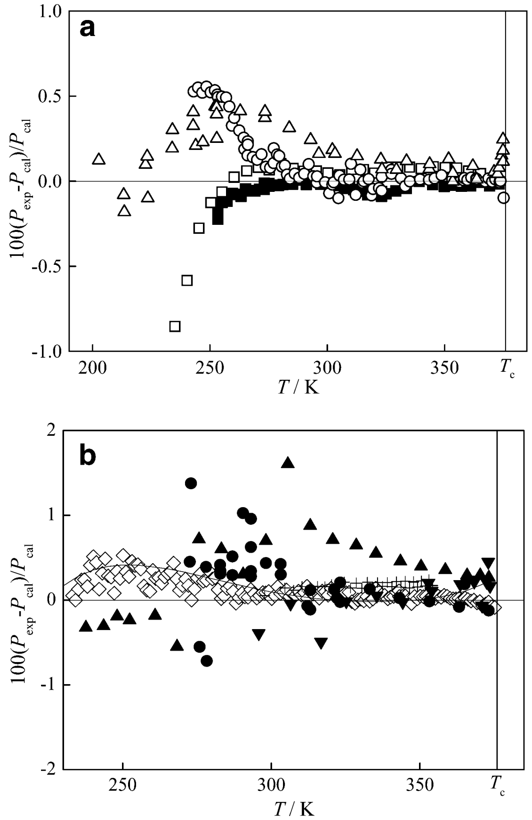

Figure 4. Relative deviations of experimental vapor pressure data of HFC-227ea from eq 2. (a) Symbol descriptions: ■, present work; △, Turk;[1] ○, Shi;[2] □, Di Nicola.[3] (b) Symbol descriptions: ◇, Hu;[4] +, Weber;[5] ▲, Salvi-Narkhede;[6] ●, Gruzdev;[7] ▼, Horstmann;[8] solid line, NIST.[16]

Table 3. Experimental Vapor Pressure Data of HFC-245fa

T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
255.215	21.93	288.910	103.68	344.962	639.43
255.217	21.93	288.911	103.67	347.800	688.83
259.365	27.28	291.163	113.41	347.801	688.90
259.366	27.27	291.163	113.43	351.538	757.91
259.369	27.28	291.165	113.42	351.538	757.93
263.272	33.25	292.620	119.97	351.539	757.86
263.275	33.25	292.623	120.01	351.541	757.93
263.275	33.24	295.550	134.37	354.126	808.71
267.308	40.47	295.550	134.41	354.147	809.38
267.309	40.47	295.553	134.41	357.697	883.20
267.310	40.47	298.310	149.04	362.208	984.31
271.030	48.26	298.312	149.05	362.209	984.35
271.031	48.26	298.314	149.05	364.467	1038.25
275.310	58.66	300.159	159.38	364.467	1038.23
275.312	58.66	313.126	250.20	367.101	1103.60
275.314	58.66	313.128	250.26	367.105	1103.63
279.325	69.99	313.130	250.34	371.113	1209.27
279.325	69.98	317.430	287.67	371.120	1209.32
279.326	69.98	317.430	287.72	374.811	1313.06
279.327	69.99	317.431	287.84	374.813	1313.09
283.202	82.37	321.769	329.90	374.950	1317.35
283.204	82.36	321.770	329.87	377.034	1378.94
283.205	82.37	321.770	329.90	381.377	1514.26
285.076	89.02	327.340	390.52	384.500	1617.36
285.080	89.02	327.342	390.61	388.320	1751.25
285.083	89.05	333.546	467.79	393.643	1950.82
288.909	103.68				

as for HFC-227ea, the maximum vapor pressure uncertainty of the present work was estimated to be not more than ±800 Pa for HFC-245fa.

The present vapor pressure measurements were used to develop a vapor pressure correlation for HFC-245fa with the same form as for HFC-227ea (eq 2). The critical

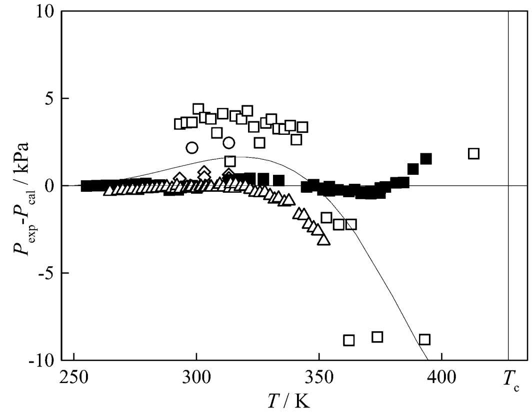

Figure 5. Absolute deviations of experimental vapor pressure data of HFC-245fa from eq 2: ■, present work; △, Di Nicola;[9] □, Sotani[10] (four points were outside of the scale); ◇, Bobbo;[11] ○, Bobbo;[12] solid line, NIST.[16]

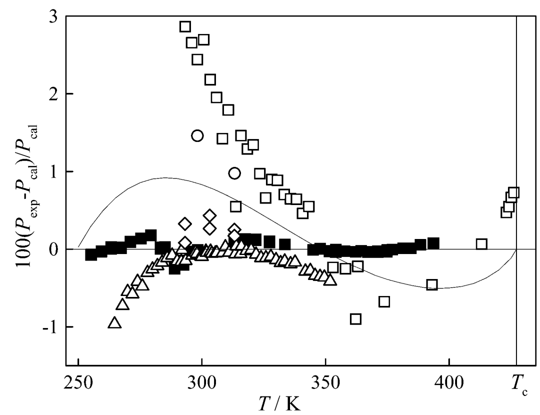

Figure 6. Relative deviations of experimental vapor pressure data of HFC-245fa from eq 2: ■, present work; △, Di Nicola;[9] ○, Sotani;[10] ◇, Bobbo;[11] ○, Bobbo;[12] solid line, NIST.[16]

temperature of HFC-245fa is T_c = 427.2 K,[16] the parameters $A_1 = -7.81829$, $A_2 = 0.975478$, $A_3 = -3.26508$, and $A_4 = -3.19006$ were obtained by fitting eq 2 to the experimental results. The critical pressure, P_c = 3638.75 kPa, was determined by extrapolating the experimental vapor pressure data to the critical temperature. The validity range of vapor pressure equation of HFC-245fa is (253−393) K. The normal boiling point temperature and the acentric factor of HFC-245fa were calculated to be T_b = 288.273 K and $\omega = 0.3759$.

Figures 5 and 6 showed the absolute and relative deviations of the available experimental vapor pressure data for HFC-245fa from eq 2. The present experimental data is well represented by eq 2, with the maximum absolute deviation of the present results from eq 2 being 1.54 kPa at 393 K and the relative RMS deviation being 0.098%. The results of Di Nicola[9] agreed well with our data below 330 K. Di Nicola's data in Figure 6 showed a negative deviation from eq 2 for temperatures below 285 K, but the maximum absolute deviation was not more than −350 Pa. However, his results were about 0.2% lower than our data above 330 K. Figure 5 shows that Sotani and Kubota's[10] results were systematically 3.5 kPa higher than eq 2 below 343 K and about 9 kPa lower from (362 to 393) K. Bobbo et al.[11,12] also reported several data points in their vapor−liquid equilibrium measurements, and their data is higher than eq 2 up to 2.44 kPa. The deviations of the calculated results of REFPROP 7.1[16] from eq 2 are also showed in Figures 5 and 6.

Conclusions

Sixty-eight vapor pressure data points were measured for HFC-227ea in the temperature range from (253 to 373) K with seventy-nine data points measured for HFC-245fa from (255 to 393) K. Vapor pressure correlations were developed for HFC-227ea, and HFC-245fa used the present data and previous data available in the literatures. The normal boiling points and acentric factors for HFC-227ea and HFC-245fa were also determined.

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