International Journal of Thermophysics, Vol. 12, No. 6, 1991

Saturated Liquid Densities and Bubble-Point Pressures of the Binary HFC 152a + HCFC 142b System

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Received March 5, 1991

Forty-eight sets of the saturated liquid densities and bubble-point pressures of the binary HFC 152a + HCFC 142b system were measured with a magnetic densimeter coupled with a variable-volume cell. The measurements obtained at four compositions, 20, 40, 60, and 80 wt%, of HFC 152a cover a range of temperatures from 280 to 400 K. The experimental uncertainties in temperature, pressure, density, and composition were estimated to be within ±15 mK, ±20 kPa, ±0.2%, and between −0.14 and ±0.01 wt% HFC 152a (−0.01 and +0.14 wt% HCFC 142b), respectively. The purities of the samples were 99.9 wt% for HFC 152a and 99.8 wt% for HCFC 142b. A binary interaction parameter, k_{ij}, in the Peng–Robinson equation of state was determined as a function of temperature for representing the bubble-point pressures. On the other hand, two constant binary-interaction parameters, k_{ij} and l_{ij}, were introduced into the mixing rule of the Hankinson–Brobst–Thomson equation for representing the saturated liquid densities.

KEY WORDS: bubble-point pressure; HCFC 142b (CH_3CClF_2); HFC 152a (CH_3CHF_2); mixtures; refrigerants; saturated liquid density.

1. INTRODUCTION

The ozone depletion and global warming by CFCs are worldwide issues. Mixtures of existing HCFCs and/or HFCs, such as HCFC 22 ($CHClF_2$, chlorodifluoromethane), HCFC 142b (CH_3CClF_2, 1-chloro-1,1-difluoroethane), and HFC 152a (CH_3CHF_2, 1,1-difluoroethane), are possible working fluids for refrigeration and heat-pumping equipment to replace

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0195-928X/91/1100-1029$06.50/0

CFCs, not only because of their low ODP (ozone depletion potential), low GWP (global warming potential), and low toxicity, but also due to the possibility of improving equipment efficiency with a nonazeotropic mixture.

The authors have already reported the saturated liquid densities and bubble-point pressures for two environmentally acceptable binary refrigerant systems, namely, HCFC 22 + HFC 152a [1] and HCFC 22 + HCFC 142b [2]. The present paper reports saturated liquid densities and bubble-point pressures of the binary HFC 152a + HCFC 142b system.

2. EXPERIMENTAL

A magnetic densimeter coupled with a variable-volume cell accompanying a metallic bellows was used for all the measurements. The apparatus and procedure were described in detail in previous publications [1, 3]. The experimental uncertainties in temperature, pressure, density, and composition of the first component (HFC 152a) were estimated to be within ±15 mK, ±20 kPa, and ±0.2% and between −0.14 and +0.01 wt%, respectively. The purities of the samples were 99.9 wt% for HFC 152a and 99.8 wt% for HCFC 142b.

3. RESULTS

The saturated-liquid densities and bubble-point pressures of the binary HFC 152a + HCFC 142b system were measured at temperatures from 280 to 400 K at 10 K intervals at four compositions of HFC 152a, 20, 40, 60, and 80 wt%. A total of 48 data points was obtained. The experimental results are presented in Table I.

Figure 1 shows the temperature dependence of the bubble-point pressures along four composition isoplethes. The solid curves for the pure refrigerants were calculated from the vapor-pressure correlations developed by Higashi et al. [4] for HFC 152a and by Yada et al. [5] for HCFC 142b. The other four curves for the mixtures were calculated from the Peng–Robinson (PR) equation of state [6] with the optimum binary interaction parameter, k_{ij}, for each temperature. These four curves change abruptly near the critical temperature, since the calculation did not converge at higher temperatures.

Figure 2 shows the temperature dependence of the saturated-liquid densities along four composition isoplethes. The six solid curves including those for the pure components were calculated from the Hankinson–Brobst–Thomson (HBT) equation [7] with a single binary parameter, k_{ij}, in the mixing rule for the critical temperature.

Table I. Saturated Liquid Densities and Bubble-Point Pressures of the Binary HFC 152a + HCFC 142b System

No.	T (K)	P (MPa)	ρ ($\mathrm{kg \cdot m^{-3}}$)	x (wt%)	x (mol%)
1	280.010	0.25	1099.2	20.03	27.59
2	290.004	0.33	1075.2	20.03	27.59
3	300.004	0.45	1050.2	20.03	27.59
4	310.001	0.60	1024.0	20.03	27.59
5	320.003	0.77	995.9	20.03	27.59
6	330.002	0.98	966.3	20.03	27.59
7	340.002	1.25	934.7	20.03	27.59
8	350.002	1.56	900.4	20.03	27.59
9	360.003	1.91	864.0	19.98	27.52
10	370.000	2.33	821.4	19.98	27.52
11	380.002	2.81	770.6	19.98	27.52
12	390.003	3.37	704.6	19.98	27.52
13	400.009	4.01	596.0	19.98	27.52
14	280.000	0.29	1053.7	40.01	50.37
15	289.999	0.39	1029.7	40.01	50.37
16	300.004	0.53	1004.7	40.01	50.37
17	310.001	0.68	978.5	40.01	50.37
18	320.002	0.90	949.7	40.01	50.37
19	330.002	1.13	919.9	40.01	50.37
20	340.001	1.43	887.6	40.01	50.37
21	350.003	1.76	851.9	40.01	50.37
22	360.003	2.16	812.4	40.02	50.38
23	370.005	2.64	766.6	40.02	50.38
24	380.002	3.17	709.8	40.02	50.38
25	390.003	3.81	629.6	40.02	50.38
26	280.000	0.32	1012.6	60.02	69.55
27	290.004	0.42	988.8	60.02	69.55
28	300.004	0.58	963.6	60.02	69.55
29	310.001	0.76	937.2	60.02	69.55
30	320.002	0.99	908.0	60.02	69.55
31	330.002	1.24	877.7	60.02	69.55
32	340.002	1.56	845.0	60.02	69.55
33	350.002	1.93	808.1	60.02	69.55
34	360.003	2.37	769.8	59.98	69.52
35	370.005	2.89	720.9	59.98	69.52
36	380.002	3.50	657.9	59.98	69.52
37	390.003	4.19	553.9	59.98	69.52
38	280.000	0.36	973.9	80.00	85.89
39	290.004	0.47	949.9	80.00	85.89
40	299.999	0.61	924.8	80.00	85.89
41	310.001	0.82	898.6	80.00	85.89
42	320.002	1.05	870.8	80.00	85.89
43	330.002	1.33	840.4	80.00	85.89
44	340.002	1.66	807.0	80.00	85.89
45	350.003	2.07	769.8	80.00	85.89
46	360.003	2.56	728.2	79.95	85.85
47	370.005	3.12	676.9	79.95	85.85
48	380.002	3.76	606.7	79.95	85.85

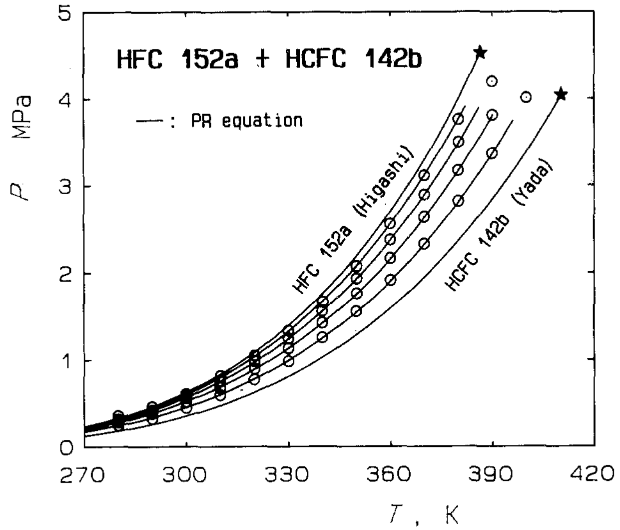

Fig. 1. Bubble-point pressures.

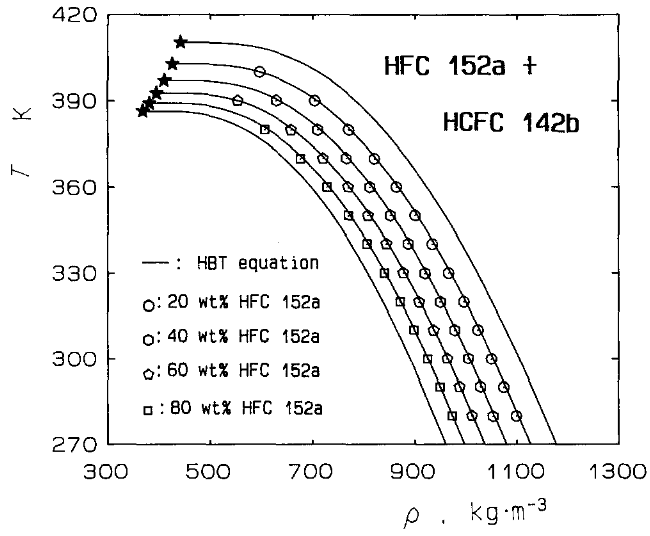

Fig. 2. Saturated liquid densities.

4. DISCUSSION

Figure 3 shows the composition dependence of the 13 isothermal dew- and bubble-point pressures. In Fig. 3, circles are the present measurements and triangles are calculated vapor pressures for the pure components from the correlations [4, 5]. The bubble-point pressures of this system show a positive deviation from Raoult's law except at higher temperatures, above 360 K, and this tendency becomes significant at lower temperatures. Therefore, the binary-interaction parameter in the PR equation of state depends on temperature as given in Table II. Pure-component parameters used for the calculation are the critical temperature, T_c, and the critical pressure, P_c, given in Table III, and Pitzer's acentric factor, ω, calculated from the vapor-pressure correlations [4, 5]. The mixing rule for parameters a and b in the PR equation used here is the one reported in the original reference [6]. Figure 4 shows the pressure deviations from the PR equation. Most of

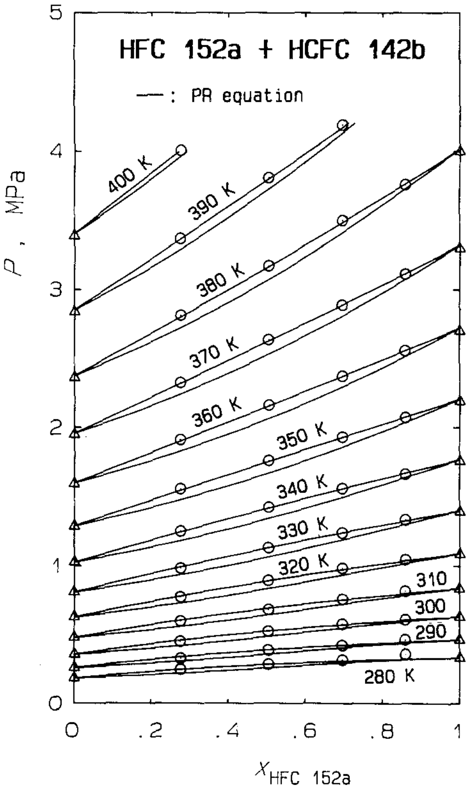

Fig. 3. Vapor–liquid equilibria.

Table II. The Optimum Binary Interaction Parameters in the PR Equation of State[a]

T (K)	k_{ij}
280	0.036
290	0.030
300	0.028
310	0.024
320	0.020
330	0.016
340	0.012
350	0.008
360	0.007
370	0.007
380	0.007
390	0.010
400	0.015

[a] The acentric factors, ω, used for the calculation are 0.2752 for HFC 152a and 0.2294 for HCFC 142b. The other parameters including the critical parameters used for the calculation are given in Table III.

Table III. Critical Parameters and Constants in the HBT Equation

	HFC 152a	HCFC 142b	HFC 152a + HCFC 142b
T_c (K)	386.44[a]	410.29[b]	—
P_c (MPa)	4.5198[a]	4.041[c]	—
ρ_c (kg · m^{-3})	368[a]	446[b]	—
M (g · mol^{-1})	66.051	100.496	—
V_c (cm^3 · mol^{-1})	179.49[d]	225.33[d]	—
ω_{SRK}	0.2814	0.2349	—
V^* (cm^3 · mol^{-1})	175.9	223.6	—
k_{ij}	—	—	+0.007
l_{ij}	—	—	+0.25

[a] From Higashi et al. [4].
[b] From Tanikawa et al. [11].
[c] From Yada et al. [5].
[d] $V_c = M/\rho_c * 1000$.

the results were represented within 20 kPa by the PR equation with the optimum binary parameter, which depends on temperature.

Figure 5 shows the composition dependence of the 13 isothermal saturated-liquid molar volumes. Since this system shows positive deviations from Raoult's law for temperatures below 360 K, the excess volumes must be positive and the experimental saturated-liquid molar volumes also show slightly positive deviations from the molar average at lower temperatures. Since the HBT equation does not represent these deviations from ideal mixing, the calculated curves deviate toward smaller volume values from the experimental results. Figure 6 illustrates the density deviations from the HBT equation with a single binary parameter. This binary parameter was applied to the mixing rule for the critical temperature. Without any binary parameter, the deviation increases especially at higher temperatures. With the use of a single binary parameter, all the present results show negative deviations as shown in Fig. 6. The values represented by the solid curves in Fig. 6 were calculated from the saturated-liquid density correlations developed by Sato et al. [8] for HFC 152a and by Maezawa et al. [9] for HCFC 142b.

The HBT equation includes three pure-component parameters: the critical temperature, T_c, the acentric factor, ω_{SRK}, in the Soave–Redlich–Kwong (SRK) equation of state [10] for fitting the vapor pressure of the pure component, and the empirical critical molar volume, V^*, for fitting the saturated-liquid density of the pure component. These parameters were

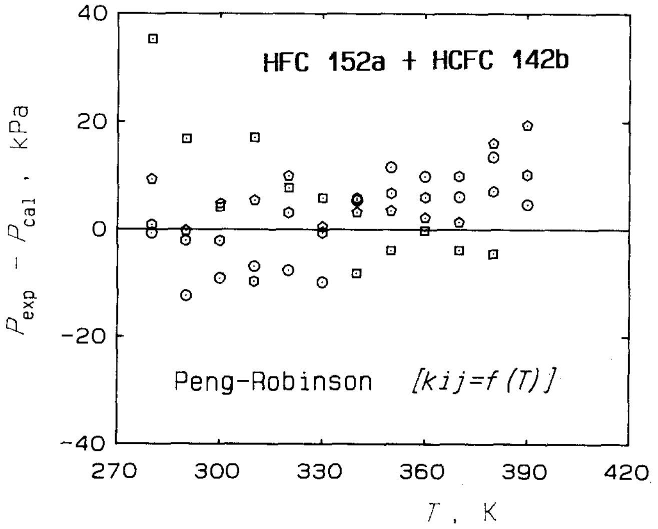

Fig. 4. Pressure deviations from the PR equation. See Fig. 2 for key.

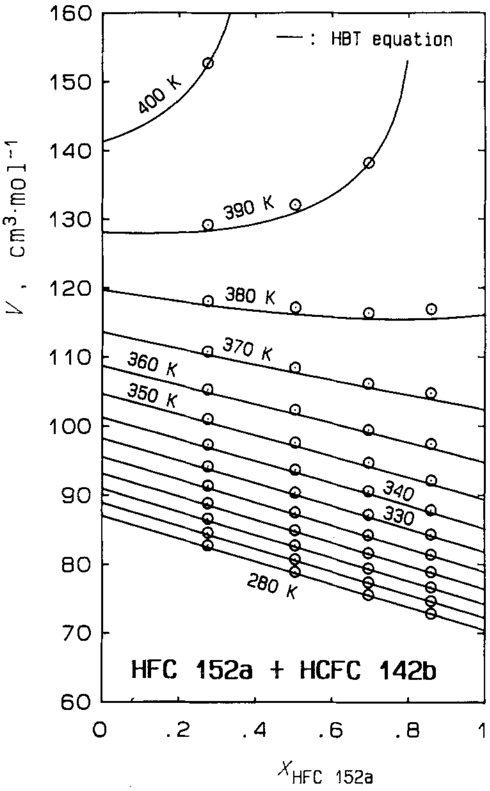

Fig. 5. Saturated liquid molar volume.

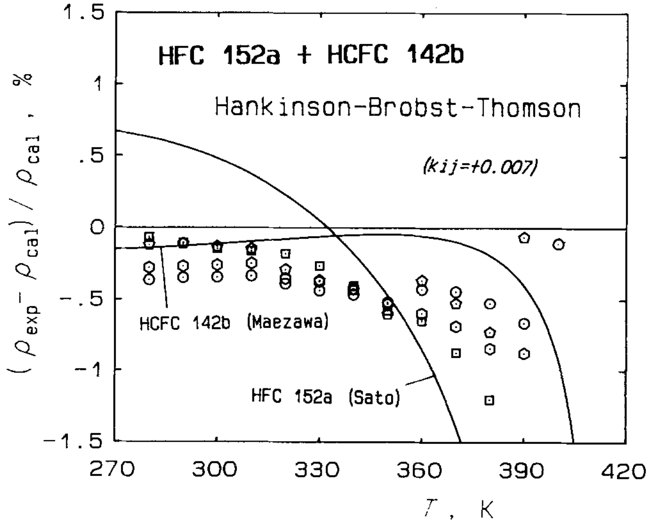

Fig. 6. Density deviations from the HBT equation with a single interaction parameter, k_{ij}. See Fig. 2 for key.

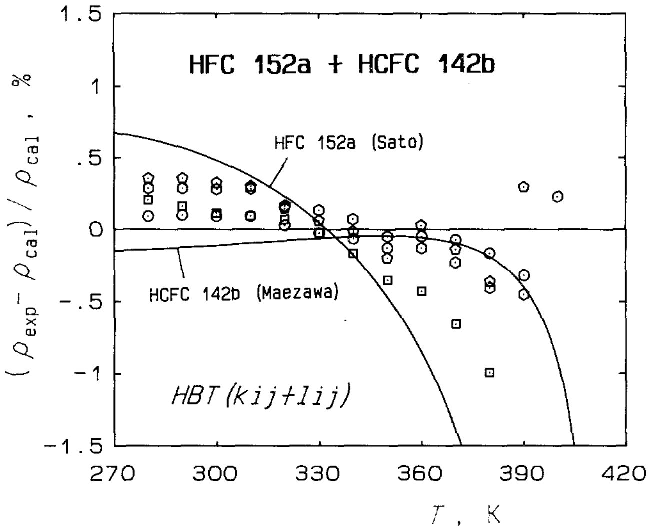

Fig. 7. Density deviations from the HBT equation with two interaction parameters, k_{ij} and l_{ij}. See Fig. 2 for key.

determined from our previous vapor-pressure measurements [4, 5] and saturated-liquid density measurements [8, 9], and their values are given in Table III. The acentric factor, ω_{SRK}, is expressed as a molar average for the mixture. However, the bubble-point pressures of this system clearly indicate a different behavior from the vapor-pressures of the pure components, and therefore, the acentric factors of the mixture should be definitely smaller than those of the pure components. Hence, we introduced an additional binary parameter, l_{ij}, into the mixing rule of the acentric factor. Figure 7 shows the density deviations from the HBT equation with the two optimum binary parameters. Except for a few points of the 80 wt% HFC 152a mixture (square symbols) at higher temperatures, the measured results are well represented within 0.5%.

ACKNOWLEDGMENT

We acknowledge the Grant-in-Aid for Scientific Research Fund in 1989–1990 (Project No. 01790369) of the Ministry of Education, Science and Culture, Japan.

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