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Vapor-Liquid Equilibria of HFC-32/*n*-Butane Mixtures

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The vapor-liquid equilibria of HFC-32 and *n*-butane mixtures were measured in a temperature range of 283.15 to 313.15 K using a circulation method. The experimental standard uncertainties of temperature, pressure, and composition measurements were estimated to be within 10 mK, 2 kPa, and 0.2% in mole fraction, respectively. The measured data were correlated with the Peng–Robinson (PR) equation of state using Wong and Sandler mixing rules. The relative deviations of the measured bubble-point pressure from the calculated bubble-point pressure as a function of the measured bubble-point pressure were found to be less than 2.5%.

KEY WORDS: circulation method; HFC-32; mixture; *n*-butane; Peng–Robinson equation of state; vapor-liquid equilibrium; Wong and Sandler mixing rules.

1. INTRODUCTION

Many hydrofluorocarbons (HFCs) have been used as refrigerants in air conditioners and freezers due to the following four advantages: (i) low toxicity, (ii) no or low flammability, (iii) good coefficient of performance (COP), and (iv) zero ozone depletion potential (ODP). However, HFCs have a very high global warming potential (GWP). For preventing or minimizing global warming, natural refrigerants with low GWP are being substituted for HFCs.

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As for the natural refrigerants, for example, CO_2, ammonia, and hydrocarbons (HCs) have some disadvantages. When CO_2 is used as the refrigerant in air conditioners, durable mechanical structures are required for the air conditioners because of its relatively high vapor pressure. In the case of ammonia, it is toxic, and in the case of HCs, their flammability can be a problem.

In order to overcome these disadvantages, a mixture of HCs and HFCs with low flammability has been applied. The HFC/HC mixture may have lower flammability and better COP than those of pure HCs.

Recently, experimental data on the vapor-liquid equilibria (VLE) of HFC/HC mixtures have been reported; propane [1–3] and *iso*-butane [4–6] were selected as the HCs in the mixtures. However, few experimental data on VLE of HFCs/*n*-butane [7] have been reported because of the difficulty in measuring the VLE of these mixtures due to the low vapor pressure of *n*-butane. In this current study, using an apparatus [8] for precise measurements of the pressure, temperature, and composition, VLE data for HFC-32/*n*-butane mixtures have been obtained over a temperature range of 283.15 to 313.15 K. In addition to the measurements, the experimental data were correlated with the Peng–Robinson equation of state [9] using Wong and Sandler mixing rules [10, 11].

2. EXPERIMENTAL

2.1. Sample Purity

The samples of pure *n*-butane and pure HFC-32 were supplied by Takachiho Co., Ltd. and Asahi Glass Co., Ltd., respectively. The manufacturers stated that the purites of pure *n*-butane and pure HFC-32 were 99.95 and 99.98% in mass fractions, respectively. These samples were used in this study without further purification.

2.2. Apparatus

Figure 1 shows a schematic drawing of the apparatus used for measuring VLE of the mixtures by the circulation method. Details of the apparatus are given in our previous report [8]. The apparatus consists of a gas chromatograph (GC), a liquid thermostat bath (LT) with a vapor-liquid cell (VL), a device for pressurizing a sampled mixture with helium gas (HC-VS-LS), and an air thermostat bath (AT) for heating the pressurized mixtures. An ethylene glycol plus water solution is used as the bath fluid in LT. The temperature of this solution is controlled constant with a small fluctuation of less than 0.5 mK using a computer-based PID algorithm (C). The internal volume of the cell is about 163 cm^3.

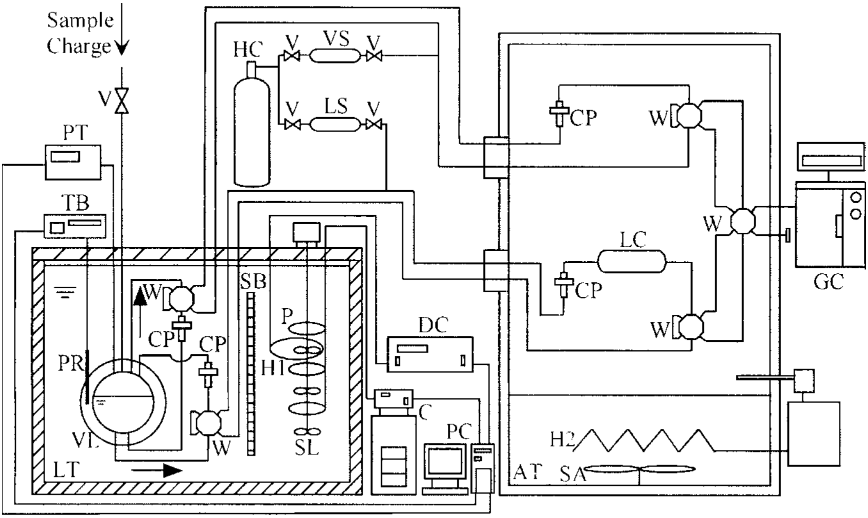

Fig. 1. Schematic of the vapor-liquid equilibrium apparatus. LT, liquid thermostat bath; VL, vapor-liquid cell; PR, 100 Ω standard platinum resistance thermometer; CP, circulation pump; W, six-way switching valve; SB, shield board; P, cooling coil; SL, SA, stirrer; H1, H2, heater; TB, thermometer bridge; PT, pressure transducer; C, liquid circulation thermostat bath; DC, DC power supply; PC, personal computer; HC, helium cylinder; LS, helium supercharge cylinder for liquid sample; VS, helium supercharge cylinder for vapor sample; LC, cylinder for liquid sample; AT, air thermostat bath; GC, gas chromatograph; V, valve.

The equilibrium pressure is measured by a calibrated pressure transducer (PT; Paroscientific, 2900AT). The standard uncertainty of the pressure measurement is estimated to be 0.01% of the pressure reading plus 0.01% of full scale. The full scale of this pressure transducer is 6.2 MPa. The amplitude of a pressure oscillation caused by the circulation method was about 0.5 kPa, so the total standard uncertainty of the pressure measurement is estimated to be 2 kPa. The equilibrium temperature is measured by monitoring the resistance of a 100 Ω platinum wire (JPt100) using an ac bridge circuit (TB; Automatic Systems Laboratories, F-17A) based on ITS-90. Considering the effects of self-heating, temperature drift, and the uncertainty in measuring the resistance ratio with the ac bridge, the standard uncertainty of the temperature measurement is estimated to be 10 mK. The compositions of both phases are measured by a gas chromatograph (Shimadzu, GC-8A) equipped with a Porapak-Q column (2 m long, ID: 3 mm, mesh range: 50/80). It was calibrated as follows.

(1) The peak areas for two pure components, S_1 and S_2, are measured independently by the gas chromatograph, where each

of the two pure components is sampled in a constant volume tube. This tube samples the two pure components at nearly the same temperature and pressure, resulting in sampling pure components of nearly the same amount of substance.

(2) Some synthesized mixtures of known mole fraction, R_1 and R_2, are prepared by blending the pure components gravimetrically.

(3) Two peak areas of the gas chromatograph for the mixtures, S_1^{m} and S_2^{m}, are measured.

(4) The mole fraction of the mixtures, R_1^{m} and R_2^{m}, are calculated using the following equations:

$$R_1^{\mathrm{m}} = \frac{S_2 S_1^{\mathrm{m}}}{S_2 S_1^{\mathrm{m}} + S_1 S_2^{\mathrm{m}}}, \qquad R_2^{\mathrm{m}} = 1 - R_1^{\mathrm{m}}.$$

(5) By examining the correlation between R_1 and R_1^{m}, the standard uncertainty in the composition measurement is estimated to be 0.2% in the amount-of-substance fraction.

2.3. Experimental Procedures

The VLE of the mixtures were measured by the circulation method where both vapor and liquid phases were continuously recirculated independently in the two sample loops [8]. When the temperature was kept constant with fluctuations of less than 0.5 mK over 15 minutes, this condition was regarded as thermal equilibrium. When the condition was satisfied, the equilibrium pressure was measured and the six-way switching valves of both phases (W in LT) were simultaneously turned so that the mixtures sampled in the sample loops were carried to the helium pressurization system. In this system, the sampled mixtures were pressurized to about 0.3 MPa. The pressurized sampled mixtures were then sent to the gas chromatograph (GC). These procedures were repeated at least three times to determine the equilibrium compositions of both phases. The standard deviations of the measured compositions were within 0.2% in mole fraction, which is the dominant uncertainty in the present measurements.

3. CORRELATION

In this study, the measured VLE data were correlated with the following Peng–Robinson equation of state [9]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}, \tag{1}$$

$$a(T) = \left[0.457232\,\frac{R^2T_c^2}{P_c}\right]\alpha(T), \tag{2}$$

$$b = 0.077796\,\frac{RT_c}{P_c}, \tag{3}$$

with

$$\alpha(T) = [1+\kappa(1-\sqrt{T_c/T})]^2, \tag{4}$$

and

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2, \tag{5}$$

where $a(T)$ is the energy parameter which is a function of the absolute temperature T, b is the excluded volume parameter, P_c is the critical pressure, T_c is the critical temperature, ω is the acentric factor, P is the pressure, v is the molar volume, and R is the universal gas constant ($8.314\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$). The critical properties and acentric factors of HFC-32 and *n*-butane are given in Table I [12].

In order to determine the mixing coefficients a_m and b_m, the Wong and Sandler mixing rules [9, 10] were used in this study. They are expressed as

$$a_m = b_m\left(\sum_i x_i\,\frac{a_i}{b_i} + \frac{A_\infty^E}{C}\right), \tag{6}$$

$$b_m = \frac{\sum_i \sum_j x_i x_j \frac{1}{2}[(b_i - a_i/RT) + (b_j - a_j/RT)](1-k_{ij})}{1 - A_\infty^E/CRT - \sum_i x_i a_i/RTb_i}, \tag{7}$$

with

$$A_\infty^E = RT\sum_i x_i\,\frac{\sum_j x_j G_{ji}\tau_{ji}}{\sum_k x_k G_{ki}}, \tag{8}$$

$$C = \ln(\sqrt{2}-1)/\sqrt{2}, \tag{9}$$

Table I. Characteristic Properties of the Pure Components

Component	T_c (K)	P_c (MPa)	ω
HFC-32	351.255	5.782	0.27680
n-Butane	425.160	3.796	0.19954

and

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ji}), \tag{10}$$

$$\tau_{ij} = A_{ij}/RT, \tag{11}$$

where A_{∞}^{E} is the excess Helmholtz free energy at infinite pressure, and C is a numerical constant. The nonrandomness parameter, α_{ij}, is set to 0.3 for all the binary mixtures considered in this study, as proposed by Lim [5].

When the binary interaction parameter k_{ij} and the binary parameters of the Wong and Sandler mixing rules, A_{ij} and A_{ji}, are known, we can calculate the equilibrium pressure P and the bubble point composition y_1 for component 1 from the equilibrium temperature T and the dew point composition x_1 for component 1. The procedure for calculating P and y_1 is as follows. When P and y_1 are assumed to be arbitrary values, Eq. (1) can be rewritten to a cubic equation on the molar volume v, and this cubic equation yields one or three roots. In the three roots, the largest root corresponds to the molar volume of the vapor, v^{V}, while the smallest root corresponds to that of the liquid, v^{L}. Using v^{V} and v^{L}, fugacity ($f_1^{V}, f_1^{L}, f_2^{V}$, and f_2^{L}) of each component (1 or 2) in each phase (V or L) is calculated by the equations shown in the appendix of Ref. 10. When the conditions, $f_1^{L} = f_1^{V}$ and $f_2^{L} = f_2^{V}$, are satisfied, the assumed values are equal to the equilibrium pressure P and the bubble point composition y_1. Both P and y_1 for given T and x_1 are thus determined by iteration.

The parameters, k_{ij}, A_{ij}, and A_{ji}, are determined by minimizing the following objective function,

$$\text{obj} = \frac{1}{N}\sum_{i}^{N}\left(\frac{P_{i,\text{exp}} - P_{i,\text{cal}}}{P_{i,\text{exp}}}\right)^2, \tag{12}$$

where N is the number of experimental points.

4. RESULTS

Vapor-liquid equilibria of HFC-32/n-butane mixtures were measured at four temperatures (283.15, 293.15, 303.15, and 313.15 K). Figure 2 shows the results. Table II lists the measured data. In Fig. 2, the isotherms calculated using the Peng–Robinson equation of state with the Wong and Sandler mixing rules are also shown. Table III lists three binary parameters (k_{12}, A_{12}, and A_{21}) and an average deviation of the pressure δP for each isotherm. The three parameters are almost independent of temperature, but a slight dependence is observed. As shown in Fig. 2, the difference between

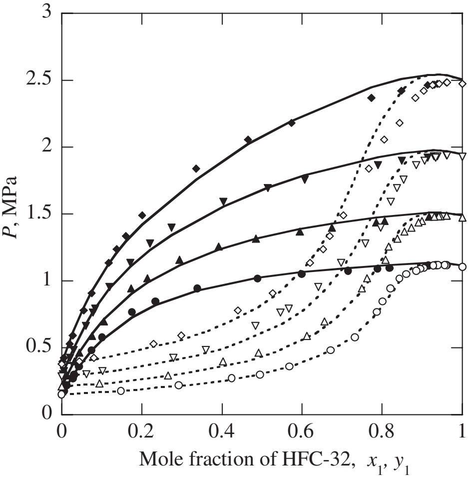

Fig. 2. Vapor-liquid equilibria of HFC-32(1)/*n*-butane(2) mixtures. (●) bubble point at 283.15 K; (○) dew point at 283.15 K; (▲) bubble point at 293.15 K; (△) dew point at 293.15 K; (▼) bubble point at 303.15 K; (▽) dew point at 303.15 K; (◆) bubble point at 313.15 K; (◇) dew point at 313.15 K. Lines represent the correlation with Peng–Robinson equation of state using the Wong and Sandler mixing rules.

the experimental data and the calculated results is smaller at lower temperatures. As shown by δP in Table III, however, the relative differences in the measured and calculated pressures are within 2.5% at all temperatures. Since the difference between vapor pressure of pure HFC-32 and one of pure *n*-butane is large, the variation of pressure against mole fraction of HFC-32 in Fig. 2 is steep below 0.4 mole fraction. Therefore, one of the reasons for this deviation may be attributed to the fact that a slight difference in measuring the composition generates a large pressure difference below 0.4 mole fraction.

Unfortunately, we could not compare our data with the results calculated from REFPROP (Ver. 6.01) [12] because no mixing parameters for HFC-32/*n*-butane are found. Figure 2 shows that the azeotropic composition for each isotherm is about 95% in mole fraction of HFC-32. The azeotropic compositions and pressures at specified temperatures from the measured and calculated data are shown in Table IV. The azeotropic compositions from the calculated data are smaller than those from the experimental data by 2.2% in mole fraction. In contrast to this tendency,

Table II. Vapor-Liquid Equilibrium Data for HFC-32(1)/*n*-Butane(2) Mixtures

	Mole fraction of HFC-32			Mole fraction of HFC-32	
P (MPa)	x_1	y_1	P (MPa)	x_1	y_1
	$T = 283.150$ K			$T = 293.150$ K	
1.1069	1.0000	1.0000	1.4748	1.0000	1.0000
1.1192	0.9603	0.9565	1.4868	0.9610	0.9608
1.1190	0.9369	0.9401	1.4853	0.9373	0.9454
1.1183	0.9337	0.9403	1.4842	0.9330	0.9409
1.1165	0.9156	0.9282	1.4807	0.9171	0.9304
1.0971	0.8183	0.9050	1.4494	0.8064	0.8997
1.0906	0.7881	0.8948	1.4389	0.7852	0.8900
1.0749	0.7148	0.8852	1.3986	0.6740	0.8729
1.0481	0.5989	0.8600	1.3677	0.5945	0.8559
1.0182	0.4893	0.8430	1.3163	0.4850	0.8377
0.9433	0.3385	0.8199	1.2582	0.3915	0.8162
0.8464	0.2343	0.8005	1.1582	0.2938	0.8078
0.7655	0.1752	0.7866	1.0202	0.2139	0.7625
0.5793	0.1012	0.7311	0.9449	0.1738	0.7492
0.4806	0.0747	0.6715	0.6991	0.1051	0.6561
0.3603	0.0423	0.5680	0.5899	0.0759	0.6117
0.3008	0.0305	0.4941	0.4658	0.0445	0.4916
0.2725	0.0273	0.4239	0.3986	0.0322	0.4030
0.2195	0.0127	0.2921	0.2931	0.0130	0.2659
0.1772	0.0055	0.1477	0.2331	0.0042	0.0946
0.1521	0.0000	0.0000	0.2123	0.0000	0.0000
	$T = 303.150$ K			$T = 313.150$ K	
1.9276	1.0000	1.0000	2.4751	1.0000	1.0000
1.9376	0.9611	0.9618	2.4822	0.9609	0.9614
1.9313	0.9293	0.9381	2.4745	0.9378	0.9419
1.9231	0.9139	0.9327	2.4683	0.9294	0.9265
1.8993	0.8485	0.9058	2.4637	0.9130	0.9252
1.8646	0.7898	0.8855	2.4219	0.8476	0.9040
1.7570	0.6062	0.8535	2.3671	0.7731	0.8830
1.6954	0.5148	0.8371	2.1825	0.5738	0.8435
1.5929	0.4040	0.8214	2.0559	0.4655	0.8048
1.3977	0.2742	0.7959	1.8383	0.3360	0.7666
1.2806	0.2204	0.7577	1.4912	0.2009	0.7033
1.1371	0.1711	0.6977	1.3353	0.1603	0.6692
0.9555	0.1202	0.6402	1.2358	0.1371	0.6525
0.7927	0.0839	0.5670	1.1337	0.1169	0.6197
0.7622	0.0784	0.5458	0.9074	0.0749	0.5261
0.6637	0.0599	0.4835	0.7796	0.0551	0.4402
0.4821	0.0291	0.3593	0.5927	0.0280	0.2980
0.4265	0.0205	0.2785	0.5316	0.0195	0.2291
0.3270	0.0060	0.1020	0.4243	0.0057	0.0806
0.3043	0.0028	0.0619	0.3995	0.0027	0.0435
0.28564	0.0000	0.0000	0.3792	0.0000	0.0000

Table III. Values of Binary Parameters and δP for HFC-32/*n*-Butane Mixtures

T (K)	k_{12}	A_{12}	A_{21}	δP (%)[a]
283.150	0.3378	5088.9	2804.2	1.932
293.150	0.3450	5054.5	2727.7	1.843
303.150	0.3436	5227.7	2763.7	1.928
313.150	0.3368	5498.0	2765.6	2.357

[a] $\delta P = (1/N) \sum |(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}|$.

the azeotropic pressures from the calculated data are larger than those from the experimental data by 35 kPa. It is also found that the azeotropic compositions are almost independent of temperature.

5. CONCLUSION

The vapor-liquid equilibria of *n*-butane/HFC-32 mixtures were measured in the temperature range of 283.15 to 313.15 K. The measured VLE data were correlated with the Peng–Robinson equation of state using the Wong and Sandler mixing rules. The result has shown that three binary parameters (k_{12}, A_{12}, and A_{21}) in the equations are almost independent of temperature. Azeotropic compositions were found to be about 95% in mole fraction of HFC-32. The azeotropic compositions were almost independent of temperature.

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Table IV. Azeotropic Values for HFC-32/*n*-Butane Mixtures

	Experimental results		Calculated results	
T (K)	x_1	P (MPa)	x_1	P (MPa)
283.150	0.9466	1.119	0.9292	1.135
293.150	0.9570	1.487	0.9325	1.511
303.150	0.9583	1.938	0.9324	1.976
313.150	0.9523	2.482	0.9331	2.542

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