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Vapor−Liquid Equilibria for the Difluoromethane (HFC-32) + Pentafluoroethane (HFC-125) System

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Isothermal vapor−liquid equilibrium data of the binary system difluoromethane (HFC-32) + pentafluoroethane (HFC-125) were measured in the temperature range from 268.15 K to 308.15 K at 10 K intervals and in the composition range from 0.1 to 0.8 mole fraction. Temperature, pressure, and compositions of the liquid and vapor phases were measured with a circulation type apparatus. The experimental data were correlated with the Carnahan−Starling−De Santis, Peng−Robinson, and Redlich−Kwong−Soave equations of state.

Introduction

As a result of the regulation of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), pure HFCs and hydrocarbons (HCs) and mixtures of these fluids are being investigated as alternative refrigerants. Vapor−liquid equilibrium data are required as one of the important basic properties in evaluating the performance of refrigeration cycles and determining their optimal composition. Therefore, accurate and reliable information on the thermophysical properties of these refrigerants are needed. In this study, isothermal vapor−liquid equilibrium data of the binary system difluoromethane (HFC-32) + pentafluoroethane (HFC-125) were measured in the temperature range from 268.15 K to 308.15 K and correlated with the Carnahan−Starling−De Santis (CSD), Peng−Robinson (PR), and Redlich−Kwong−Soave (RKS) equations of state.

Experimental Section

Chemicals. The samples of pure HFC-32 were supplied by Ulsan Chemical Co., and the HFC-125 was from Du Pont Co. The manufacturers stated that the purity of samples was 99.9 mass %. These samples were used without further purification.

Apparatus. Phase equilibrium experimental methods are classified as either static, flow, or circulation, depending upon how the mixture is equilibrated. In this study the circulation method is used, and the apparatus for measuring the vapor−liquid equilibrium is shown schematically in Figure 1. The apparatus consists of an equilibrium unit, a sampling and analysis unit, and a supply unit. The most important unit is the equilibrium unit that consists of an equilibrium cell, a magnetic pump, and a constant temperature-controlled bath. The recirculation apparatus and the procedures used in this work are described only briefly here, as they have already been presented in more detail elsewhere.[1,2]

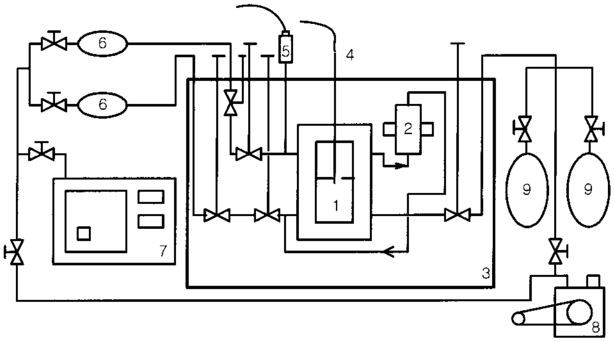

Figure 1. Schematic diagram of the vapor−liquid equilibrium apparatus: 1, equilibrium cell; 2, magnetic pump; 3, isothermal bath; 4, platinum resistance thermometer; 5, pressure transducer; 6, sample cylinder; 7, gas chromatograph; 8, vacuum pump; 9, refrigerant vessel.

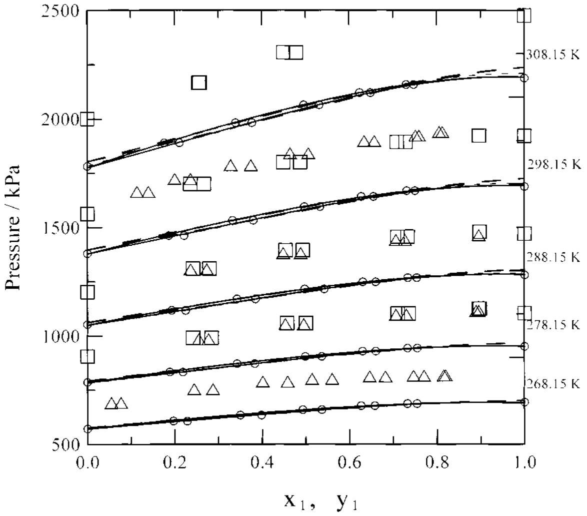

Figure 2. Vapor−liquid equilibrium data for the HFC-32 + HFC-125 system: ○, this work; —, Carnahan−Starling−De Santis (CSD) equations of state; - - -, Peng−Robinson (PR) equations of state; — — —, Redlich−Kwong−Soave (RKS) equations of state; □, Higsahi;[3] △, Kobayashi and Nishiumi.[4]

The equilibrium cell is made of type 316 stainless steel with an inner volume of about 128 cm^3. The magnetic pump circulates the vapor phase to ensure proper mixing and to reach equilibrium quickly. The equilibrium cell and the magnetic pump are immersed in the isothermal bath filled with silicon oil. The temperature of the isothermal bath was maintained at its set point by a circulator. The cell temperature was maintained within ±0.02 K for >1 h. The

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Table 1. Vapor−Liquid Equilibrium Data for the HFC-32 + HFC-125 System

	mole fraction of HFC-32			mole fraction of HFC-32	
P/kPa	liquid	vapor	P/kPa	liquid	vapor
		T = 268.15 K			
571.3	0.0000	0.0000	676.7	0.6265	0.6578
606.8	0.1966	0.2282	686.6	0.7323	0.7542
634.3	0.3494	0.3979	693.8	1.0000	1.0000
658.8	0.4929	0.5363			
		T = 278.15 K			
785.4	0.0000	0.0000	929.4	0.6299	0.6603
833.1	0.1883	0.2185	943.8	0.7326	0.7548
872.2	0.3422	0.3827	951.8	1.0000	1.0000
905.2	0.4984	0.5361			
		T = 288.15 K			
1052.8	0.0000	0.0000	1248.0	0.6303	0.6601
1117.4	0.1928	0.2247	1267.9	0.7331	0.7536
1170.2	0.3419	0.3845	1281.0	1.0000	1.0000
1215.5	0.4975	0.5419			
		T = 298.15 K			
1380.6	0.0000	0.0000	1643.0	0.6273	0.6551
1453.0	0.1864	0.2213	1669.7	0.7312	0.7499
1533.8	0.3323	0.3794	1689.6	1.0000	1.0000
1596.6	0.4964	0.5325			
		T = 308.15 K			
1782.9	0.0000	0.0000	2121.9	0.6237	0.6486
1890.5	0.1763	0.2108	2158.9	0.7300	0.7469
1983.5	0.3391	0.3765	2189.4	1.0000	1.0000
2065.9	0.4953	0.5310			

cell temperature was measured with a 100 Ω platinum resistance sensor and a precision thermometer (Yokogawa, 7563). The thermometer was calibrated against the ITS-90 scale. The uncertainty in the temperature measurements was estimated to be within ±0.02 K. The pressure is measured with a pressure transducer (Druck, PDCR 922). The pressure transducer calibration was checked against a quartz crystal pressure transducer after each series of experiments. The uncertainty of the pressure measurement is estimated to be within ±0.4%. After the equilibrium was reached, the vapor and liquid samples for analyzing compositions were trapped in a space between two valves and introduced into evacuated cylinders. The space between two valves for the liquid sample is about 0.1 cm^3. The volume of the cylinder is sufficient for the liquid sample to evaporate. The compositions of the vapor and liquid samples are determined using a gas chromatograph (HP 5890II) equipped with a thermal conductivity detector. The column is a Porapak-Q column (1.83 m long; 3.18 mm diameter; mesh range, 80/100). The gas chromatograph is calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. The uncertainty of the composition measurements is estimated to be within ±0.3 mol %. The experimental data at one condition were obtained at least three times in order to ensure accuracy.

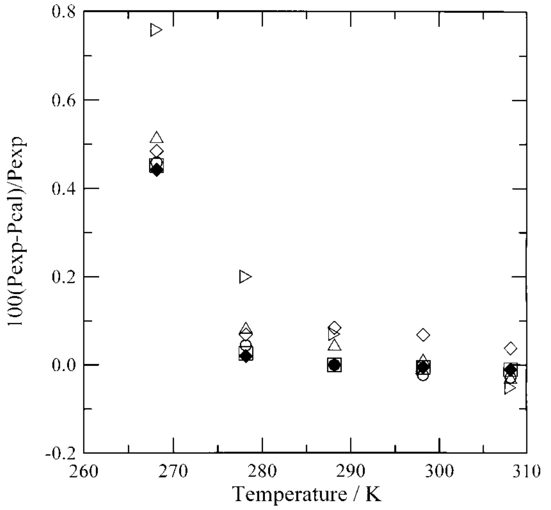

Figure 3. Comparison of the vapor pressure for HFC-32 between the experimental data and that of Weber et al.:[6] ◆, this work; ○, REFPROP 6.01;[5] sideways triangle, Widiatomo et al.;[7] △, Zhang et al.;[8] □, Defigaugh et al.;[9] ◇, ASHRAE handbook.[10]

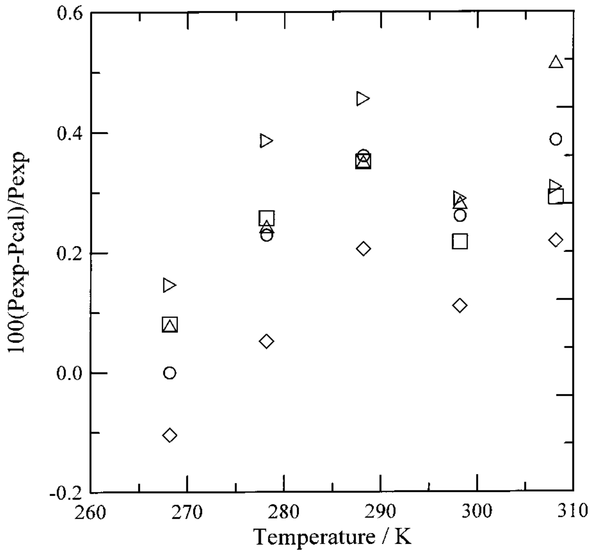

Figure 4. Comparison of the vapor pressure for HFC-125 between the experimental data and that of Piao et al.:[11] □, this work; ○, REFPROP 6.01;[5] △, Weber et al.;[6] sideways triangle, Zhang et al.;[8] ◇, ASHRAE handbook.[10]

Table 2. Critical Properties and Acentric Factor of Pure Components

	HFC-32	HFC-125
critical temperature, T_c/K	351.255[a]	339.33[b]
critical pressure, P_c/kPa	5782[b]	3629.0[b]
acentric factor	0.2768[b]	0.3035[b]

[a] Kuwabara et al.[17] [b] REFPROP 6.01.

Table 3. Coefficients of the CSD EOS Used for Data Correlation (Huber et al.[15])

	HFC-32	HFC-125
a_0/kPa·L^2·mol^{-2}	1662.2699	3427.9219
a_1/K^{-1}	$-2.197\,522\,7 \times 10^{-3}$	$-3.174\,613\,2 \times 10^{-3}$
a_2/K^{-2}	$-8.889\,027 \times 10^{-6}$	$-1.757\,286\,1 \times 10^{-6}$
b_0/L·mol^{-1}	0.077 987 924	0.149 380 43
b_1/L·mol^{-1}·K^{-1}	$-0.752\,381\,02 \times 10^{-4}$	$-1.808\,510\,7 \times 10^{-4}$
b_2/L·mol^{-1}·K^{-2}	$-0.583\,310\,54 \times 10^{-7}$	$-1.188\,133\,1 \times 10^{-7}$

Results and Discussion

Vapor−liquid equilibrium data for the binary system of HFC-32 + HFC-125 were measured in the temperature range from 268.15 to 308.15 K at 10 K intervals. Experimental data for the vapor−liquid equilibrium for HFC-32 + HFC-125 have been published by Higashi[3] and Kobayashi and Nishiumi.[4] These data are presented in Table 1 and in Figure 2. For the vapor pressure of pure components, the comparison between the present data and the correlation by Weber and Silva for HFC-32 is shown in Figure 3, whereas that by Piao et al. for HFC-125 is shown in Figure 4. The relative deviations of the vapor pressure of HFC-32 from REFPROP 6.01[5] and the Weber and Silva's[6] correlation are within −0.03% to 0.45% and −0.01% to 0.44%, respectively. The relative deviations of the vapor pressure of HFC-125 from REFPROP 6.01 and Piao's[11]

Table 4. Binary Interaction Parameters for the HFC-32 + HFC-125a System and Deviation of Pressure and Vapor Mole Fraction of HFC-32 from Equations of State

T/K	k_{12}	$\delta(\Delta P/P)^a$/%	δy^b
Canahan–Starling–De Santis			
268.15	−0.0151	0.293	0.0049
278.15	−0.0130	0.139	0.0046
288.15	−0.0110	0.149	0.0036
298.15	−0.0088	0.183	0.0025
308.15	−0.0057	0.117	0.0018
Average		0.176	0.0035
Peng–Robinson			
268.15	0.0010	0.280	0.0051
278.15	0.0020	0.180	0.0068
288.15	0.0030	0.196	0.0033
298.15	0.0038	0.212	0.0021
308.15	0.0054	0.219	0.0026
Average		0.217	0.0040
Redlich–Kwong–Soave			
268.15	−0.0037	0.522	0.0031
278.15	−0.0036	0.488	0.0048
288.15	−0.0033	0.581	0.0026
298.15	−0.0026	0.676	0.0045
308.15	−0.0005	0.633	0.0036
Average		0.580	0.0037

[a] $\delta(\Delta P/P) = (100/N)\Sigma(|P_{\mathrm{exp},i} - P_{\mathrm{cal},i}|/P_{\mathrm{exp},i})_i$. [b] $\delta y = (1/N)\Sigma(|y_{\mathrm{exp},i} - y_{\mathrm{cal},i}|)_i$.

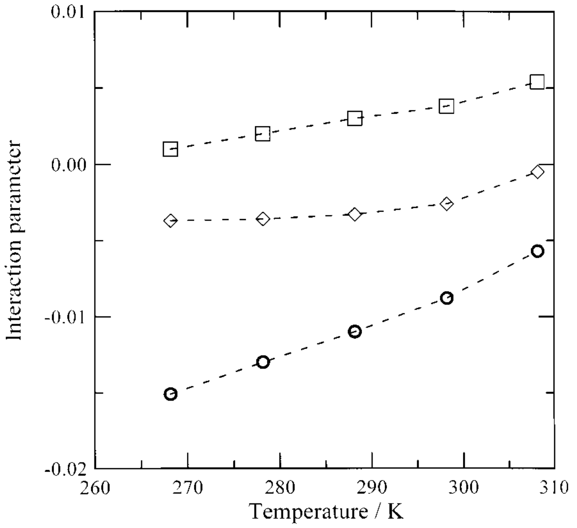

Figure 5. Binary interaction parameter in Carnahan–Starling–De Santis, Peng–Robinsion, and Redlich–Kwong–Soave equations of state for the HFC-32 + HFC-125 system at several temperatures: ○, CSD; ◇, RKS; □, PR.

correlation are within 0.22% to 0.38% and 0.08% to 0.35%, respectively.

The experimental results were correlated with the Carnahan–Starling–De Santis,[12] Peng–Robinson,[13] and Redlich–Kwong–Soave[14] equations of state using the van der Waals mixing rules. The mixing rules are given by

$$a = \sum\sum x_i y_j a_{ij} \tag{1}$$

$$b = \sum\sum x_i y_j b_{ij} \tag{2}$$

$$a_{12} = (1 - k_{12})(a_{11}a_{22})^{1/2} \tag{3}$$

$$b_{12} = (b_{11}^{1/3} + b_{22}^{1/3})^3/8 \tag{4}$$

where k_{12} is the binary interaction parameter. The critical properties and acentric factors used are given in Table 2.

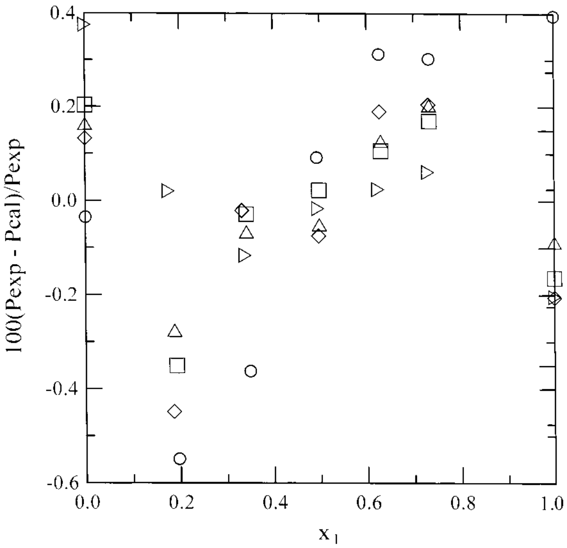

Figure 6. Deviation of the bubble point pressure for the HFC-32 + HFC-125 system between the measured data and the calculated results from the Carnahan–Starling–De Santis equation of state: percent deviation = $100(P_{\mathrm{exp}} - P_{\mathrm{cal}})/P_{\mathrm{exp}}$: ○, 268.15 K; △, 278.15 K; □, 288.15 K; ◇, 298.15 K; sideways triangle, 308.15 K.

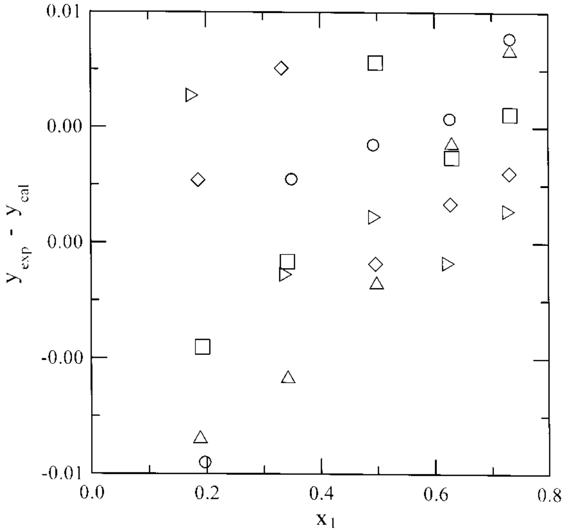

Figure 7. Deviation of the vapor-phase mole fraction of HFC-32 for the HFC-32 + HFC-125 system between the measured data and the calculated results from the Carnahan–Starling–De Santis equation of state; deviation = $y_{\mathrm{exp}} - y_{\mathrm{cal}}$: ○, 268.15 K; △, 278.15 K; □, 288.15 K; ◇, 298.15 K; sideways triangle, 308.15 K.

The coefficients of the CSD equation of state were cited from REFPROP 5.0.[15] They are listed in Table 3.

The binary interaction parameter, k_{12}, was determined by minimizing the objective function.

$$\mathrm{Obj} = \sum_{i=1}^{N}\left(\frac{P_{\mathrm{cal},i} - P_{\mathrm{exp},i}}{P_{\mathrm{exp},i}}\right)^2 \tag{5}$$

where N is the number of experimental points. For five temperatures, that is, 268.15, 278.15, 288.15, 298.15, and 308.15 K, the binary interaction parameters were determined and are presented in Table 4 and in Figure 5. In Figure 5, it is evident that the binary interaction parameters for all equation of state increase slightly as the temperature increases. The binary interaction parameter for the CSD equation of state has a stronger temperature dependence than those for the RKS and PR equations of state.

The relative deviations between measured pressure and vapor-phase mole fraction of HFC-32 and calculated results from equations of state are given in Table 4. In Table 4, the average deviation between the measured pressure and calculated results from the CSD equation of state is about 0.18% and that from the PR equation of state is about 0.22%. The average deviation from the RKS equation of state is about 0.58%. As a result, the CSD equation of state correlates the experimental data better than the PR and RKS equations of state.

Figures 6 and 7 show comparisons of the relative pressure and vapor-phase mole fraction of HFC-32 between the measured data and the calculated results from the CSD equation of state. As show in Figure 6, the present data were in good agreement with the calculated results from the CSD equation of state, and the deviations were within ±0.4%, except for two points.

Conclusions

Isothermal vapor−liquid equilibrium data of the binary system HFC-32 + HFC-125 were obtained at 35 conditions over the temperature range from 268.15 K to 308.15 K at 10 K intervals. The experimental data were correlated with the Carnahan−Starling−De Santis, Peng−Robinson, and Redlich−Kwong−Soave equations of state. The Carnahan−Starling−De Santis equation of state correlates the experimental data better than the Peng−Robinson and Redlich−Kwong−Soave equations of state.

Nomenclature

a, a_0, a_1, a_2 = coefficients of the equation of state
b, b_0, b_1, b_2 = coefficients of the equation of state
k_{12} = interaction parameter
Obj = objective function
N = number of data
P = pressure
T = temperature
x = liquid-phase mole fraction
y = vapor-phase mole fraction

Subscripts

1 = composition 1
2 = composition 2
c = critical point
cal = calculation
exp = experiment
i = composition i
j = composition j

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