Vapor−Liquid Equilibria for 1,1-Difluoroethane + Acetylene and 1,1-Difluoroethane + 1,1-Dichloroethane at 303.2 K and 323.2 K

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Isothermal vapor−liquid equilibria for 1,1-difluoroethane (HFC-152a) + acetylene and 1,1-difluoroethane + 1,1-dichloroethane (HCC-150a) were measured in a circulation type apparatus at 303.2 K and 323.2 K. The experimental data were correlated with the Peng−Robinson equation of state using the Wong and Sandler mixing rule, and the relevant parameters are presented.

Introduction

1,1-Difluoroethane (HFC-152a) is one of the promising replacements for dichlorodifluoromethane (CFC-12) as a refrigerant, a foam-blowing agent, and a propellant. Acetylene or 1,1-dichloroethane (HCC-150a) can be used as a raw material to produce HFC-152a by hydrofluorination (Rao, 1993; Ozawa *et al.*, 1975). In the manufacturing process of HFC-152a, it is necessary to have vapor−liquid equilibrium data to separate the raw material from the product. However, no experimental data have been previously reported in the literature.

In this work, we measured the vapor−liquid equilibria for the two binary systems HFC-152a + acetylene and HFC-152a + HCC-150a at 303.2 K and 323.2 K. The experimental data were correlated with the Peng−Robinson (1976) equation of state using the Wong and Sandler (1992) mixing rule.

Experimental Section

Chemicals. The purities of the chemicals used in this work were guaranteed by the manufacturers as shown in Table 1. They were used without any further purification.

Table 1. Origin and Purity of the Chemicals

component	origin	purity/mass %
HFC-152a	Dupont	>99.9
acetylene	Shin-Yang Chemical Co., Korea	>99.9
HCC-150a	JANSSEN CHIMICA Co.	>99.9

Experimental Apparatus. Vapor−liquid equilibria were measured in a circulation apparatus in which both phases were continuously recirculated. The experimental apparatus used in this work is the same as that discussed elsewhere (Lim *et al.*, 1994). The system consists of four major parts: an equilibrium cell, duplex circulation pump, vapor and liquid sampling valves, and a temperature-controlled air bath. The stainless steel equilibrium cell (Penberthy-Houdaile Co.) was equipped with dual glass windows for visual observation of the phases at equilibrium. The volume of the equilibrium cell was about 80 cm^3. The temperatures in the cell were measured by a K-type thermocouple (OMEGA Co.), with an uncertainty in the temperature measurement estimated to be ±0.1 K. The pressure in the cell was measured by a Heise pressure gauge (Model CMM 104637). The uncertainty of the pressure measurement is estimated to be within ±0.01 bar. A dual-head circulation pump (Milton Roy Co.) was used to circulate the liquid at one head and the vapor at the other. A temperature control system was equipped to maintain the system temperature constant within ±0.1 K. Two six-port sampling valves (Rheodyne Instruments, Model 7413) were used to collect the circulating vapor and liquid phase samples. They were directly connected to a gas chromatograph (HP-5890 series II) equipped with a thermal conductivity detector and a column packed with Porapak Q. Except for the duplex circulation pump, all the equilibrium apparatus was located in a temperature-controlled air bath.

Experimental Procedure. After the whole system had been evacuated by a vacuum pump, a certain amount of HFC-152a (for HFC-152a + acetylene) or HCC-150a (for HFC-152a + HCC-150a) was introduced into the cell. By controlling the temperature of the air bath, the temperature of the entire system was maintained constant. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of acetylene (for HFC-152a + acetylene) or HFC-152a (for HFC-152a + HCC-150a) was supplied to the cell from a charging cylinder. Both vapor and liquid phases were allowed to circulate for about 1 h to ensure equilibrium. After equilibrium was attained, the pressure was measured and then vapor and liquid samples were taken from the recycling lines by use of the vapor sampling valve with the loop volume of 5 μL and the liquid sampling valve with the loop volume of 1 μL, respectively. They were directly injected into the gas chromatograph which is connected on-line to both vapor and liquid sampling valves.

To obtain reliable values, we measured the equilibrium concentration at least three times in a row. Average deviations of the equilibrium concentration were within ±0.002 and ±0.001 (mole fraction) for liquid and vapor phases, respectively.

Results and Discussion

The experimental vapor−liquid equilibrium (VLE) results for the binary systems of HFC-152a (1) + acetylene (2) and HFC-152a (1) + HCC-150a (2) at 303.2 K and 323.2 K are given in Tables 2 and 3, respectively. Each table lists the measured mole fraction of the liquid and vapor

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Table 2. Vapor−Liquid Equilibria for HFC-152a (1) + Acetylene (2)

x_1	y_1	P/bar
	T/K = 303.2	
1.0000	1.0000	7.01
0.9620	0.8428	7.80
0.8717	0.6151	8.50
0.7491	0.4016	11.75
0.5757	0.2397	17.75
0.4315	0.1630	25.00
0.3044	0.1095	32.49
0.1986	0.0622	39.20
0.0907	0.0373	47.20
0.0000	0.0000	54.76
	T/K = 323.2	
1.0000	1.0000	11.86
0.9688	0.8984	12.29
0.8892	0.6918	14.25
0.7433	0.4619	19.00
0.5951	0.3160	25.50
0.4391	0.2134	35.57
0.2992	0.1476	46.06
0.2228	0.1105	52.30
0.0968	0.0793	65.75

Table 3. Vapor−Liquid Equilibria for HFC-152a (1) + HCC-150a (2)

x_1	y_1	P/bar
	T/K = 303.2	
0.1063	0.6934	1.34
0.1936	0.8031	2.05
0.2776	0.8600	2.81
0.3724	0.8906	3.36
0.5276	0.9266	4.31
0.6076	0.9403	4.70
0.7051	0.9526	5.30
0.7990	0.9655	5.95
0.8810	0.9771	6.39
0.9500	0.9851	6.85
	T/K = 323.2	
0.1016	0.6342	1.58
0.1643	0.7578	2.77
0.2721	0.8250	4.40
0.3408	0.8551	5.15
0.4876	0.9015	6.70
0.5320	0.9109	7.08
0.6176	0.9281	7.91
0.7613	0.9522	9.42
0.8274	0.9636	10.16
0.9385	0.9822	11.47

phases, pressures, and temperatures in equilibrium. The VLE data were correlated with the Peng−Robinson (1976) equation of state. The Peng−Robinson equation of state is expressed as follows:

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

$$a = (0.457235R^2T_c^{\ 2}/P_c)\alpha(T) \tag{2}$$

$$b = 0.077796RT_c/P_c \tag{3}$$

$$\alpha(T) = [1 + \kappa(1 - T_r^{\ 0.5})]^2 \tag{4}$$

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

where the parameter a is a function of temperature, b is constant, κ is a constant characteristic of each substance, ω is the acentric factor, P is pressure, P_c is the critical pressure, T is absolute temperature, T_c is the critical temperature, T_r is the reduced temperature, and v is molar volume.

Table 4. Characteristic Properties of the Chemicals

component	T_c/K	P_c/bar	ω	source
HFC-152a	386.6	45.0	0.256	TRC Tables (1996)
acetylene	308.32	61.39	0.190	TRC Tables (1996)
HCC-150a	523.0	51.0	0.240	TRC Tables (1996)

Table 5. Values of Binary Parameters and AAD (%) of *P*

		δP^b/%	
system	NRTL params^a	303.2 K	323.2 K
HFC-152a + acetylene	$k_{ij} = 0.0935$ $A_{ij} = -336.15$ $A_{ji} = -469.12$	1.14	2.03
HFC-152a + HCC-150a	$k_{ij} = -0.6935$ $A_{ij} = 2787.67$ $A_{ji} = 462.31$	1.26	6.52

[a] Binary parameters for both systems were obtained at 303.2 K and the units of A_{ij} and A_{ji} are cal/mol. [b] $\delta P = (1/N)\sum_i^N|(P_{\text{exptl},,i} - P_{\text{calcd},i}/P_{\text{exptl},i}| \times 100$.

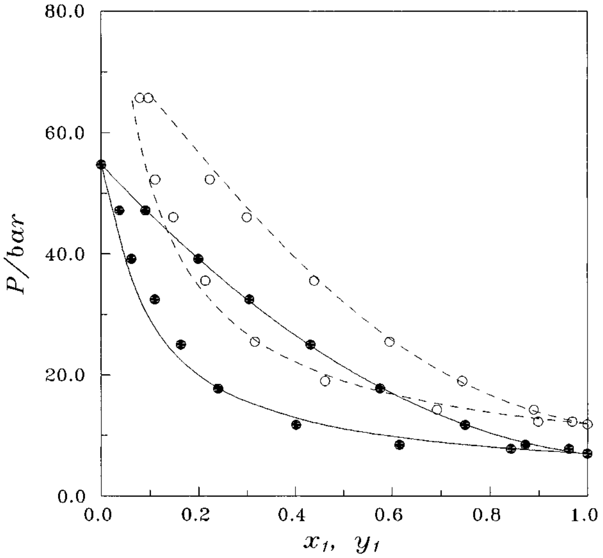

Figure 1. $P-x-y$ diagram for the HFC-152a (1) + acetylene (2) system at 303.2 K and 323.2 K: (●) experimental at 303.2 K; (○) experimental at 323.2 K; (—) calculated at 303.2 K; (- - -) calculated at 323.2 K.

The critical properties (T_c, P_c) and acentric factors (ω) of HFC-152a, acetylene, and HCC-150a used to calculate the parameters for the Peng−Robinson equation of state are taken from TRC databases (1996) and given in Table 4.

In this work, we used the Wong and Sandler (1992) mixing rule to obtain equation of state parameters for a mixture of the pure components. Wong and Sandler equated the excess Helmholtz free energy at infinite pressure from an equation of state to the excess Helmholtz free energy from any activity coefficient model, in such a way that a mixing rule is obtained which simultaneously satisfies the quadratic composition dependence of the second virial coefficient but also behaves like an activity coefficient model at high density (Huang *et al.*, 1994). This mixing rule for a cubic equation of state can be written as

$$b_m = \frac{\sum_i\sum_j x_ix_j(b - a/RT)_{ij}}{(1 - A_\infty^E/CRT - \sum_i x_ia_i/RTb_i)} \tag{6}$$

with

$$(b - a/RT)_{ij} = \frac{1}{2}[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \qquad (7)$$

and

$$\frac{a_{\mathrm{m}}}{b_{\mathrm{m}}} = \sum_i x_i \frac{a_i}{b_i} + \frac{A^{\mathrm{E}}_{\infty}}{C} \qquad (8)$$

where C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the Peng−Robinson equation (1976) used in this work. Also, A^{E}_{∞} is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy model (Wong *et al.*, 1992); in this study we use the NRTL model (Renon and Prausnitz, 1968):

$$\frac{A^{\mathrm{E}}_{\infty}}{RT} = \sum_i x_i \frac{\left(\sum_j x_j G_{ji} \tau_{ji}\right)}{\sum_k x_k G_{ki}} \qquad (9)$$

with

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \qquad \text{and} \qquad \tau_{ij} = \mathrm{A}_{ij}/(\mathrm{RT}) \qquad (10)$$

where G_{ij} is the local composition factor for the NRTL model, τ_{ij} is the NRTL model binary interaction parameter, $A_j = (g_{ij} - g_{jj})$ and g_{ij} are energy parameters characteristic of the i−j interaction, and α is the NRTL model parameter. We have set α_{ij} equal to 0.3 for all the binary mixtures studied here.

The Marquardt algorithm (Kuester and Mize, 1973) was applied to obtain the parameters with the following objective function:

$$\mathrm{obj} = \sum_j \left[\left(\frac{P_{j,\mathrm{exptl}} - P_{j,\mathrm{calcd}}}{P_{j,\mathrm{exptl}}} \right) \times 100 \right]^2 \qquad (11)$$

In these calculations the VLE at 323.2 K were predicted using the model parameters obtained at 303.2 K. Because the temperature ranges of the two binary systems studied here were relatively short, k_{ij}, A_{ij}, and A_{ji} were fixed with the values obtained at 303.2 K. All the binary parameters of both systems and the average absolute deviations (AAD) between measured and calculated values are listed in Table 5. Figure 1 shows the comparison of measured and calculated values for the HFC-152a (1) + acetylene (2) system at 303.2 K and 323.2 K, respectively. As shown in this figure and by the low average absolute deviations, the calculated values give a good agreement with the experimental data. This system exhibits a critical point at about 68 bar and 323.2 K.

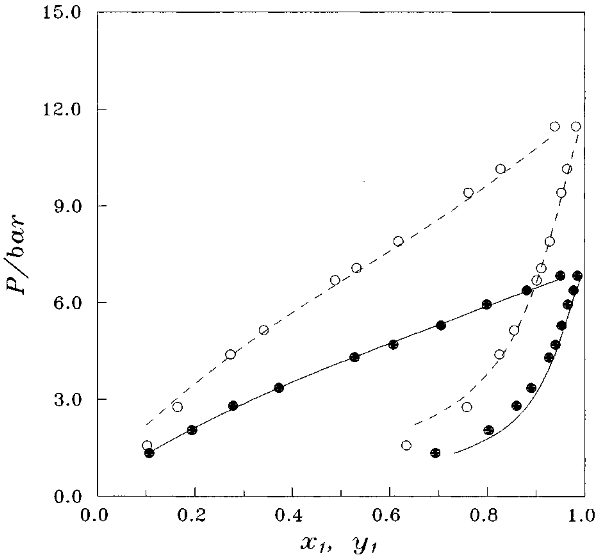

Figure 2. P−x−y diagram for the HFC-152a (1) + HCC-150a (2) system at 303.2 K and 323.2 K: (●) experimental at 303.2 K; (○) experimental at 323.2 K; (—) calculated at 303.2 K; (- - -) calculated at 323.2 K.

Figure 2 illustrates the comparison of measured and calculated values for the system of HFC-152a (1) + HCC-150a (2) at 303.2 K and 323.2 K, respectively. As given in Table 5, the AAD at 323.2 K for this system was a little larger than that for the HFC-152a (1) + acetylene (2) system. The calculated data, however, appeared to have good agreement with experimental values at both temperatures, as seen in Figure 2.

From these results, the NRTL binary parameters obtained in this work can be used for the prediction of VLE in the range of temperatures studied.

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