Vapor−Liquid Equilibria for Difluoromethane + Dichloromethane at 303.2 and 313.2 K and 1,1-Difluoroethane + Vinyl Chloride at 303.2 and 323.2 K

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Isothermal vapor−liquid equilibria for difluoromethane (HFC-32) + dichloromethane at 303.2 K and 313.2 K and 1,1-difluoroethane (HFC-152a) + vinyl chloride at 303.2 K and 323.2 K were measured in a circulation-type apparatus. 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

Difluoromethane (HFC-32: CH_2F_2) and 1,1-difluoroethane (HFC-152a: $C_2H_4F_2$) are promising alternative refrigerants in place of chlorodifluoromethane (HCFC-22: $CHClF_2$) and dichlorodifluoromethane (CFC-12: CCl_2F_2), respectively. The ozone depletion potentials (ODP) of HFC-32 and HFC-152a are null since they do not contain chlorine atoms. Their global warming potentials (GWP) are less than those of HCFC-22 and CFC-12 because they contain more hydrogen atoms and thus have a shorter atmospheric lifetime (Lisal and Vacek, 1996).

In the manufacturing process of HFC-32 and HFC-152a, dichloromethane (CH_2Cl_2) and vinyl chloride (C_2H_3Cl) are used as a raw material to produce HFC-32 and HFC-152a by hydrofluorination, respectively. Therefore, 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 isothermal vapor−liquid equilibria (VLE) for the two binary systems HFC-32 + dichloromethane at 303.2 K and 313.2 K and HFC-152a + vinyl chloride at 303.2 K and 323.2 K. The experimental data were correlated with the Peng−Robinson equation of state (Peng and Robinson, 1976) using the Wong−Sandler mixing rule (Wong and Sandler, 1992).

Experimental Section

Chemicals. The high-grade chemicals having purities more than 99.9 wt %, as shown in Table 1 , were used for the measurements of VLE. The purities of the chemicals were guaranteed by the manufacturers and they were used without any further purification.

Experimental Apparatus. The experimental equipment used to measure the isothermal VLE in this work is a circulation-type apparatus in which both phases were continuously recirculated. The explanation of the experimental apparatus and the procedure has been reported in our previous publications (Lim and Kim, 1996; Lim *et al.*, 1994, 1996).

The system consists of four major parts: an equilibrium cell, a 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.) and a digital indicator (OMEGA model DP41-TC) that was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of ±0.1 K. The pressure in the cell was measured by a Heise pressure gauge (Model CMM 104637) that was calibrated by a dead weight gauge (NAGANO KEIKI PD12) with the uncertainty of the pressure measurement 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 (Alltech Co.). Except for the duplex circulation pump, all the equilibrium apparatus was located in a temperature-controlled air bath.

Table 1. Origin and Purity of the Chemicals

component	origin	purity/ (mass %)
HFC-32	KIST, Soeul, Korea	>99.9
dichloromethane	Samsung Fine Chemicals Co., Ulsan, Korea	>99.9
HFC-152a	DuPont	>99.9
vinyl chloride	Hanyang Chem. Co., Daejon, Korea	>99.9

Experimental Procedure. Experiments for a binary system were performed by the following procedure. The whole system was evacuated by a vacuum pump to remove all the inert gases. A certain amount of dichloromethane (for HFC-32 + dichloromethane) or vinyl chloride (for HFC-152a + vinyl chloride) was introduced into the cell, and then the temperature of the entire system was maintained constant by controlling the temperature of the air bath. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of HFC-32 (for HFC-32 + dichloromethane) or HFC-152a (for HFC-152a + vinyl chloride) 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. When the equilibrium was attained, the pressure was measured and then vapor and liquid samples were taken from the recycling lines by the vapor and liquid

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Table 2. Vapor−Liquid Equilibria for HFC-32 (1) + Dichloromethane (2)

x_1	y_1	P/bar	x_1	y_1	P/bar
		T/K = 303.2			
0.0000	0.0000	0.72	0.6158	0.9482	13.52
0.0398	0.5960	2.29	0.7142	0.9592	14.88
0.1190	0.7666	4.06	0.8054	0.9696	16.44
0.2398	0.8701	6.71	0.8705	0.9783	17.35
0.3049	0.9036	8.39	1.0000	1.0000	19.26
0.4699	0.9371	11.54			
		T/K = 313.2			
0.0000	0.0000	1.01	0.6074	0.9444	17.19
0.0390	0.5448	2.85	0.7136	0.9521	19.05
0.1162	0.7560	5.01	0.8012	0.9654	20.86
0.2241	0.8499	8.07	0.8624	0.9712	21.75
0.2857	0.8845	10.23	1.0000	1.0000	24.77
0.4391	0.9115	13.72			

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

x_1	y_1	P/bar	x_1	y_1	P/bar
		T/K = 303.2			
0.0000	0.0000	4.66	0.6701	0.7278	6.71
0.0982	0.1724	5.25	0.7717	0.8108	6.85
0.1387	0.2172	5.41	0.7839	0.8172	6.85
0.2060	0.3038	5.71	0.8278	0.8583	6.86
0.3269	0.4302	6.09	0.9128	0.9269	6.89
0.4719	0.5672	6.38	0.9724	0.9763	6.95
0.5066	0.5951	6.50	1.0000	1.0000	7.01
		T/K = 323.2			
0.0000	0.0000	7.34	0.5981	0.6456	10.72
0.0410	0.0707	7.83	0.6546	0.7041	10.93
0.0947	0.1565	8.35	0.7539	0.7868	11.18
0.1375	0.2054	8.66	0.7945	0.8318	11.32
0.1742	0.2620	8.83	0.8292	0.8497	11.40
0.2436	0.3383	9.38	0.9133	0.9247	11.62
0.3153	0.4071	9.73	0.9716	0.9748	11.80
0.3545	0.4426	9.83	1.0000	1.0000	11.91
0.5049	0.5782	10.47			

Table 4. Characteristic Properties of the Chemicals

component	T_c/K	P_c/bar	ω	source
HFC-32	351.6	58.3	0.271	TRC Tables (1996)
dichloromethane	510.0	61.0	0.190	TRC Tables (1996)
HFC-152a	386.6	45.0	0.256	TRC Tables (1996)
vinyl chloride	425.0	51.5	0.122	Reid et al. (1987)

sampling valves (loop volumes: 5 μL for vapor, 1 μL for liquid), respectively. The compositions of the samples were measured by immediately injecting them into the gas chromatograph that is connected on-line to both vapor and liquid sampling valves. We measured the equilibrium concentration at least three times in a row to obtain reliable values. Average deviations of the equilibrium concentration were within ±0.002 and ±0.001 (mole fraction basis) for liquid and vapor phases, respectively.

Results and Discussion

The experimental vapor−liquid equilibrium results for the binary systems of HFC-32 (1) + dichloromethane (2) at 303.2 K and 313.2 K and HFC-152a (1) + vinyl chloride (2) at 303.2 K and 323.2 K are given in Tables 2 and 3, respectively. Each table lists the measured compositions of the liquid and vapor phases in mole fraction and the equilibrium pressures and temperatures. The VLE data were correlated with the Peng−Robinson equation of state (PR-EOS). The PR-EOS is expressed as follows:

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

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

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

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

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

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. The critical properties (T_c, P_c) and the acentric factors (ω) of HFC-32, dichloromethane, HFC-152a, and vinyl chloride used to calculate the parameters for the PR-EOS are given in Table 4.

The experimental binary VLE data given in Tables 1 and 2 were correlated with the PR-EOS. In this work the Wong−Sandler mixing rule (1992) was applied to obtain the equation of state parameters for a binary mixture from those of the pure components. Wong and Sandler equated the excess Helmholtz free energy at infinite pressure from an equation of state to that 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

$$b_m = \frac{\sum_i\sum_j x_i x_j (b - a/RT)_{ij}}{\left(1 - A^E_\infty/CRT - \sum_i x_i a_i/RTb_i\right)} \tag{6}$$

with

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

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A^E_\infty}{C} \tag{8}$$

where C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR-EOS (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).

When the NRTL model (Renon and Prausnitz, 1968) is used, A^E_∞ can be expressed as

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

with

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \quad \text{and} \quad \tau_{ij} = A_{ij}/(RT) \tag{10}$$

where G_{ij} is the local composition factor for the NRTL model, τ_{ij} is the binary interaction parameter, $A_{ij} = (g_{ij} - g_{jj})$ and g_{ij} are energy parameters characteristic of the i−j

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

		δP^b/%		
system	NRTL params[a]	303.2 K	313.2 K	323.2 K
HFC-32 + dichloromethane	$k_{ij} = 0.3965$ $A_{ij} = 7.8097$ $A_{ji} = -3.8015$	1.90	2.21	
HFC-152a + vinyl chloride	$k_{ij} = -0.8367$ $A_{ij} = 5.9931$ $A_{ji} = 4.6996$	0.45		1.92

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

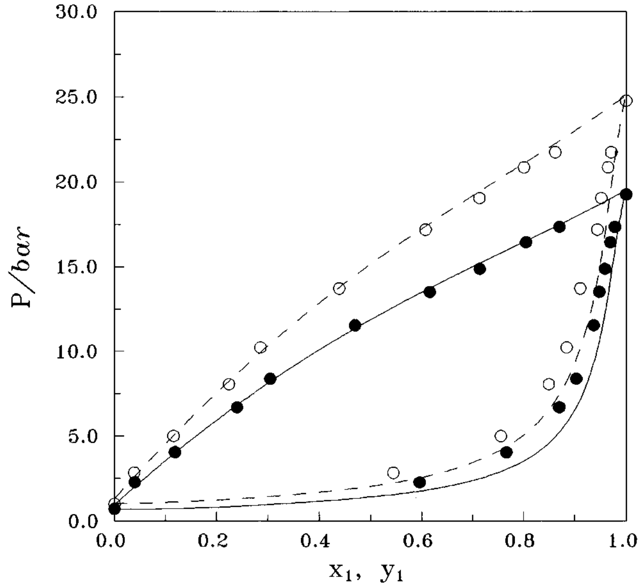

Figure 1. $P-x-y$ diagram for the HFC-32 (1) + dichloromethane (2) system at 303.2 K and 313.2 K: (●) experimental at 303.2 K; (○) experimental at 313.2 K; (—) calculated at 303.2 K; (- - -) calculated at 313.2 K.

interaction, and α is the NRTL model parameter which is set to 0.3 for all the binary mixtures studied here.

The model contains three adjustable binary parameters (k_{ij}, A_{ij} and A_{ji}). The Marquardt algorithm (Kuester and Mize, 1973) was applied to regress the binary parameters and the following objective function was used:

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

where $P_{i,\text{exptl}}$ and $P_{i,\text{calcd}}$ are the experimental and calculated pressure, respectively.

The binary parameters (k_{ij}, A_{ij}, and A_{ji}) for the two binary systems and the average absolute deviations (AAD) between measured and calculated values are shown in Table 5. In these calculations, in order to observe the prediction capability of the PR-EOS with the Wong−Sandler mixing rule, the binary parameters were regressed using the VLE data only at the lowest temperature of each system, i.e., 303.2 K for both binary systems. In other words, the isothermal VLE at higher temperatures (313.2 K for HFC-32 + dichloromethane and 323.2 K for HFC-152a + vinyl chloride) were predicted using the model parameters obtained at the lowest temperature (303.2 K). It is reasonable to apply the binary parameters obtained at one temperature to the other temperatures, since the temperature ranges studied here are relatively short.

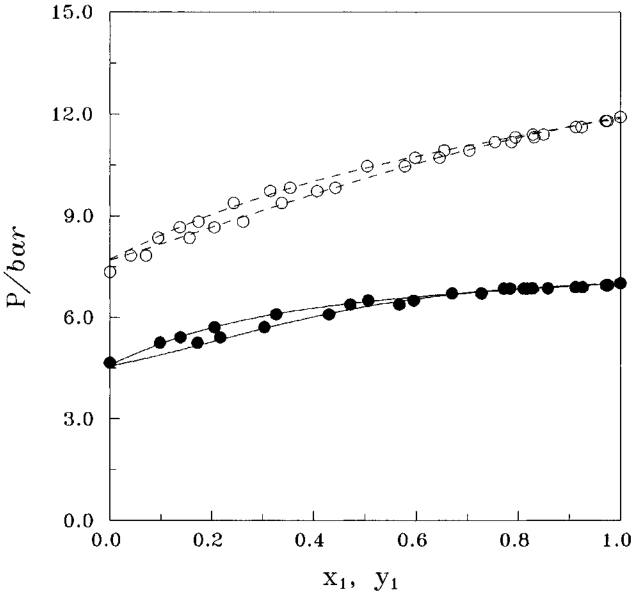

Figure 2. $P-x-y$ diagram for the HFC-152a (1) + vinyl chloride (2) system at 303.2 K and 323.2 K: (●) experimental at 303.2 K; (○) experimental at 323.2 K; (—) calculated at 303.2 K; (- - -) calculated at 323.2 K.

Figure 1 shows the experimental and calculated isothermal VLE for the HFC-32 (1) + dichloromethane (2) system at 303.2 K and 313.2 K. As shown in this figure and by the low average absolute deviations given in Table 5, the calculated values give a good agreement with the experimental ones.

Figure 2 illustrates the comparison of measured and calculated values for the system HFC-152a (1) + vinyl chloride (2) at 303.2 K and 323.2 K. The calculated values were observed to have relatively good agreements with the experimental ones at both temperatures. In conclusion, the NRTL binary parameters obtained in this work can be used for the prediction of VLE in the range of temperatures studied.

Conclusions

The isothermal VLE between HFC-32 + dichloromethane and HFC-152a + vinyl chloride at several temperatures were measured using a circulation-type apparatus. These experimental data would be valuable, since no or very few VLE data for the systems containing the above compounds are available. The experimental data were well correlated with the Peng−Robinson equation of state using the Wong−Sandler mixing rule. The binary parameters obtained in this work can be used for the prediction of VLE in the range of temperatures studied.

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