# Vapor−Liquid Equilibria of the Difluoromethane + Dimethyl Ether and 1,1,1,2-Tetrafluoroethane + Dimethyl Ether Systems

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Binary vapor−liquid equilibrium data were measured for the difluoromethane (HFC-32) + dimethyl ether (DME) and 1,1,1,2-tetrafluoroethane (HFC-134a) + dimethyl ether (DME) systems at temperature from (313.15 to 343.15) K. These experiments were carried out with a circulating-type apparatus with on-line gas chromatography. The experimental data were correlated well by Peng−Robinson equation of state using the Wong−Sandler mixing rules.

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## Introduction

The production and use of refrigerants with high ozone-depletion potentials (ODPs) such as the chlorofluorocarbons (CFCs) have been regulated as a consequence of the Montreal Protocol in 1987. Hydrofluorocarbons (HFCs) are proposed as promising alternative refrigerants to substitute for CFCs because of their zero ODPs and low global warming potentials (GWPs). With HFCs, dimethyl ether (DME) has been used as an alternative refrigerant of CFCs because of its environmentally friendly properties. DME has zero ODPs and is non-toxic.[1−4]

Thermodynamic properties of the mixtures, such as vapor−liquid equilibria (VLE), are important to decide the optimal compositions of the mixtures and to evaluate the performance of the refrigeration cycles. In this work, we measured the isothermal VLE data for the two binary systems, difluoromethane (HFC-32) + DME and 1,1,1,2-tetrafluoroethane (HFC134a) + DME, at temperatures from (313.15 to 343.15) K at 10 K intervals. The experimental data were correlated by the Peng−Robinson equation[6] of state with the Wong−Sandler mixing rules.[7]

## Experimental Section

***Chemicals.*** DME of 99.9 % purity was supplied by LG Chem. Ltd., and HFC-32 and HFC-134a with purity 99.8 mass % were obtained from Ulsan Chemical Co. All components were used without further purification in these experiments.

***Apparatus.*** The measurement of the VLE data was conducted in a circulation-type apparatus. The details of this apparatus were given in our previous studies.[5] The equilibrium cell was made of 316 stainless steel with an inner volume of about 320 mL. It was equipped with two windows and two magnetic pumps. Because two magnetic pumps were forced to circulate vapor and liquid phase separately, equilibrium was quickly reached. The temperature in the cell was measured with a 100 Ω platinum resistance thermometer (Hart Scientific Co., model 5627) and a digital indicator (Hart Scientific Co., model 1502A) with an accuracy of 0.05 K. The pressure of the cell was measured with pressure transducer (Sensotec Co., model Super TJE (0 to 1500) psia) connected to a digital indicator (Laurel, model L20010WM1). An accuracy of the digital pressure gauge is 0.05 %. To trap the liquid and vapor sample, we used two sampling valves (Rheodyne Instruments, model 7413 with a 0.5 $\mu$L sampling loop for liquid and model 7010 with a 10 $\mu$L sampling loop for vapor). A gas chromatograph, which used helium gas as a carrier, was connected on-line to the equilibrium apparatus

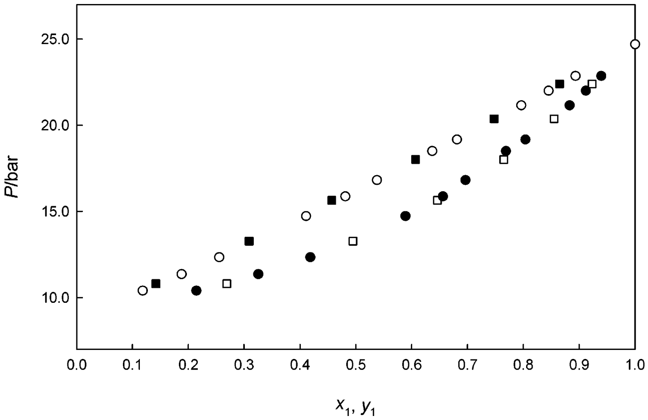

**Figure 1.** Comparative data of the HFC-32 (1) + DME (2) system at 313.15 K: ■ and □, experimental data of Richon and co-workers;[3,4] ○ and ●, this study.

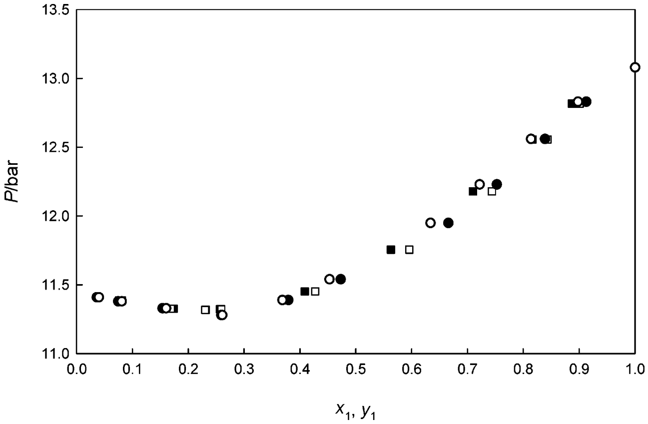

**Figure 2.** Comparative data of the HFC-134a (1) + DME (2) system at 313.15 K: ■ and □, experimental data of Richon and co-workers;[3,4] ○ and ●, this study.

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**Table 1. Critical Properties and Acentric Factors of Pure Components[a]**

| | HFC-32 | HFC-134a | dimethyl ether |
|---|---|---|---|
| $T_c$/K | 351.26 | 374.18 | 401.10 |
| $P_c$/bar | 57.84 | 40.56 | 53.7 |
| $\omega$ | 0.2771 | 0.3268 | 0.2002 |

[a] Aspen Property Databank.

**Table 2. Vapor−Liquid Equilibrium Data for the HFC-32 (1) + DME (2) System**

| $P_{\mathrm{exptl}}$/bar | $y_{1,\mathrm{exptl}}$ | $x_{1,\mathrm{exptl}}$ | $P_{\mathrm{caled}}$/bar | $y_{1,\mathrm{caled}}$ | $\Delta P$/bar[a] | $\Delta y_1$[b] |
|---|---|---|---|---|---|---|
| $T = 313.15$ K | | | | | | |
| 10.40 | 0.2145 | 0.1186 | 10.40 | 0.2227 | 0.00 | 0.0082 |
| 11.36 | 0.3256 | 0.1881 | 11.36 | 0.3307 | 0.00 | 0.0051 |
| 12.34 | 0.4187 | 0.2555 | 12.35 | 0.4216 | 0.01 | 0.0029 |
| 14.73 | 0.5893 | 0.4108 | 14.74 | 0.5909 | 0.01 | 0.0017 |
| 15.87 | 0.6561 | 0.4815 | 15.87 | 0.6543 | 0.00 | −0.0019 |
| 16.82 | 0.6966 | 0.5381 | 16.79 | 0.7005 | −0.03 | 0.0039 |
| 18.50 | 0.7687 | 0.6370 | 18.43 | 0.7742 | −0.07 | 0.0055 |
| 19.17 | 0.8036 | 0.6811 | 19.18 | 0.8048 | 0.01 | 0.0012 |
| 21.15 | 0.8828 | 0.7964 | 21.18 | 0.8801 | 0.03 | −0.0027 |
| 22.00 | 0.9119 | 0.8454 | 22.04 | 0.9105 | 0.04 | −0.0015 |
| 22.86 | 0.9395 | 0.8936 | 22.90 | 0.9394 | 0.04 | −0.0001 |
| 24.69 | 1.0000 | 1.0000 | 24.77 | 1.0000 | 0.08 | 0.0000 |
| $T = 323.15$ K | | | | | | |
| 12.28 | 0.0849 | 0.0510 | 12.25 | 0.0992 | −0.03 | 0.0144 |
| 13.23 | 0.1864 | 0.1106 | 13.22 | 0.2032 | −0.01 | 0.0168 |
| 14.24 | 0.2850 | 0.1693 | 14.22 | 0.2941 | −0.02 | 0.0091 |
| 15.26 | 0.3671 | 0.2265 | 15.24 | 0.3733 | −0.02 | 0.0063 |
| 16.65 | 0.4624 | 0.3012 | 16.61 | 0.4647 | −0.04 | 0.0022 |
| 17.83 | 0.5371 | 0.3662 | 17.84 | 0.5349 | 0.01 | −0.0022 |
| 20.16 | 0.6476 | 0.4832 | 20.15 | 0.6444 | −0.01 | −0.0032 |
| 21.46 | 0.7017 | 0.5459 | 21.42 | 0.6962 | −0.04 | −0.0055 |
| 23.00 | 0.7569 | 0.6200 | 22.97 | 0.7528 | −0.03 | −0.0041 |
| 24.35 | 0.8018 | 0.6838 | 24.33 | 0.7984 | −0.02 | −0.0034 |
| 25.40 | 0.8367 | 0.7353 | 25.45 | 0.8337 | 0.05 | −0.0030 |
| 27.32 | 0.8923 | 0.8239 | 27.43 | 0.8918 | 0.11 | −0.0005 |
| 28.87 | 0.9326 | 0.8903 | 28.94 | 0.9336 | 0.07 | 0.0010 |
| 30.28 | 0.9701 | 0.9516 | 30.34 | 0.9711 | 0.06 | 0.0010 |
| 31.38 | 1.0000 | 1.0000 | 31.45 | 1.0000 | 0.07 | 0.0000 |
| $T = 333.15$ K | | | | | | |
| 15.41 | 0.0879 | 0.0475 | 15.44 | 0.0888 | 0.03 | 0.0009 |
| 16.75 | 0.1954 | 0.1139 | 16.75 | 0.2003 | 0.00 | 0.0050 |
| 18.57 | 0.3264 | 0.2013 | 18.58 | 0.3279 | 0.01 | 0.0015 |
| 20.85 | 0.4549 | 0.3037 | 20.85 | 0.4543 | 0.00 | −0.0006 |
| 25.81 | 0.6559 | 0.5100 | 25.80 | 0.6547 | −0.01 | −0.0012 |
| 26.72 | 0.6851 | 0.5434 | 26.65 | 0.6822 | −0.07 | −0.0029 |
| 28.78 | 0.7480 | 0.6243 | 28.75 | 0.7450 | −0.03 | −0.0030 |
| 29.54 | 0.7703 | 0.6546 | 29.55 | 0.7673 | 0.01 | −0.0030 |
| 30.88 | 0.8028 | 0.7018 | 30.83 | 0.8011 | −0.05 | −0.0017 |
| 33.41 | 0.8668 | 0.7984 | 33.52 | 0.8674 | 0.11 | 0.0006 |
| 35.63 | 0.9175 | 0.8767 | 35.78 | 0.9194 | 0.15 | 0.0019 |
| 37.74 | 0.9659 | 0.9501 | 37.95 | 0.9675 | 0.21 | 0.0016 |
| 39.34 | 1.0000 | 1.0000 | 39.44 | 1.0000 | 0.10 | 0.0000 |
| $T = 343.15$ K | | | | | | |
| 20.78 | 0.1930 | 0.1120 | 20.83 | 0.1891 | 0.05 | −0.0039 |
| 22.39 | 0.2877 | 0.1765 | 22.43 | 0.2820 | 0.04 | −0.0057 |
| 23.97 | 0.3654 | 0.2362 | 23.98 | 0.3594 | 0.01 | −0.0060 |
| 26.65 | 0.4774 | 0.3339 | 26.63 | 0.4711 | −0.02 | −0.0063 |
| 29.38 | 0.5686 | 0.4281 | 29.32 | 0.5645 | −0.06 | −0.0041 |
| 31.24 | 0.6251 | 0.4919 | 31.22 | 0.6215 | −0.02 | −0.0036 |
| 32.19 | 0.6519 | 0.5230 | 32.16 | 0.6478 | −0.03 | −0.0041 |
| 34.23 | 0.7028 | 0.5870 | 34.16 | 0.6994 | −0.07 | −0.0034 |
| 35.29 | 0.7310 | 0.6235 | 35.32 | 0.7275 | 0.03 | −0.0035 |
| 39.36 | 0.8193 | 0.7470 | 39.45 | 0.8181 | 0.09 | −0.0011 |
| 42.11 | 0.8738 | 0.8250 | 42.22 | 0.8736 | 0.11 | −0.0003 |
| 44.12 | 0.9096 | 0.8777 | 44.16 | 0.9110 | 0.04 | 0.0014 |
| 45.60 | 0.9377 | 0.9175 | 45.68 | 0.9396 | 0.08 | 0.0019 |
| 46.86 | 0.9641 | 0.9548 | 47.13 | 0.9667 | 0.27 | 0.0025 |
| 48.84 | 1.0000 | 1.0000 | 48.92 | 1.0000 | 0.08 | 0.0000 |

[a] $\Delta P = P_{\mathrm{cal}} - P_{\mathrm{exp}}$. [b] $\Delta y_1 = y_{\mathrm{cal}} - y_{\mathrm{exp}}$.

with a thermal conductivity detector (TCD) and equipped Porapak-Q column(1.83 m long; 3.18 mm diameter; mesh range, 80/100).

**Table 3. Vapor−Liquid Equilibrium Data for the HFC-134a (1) + DME (2) System**

| $P_{\mathrm{exptl}}$/bar | $y_{1,\mathrm{exptl}}$ | $x_{1,\mathrm{exptl}}$ | $P_{\mathrm{caled}}$/bar | $y_{1,\mathrm{caled}}$ | $\Delta P$/bar[a] | $\Delta y_1$[b] |
|---|---|---|---|---|---|---|
| $T = 313.15$ K | | | | | | |
| 8.84 | 0.0245 | 0.0309 | 8.84 | 0.0264 | 0.00 | −0.0045 |
| 8.80 | 0.0682 | 0.0806 | 8.77 | 0.0727 | −0.03 | −0.0078 |
| 8.78 | 0.0835 | 0.0980 | 8.75 | 0.0899 | −0.03 | −0.0082 |
| 8.76 | 0.1115 | 0.1282 | 8.72 | 0.1206 | −0.04 | −0.0076 |
| 8.69 | 0.2210 | 0.2368 | 8.69 | 0.2377 | 0.00 | 0.0008 |
| 8.72 | 0.3072 | 0.3154 | 8.71 | 0.3255 | −0.01 | 0.0101 |
| 8.78 | 0.4300 | 0.4258 | 8.81 | 0.4488 | 0.03 | 0.0229 |
| 8.97 | 0.5511 | 0.5344 | 8.97 | 0.5668 | 0.00 | 0.0324 |
| 9.20 | 0.6746 | 0.6492 | 9.19 | 0.6861 | −0.01 | 0.0369 |
| 9.53 | 0.8026 | 0.7779 | 9.49 | 0.8115 | −0.04 | 0.0335 |
| 9.85 | 0.9101 | 0.8952 | 9.82 | 0.9163 | −0.03 | 0.0211 |
| 10.08 | 1.0000 | 1.0000 | 10.15 | 1.0000 | 0.07 | 0.0000 |
| $T = 323.15$ K | | | | | | |
| 11.41 | 0.0361 | 0.0400 | 11.41 | 0.0364 | 0.00 | −0.0036 |
| 11.38 | 0.0744 | 0.0808 | 11.36 | 0.0756 | −0.02 | −0.0051 |
| 11.33 | 0.1539 | 0.1605 | 11.30 | 0.1571 | −0.03 | −0.0034 |
| 11.28 | 0.2592 | 0.2609 | 11.30 | 0.2662 | 0.02 | 0.0053 |
| 11.39 | 0.3792 | 0.3685 | 11.40 | 0.3866 | 0.01 | 0.0181 |
| 11.54 | 0.4730 | 0.4530 | 11.53 | 0.4808 | −0.01 | 0.0278 |
| 11.95 | 0.6658 | 0.6338 | 11.97 | 0.6726 | 0.02 | 0.0387 |
| 12.23 | 0.7524 | 0.7217 | 12.24 | 0.7585 | 0.01 | 0.0369 |
| 12.56 | 0.8389 | 0.8139 | 12.54 | 0.8431 | −0.02 | 0.0292 |
| 12.83 | 0.9129 | 0.8979 | 12.83 | 0.9157 | 0.00 | 0.0177 |
| 13.08 | 1.0000 | 1.0000 | 13.18 | 1.0000 | 0.10 | 0.0000 |
| $T = 333.15$ K | | | | | | |
| 14.48 | 0.0453 | 0.0489 | 14.48 | 0.0461 | 0.00 | −0.0028 |
| 14.46 | 0.0870 | 0.0919 | 14.44 | 0.0889 | −0.02 | −0.0031 |
| 14.45 | 0.1420 | 0.1473 | 14.41 | 0.1463 | −0.04 | −0.0010 |
| 14.47 | 0.2774 | 0.2760 | 14.47 | 0.2857 | 0.00 | 0.0097 |
| 14.66 | 0.4063 | 0.3934 | 14.66 | 0.4147 | 0.00 | 0.0213 |
| 15.06 | 0.5788 | 0.5547 | 15.07 | 0.5868 | 0.01 | 0.0321 |
| 15.55 | 0.7251 | 0.6971 | 15.57 | 0.7296 | 0.01 | 0.0325 |
| 15.95 | 0.8194 | 0.7964 | 15.96 | 0.8231 | 0.01 | 0.0268 |
| 16.27 | 0.8853 | 0.8689 | 16.26 | 0.8883 | −0.01 | 0.0194 |
| 16.46 | 0.9217 | 0.9101 | 16.44 | 0.9242 | −0.02 | 0.0141 |
| 16.73 | 1.0000 | 1.0000 | 16.84 | 1.0000 | 0.11 | 0.0000 |
| $T = 343.15$ K | | | | | | |
| 18.16 | 0.0101 | 0.0102 | 18.20 | 0.0097 | 0.04 | −0.0006 |
| 18.15 | 0.0841 | 0.0858 | 18.14 | 0.0848 | −0.01 | −0.0010 |
| 18.16 | 0.1662 | 0.1667 | 18.15 | 0.1696 | −0.01 | 0.0029 |
| 18.30 | 0.2970 | 0.2903 | 18.30 | 0.3028 | 0.00 | 0.0126 |
| 18.54 | 0.4228 | 0.4054 | 18.57 | 0.4266 | 0.03 | 0.0212 |
| 18.98 | 0.5639 | 0.5386 | 19.01 | 0.5661 | 0.03 | 0.0275 |
| 19.57 | 0.7023 | 0.6770 | 19.57 | 0.7048 | 0.00 | 0.0278 |
| 20.15 | 0.8125 | 0.7892 | 20.10 | 0.8122 | −0.05 | 0.0230 |
| 20.50 | 0.8769 | 0.8588 | 20.45 | 0.8763 | −0.05 | 0.0175 |
| 21.06 | 1.0000 | 1.0000 | 21.23 | 1.0000 | 0.17 | 0.0000 |

[a] $\Delta P = P_{\mathrm{cal}} - P_{\mathrm{exp}}$. [b] $\Delta y_1 = y_{\mathrm{cal}} - y_{\mathrm{exp}}$.

***Experimental Procedure.*** The whole system was evacuated with a vacuum pump to remove all the impurities. Next, a certain amount of DME was injected into the cell. Then, a proper amount of HFCs was charged. After the target temperature was reached, two magnetic pumps were started to circulate vapor and liquid phases. When the equilibrium was reached, the vapor and liquid samples were taken into the gas chromatograph, and the compositions were measured. The equilibrium compositions of each phase were measured at least five times in a row to obtain reliable average values. Deviations of the equilibrium composition were less than 0.0005 in the mole fraction.

## Results and Discussion

VLE data for the binary systems, HFC-32 (1) + DME (2) and HFC-134a (1) + DME (2), were measured in a temperature range from (313.15 to 343.15) K. We found that Richon and co-workers reported the data for the same system at different temperature ranges.[3,4] Thus, we compared our data to those in

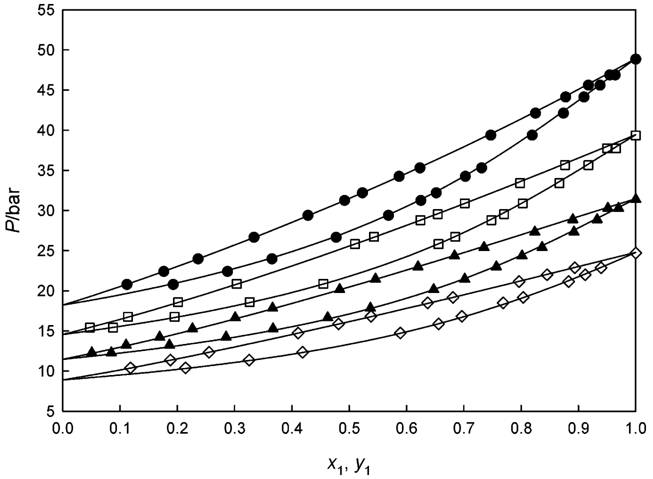

**Figure 3.** Vapor−liquid equilibria of the HFC-32 (1) + DME (2) system: —, PR EOS using Wong−Sandler mixing rules. ●, experimental data at 343 K; □, 333.15 K; ▲, 323.15 K; ◇, 313.15 K.

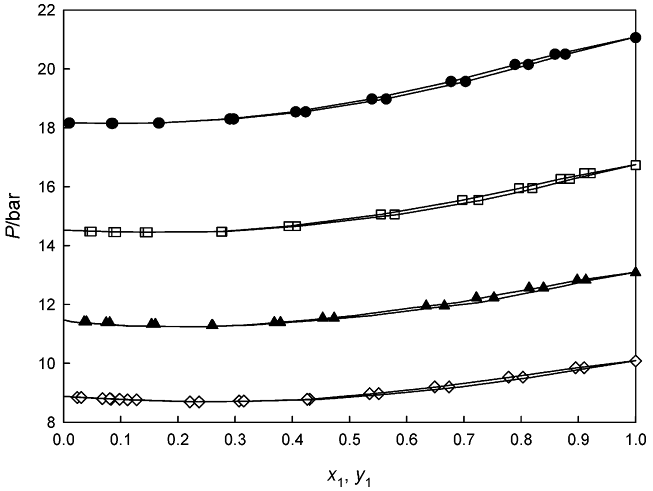

**Figure 4.** Vapor−liquid equilibria of the HFC-134a (1) + DME (2) system: —, PR EOS using Wong−Sandler mixing rules. ●, experimental data at 343 K; □, 333.15 K; ▲, 323.15 K; ◇, 313.15 K.

the literature. Figures 1 and 2 show the comparison at 313.15 K; good results were obtained. Experimental data for each system are given in Tables 2 and 3. Experimental data were correlated with the Peng−Robinson[6] equation of state (PR EOS) using the Wong−Sandler mixing rules.[7] The PR EOS and the Wong−Sandler mixing rules are expressed as follows:

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

$$a(T) = 0.45724\frac{R^2{T_c}^2}{P_c}\alpha(T) \tag{2}$$

$$b(T_c) = 0.07780\frac{RT_c}{P_c} \tag{3}$$

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

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

where $T_c$ is the critical temperature, $P_c$ is the critical pressure, $T_r$ is the reduced temperature, and $\omega$ is the acentric factor. The critical properties and acentric factors are listed in Table 1.

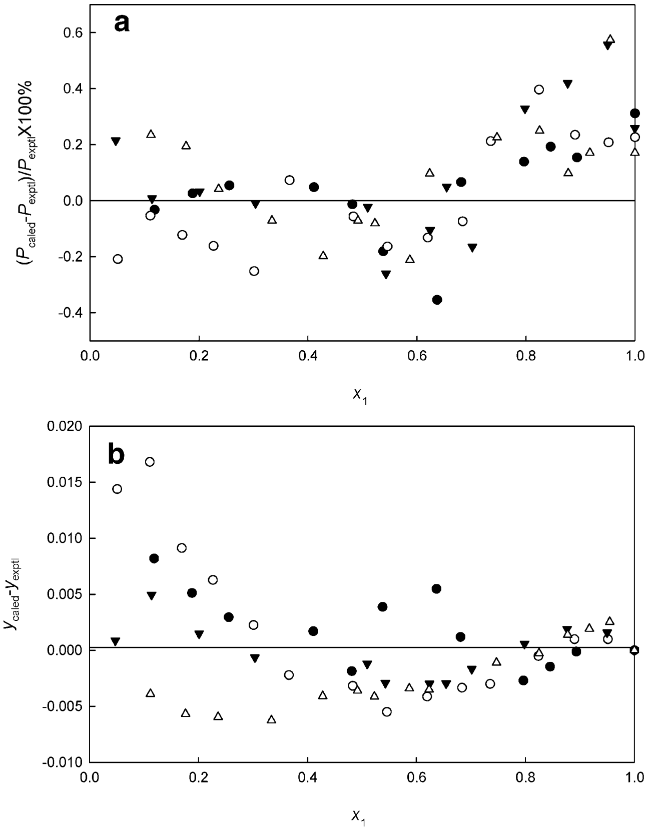

**Figure 5.** Deviation of the HFC-32 (1) + DME (2) system: (a) deviation of pressure and (b) deviation of vapor mole fraction. ●, experimental data at 313.15 K; ○, 323.15 K; ▼, 333.15 K; △, 343.15 K.

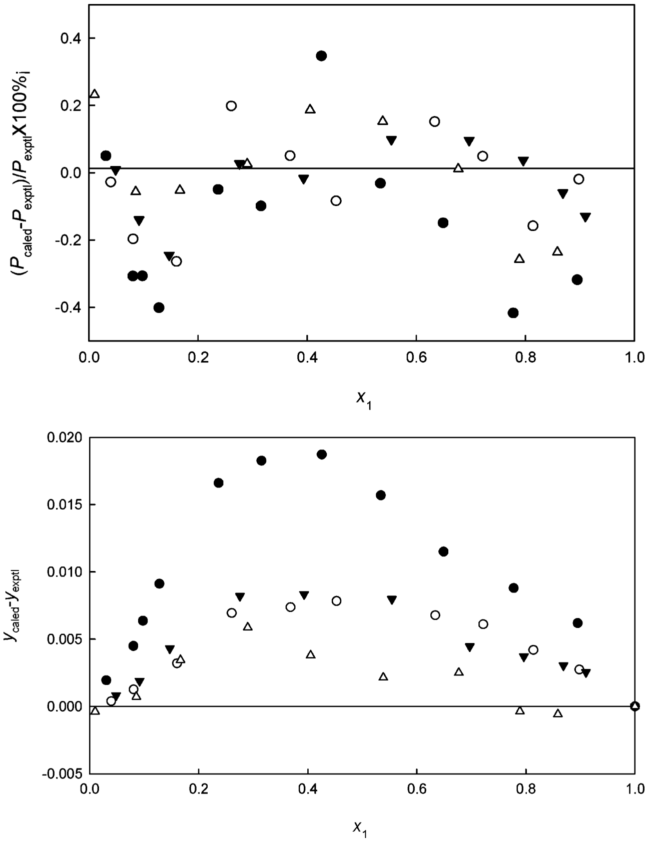

**Figure 6.** Deviation of the HFC-134a (1) + DME (2) system: (a) deviation of pressure and (b) deviation of vapor mole fraction. ●, experimental data at 313.15 K; ○, 323.15 K; ▼, 333.15 K; △, 343.15 K.

**Table 4. Binary Parameters and AAD (%)**

| $T$/K | binary parameters[a] | | AAD$P$[b]/% | AAD$y$[c] |
|---|---|---|---|---|
| | HFC-32 + DME | | | |
| | $k_{ij}$ | −0.31848 | 0.130 | 0.0029 |
| 313.15 | $A_{ij}$ | −475.36 | | |
| | $A_{ji}$ | 187.2982 | | |
| | $k_{ij}$ | −0.20037 | 0.172 | 0.0048 |
| 323.15 | $A_{ij}$ | −558.458 | | |
| | $A_{ji}$ | 128.0031 | | |
| | $k_{ij}$ | −0.12306 | 0.187 | 0.0018 |
| 333.15 | $A_{ij}$ | −596.239 | | |
| | $A_{ji}$ | 73.82621 | | |
| | $k_{ij}$ | −0.08792 | 0.179 | 0.0032 |
| 343.15 | $A_{ij}$ | −642.458 | | |
| | $A_{ji}$ | 57.95562 | | |
| | $k_{ij}$ | −0.15107 | 0.188 | 0.0033 |
| overall | $A_{ij}$ | −581.08 | | |
| | $A_{ji}$ | 93.63736 | | |
| | HFC-134a + DME | | | |
| | $k_{ij}$ | −0.30141 | 0.266 | 0.0098 |
| 313.15 | $A_{ij}$ | 165.4623 | | |
| | $A_{ji}$ | −5.17205 | | |
| | $k_{ij}$ | −0.11128 | 0.176 | 0.0043 |
| 323.15 | $A_{ij}$ | 510.1168 | | |
| | $A_{ji}$ | −343.899 | | |
| | $k_{ij}$ | −0.1585 | 0.137 | 0.0041 |
| 333.15 | $A_{ij}$ | 343.9054 | | |
| | $A_{ji}$ | −214.227 | | |
| | $k_{ij}$ | −0.18558 | 0.199 | 0.0020 |
| 343.15 | $A_{ij}$ | 228.3719 | | |
| | $A_{ji}$ | −98.3347 | | |
| | $k_{ij}$ | −0.01507 | 0.178 | 0.0052 |
| overall | $A_{ij}$ | 724.7465 | | |
| | $A_{ji}$ | −487.877 | | |

[a] The unit of $A_{ij}$ and $A_{ji}$ is K. [b] AAD$P$ = $(100/N)\sum_i^N(|P_{i,\mathrm{cal}} - P_{i,\mathrm{exp}}|/P_{i,\mathrm{exp}})$. [c] AAD$y$ = $(1/N)\sum_i^N|y_{i,\mathrm{cal}} - y_{i,\mathrm{exp}}|$.

**Table 5. Calculated Azeotropic Compositions and Pressures for the HFC-134a + DME System**

| $T$/K | $x_1$ | $P$/bar | $T$/K | $x_1$ | $P$/bar |
|---|---|---|---|---|---|
| 313.15 | 0.2277 | 8.69 | 333.15 | 0.1645 | 14.41 |
| 323.15 | 0.2022 | 11.29 | 343.15 | 0.1139 | 18.13 |

The Wong−Sandler mixing rule is represented as follows:

$$b_\mathrm{m} = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^\mathrm{E}}{CRT}} \tag{6}$$

$$a_\mathrm{m} = b_\mathrm{m}\left(\sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^\mathrm{E}}{C}\right) \tag{7}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)}{2}(1 - k_{ij}) \tag{8}$$

where $C = \ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR EOS. Because the excess Helmholtz free energy of mixing at infinite pressure is assumed equal to the excess Gibbs free energy ($G^\mathrm{E}$) at low pressure, the $G^\mathrm{E}$ model is used in place of $A_\infty^\mathrm{E}$. We used the NRTL model[8] as a $G^\mathrm{E}$ model in this study:

$$\frac{G^\mathrm{E}}{RT} = \sum_i x_i \frac{\sum_i x_i \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} \tag{9}$$

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

$$\tau_{ij} = A_{ij}/T \tag{11}$$

where $\tau_{ij}$ and $\tau_{ji}$ are the interaction parameters and $\alpha_{ij}$ is the non-randomness parameter. We fixed the non-randomness parameter $\alpha_{ij}$ to 0.3 in this study. The Marquardt algorithm was used to minimize the following objective function:

$$\mathrm{OF} = \sum_i^N \left|\frac{P_\mathrm{exp} - P_\mathrm{cal}}{P_\mathrm{exp}}\right| \tag{12}$$

where $N$ is the number of experimental data points and $P_\mathrm{exp}$ and $P_\mathrm{cal}$ are the experimental and the calculated pressures, respectively.

As shown in Figures 3 and 4, the calculated results give a good agreement with the experimental data at each temperature. The overall deviation values of pressure and vapor composition were 0.188 % and 0.0033 for the HFC-32 + DME system and 0.178 % and 0.0052 for the HFC-134a + DME system, respectively. Figures 5 and 6 show the deviations of $P$ and $y$ of each system between the measured data and the calculated values. Binary parameters and the average absolute deviations of $P$ and $y$ are given in Table 4. In the HFC-134a + DME system, azeotropic behaviors were found, and the calculated azeotropic compositions and pressures are listed in Table 5.

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