*J. Chem. Eng. Data* **1996,** *41,* 443−445 **443**

# Vapor−Liquid Equilibria for the Systems Difluoromethane + Chlorodifluoromethane, Difluoromethane + Dichlorodifluoromethane, and Difluoromethane + Chloromethane at 10.0 °C

**Yun Whan Kang* and Kun Yong Chung**

CFC Alternatives Technology Center, KIST, P.O. Box 131, Cheongryang, Seoul, Korea

Isothermal vapor−liquid equilibria for the three binary systems (difluoromethane + chlorodifluoromethane, difluoromethane + dichlorodifluoromethane, and difluoromethane + chloromethane) have been measured at 10.0 °C. The experimental data for the binary systems are correlated with the Wilson equation and the relevant parameters are presented. The difluoromethane + dichlorodifluoromethane system forms a minimum boiling azeotrope, but the others do not.

## Introduction

Difluoromethane (hereinafter referred to as HFC-32), which is presently under consideration as a compound in refrigerant mixtures, is normally manufactured by the fluorination of dichloromethane with hydrogen fluoride. A small amount of chlorodifluoromethane (hereinafter referred to as HCFC-22), dichlorodifluoromethane (hereinafter referred to as CFC-12), and chloromethane (hereinafter referred to as HCC-40), which have higher normal boiling points than HFC-32, are produced by side reactions. The normal boiling points of the pure components HFC-32, HCFC-22, CFC-12, and HCC-40 are (−51.65, −40.81, −29.79, and −24.04) °C, respectively. These byproducts may be impurities in the product and may affect the economics of the HFC-32 preparation process. If a trace amount of the byproduct is not removed from the process, it may build up to very large levels in a recycle loop. To determine the most efficient separation system and to design separation equipment, knowledge of the vapor−liquid equilibria for the binary systems composed of HFC-32 and these byproducts is essential. However, experimental data have not yet been reported in the literature. In this study, the isothermal vapor−liquid equilibria for the three binary systems HFC-32 + HCFC-22, HFC-32 + CFC-12, and HFC-32 + HCC-40 at 10.0 °C were measured and correlated with the Wilson equation.

## Experimental Section

***Chemicals.*** HFC-32 which is prepared in our pilot plant was used. HCFC-22 and CFC-12 (Ulsan Chemical Co., Korea) and HCC-40 (Samsung Fine Chem., Co.) were of guaranteed reagent grade and were used without any further purification. A chromatographic analysis on the reagents showed major peak areas of more than 99.8%.

***Apparatus and Procedure.*** The static equilibrium apparatus and the procedures used for this work are described by Kang and Lee (1996). The equilibrium temperature was measured with a T-type thermocouple converter (Yokogawa Electric Corp., Model STED-210-TT*B) having an accuracy of ±0.1 °C. The equilibrium pressure was determined by a gauge pressure transmitter (Yokogawa Electric Corp., Model UNE43-SBS3*B) and a barometer having an accuracy of ±0.5 and ±0.05 kPa, respectively.

**Table 1. Vapor−Liquid Equilibria for HFC-32 (1) + HCFC-22 (2) at 10.0 °C**

| $P$/MPa | $x_1$ | $y_1$ |
|---|---|---|
| 0.6772 | 0.0000 | 0.0000 |
| 0.7326 | 0.1135 | 0.1683 |
| 0.7774 | 0.2077 | 0.2916 |
| 0.8195 | 0.2990 | 0.3991 |
| 0.8666 | 0.4062 | 0.5108 |
| 0.9080 | 0.5025 | 0.6040 |
| 0.9496 | 0.6016 | 0.6915 |
| 0.9901 | 0.7025 | 0.7719 |
| 0.9042 | 0.5041 | 0.6049 |
| 0.9894 | 0.7022 | 0.7868 |
| 1.0263 | 0.7999 | 0.8510 |
| 1.0645 | 0.9012 | 0.9275 |
| 1.1035 | 1.0000 | 1.0000 |

**Table 2. Vapor−Liquid Equilibria for HFC-32 (1) + CFC-12 (2) at 10.0 °C**

| $P$/MPa | $x_1$ | $y_1$ |
|---|---|---|
| 0.4204 | 0.0000 | 0.0000 |
| 0.6130 | 0.0805 | 0.3263 |
| 0.7826 | 0.1802 | 0.5023 |
| 0.8976 | 0.2828 | 0.5909 |
| 0.9825 | 0.3884 | 0.6535 |
| 1.0391 | 0.4963 | 0.6995 |
| 1.0813 | 0.6004 | 0.7389 |
| 1.1123 | 0.7017 | 0.7784 |
| 1.1233 | 0.7792 | 0.8144 |
| 1.1362 | 0.8583 | 0.8625 |
| 1.1335 | 0.8937 | 0.8906 |
| 1.1311 | 0.9155 | 0.9069 |
| 1.1273 | 0.9368 | 0.9259 |
| 1.1195 | 0.9577 | 0.9468 |
| 1.1161 | 0.9718 | 0.9630 |
| 1.1035 | 1.0000 | 1.0000 |

The compositions of the vapor phase were measured by a GowMac gas chromatograph provided with a thermal conductivity detector. The total mass of the vapor phase samples used for three chromatographic analyses to obtain one VLE value was approximately 0.3 g. The mass of each sample was calculated with the estimated vapor density at the pressure of the sampling cylinder. A 6 m long with 3.2 mm diameter Porapak Q column was operated at 160 °C, with the detector at 200 °C and the injector at 200 °C. The peak area percents were converted to the mass percents using the weight factors determined by the analysis of mixtures of known compositions. The compositions of the liquid phase were calculated by the correction

0021-9568/96/1741-0443$12.00/0 © 1996 American Chemical Society

**Table 3. Vapor−Liquid Equilibria for HFC-32 (1) + HCC-40 (2) at 10.0 °C**

| $P$/MPa | $x_1$ | $y_1$ |
|---|---|---|
| 0.3619 | 0.0000 | 0.0000 |
| 0.5046 | 0.0976 | 0.3243 |
| 0.6048 | 0.1909 | 0.4811 |
| 0.7035 | 0.3004 | 0.5968 |
| 0.7765 | 0.3985 | 0.6694 |
| 0.8437 | 0.4998 | 0.7313 |
| 0.9014 | 0.5997 | 0.7845 |
| 0.9556 | 0.6999 | 0.8344 |
| 0.8409 | 0.5015 | 0.7307 |
| 0.9547 | 0.7002 | 0.8341 |
| 1.0076 | 0.8015 | 0.8872 |
| 1.0548 | 0.9005 | 0.9398 |
| 1.1035 | 1.0000 | 1.0000 |

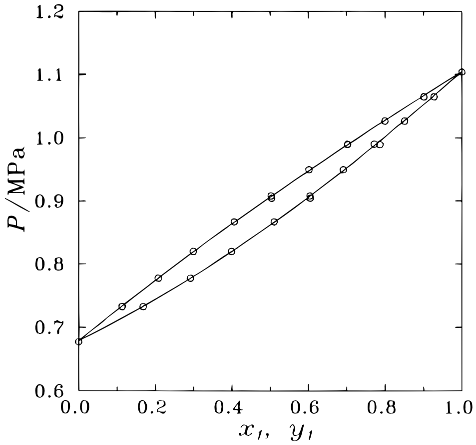

**Figure 1.** Equilibrium curve for HFC-32 (1) + HCFC-22 (2) at 10.0 °C: (○) experimental; (—) Wilson equation.

of the mass existing in the vapor phase. The densities of both phases were estimated by using the cubic equation of state proposed by Peng and Robinson (1976). The standard deviations of the vapor and liquid phase compositions were ±0.003 and ±0.001 mole fraction, respectively.

## Results and Discussion

The experimental vapor−liquid equilibrium data at 10.0 °C for the three binary HFC-32 + HCFC-22, HFC-32 + CFC-12, and HFC-32 + HCC-40 systems are shown in Tables 1−3 and in Figures 1−3. HFC-32 + CFC-12 forms a minimum boiling azeotrope at the experimental temperature, but the others do not. The equation of vapor−liquid equilibrium for any component $i$ is

$$y_i\phi_i P = x_i\gamma_i\phi_i^{s}P_i^{s}\exp((P - P_i^{s})v_i^{L}/RT) \tag{1}$$

where $y_i$ is the vapor-phase mole fraction, $\phi_i$ is the fugacity coefficient, $P$ is the pressure, $x_i$ is the liquid-phase mole fraction, $\gamma_i$ is the activity coefficient, $v_i^{L}$ is the saturated-liquid molar volume, $T$ is the temperature, and the superscript s indicates the saturation state. The fugacity coefficient $\phi_i$ was calculated by the PR EOS not using a binary parameter. The vapor pressures of the pure components were calculated from an equation of the form

$$\ln(P_i^{s}/\mathrm{Pa}) = C_1 + C_2/(T/K) + C_3(T/\mathrm{K}) + C_4\ln(T/\mathrm{K}) \tag{2}$$

The liquid molar volume $v^{L}$ at a given temperature was calculated from the modified Rackett equation (Spencer and Danner, 1972):

$$v^{L} = (RT_c/P_c)Z_{RA}^{1+(1-T_r)^{2/7}} \tag{3}$$

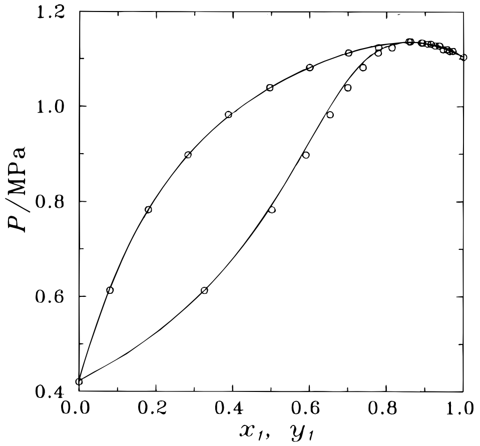

**Figure 2.** Equilibrium curve for HFC-32 (1) + CFC-12 (2) at 10.0 °C: (○) experimental; (—) Wilson equation.

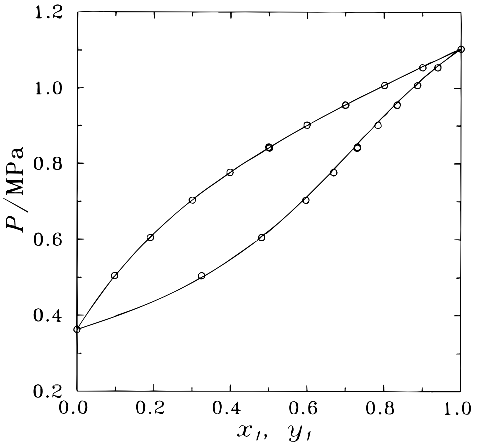

**Figure 3.** Equilibrium curve for HFC-32 (1) + HCC-40 (2) at 10.0 °C: (○) experimental; (—) Wilson equation.

The physical properties from Sato et al. (1994) and the recalculated constants $C_1$−$C_4$ of the pure components in the above equations from Reid et al. (1988) are presented in Table 4. The activity coefficients in the liquid phase are correlated with the Wilson (1964) equation:

$$\ln\gamma_i = 1 - \ln\left(\sum_j \Lambda_{ij}x_j\right) - \sum_k \frac{\Lambda_{ki}x_k}{\sum_j \Lambda_{kj}x_j} \tag{4}$$

where

$$\Lambda_{ij} = \frac{v_j^{L}}{v_i^{L}}\exp\left(-\frac{\Delta\lambda_{ij}}{RT}\right) \tag{5}$$

The binary interaction parameters of the Wilson equation, $\Delta\lambda_{ij}$, were evaluated by a nonlinear regression method based on the maximum-likelihood principle (Anderson et al., 1978), as implemented in the computer programs published by Prausnitz et al. (1980), with the following objective function ($Z$):

$$Z = \left\{\sum_j \frac{(P^j_{\mathrm{exptl}} - P^j_{\mathrm{calcd}})^2}{{\sigma_P}^2} + \frac{(T^j_{\mathrm{exptl}} - T^j_{\mathrm{calcd}})^2}{{\sigma_T}^2} + \frac{(x^j_{1,\mathrm{exptl}} - x^j_{1,\mathrm{calcd}})^2}{{\sigma_{x_1}}^2} + \frac{(y^j_{1,\mathrm{exptl}} - y^j_{1,\mathrm{calcd}})^2}{{\sigma_{y_1}}^2}\right\} \tag{6}$$

**Table 4. Physical Properties and Constants for the Vapor Pressure Correlation of the Pure Components**

| component | $T_c$/K | $P_c$/MPa | $\omega$ | $Z_{RA}$ | $C_1$ | $C_2$ | $100C_3$ | $C_4$ |
|---|---|---|---|---|---|---|---|---|
| HFC-32 | 351.26 | 5.777 | 0.277 | 0.244 | 89.742 | −4124.5 | 2.0285 | −11.868 |
| HCFC-22 | 369.30 | 4.970 | 0.221 | 0.267 | 97.559 | −4447.2 | 2.1188 | −13.182 |
| CFC-12 | 384.92 | 4.129 | 0.179 | 0.280 | 82.640 | −4127.3 | 1.6346 | −10.581 |
| HCC-40 | 416.27 | 6.700 | 0.153 | 0.270 | 95.401 | −4620.9 | 1.9537 | −12.720 |

**Table 5. Wilson Parameters and Standard Deviations of the Measured Variables for the Binary Systems at 10.0 °C**

| | | | standard deviations | | | |
|---|---|---|---|---|---|---|
| system comp 1 + comp 2 | $\Delta\lambda_{12}$/ kJ·mol$^{-1}$ | $\Delta\lambda_{21}$/ kJ·mol$^{-1}$ | $P$/ kPa | $T$/ K | $x_1$/ % | $y_1$/ % |
| HFC-32 + HCFC-22 | 0.706 | −0.534 | 0.0 | 0.04 | 0.02 | 0.15 |
| HFC-32 + CFC-12 | 2.874 | 0.116 | 0.0 | 0.04 | 0.03 | 0.57 |
| HFC-32 + HCC-40 | 1.483 | 0.126 | 0.0 | 0.04 | 0.04 | 0.52 |

where $\sigma$ is the estimated standard deviation of each of the measured variables, i.e. pressure, temperature, and liquid-phase and vapor-phase mole fractions. In data reduction, we chose $\sigma_P = 0.5$ kPa, $\sigma_T = 0.1$ °C, $\sigma_{x_1} = 0.001$, and $\sigma_{y_1} = 0.003$. The binary interaction parameters obtained by data reduction and the standard deviations of the measured variables of the binary systems are presented in Table 5. The experimental and calculated equilibrium data for the three binary systems HFC-32 + HCFC-22, HFC-32 + CFC-12, HFC-32 + HCC-40 at 10.0 °C are shown in Figures 1−3. As shown in these figures and the low standard deviations in Table 5, the calculated results are in good agreement with the experimental values.

## Literature Cited

Anderson, T. F.; Abrams, D. S.; Grens, E. A. Evaluation of Parameters for Nonlinear Thermodynamics Models. *AIChE J.* **1978**, *24*, 20−29.

Kang, Y. W.; Lee, Y. Y. Vapor-Liquid Equilibria for the Systems Composed of 1-Chloro-1,1-difluoroethane, 1,1-Dichloro-1-fluoroethane, and 1,1,1-Trichloroethane at 50.1 °C. *J. Chem. Eng. Data* **1996**, *41*, 303−305.

Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connel, J. P. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1980.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*; McGraw-Hill: New York, 1988.

Sato, H.; Higashi, Y.; Okada, M.; Takaishi, Y.; Kagawa, N.; Fukushima, M. *JAR Thermodynamics Tables, Vol. 1*; Japanese Association of Refrigeration: Tokyo, 1994.

Spencer, C. F.; Danner, R. P. Improved Equation for Prediction of Saturated Liquid Density. *J. Chem. Eng. Data* **1972**, *17*, 236−241.

Wilson, G. M. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

Received for review October 23, 1995. Accepted January 16, 1996. This work was supported by MOST of the Republic of Korea (Project 2N1370R).[⊗]

JE9502657

---

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1996.