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Vapor–Liquid Equilibria for the Binary Difluoromethane (R-32) + Propane (R-290) Mixture

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The vapor–liquid equilibrium of the mixture composed of difluoromethane (R-32) and propane (R-290) was studied in the temperature range between 273.15 and 313.15 K. The experimental uncertainties of temperature, pressure, and composition measurements were estimated to be within ±10 mK, ±3 kPa, and ±0.4 mol%, respectively. Comparisons between the present data and available experimental data were made using the Helmholtz free energy mixture model (HMM) adopted in the thermophysical properties program package, REFPROP 6.0, as a baseline. In addition, the existence of an azeotrope and the determination of new adjustable parameters for HMM for the R-32 + R-290 mixture are discussed.

KEY WORDS: alternative refrigerants; azeotropic mixture; Helmholtz free energy mixture model; R-32 + R-290 mixture; REFPROP 6.0; vapor–liquid equilibria.

1. INTRODUCTION

Because of their low ozone-depleting potentials and low global warming potentials, refrigerant mixtures including hydrocarbons and HFC refrigerants are expected to be considered as alternative refrigerants for chlorodifluoromethane (R-22). R-22 is currently a working fluid in refrigerators and heat pump systems. However, reliable information on the thermophysical properties of these mixtures is very scarce. The present author has measured the vapor–liquid equilibrium for several kinds of refrigerant mixtures, that is, difluoromethane (R-32) + 1,1,1-tetrafluoroethane (R-134a)

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[1], difluoromethane + pentafluoroethane (R-125) [2], and propane (R-290) + isobutane (R-600a) [3]. In this paper, the vapor–liquid equilibrium (VLE) of the mixture composed of difluoromethane and propane was studied in the temperature range between 273.15 and 313.15 K. The only VLE data available for comparison are those of Holcomb et al. [4]. The present data were compared to the data of Holcomb et al. as well as the Helmholtz free energy mixture model (HMM) [5] adopted in the thermophysical properties program package, REFPROP 6.0 [6]. In addition, the existence of an azeotrope as well as the possibility of liquid–liquid equilibrium are discussed.

2. EXPERIMENTAL APPARATUS

The experimental apparatus at Iwaki Meisei University for measuring the vapor–liquid equilibrium has been described in detail [1, 2]. Temperatures were measured with a 100-Ω platinum resistance thermometer immersed in the thermostated bath. This thermometer was located in the vicinity of the equilibrium cell and calibrated against ITS-90 using a 25-Ω standard platinum resistance thermometer. The uncertainty of temperature measurements is estimated to be within ±10 mK. The pressure of the sample was measured with a diaphragm semiconductor strain-gauge pressure transducer. This pressure transducer was installed in the cell and can measure the fluid pressure directly. The pressure transducer was calibrated against the quartz crystal pressure transducer after every series of experiments. The uncertainty of the pressure measurements is estimated to be within ±3 kPa. Compositions of the vapor phase (dew-point composition) and the liquid phase (bubble-point composition) for the mixtures were determined with a gas chromatograph equipped with a thermal conductivity detector. A Porapak-Q[3] column was used. The gas chromatograph was 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 ±0.4 mol%.

The sample of pure R-32 was furnished by Asahi Glass Co. Ltd.[3] The stated sample purity was 99.98 mass% R-32. The sample of R-32 was used without further purification. The pure R-290 was furnished by Sumitomo Seika Co.[3] It seems to be difficult to remove the impurities from propane;

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[3] In order to describe materials and experimental procedures adequately, it is occasionally necessary to identify commercial products by manufacturer's name or label. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the particular material or equipment is necessarily the best available for the purpose.

the sample used was not less than 99 mass% R-290. The sample of R-290 was used after degassing in liquid nitrogen several times.

3. RESULTS

The experimental results for the vapor–liquid equilibrium (VLE) for R-32 + R-290 are given in Table I. Measurements were made along five isotherms, i.e., 273.15, 283.15, 293.15, 303.15, and 313.15 K. The distribution of VLE results for the R-32 + R-290 mixture is shown in Fig. 1 on a pressure–composition diagram. In this figure, the solid lines are the predicted values calculated from REFPROP 6.0 along the same five isotherms. For this mixture, the program package REFPROP 6.0 shows an azeotrope near 65 to 70 mol% R-32. The present data are composed of four series of nearly constant composition data, that is, 20 mol% R-32 in liquid, 40 mol% R-32 in liquid, 80 mol% R-32 in liquid, and 90 mol% R-32 in liquid. The data at 20 mol% R-32 in liquid and 40 mol% R-32 in liquid have liquid compositions that are lower than their equilibrium vapor compositions, whereas the data at 80 mol% R-32 in liquid and 90 mol% R-32

Table I. Vapor–Liquid Equilibrium Data of the R-32(A) + R-290(B) Mixture

T (K)	P (kPa)	x_A[a]	y_A[a]
273.15	880.0	0.1668	0.4914
273.15	1019.0	0.3955	0.6062
273.15	1050.1	0.7734	0.7431
273.15	988.0	0.9026	0.7911
283.15	1148.3	0.1713	0.4781
283.15	1340.8	0.3889	0.5974
283.15	1396.1	0.7711	0.7406
283.15	1317.4	0.8983	0.8041
293.15	1495.3	0.1898	0.4716
293.15	1741.0	0.4074	0.5948
293.15	1820.3	0.7699	0.7393
293.15	1726.4	0.8943	0.8135
303.15	1822.2	0.1816	0.4338
303.15	2185.7	0.4014	0.5754
303.15	2328.0	0.7698	0.7392
303.15	2212.4	0.8957	0.8264
313.15	2295.2	0.2306	0.4366
313.15	2739.6	0.4158	0.5681
313.15	2943.0	0.7375	0.7218
313.15	2810.0	0.8856	0.8299

[a] Mole fractions.

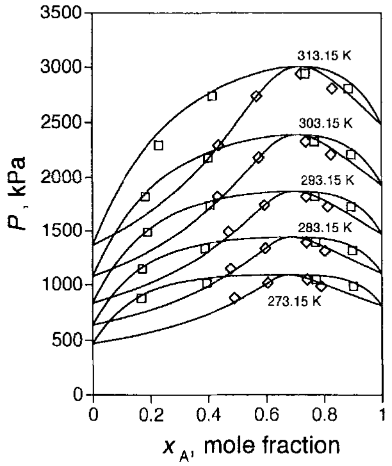

Fig. 1. Experimental VLE data for the R-32(A) + R-290(B) mixture. Solid lines are from REFPROP 6.0 using the original adjustable parameters. (□) Bubble point; (◇) dew point.

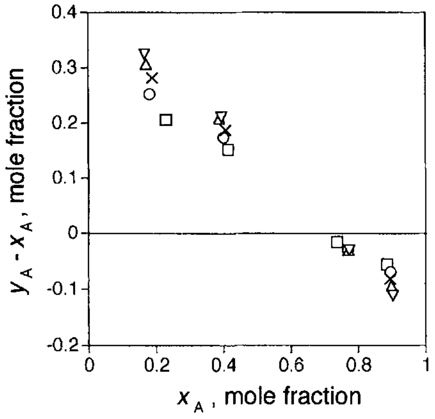

Fig. 2. Plot of the difference between dew-point and bubble-point compositions ($y_A - x_A$) against bubble-point composition x_A for the R-32(A) + R-290 (B) mixture. (▽) 273.15 K; (△) 283.15 K; (×) 293.15 K; (○) 303.15 K; (□) 313.15 K.

in liquid have liquid compositions that are higher than their equilibrium vapor compositions. This result means the azeotrope apparently exists near 70 mol% R-32.

The only other experimental VLE data available for the R-32 + R-290 mixture is the data set of Holcomb et al. [4]. They reported the VLE data for this mixture at temperatures between 280 and 340 K and showed that this mixture has a strong positive pressure azeotrope. For this mixture, they also showed the liquid phase separated into two phases at temperatures below 310 K. Unfortunately, the present VLE cell does not have a window. Therefore, the existence of the liquid–liquid–vapor interface could not be observed directly. However, an azeotrope could be confirmed near 70 mol% R-32.

The plot of the difference between the dew-point composition y_A and the bubble-point composition x_A, that is, $(y_A - x_A)$, versus the bubble-point

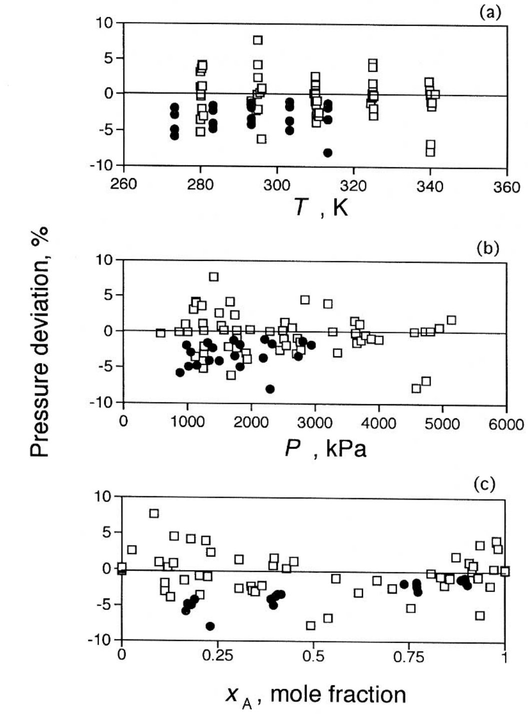

Fig. 3. Bubble-point pressure deviations between the experimental VLE data and the Helmholtz free energy mixture model. (a) Versus temperature; (b) versus pressure; (c) versus composition. (●) Present work; (□) Holcomb et al. [4].

composition x_A is shown in Fig. 2 for the present measurements. An azeotrope near 70 mol% R-32 can also be confirmed from Fig. 2.

4. DISCUSSION

4.1. Bubble-Point Pressures

The bubble-point pressure comparisons among the present VLE data, the data of Holcomb et al. [4], and the calculated results of the Helmholtz free energy mixture model (HMM) [5] are shown in Fig. 3. These deviations are plotted against the temperature, pressure, and composition. With respect to the adjustable parameters for the HMM in this calculation, the values adopted in REFPROP 6.0 [6] are used. Moreover, Fig. 4 shows the bubble-point pressure deviations against composition taking into consideration the temperature dependence. As shown in Fig. 3, the pressure deviations of the present data are within the deviations of the data by Holcomb et al. All of the present data show negative deviations compared to the calculated results of HMM. Both data sets cover a wide composition range approaching the pure components on both ends. Because this mixture has an azeotrope, the pressure deviations near the pure component become larger. This is because the slope of (dP/dx) becomes larger as x approaches either zero or unity. One point on the 295 K isotherm of Holcomb et al. looks slightly high. From Fig. 3, although all of the present

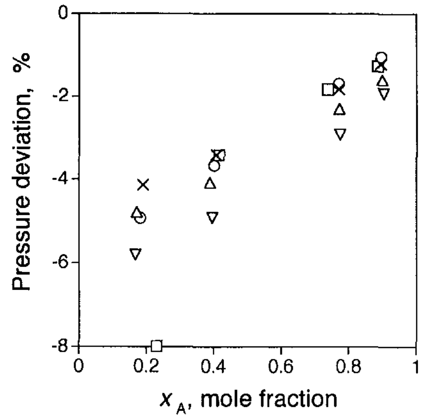

Fig. 4. Bubble-point pressure deviations between the present experimental VLE data and the Helmholtz free energy mixture model. (▽) 273.15 K; (△) 283.15 K; (×) 293.15 K; (○) 303.15 K; (□) 313.15 K.

data as well as the data of Holcomb et al. look evenly scattered when plotted against composition and pressure, it is found that these data deviate systematically from the calculated values of HMM when plotted against temperature. This systematic deviation may occur from inadequate adjustable parameters in the HMM.

4.2. Dew-Point Compositions

The dew-point composition deviation plots for the experimental VLE data compared to the HMM are shown in Fig. 5. The deviations are plotted against temperature, pressure, and bubble-point composition. The present data are in good agreement with those of Holcomb et al. The present data near 75 mol% R-32 for the dew-point composition show a large, positive

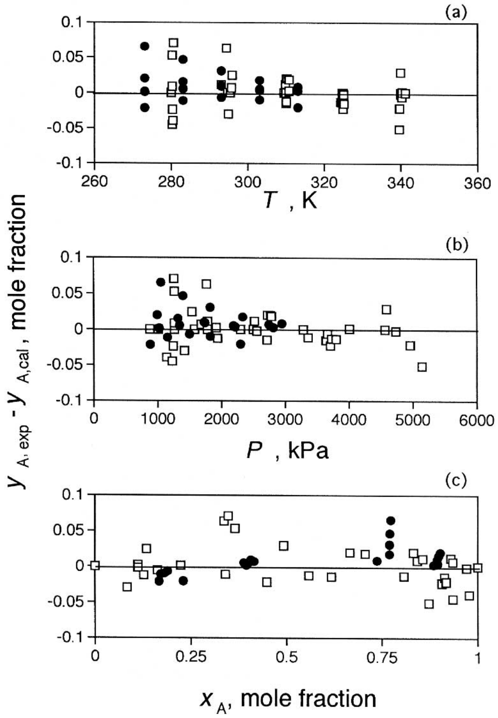

Fig. 5. Dew-point composition deviations between the experimental VLE data and the Helmholtz free energy mixture model. (a) Versus temperature; (b) versus pressure; (c) versus composition. (●) Present work; (□) Holcomb et al. [4].

Table II. Adjustable Parameters in the Helmholtz Free Energy Model for the R-32 + R-290 Mixture

	ζ	ξ	F_{pq}
Present work	−86.928	−0.010706	−0.671190
Original REFPROP 6.0	−87.022	−0.009759	−1.1135260

deviation. These data were near the azeotrope and are more sensitive to temperature and composition uncertainties.

4.3. New Adjustable Parameters for the R-32 + R-290 Mixture for the Helmholtz Free Energy Mixture Model (HMM)

Based upon the present VLE data, new adjustable parameters of the R-32 + R-290 mixture for HMM [5] were determined for the sake of comparison with the data of Holcomb et al. Three adjustable parameters were used in HMM for the R-32 + R-290 mixture: ζ, ξ, and F_{pq}. In Table II, the new parameters are summarized together with those of the original REFPROP 6.0 [6]. The VLE lines on a pressure–composition diagram were recalculated (shown in Fig. 6) by using the new parameters

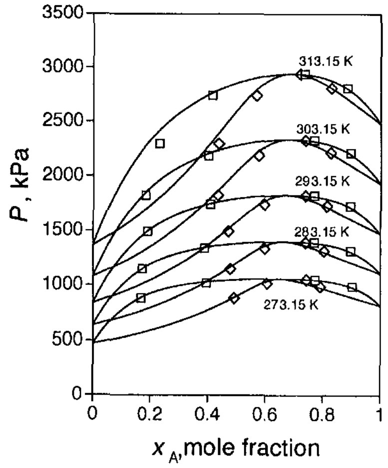

Fig. 6. Experimental VLE data for the R-32(A) + R-290(B) mixture. Solid lines are from the Helmholtz free energy mixture model using the new adjustable parameters in Table II. (□) Bubble point; (◇) dew point.

in the HMM for the R-32 + R-290 mixture, Moreover, the deviation plots in Fig. 3 for the bubble-point pressure deviations and Fig. 4 for the dew-point composition deviations were converted to Figs. 7 and 8, respectively. Using the new parameters in the HMM, REFPROP 6.0 reproduces the present bubble-point pressure data with an absolute average deviation (AAD) of 0.59%, except for one data point of 2295.2 kPa at 313.15 K. Furthermore, with the new parameters, the HMM reproduces all of the present dew-point composition data with an AAD of 0.0117. With respect to the data of Holcomb et al., the calculated results by the HMM with new parameters were improved except for regions near the pure components and near the azeotrope.

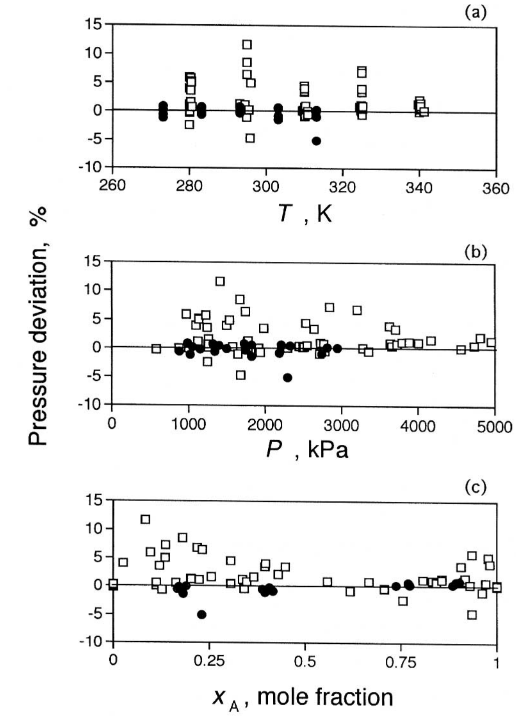

Fig. 7. Bubble-point pressure deviations between the experimental VLE data and the Helmholtz free energy mixture model using new adjustable parameters in Table II. (a) Versus temperature; (b) versus pressure; (c) versus composition. (●) Present work; (□) Holcomb et al. [4].

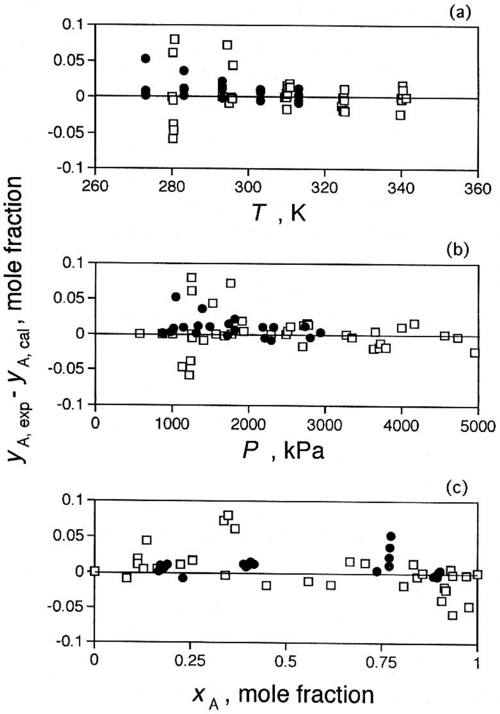

Fig. 8. Dew-point composition deviations between the experimental VLE data and the Helmholtz free energy mixture model using new adjustable parameters in Table II. (a) Versus temperature, (b) versus pressure, (c) versus composition. (●) Present work; (□) Holcomb et al. [4].

4.4. Prediction nf the Azeotropic Composition

As described previously, this mixture shows azeotropic behavior. On the basis of the difference between the dew-point and the bubble-point compositions $(y_A - x_A)$ plotted versus the bubble-point composition x_A, the azeotropic composition for each temperature can be determined analytically. Assuming that the R-32 + R-290 mixture is azeotropic, along an isotherm the differences between the dew-point and the bubble-point compositions might be fitted with a cubic as a function of the bubble-point composition. In this study, the experimental data of $(y_A - x_A)$ in Fig. 2 were fitted with a cubic polynomial equation. The azeotropic compositions were calculated as one of the solutions of these cubic equations. The

Table III. Predicted Azeotropic Composition of the R-32(A) + R-290(B) Mixture Using $(y_A - x_A) = a_1 x_A^3 + a_2 x_A^2 + a_3 x_A + a_4$

T (K)	a_1	a_2	a_3	a_4	Azeotropic composition	AAD
273.15	0.338	−0.681	−0.199	0.375	0.7274	0.0003
283.15	0.734	−1.267	0.077	0.327	0.7193	0.0001
293.15	0.987	−1.638	0.269	0.283	0.7127	0.0002
303.15	1.178	−1.933	0.456	0.226	0.7040	0.0004
313.15	1.519	−2.560	0.876	0.122	0.7038	0.0006

azeotropic compositions of the R-32 + R-290 mixture for each temperature are shown in Table III. Although a check by experiment was not made, these azeotropic compositions were in good agreement with the results on a pressure-composition diagram.

5. CONCLUSION

The vapor-liquid equilibrium for the binary R-32 + R-290 mixture was measured in the temperature range between 273.15 and 313.15 K. It was confirmed that this mixture shows azeotropic behavior at a composition near 0.7 R-32 mole fraction. Although it has been observed that this mixture exhibits liquid–liquid–vapor behavior [4], the author can not verify this behavior based on the experimental data of this study. It is necessary to obtain additional data over a wider temperature range in order to confirm, the existence of liquid–liquid–vapor equilibrium as well as to determine the upper critical solution temperature.

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REFERENCES

1. Y. Higashi, *Int. J. Thermophys.* **16**:1175 (1995).
2. Y. Higashi, *J. Chem. Eng. Data* **42**:1269 (1997).

3. Y. Higashi, M. Funakura, and Y. Yoshida, *Proc. Int. Conf. "CFCs, The Day After,"* Padova, Italy (1994), p. 493.
4. C. D. Holcomb, J. W. Magee, J. L. Scott, S. L. Outcalt, and W. M. Haynes, *NIST Technical Note* 1397 (1997).
5. E. W. Lemmon and R. T. Jacobsen, *Int. J. Thermophys.*, in press.
6. M. O. McLinden, S. A. Klein, E. W. Lemmon, and A. P. Peskin, *NIST Standard Reference Database 23—REFPROP*, Version 6.0 (NIST, Boulder, CO, 1998).