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VAPOR-LIQUID EQUILIBRIUM OF DIFLUOROMETHANE (R-32) + PROPANE (R-290) SYSTEM IN THE TEMPERATURE RANGE OF 293-313 K

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ABSTRACT   Isothermal vapor-liquid equilibrium (VLE) data have been measured for the systems of difluoromethane (HFC-32)+propane (HC-290) system in the temperature range of 293-313 K. An apparatus for the measurement of vapor-liquid equilibrium data was designed as a circulation type apparatus by injecting vapor through liquid pool using a magnetic pump. The experiment was performed to measure temperature, pressure, liquid and vapor compositions of the refrigerant mixture. The experimental results were correlated with the Margules equation with four adjusting parameters, and the absolute average deviation of bubble-point pressure for HFC-32 + HC-290 system from the Margules equation was 0.35%. Also the absolute average deviation for the dew-point composition for HFC-32 + HC-290 system was 0.045 mole fraction for the temperature range investigated. The refrigerant mixture forms an azeotrope near the mole fraction of 0.7 of R-32.

Keywords: HFC-32, HC-290, Vapor-liquid equilibrium, Azeotrope, Margules equation, Composition

1. INTRODUCTION

Because of their low ozone-depleting potentials and low global warming potentials, refrigerant mixtures including hydrocarbons (HC) and hydrofluorocarbon (HFC) refrigerants are considered as alternatives. Many researchers[1-4] have studies the vapor-liquid equilibrium (VLE) for the system of hydrocarbon and HFC mixture systems. However, reliable information on the thermophysical properties of these mixtures is not sufficient. As far as the properties are concerned, VLE data should be obtained to design new systems or to retrofit present systems. In this study, VLE data for the systems of HFC-32+HC-290 in the temperature range of 293-313 K were obtained. The experimental data are correlated with the Margules equation for excess Gibb's free energy (binary mixtures) with four adjusting parameters. The comparison of the test result in this study with the result of Higashi[1] showed that the experimental data were in good agreement with theirs.

2. EXPERIMENTS AND DATA ACQUISITION

2.1 Refrigerants

In this study refrigerants mixtures of HFC-32 and HC-290 are selected as test fluid. HFC-32 with a purity of 99.9% was supplied by Nippon Sanso in Japan and HC-290 with a purity of 99.95% was supplied by Messer Griesheim in Germany.
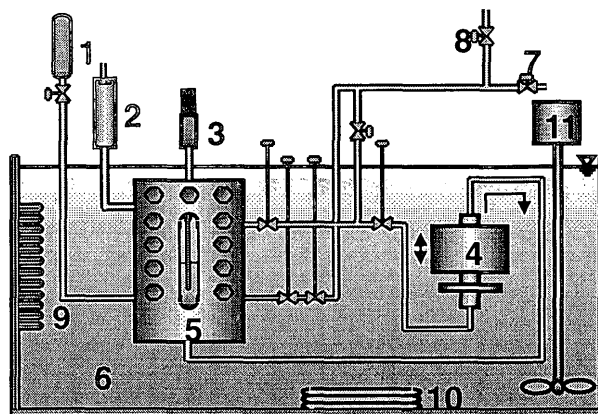
2.2 Apparatus and data acquisition

Fig. 1 Schematic diagram of experimental apparatus; 1. charging cylinder, 2. pressure transducer, 3. resistance thermometer, 4. magnetic pump, 5. equilibrium cell, 6. isothermal bath, 7. sampling port, 8. vacuum pump, 9. evaporator, 10. heater, 11. stirrer.

The schematic diagram of the experimental setup is shown in Fig. 1. This consists mainly of an equilibrium cell, isothermal bath filled with water, temperature control system composed of a platinum resistance thermometer, power controller, heater and refrigerator, and magnetic pump.[5] The equilibrium cell was made of SUS316 with an inner volume of about 150 cm^3 and a height of 120 mm. It was fully immersed in the isothermal bath to keep constant temperature and the temperature control system

Table 1 Vapor-liquid equilibrium data of R32+R290

P (kPa)	Mole fraction of R32	
	Liquid	vapor
T = 293.15 K		
837.5	0	0
1367	0.133	0.401
1515	0.217	0.479
1699	0.329	0.529
1703	0.366	0.555
1758	0.435	0.574
1793	0.496	0.609
1817	0.599	0.651
1817	0.710	0.699
1781	0.830	0.755
1720	0.888	0.810
1475	1	1
T = 303.15 K		
1081	0	0
1694	0.129	0.372
1888	0.204	0.452
2135	0.328	0.523
2149	0.353	0.551
2232	0.411	0.579
2283	0.503	0.617
2324	0.608	0.662
2331	0.719	0.711
2282	0.832	0.774
2182	0.911	0.847
1929	1	1
T = 313.15 K		
1372	0	0
2068	0.126	0.339
2315	0.194	0.423
2644	0.331	0.529
2666	0.347	0.531
2787	0.422	0.574
2864	0.505	0.611
2928	0.614	0.666
2943	0.704	0.709
2886	0.834	0.784
2767	0.912	0.858
2479	1	1

Fig. 2 VLE diagram of R32+R290 system.

keeps the temperature fluctuation of the bath within ±0.01 K. The refrigerant mixture is circulated by a magnetic pump.[6]

After a steady state is reached, a small amount of vapor and liquid were sampled out of the cell. The vapor and liquid samples were analyzed by a gas chromatograph (Hewlett-Packard, 5890 series II plus), which uses helium as a carrier gas with a thermal conductivity detector and a Chromosorb 102 column. For liquid sampling, liquid samples were trapped in a space between two valves and introduced into a pre-evacuated expansion cell. The uncertainty of composition analysis was estimated to be within ±0.005 in mole fraction. Temperatures were measured with a Pt-100 Ω resistance thermometer (Automatic Systems Laboratories, F250), and the uncertainty of temperature measurement was estimated to be within ±0.01 K. The pressure was measured with a pressure transducer (Sensotec, super THE-AP112), and the uncertainty of pressure measurement was estimated to be
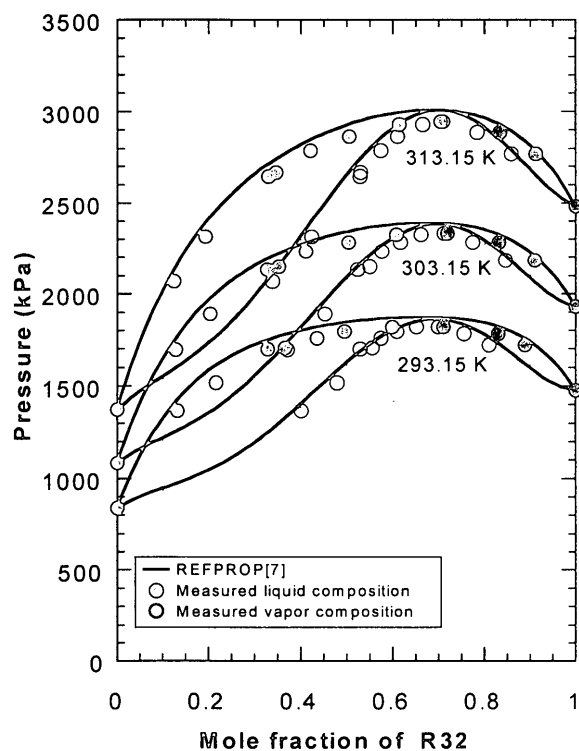
within ±0.1%.

3. RESULTS AND DISCUSSION

3.1 VLE data

Vapor–liquid equilibrium for the mixtures of R32+R290 and the vapor pressures for their pure components were represented in Table 1. When the vapor pressure data of pure R32 and R290 were compared with those given in REFPROP[7], the relative deviations of the experimental results were 0.048% and 0.21%, respectively. Fig. 2 shows the VLE data of R32 + R290 system measured in the temperature range of 293-313 K with respect to mole fraction of R-32. REFPROP[7] generally overpredicts the bubble and dew point pressures for the whole range of composition, which represents the interaction parameters used in the prediction should be slightly changed. Fig. 3 shows the difference between the dew-point composition and the bubble composition versus the bubble-point composition of R-32. It shows gradual variation of y-x values, which means the experiment was performed satisfactorily. The data by Higashi[1] was compared with our experimental data, and it shows a good agreement.

3.2 Data reduction method

In predicting VLE based on experimental data, the concepts of excess Gibb's free energy and the activity coefficient were used for estimating the relations of pressure and vapor-liquid mole fractions. The Margules equation was used for fitting formula. The advantage of this approach lies in the flexibility in selecting the number of
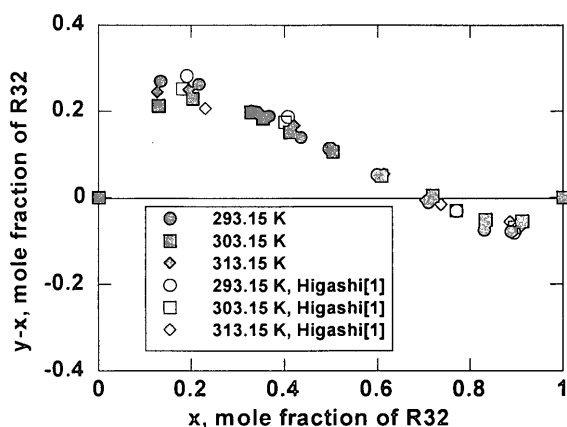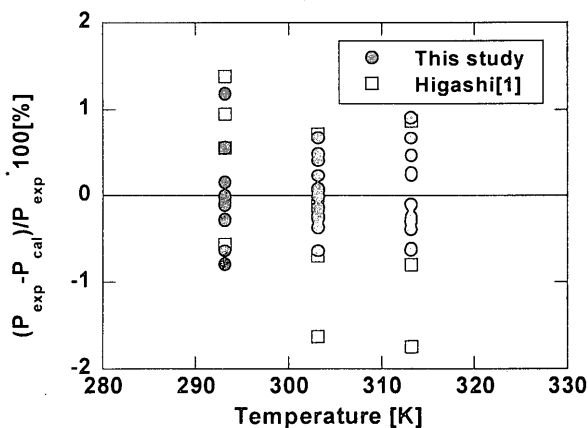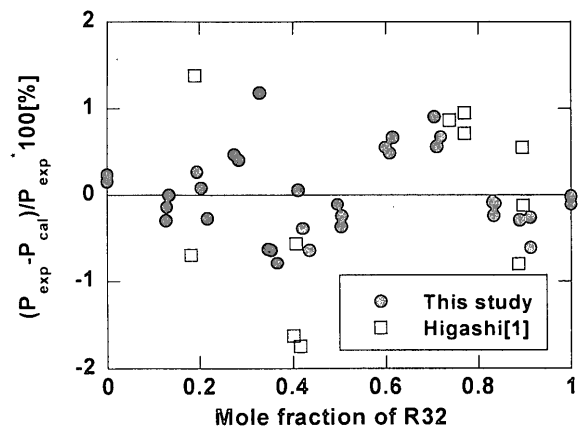
Fig. 3 Plot of the difference between dew-point and bubble-point compositions against bubble-point composition of R32+R290.

Table 2 Adjusting parameters in Margules equation

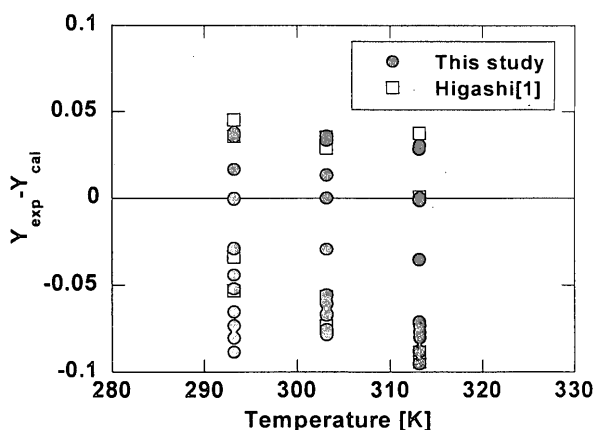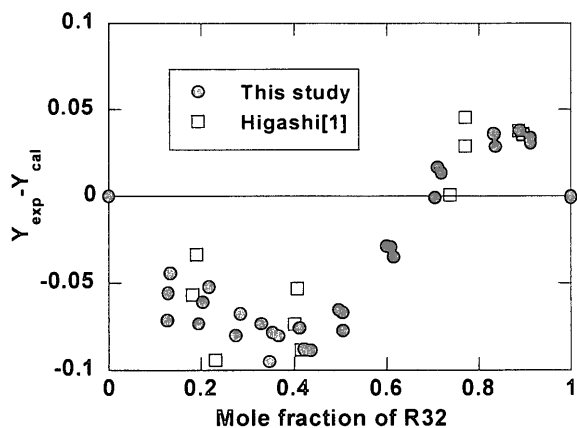| T (K)	A	B	C	D
293.15	1.630	1.853	-1.416	2.047
303.15	1.645	1.646	-1.117	1.688
313.15	1.659	1.476	-0.7667	1.506

(a) as a function of temperature

(b) as a function of mole fraction of R32

Fig. 4 Bubble-point pressure deviation of R32+R290 system from Margules equation.

(a) as a function of temperature

(b) as a function of mole fraction of R32

Fig. 5 Dew-point composition deviation of R32+R290 system from Margules equation.

adjusting parameters in the Margules equation. In this study, four parameters were used to fit experimental data using Margules equation as

$$\frac{G^{E}}{RTx_{1}x_{2}} = Ax_{1} + Bx_{2} - (Cx_{1} + Dx_{2})x_{1}x_{2} \quad (1)$$

shown in Eq. (1). A, B, C and D are adjusting parameters in the Margules equation, and they should be determined to minimize the following objective function in Eq. (2). The values of adjusting parameters are shown in Table 2.

$$obf = \sum_{i=1}^{N}[\frac{P_{cal}}{P_{exp}} - 1]^{2} \quad (2)$$

Fig. 4 shows the relative bubble point pressure deviation of R32+R290 system from Margules equation as a function of temperature and mole fraction of R32, respectively. The absolute average deviation is 0.35% for bubble point pressure deviation in the temperature range of this study. Also, Fig. 5 shows the deviation of measured data from the Margules equation for dew-point composition for R32+R290 system as a function of temperature and

mole fraction of R32. The absolute average deviation was 0.045 mole fraction.

Azeotropic compositions can be determined from the fitting using Margules equation. For the temperature of 293.15 K, the azeotropic composition is about 0.685. And for 303.15 and 313.15 K, it is about 0.700 and 0.718.

4. CONCLUSION

In this study, the circulation type VLE cell was made and vapor-liquid equilibrium data for R32+R290 including the vapor pressure data for pure components were obtained in the temperature range of 292-313 K. The experimental results were fitted by Margules equation with four adjustable parameters. Bubble point pressure deviation and dew point composition deviation of R32+R290 system from Margules equation were 0.35% and 0.045 mole fraction, respectively. Azeotropes are formed near the mole fraction of 0.7 of R-32 in the refrigerant mixture.

ACKNOWLEDGMENTS

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