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Vapor−Liquid Equilibrium Measurements for the Ethane + Hexafluoroethane System over a Temperature Range from (199.64 to 242.93) K

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Vapor−liquid equilibrium (VLE) data for the ethane (R170) + hexafluoroethane (R116) system were measured at temperatures of (199.64, 213.06, 228.28, and 242.93) K. The measurements were carried out with an apparatus based on the recirculation method. The measured VLE data for this binary system of R170 + R116 show azeotropic behaviors at certain compositions. The experimental results were correlated with the Peng−Robinson equation of state using the Panagiotopoulos−Reid mixing rule.

Introduction

In recent years, great achievements have been made in the development of mixed-gases Joule−Thomson refrigerators (MJTRs).[1−5] With the successful application of oil-lubricated commercial compressor to MJTRs, this type of MJTR becomes more competitive with other types of refrigerators. Obviously, one of the most important and difficult tasks in the design of such refrigerators is the precise prediction of the properties of mixtures, including the VLE behavior. Moreover, in the traditional cascade refrigeration system for −80 °C refrigeration applications, refrigerants used in the lower temperature stage are R13, R503, and R508B. The former two have an ozone depletion effect. The later one has a large global warming potential (GWP) value because of its HFC and FC components. So, to find a new refrigerant for use in two-stage cascade refrigeration system is significant in refrigeration applications.

No VLE data are available in any literature for the R170 + R116 system. Therefore, the VLE measurements for the R170 + R116 system are important both for practical refrigeration applications and for contributing valuable data to theoretical model development. In this work, the VLE data were measured for the R170 + R116 system over a temperature range from (199.64 to 242.93) K.

Experimental Section

Chemicals. R170 (ethane, C_2H_6) was supplied by Airgas with a declared mole fraction purity of >99.95 %, and R116 (hexafluoroethane, C_2F_6) was supplied by Huayu Special Gases with a declared mole fraction purity of >99.99 %. All samples were used without further purification.

Apparatus. The experimental apparatus used in these VLE data measurements is similar to that described by Dorau et al.[6] and is shown in Figure 1. The equilibrium cell made of stainless steel with a volume of 300 cm^3 was immersed in a liquid bath. To accelerate thermodynamic equilibrium process, the experimental apparatus was designed according to the recirculation method. That is, the vapor phase in the equilibrium cell was driven by a self-made electromagnetic recirculation pump and passed sequentially through a counter-current heat exchanger, recirculation pump, and precooling coils. Finally, the returning vapor phase was distributed by a nozzle at the bottom of the cell to mix evenly with the liquid phase. To ensure thermodynamic equilibrium of the cell, the flow rate of the vapor phase was regulated ranging from (3 to 10) mL·s^{-1}. Vapor composition was sampled through a capillary in the recirculation loop. Three liquid-sampling capillaries were located at different locations and elevations in the cell, which ensures a homogeneous liquid sampling.

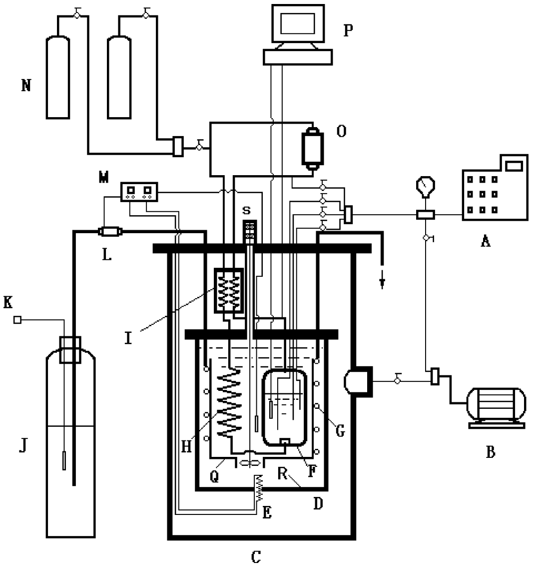

Figure 1. Schematic diagram of the experimental apparatus: A, gas chromatograph; B, vacuum pump; C, vacuum vessel; D, cryostat; E, electric heater; F, equilibrium cell; G, liquid nitrogen cooling coils; H, precooling coils; I, heat exchanger; J, liquid nitrogen dewar; K, liquid nitrogen pressure controller; L, electromagnetic valve; M, temperature controller; N, feed cylinder; O, electromagnetic recirculation pump; P, temperature and pressure indicator; Q, inner tank; R, outer tank; S, stirrer.

The cryostat was filled with liquid R12 (dichlorodifluoromethane) as the liquid bath. A stirrer fixed at the bottom

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Table 1. Experimental Data for the R170 (1) + R116 (2) System

T = 199.64 K			T = 213.06 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.1287	0.0000	0.0000	0.2434	0.0000	0.0000
0.2056	0.1633	0.4167	0.3727	0.1827	0.4198
0.2392	0.2636	0.5410	0.4270	0.3257	0.5321
0.2613	0.4662	0.6311	0.4581	0.4822	0.6140
0.2655	0.5732	0.6595	0.4665	0.6071	0.6587
0.2667	0.6444	0.6791	0.4691	0.6499	0.6724
0.2671	0.6875	0.6906	0.4682	0.6960	0.6878
0.2664	0.7354	0.7051	0.4664	0.7582	0.7195

T = 228.28 K			T = 242.93 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.4531	0.0000	0.0000	0.7651	0.0000	0.0000
0.6411	0.1782	0.3661	1.0154	0.1731	0.3181
0.7654	0.3971	0.5462	1.1367	0.2805	0.4314
0.8006	0.5540	0.6245	1.2037	0.3820	0.5103
0.8088	0.6471	0.6608	1.2394	0.4567	0.5564
0.8077	0.7098	0.6881	1.2790	0.6170	0.6418
0.8037	0.7569	0.7141	1.2806	0.6408	0.6540
0.7967	0.8040	0.7421	1.2801	0.6958	0.6818
			1.2742	0.7412	0.7076
			1.2604	0.7977	0.7439

of the liquid bath tank was used to drive the liquid to ensure an even temperature distribution in the tank. The liquid bath was cooled by liquid nitrogen coils and heated with an electric heater, and its temperature was measured by a calibrated Pt100 resistance thermometer as an input signal for the temperature controller. The temperature of the cryostat was controlled by a Shimaden SR 253 digital controller by heating and cooling the liquid bath. The temperature fluctuation in the cryostat is ± 0.01 K.

A Pt25 standard resistance thermometer was inserted into the liquid phase in the cell. The Pt25 thermometer was calibrated by the Cryogenic Metrology Station of the Chinese Academy of Sciences with an uncertainty of ± 0.01 K. The pressure was measured by a Druck PMP 4010 pressure transducer with a full scale of 6 MPa and an uncertainty of ± 0.002 MPa. The compositions of vapor and liquid phase were analyzed by a Beifen SP 3400 gas chromatograph with an uncertainty of ± 0.001 in mole fraction.

Results

The $P-T-x-y$ data for the R170 + R116 system at four isotherms from (199.64 to 242.93) K are presented in Table 1. The azeotropic composition changes with the temperature. Generally, as the temperature increases, a pressure maximum (or positive) azeotrope in a binary system moves toward the more volatile component.[7] However, the azeotropic compositions of the R170 + R116 system move toward the less volatile component with an increase of temperature.

Correlations and Discussion

In this work, the experimental data were correlated with the Peng–Robinson (PR)[8] equation of state using the mixing rule of Panagiotopoulos–Reid.[9] The PR equation has the form:

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

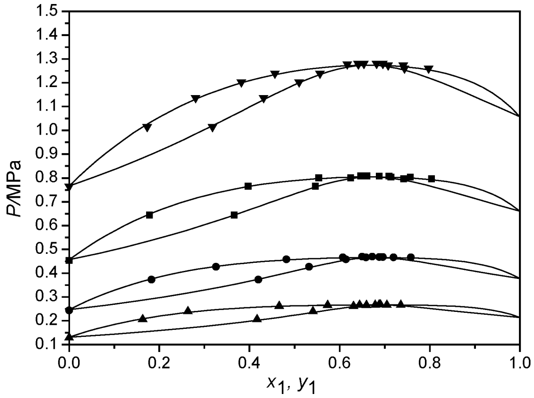

Figure 2. Vapor–liquid equilibrium for the R170 (1) + R116 (2) system at different temperatures: ▲, 199.64 K; ●, 213.06 K; ■, 228.28 K; ▼, 242.93 K; —, calculated with the PR equation and the Panagiotopoulos–Reid mixing rule.

Table 2. Interaction Parameters of the Panagiotopoulos–Reid Mixing Rule Gained for the PR Equation

T/K	k_{12}	k_{21}
199.64	0.1273	0.1295
213.06	0.1312	0.1304
228.28	0.1336	0.1303
242.43	0.1344	0.1293

with

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

$$b = 0.077796\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T) = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{\,0.5})]^2 \tag{4}$$

$$T_r = \frac{T}{T_c} \tag{5}$$

where T_c and P_c are the critical temperature and pressure, and ω is the acentric factor.

The Panagiotopoulos–Reid mixing rule is added to the original van der Waals mixing rule, which can be expressed as follows:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i x_i b_i \tag{7}$$

$$a_{ij} = (a_i a_j)^{1/2}[(1 - k_{ij}) + (k_{ij} - k_{ji})x_i] \tag{8}$$

where k_{ij} and k_{ji} are interaction parameters. The values of k_{ij} and k_{ji} regressed with the experimental data are given in Table 2. The correlated results from the PR equation with the Panagiotopoulos–Reid mixing rule are illustrated in Figure 2. The comparisons between the calculated azeotropic compositions and pressures for the R170 + R116 system with the present experimental values are shown

Table 3. Azeotropic Compositions and Pressures for the R170 (1) + R116 (2) System

T/K	$x_{1,\text{cal}}$	$x_{1,\text{expt}}$	P_{cal}/MPa	P_{expt}/MPa
199.64	0.6882	0.6922	0.2665	0.2667
213.06	0.6793	0.6837	0.4655	0.4691
228.28	0.6716	0.6766	0.8042	0.8088
242.93	0.6655	0.6675	1.2738	1.2806

in Table 3. The experimental azerotropic compositions were derived from interpolation of the two nearest values.

Conclusions

An apparatus based on the recirculation method is presented in this work. The VLE data for the R170 + R116 system were measured at four different temperatures. Azeotropic VLE behavior was observed. This binary system shows a quite good potential used as a new azeotropic refrigerant for cascade refrigeration applications at their azeotropic compositions. The model of the PR equation with the Panagiotopoulos−Reid mixing rule was used to correlate the experimental data. The interaction parameters for this model were regressed from the data. The predicted results using the PR equation of state with the Panagiotopoulos−Reid mixing rule show a good agreement with the experimental data.

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