Vapor−Liquid Equilibrium Measurements for the Nitrogen + Tetrafluoromethane System over a Temperature Range of (134.27 to 204.85) K

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The isothermal vapor−liquid equilibrium for nitrogen (N_2) + tetrafluoromethane (CF_4) system *P*, *T*, *y* data was measured at temperatures of (134.27, 143.57, 153.95, 162.70, 173.43, 185.33, 192.51, and 204.85) K, respectively. The measurements were made with vapor recirculation method, and the experimental results were correlated with the Peng−Robinson equation of state and the van der Waals mixing rule. Through an optimization, the interaction parameters at each temperature and the overall interaction parameter for the whole range of experimental data were obtained. The deviations between the correlated and measured vapor compositions were calculated and the data showed a good consistency.

Introduction

In recent years, a mixed-refrigerant cycle (MRC) Joule-Thomson refrigerator/liquefier, which could be driven by a commercial refrigeration compressor, has received attention from cryogenic researchers.[1−4] Multicomponent mixtures have been used to improve the recuperative performance and thus make the cryogenic process of gas liquefaction more efficient. A mixed refrigerant can consist of neon, nitrogen, and light hydrocarbons. Some fully fluorinated hydrocarbons, such as tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6), which are characterized by low ozone depletion potential (ODP), can also be used to reduce the refrigerant flammability.

Tetrafluoromethane has a boiling point of 145.10 K,[5] which lies just between the boiling points of methane and ethane. In a typical recuperative MRC cryo-cooler/liquefier, more than five or six components with different boiling points have been used to form an optimized mixed refrigerant that will display a good temperature glide during vapor−liquid phase change. By adding tetrafluoromethane, the mixed refrigerant may show a better temperature glide property between methane and ethane boiling temperatures and may considerably improve the thermodynamic efficiency of the cryogenic process for gas liquefaction systems.

It is important to obtain cryogenic vapor−liquid equilibrium (VLE) data of binary system with CF_4 for the accurate predication of thermodynamic properties for the multicomponent systems with CF_4. Zhu[6,7] has performed the vapor−liquid equilibrium experiments on CF_4 with methane and ethane to obtain the binary interaction parameters with the motivation of optimizing the thermodynamic efficiency of miniature mixed refrigerant Joule-Thomson refrigerators. A few earlier VLE experiments for N_2 + CF_4 system can be found in NIST/TRC VLE Floppy Book Database.[8] However, these experimental data were not sufficient for a low-temperature application.

In this work, the VLE data for N_2 + CF_4 binary system in a temperature range from (134.27 to 204.85) K were measured with a high-accuracy cryogenic visualization equilibrium apparatus, which includes a high-pressure sapphire cell in a well-controlled cryogenic air bath and a chromatogram system for vapor composition analysis. A large number of experimental data were collected and correlated, and the results are presented and discussed.

Experiment

Chemicals. The nitrogen (N_2) used for test was supplied by Guangzhou Air Factory with a declared mole fraction purity of 99.999 %, and the tetrafuoromethane (CF_4) was supplied by Beijing LINGGAS Ltd. with a declared mole fraction purity of 99.999 %. All samples were used without further purification.

Apparatus. The experimental apparatus is based on a vapor recirculation method. The apparatus was reported in our previous paper,[9] and also here some details are described. The schematic diagram is shown in Figure 1. The visualized equilibrium apparatus was manufactured by Sanchez Technologies of France. The main part of the apparatus consists of two large boxes. The upper box was made from heavy thermal insulated materials of polyurethane, which had a thickness of over 30 cm, and performed as the temperature-controlled cryogenic air bath. In the upper box, there was a sapphire cell, a connected blind cell, and the auxiliary testing parts for air circulation, liquid nitrogen supply, and temperature measurement and control. The sapphire cell is the main test section. Its temperature was measured with the high-accuracy platinum resistance thermometer. Its pressure was measured with a high-precision pressure transducer and could be regulated with the precisely controlled vapor handling measuring pump. The maximum operation pressure for this system is 50 MPa. To ensure thermodynamic equilibrium in the sapphire cell, there was a magnet-driven stirrer in the cell. The liquid nitrogen was distributed from the Dewar through a vacuum-insulated flexible hose and the electromagnetic-controlled expansion valve and throttled into the upper box to keep the cryogenic air bath at a set temperature. In the lower box, there was a two-stage vapor compression refrigeration system for cooling the air that circulated with a motorized fan inside the air bath. The refrigeration system can cool the air bath and the cells to a temperature of 208.15 K through the cooling coil placed in the upper box. The system of the compression refrigeration and cooling coil was separated from the system of the test cells and vapor circulation loop, so the test system will not be contaminated by the refrigeration system. There an electric heater was wired around with the cooling coil to balance the refrigeration capacity. Using liquid nitrogen spray cooling, the cryogenic air bath can be cooled to the lowest air bath temperature of 108.15 K. The two cooling systems can be switched automatically and function for keeping the air bath at the desired temperature.

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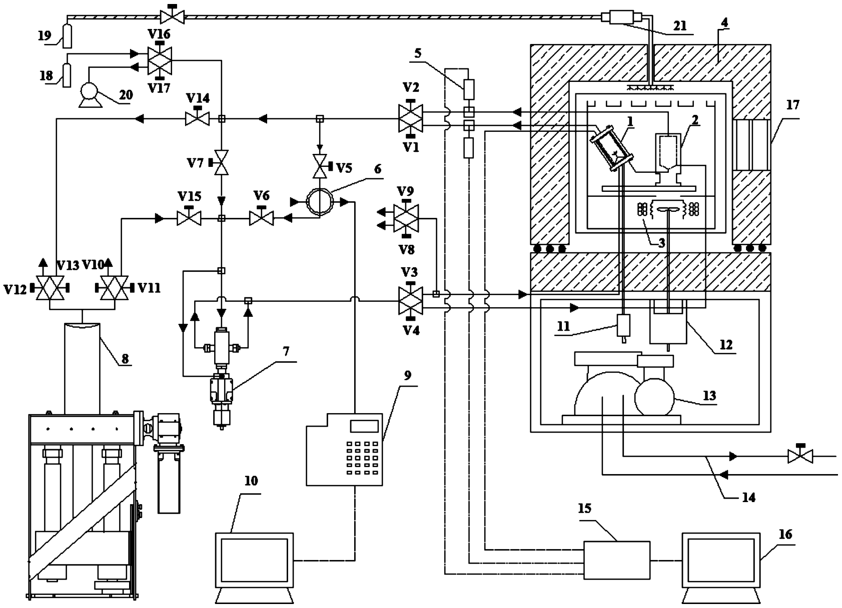

Figure 1. Schematic diagram of visualized high-pressure vapor−liquid equilibrium test setup. 1, sapphire testing cell; 2, blind cell; 3, coil heater; 4, thermal insulation; 5, absolute pressure transducer; 6, four-way sampling valve; 7, vapor recirculation pump; 8, vapor handling measuring pump; 9, gas chromatograph; 10, Agilent workstation; 11, magnetic driven stirrer; 12, fan; 13, two-stage compression refrigerator; 14, cooling water pipe; 15, controller box; 16, data acquisition computer; 17, three-layer visualized observation window; 18, gas bottle; 19, liquid nitrogen dewar; 20, vacuum pump; 21, electromagnetic control valve; V1−V17, valves.

Table 1. Comparison of Experimental Data with Calculated Optimization Data on Vapor Phase Compositions of Nitrogen (1) + Tetrafluoromethane (2) System

P/kPa	y	$\Delta(y(\text{calc}) - y)$	$\Delta(y^1(\text{calc}) - y)$	P/kPa	y	$\Delta(y(\text{calc}) - y)$	$\Delta(y^1(\text{calc}) - y)$
			T/K = 134.27				
114.1	0.6778	−0.0179	−0.0322	644.3	0.9382	0.0129	−0.0006
150.0	0.7498	−0.0038	−0.0192	671.5	0.9506	0.0154	0.0033
274.4	0.8658	0.0032	−0.0128				
			T/K = 143.57				
175.2	0.4683	0.0014	0.0092	389.0	0.7548	−0.0040	0.0072
211.7	0.551	0.0083	0.0172	614.7	0.8420	−0.0067	0.0056
228.9	0.5904	−0.0006	0.0088	1147.0	0.9068	−0.0048	0.0087
275.0	0.6582	−0.0030	0.0071	2529.2	0.9329	0.0064	0.0231
			T/K = 153.95				
242.2	0.2971	−0.0080	−0.0514	611.5	0.7055	0.0172	−0.0138
246.7	0.3085	−0.0054	−0.0485	984.7	0.8167	0.0124	−0.0142
259.8	0.3498	−0.0132	−0.0555	1317	0.8575	0.0146	−0.0096
317.9	0.4709	−0.0088	−0.0479	1630.5	0.8825	0.0136	−0.0090
355.6	0.5326	−0.0132	−0.0508				
			T/K = 162.70				
348.0	0.1180	0.0094	0.0139	739.2	0.5831	−0.0240	−0.0081
388.0	0.2114	−0.0007	0.0065	987.6	0.6588	−0.0022	0.0156
454.0	0.3185	−0.0018	0.0084	1617.5	0.7652	0.0029	0.0232
543.0	0.4090	0.0104	0.0232	3077.1	0.8425	−0.0006	0.0249
620.2	0.4745	0.0103	0.0247	3717.7	0.8430	0.0098	0.0361
			T/K =173.43				
610.5	0.1516	−0.0033	−0.0112	1491.0	0.6420	−0.0001	−0.0276
673.0	0.2394	−0.0129	−0.0247	1809.0	0.6851	0.0153	−0.0135
837.3	0.3871	−0.0111	−0.0296	2366.3	0.7440	0.0190	−0.0108
1031.8	0.5001	−0.0091	−0.0320	2682.1	0.7667	0.0192	−0.0109
1238.6	0.5754	−0.0022	−0.0278				
			T/K = 185.33				
1058.3	0.144	−0.0012	0.0052	1750.2	0.4373	−0.0077	0.0090
1081.8	0.1608	−0.0024	0.0047	2103.3	0.4943	0.0087	0.0276
1229.5	0.2447	−0.0014	0.0090	3023.3	0.5994	0.0102	0.0326
1420.1	0.3377	−0.0104	0.0030	3631.3	0.6504	−0.0041	0.0199
			T/K = 192.51				
1408.6	0.1426	−0.0009	−0.0005	2315.0	0.4299	−0.0010	−0.0048
1731.1	0.2832	−0.0034	−0.0061	2959.2	0.5240	−0.0018	−0.0062
1842.0	0.3182	−0.0027	−0.0056	3364.3	0.5576	0.0030	−0.0018
1851.1	0.3231	−0.0048	−0.0077	3915.0	0.5916	0.0064	0.0003
1955.0	0.3485	−0.0007	−0.0039				
			T/K = 204.85				
2189.4	0.1191	−0.0004	0.0050	2997.6	0.2886	−0.0007	0.0129
2360.0	0.1693	−0.0045	0.0029	3410.3	0.3473	−0.0044	0.0097
2484.3	0.1945	−0.0001	0.0084	3906.8	0.3879	0.0012	0.0171
2564.6	0.2133	−0.0014	0.0078	4520.6	0.4207	0.0051	0.0222

Table 2. Reference Parameters of N_2 and CF_4

compound	T_b/K	T_c/K	P_c/MPa	ω
N_2	77.36	126.19	3.3958	0.0898
CF_4	145.10	227.51	3.7500	0.140

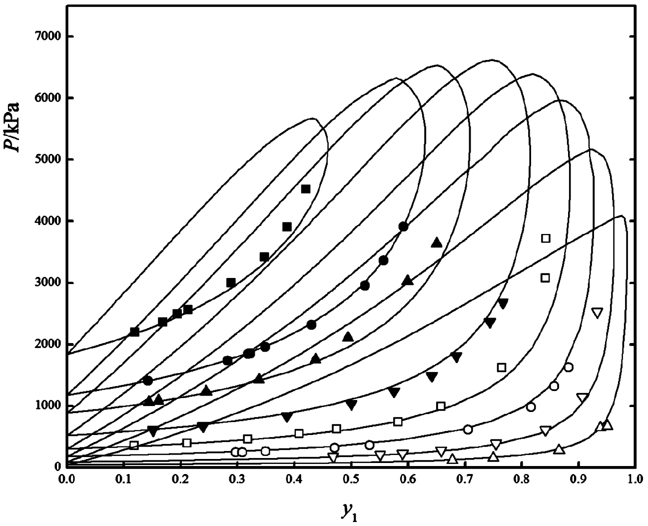

Figure 2. Vapor−liquid equilibrium for N_2 (1) + CF_4 (2) system at different temperatures: ■, T = 204.85 K; ●, T = 192.51 K; ▲, T = 185.33 K; ▼, T = 173.43 K; □, T = 162.70 K; ○, T = 153.95 K; ∇, T = 143.57 K; Δ, T = 134.27 K; —, calculated with PR equation of state and overall k_{ij} = −0.0935.

Table 4. Comparison of Literature's Data[8] and Calculated Data on Vapor Phase Composition of Nitrogen (1) + Tetrafluoromethane (2) System

T/K	209.99	197.56	171.66	161.85	147.55	116.24	107.94
P/kPa	5298	5964	6270	5962	5000	194.43	861.87
y	0.333	0.504	0.746	0.814	0.951	0.963	0.992
y^1(calc)	0.3682	0.5441	0.8042	0.870	0.9431	0.9633	0.9977

The sapphire cell and the blind cell had each a volume of 80 cm^3. The vapor phase in the cells were drawn out by a recirculation pump, sent back through the 2 mm inner diameter pipelines and valves outside the apparatus box, and finally distributed at the bottom of the cells to mix with the cryogenic liquid phase. The flow rate of the circulating vapor was regulated in (2 to 120) $cm^3 \cdot min^{-1}$. For composition analysis, the vapor was sampled by a four-way sampling valve inserted in the recirculation loop. The sampling valve, which has a 0.5 μL sampling volume, was connected with a metal capillary tube to the HP6890N gas chromatograph station. The vapor phase in the sapphire cell was sampled successfully, rather than the liquid phase, thus P, T, y results are reported.

The temperature fluctuation of the air-bath is less than ± 0.1 K, and correspondingly that of the sapphire cell is less than ± 0.01 K. Both temperatures were measured with Pt100 platinum resistance thermometers. The Pt100 in the sapphire cell was calibrated with an uncertainty of ± 0.01 K by a Pt25 standard platinum resistance, which was supplied by Yunnan Measuring Appliance Ltd. and calibrated by the Chinese National Institute of Measurement and Testing. The pressure was measured simultaneously by two absolute pressure transducers. One was Keller PA33 pressure transducer with a full scale of 50 MPa and an uncertainty of ± 0.03 MPa, and the other one was a high-precision Mensor 6100 with a full scale of 10 MPa and an uncertainty of ± 1000 Pa. The product calibration certificate was supplied by the U.S. manufacturer. The pressure data from the Mensor 6100 transducer were used in this work.

The vapor composition measurement was made using the gas chromatograph (Agilent HP6890N), which was equipped with a thermal conductivity detector (TCD). The samples of N_2 + CF_4 gas mixtures for calibration of the chromatograph curve were prepared using a gravimetrical method. The gaseous components were measured by the high-precision Sartorius CP225 balance, which has a precision of 0.1 mg in range of 220 g. All the calibration points in this test were on a linear curve and the uncertainty was less than ± 0.002 in mole fraction. The experimental composition data reported in this work were normalized with the calibration curve.

Experimental Procedure. First the cells and loading pipelines were evacuated at room temperature. The system was filled with the test gas (CF_4) and re-evacuated three times to ensure the removal of all residual gases. Then an estimated amount of CF_4 (the higher boiling-temperature substances) was charged into the system by a desired pressure. Meanwhile the air bath began to be cooled using the compression refrigeration system. Since the cooling speed was quite slow (~0.3 $K \cdot min^{-1}$) and it may take a few hours before reaching the dew point of CF_4. After a set temperature, which is above the dew point, was reached, the air bath temperature was kept steady for around 10 min and the second component, N_2 (the volatile substances), was charged into the system slowly to another desired pressure. Then the substances in the system were circulated with the vapor circulation pump to make the two components mixed uniform. During this cooling, filling, and mixing course, no condensate appeared in the system. Then the air bath was further cooled down with liquid nitrogen. When two phases (vapor and liquid) appeared in the sapphire cell (the vapor−liquid interface can be observed through the multilayer observing window fitted on the wall of the upper thermal-insulated box), the test system was kept at steady for enough long time (taking 1 to 2 h). When the equilibrium state was assumed to be reached (the cell temperature remained unchanged within ± 0.01 K and the total pressure remained unchanged within ± 1000 Pa), the equilibrium data of temperature and pressure are recorded, and then the vapor in the sapphire cell was sampled though the sampling valve and sent to the chromatograph for analyzing. For the next equilibrium test with different composition at the same temperature, a certain amount of N_2 (the volatile substances) was added into the test loop and the tested system was compressed to another pressure. Then the chemicals in the system were circulated with the circulation pump to make even mixing while to keep the two phase existing in the cell. After that, the system was left in steady for equilibrium, and then the data were recorded and the vapor in the cell was sampled for composition analysis. For equilibrium tests at different temperature set point, the above procedure was repeated.

Table 3. The Comparison of Correlated Results with Different Interaction Parameters

T/K	134.27	143.57	153.95	162.70	173.43	185.33	192.51	204.85
k_{ij} for isothermal data	−0.2164	0.0880	−0.1868	0.1009	−0.2095	0.0282	−0.1118	−0.0205
$\sum\Delta\|y(\text{calc}) - y\|/N$	0.0100	0.0044	0.0118	0.0072	0.0102	0.0058	0.0028	0.0022
overall k_{ij}	−0.0935							
$\sum\Delta\|y^1(\text{calc}) - y\|/N$	0.0136	0.0109	0.0334	0.0185	0.0209	0.0139	0.0041	0.0108

Table 5. The Mean Deviations of the Experimental Pressure from the Calculated Pressures with the Overall k_{ij}

T/K	134.27	143.57	153.95	162.70	173.43	185.33	192.51	204.85
$(\sum(P(\text{calc}) - P)/\text{N})$/kPa	40.9	−146.0	62.5	−239.6	84.1	−112.9	21.1	−104.0

Results and Correlations

The isothermal experimental P, T, y data for $N_2 + CF_4$ system were measured at eight different temperatures, (134.27, 143.57, 153.95, 162.70, 173.43, 185.33, 192.51, and 204.85) K. The experimental results are listed in Table 1.

The experimental results were correlated and optimized with Peng−Robinson Equation of State (PREoS). The PREoS is suitable for the nonpolar and even slightly polar mixtures and has been successfully applied to correlate cryogenic thermodynamic properties.[10]

To correlate the experimental results and obtain the optimal interaction parameters, the following object function[11] was minimized

$$\sigma^2 = \sum_{i=1}^{N} (y_i - y_i(\text{calc}))^2$$

where N is the number of equilibrium data points, and y_i and y_i(calc) denote the i-th experimental data and calculation data, respectively.

In this work, the PREoS with the classical van der Waals mixing rule[12] was used to correlate the measured data. The basic parameters, such as the critical temperature and pressure and the acentric factor, for the two pure substances were taken from Refprop 7.0[5] and are listed in Table 2. The only adjustable parameter for the mixing rule is the interaction parameter k_{ij}.

The value of k_{ij} optimized with isothermal experimental data at each temperature was obtained first. The values and the mean deviations of the vapor composition data are given in Table 3. The deviations of the experimental data from the calculated data with k_{ij} at different temperature, denoted with y(calc), are shown in Table 1. The optimized interaction parameters for different temperature were not a smooth function of temperature. It was better to correlate the experimental results with an overall k_{ij} by optimizing with all experimental data. The obtained overall k_{ij} and mean deviations for different temperature were also given in Table 3. The deviations of the experimental data from the calculated data with the overall k_{ij}, denoted with y^1(calc), are also listed in Table 1. All the experimental data and the correlation curves are plotted in Figure 2. It can be seen that the mean deviations for the data are rather small and the experimental data show a good consistency.

The data published in the NIST/TRC VLE Floppy Book Database[8] were collected for comparison with the present study. The literatures' data and the calculated vapor composition data with the overall k_{ij} are listed in Table 4, corresponding to each temperature and pressure. It can be seen that the literatures' data are comparable with the results of this study.

The temperature range in this study was above the critical temperature of N_2, so the retrograde phenomena could appear near to the critical point for a specified composition, as seen in Figure 2. The retrograde region is very sensitive to the composition variation, and it is most preferable to get the retrograde dew point by compressing the system in the test cell at a constant composition. However, in the present study the system could not be compressed without component added and composition varied, since the experimental apparatus was based on a vapor recirculation method and the test cell in the cryogenic air bath was not a closed system. Because of this limitation of the experimental apparatus, the retrograde condensation data were not investigated in this work.

It will be useful that the temperature and composition are used to calculate the dew point pressure and to obtain the deviations against the experimental pressure. The mean deviations between the experimental pressure and the calculated dew point pressure with overall k_{ij} were obtained and listed in Table 5. It can be found that the deviations are rather small for most of the data except for those close to the retrograde region. This can be seen in Figure 2.

Conclusions

The vapor−liquid equilibrium for $N_2 + CF_4$ has been measured using a cryogenic experimental apparatus with vapor recirculation. Through this experimental study, a total of 66 groups of P, T, y data at eight different temperatures (134.27, 143.57, 153.95, 162.70, 173.43, 185.33, 192.51, and 204.85) K have been obtained. The Peng−Robinson equation of state with the classical van der Waals mixing rule was used to correlate the results to give an optimized overall interaction parameter. It has been shown that the deviations between the experimental and calculated vapor phase composition are small and the experimental data have a good consistency. It can also be seen that the predicted results by using the overall interaction parameter have agreed very well with the experiment data.

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