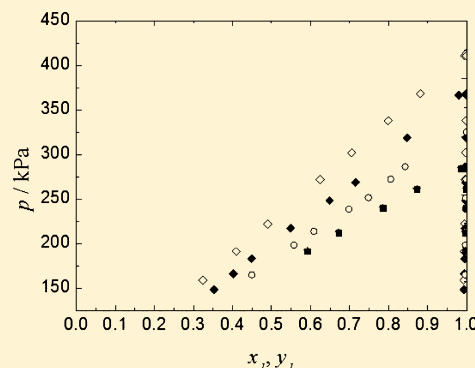


# Vapor–Liquid Equilibrium for the Mixture Methane (CH<sub>4</sub>) + Ethane (C<sub>2</sub>H<sub>6</sub>) over the Temperature Range (126.01 to 140.01) K

Xiao Hong Han, Yu Jia Zhang, Zan Jun Gao, Ying Jie Xu, Xue Jun Zhang,\* and Guang Ming Chen

Institute of Refrigeration and Cryogenics, State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China

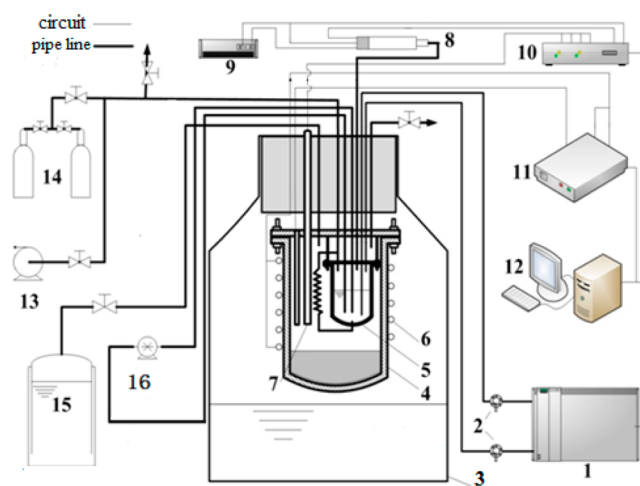
**ABSTRACT:** A single-cycle apparatus was used to measure vapor–liquid equilibrium (VLE) data for the binary system (CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>) over low temperatures of (126.01 to 140.01) K and pressures up to 0.64 MPa. The Peng–Robinson (PR) + modified Huron–Vidal mixing rule (MHV1) + Wilson model was used to correlate the experimental data for the binary system (CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>), and the interactive parameters of the Wilson model were given. The model gave satisfactory results over the range of experimental temperatures and pressure.



## 1. INTRODUCTION

At present, liquefied nature gas (LNG) has become an important commodity in the world, and the development of this industry is very rapid. In the LNG industry chain, the liquefaction and the storage and transportation of natural gas at low temperature are two main processes, and simulating and optimizing processes can minimize the cost and energy consumption. The simulation and optimization design need accurate equations of state that require vapor–liquid equilibrium data for nature gas mixtures as the basis to calculate the thermodynamic properties of natural gas. Natural gas contains a variety of components, so it is not realistic to measure vapor–liquid equilibrium data for all binary mixtures in natural gas mixture. A more reasonable way is to use experimental apparatus to measure a few accurate vapor–liquid equilibrium data for binary mixtures; then other phase equilibrium data are associated by the measured experimental data.<sup>1</sup> Further, the vapor–liquid equilibrium (VLE) data of multiple mixture of the natural gas are predicted by correlations developed with vapor–liquid equilibrium data of binary mixtures only.

Usually atmospheric pressure and high pressure containers are both used to store LNG.<sup>2</sup> The temperature of the atmospheric pressure container, which is used in large number of applications, is approximately 111 K. At many medium-scale LNG stations, LNG is stored at high pressure; namely, the pressure of the storage tanks are commonly between (0.3 and 0.6) MPa, and the working temperature of the high pressure storage is about 135 K. In addition, the proportion of methane and ethane is more than 95 % in natural gas,<sup>3</sup> therefore, the knowledge about VLE data of the binary mixtures (CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>) at the low temperature (130 to 140) K is extremely important for LNG storage in medium-scale LNG stations.



**Figure 1.** Schematic diagram of the VLE experimental system. 1, chromatograph; 2, six-way valve; 3, Dewar; 4, thermostatted bath; 5, equilibrium cell; 6, heater; 7, platinum resistance thermometer; 8, pressure transducer; 9, DC regulated power supply; 10, Keithley 2002 data acquisition/switch unit; 11, PID temperature controller; 12, PC; 13, vacuum pump; 14, sample; 15, self-pressurization Dewar; 16, circulation pump.

In 1950s to 1970s, previous researchers published a large number of papers about phase equilibrium data of the mixtures (CH<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>; seen in Table 1).<sup>4–18</sup> Because of the limitations in the measuring technology and device, the measuring range was not very wide, and most of the previous scholars devoted to

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Table 1. Previous Vapor–Liquid Investigations for the Binary Mixture ( $\text{CH}_4 + \text{C}_2\text{H}_6$ )

investigators	approximate temperatures reported (and approximate pressure)	measurement accuracy	measuring method	investigators	approximate temperatures reported (and approximate pressure)	measurement accuracy	measuring method
Guter et al. <sup>4</sup> (1940)	195 K, (0.4 to 5.2) MPa			Davalos and Anderson <sup>15</sup> (1976)	250 K, (1.3 to 6.7) MPa	temperature: $\pm 0.01$ K	flow method
Levitskaya <sup>5</sup> (1941)	178 K, 3 MPa					pressure: $\pm 0.0035$ MPa	
Bloomer et al. <sup>6</sup> (1953)	188 K, (3.0, 4.1) MPa		dew-bubble point			(0 to 3.5) MPa	
Moran <sup>7</sup> (1959)	(140 to 300) K, (0.7 to 6.9) MPa		dew-bubble point			$\pm 0.005$ MPa	
	(99 to 192) K, (0 to 0.2) MPa					(0 to 10.2) MPa	
Price and Kobayashi <sup>8</sup> (1959)	144 K, 0.7 MPa			Miller and Staveley <sup>16</sup> (1976)	116 K, (0 to 0.1) MPa	mole fraction: $\pm 0.015$	
	172 K, (0.7, 1.4) MPa			Miller et al. <sup>17</sup> (1977)	150 K, (0.03 to 1.04) MPa	temperature: $\pm 0.02$ K	vapor-recycle
	200 K, (0.7, 1.4, 2.7, 4.2) MPa				160 K, (0.06 to 1.59) MPa	pressure: $\pm 0.001$ MPa	
Ellington et al. <sup>9</sup> (1959)	228 K, (1.4, 2.7, 4.2, 5.5) MPa				170 K, (0.11 to 2.33) MPa	(0 to 0.6) MPa	
	(142 to 300) K, (0.7 to 6.4) MPa				180 K, (0.18 to 3.83) MPa	$\pm 0.005$ MPa	
Chang and Lu <sup>10</sup> (1967)	122 K, (0 to 0.2) MPa		dew-bubble point		190 K, (0.29 to 4.52) MPa	(0 to 4.6) MPa	
	171 K, (0.3 to 2.1) MPa			Gupta et al. <sup>18</sup> (1980)	260 K, (1.71 to 7.13) MPa	mole fraction: $\pm 0.001$	
Skripka et al. <sup>11</sup> (1970)	123 K, (0 to 0.2) MPa				270 K, (2.21 to 6.79) MPa	temperature: $\pm 0.02$ K	vapor-recycle
	133 K, (0 to 0.5) MPa				280 K, (2.82 to 6.37) MPa	pressure: $\pm 0.0035$ MPa	
	143 K, (0 to 0.8) MPa					(0 to 3.5) MPa	
	153 K, (0 to 1.2) MPa					$\pm 0.01$ MPa	
Hsi and Lu <sup>12</sup> (1971)	159 K, (0.2 to 1.4) MPa					(> 3.5 MPa)	
Wichterle and Kobayashi <sup>13</sup> (1972)	130 K, (0 to 0.4) MPa	temperature: $\pm 0.01$ K	vapor-recycle			mole fraction: $\pm 0.002$	
	144 K, (0 to 0.8) MPa	pressure: $\pm 0.003$ MPa		Gomes De Azevedo and Calado <sup>19</sup> (1989)	90.69 K		
	158 K, (0 to 1.5) MPa	(0 to 3) MPa			103.99 K		
	172 K, (0 to 2.5) MPa	$\pm 0.014$ MPa		Raabe et al. <sup>20</sup> (2001)	240 K, (1.52 to 6.57) MPa		static method
	186 K, (0.1 to 4.1) MPa	(0 to 14) MPa			270 K, (2.84 to 6.63) MPa		
	188 K, (3.2 to 4.3) MPa			Janisch et al. <sup>21</sup> (2007)	140 K, (0.49 to 0.62) MPa		
	190 K, (0.1 to 4.5) MPa				150 K, (0.39, 0.58) MPa		
	192 K, (0.2 to 4.8) MPa				180 K, (0.52 to 3.03) MPa		
	194 K, (4.3 to 4.9) MPa				210 K, (2.04 to 5.01) MPa		
Wilson <sup>14</sup> (1975)	111 K, (0 to 0.1) MPa						

researching VLE data of the binary mixtures ( $\text{CH}_4 + \text{C}_2\text{H}_6$ ) at relatively high temperatures (>140) K, as a result, there were limited data in low temperature ranges (120 to 140) K. For these two reasons, it is necessary to measure accurate (VLE) data of the mixture ( $\text{CH}_4 + \text{C}_2\text{H}_6$ ) at low temperatures.

The objective of the work is to provide accurate experimental measurements for the binary mixture ( $\text{CH}_4 + \text{C}_2\text{H}_6$ ) in temperature range from (126 to 140) K. The Peng–Robinson (PR) + modified Huron–Vidal mixing rule (MHV1) + Wilson model is used to correlate the experimental data, and the interactive parameters are obtained.

## 2. EXPERIMENTS

**2.1. Sample.**  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were used in the VLE experiment. Detailed information is shown in Table 2. No further purification was done on these chemicals before use.

**2.2. Experimental Equipment.** The apparatus used in this paper is a vapor-recycled type still (shown in Figure 1). Details of the apparatus have been reported by Han et al.<sup>22</sup> The vapor is continuously recycled by a circulating pump (Micropump, GAH-T23.PVS.B). The temperature of the equilibrium cell is controlled by means of a high accurate thermostat (Shimaden,

SR253, Japan), and it can be maintained within  $\pm 10$  mK. The temperature in the cell is measured by a four-head 25  $\Omega$  platinum resistance thermometer (WZPB-1, Yunnan Instrument) with an uncertainty of  $\pm 1$  mK (ITS-90). The pressure of the equilibrium cell is measured using a pressure transducer (Druck PMP4010, FS = 1.6 MPa) and an atmospheric pressure gauge (DYM-1, China). The total uncertainty of the pressure measurement system is  $\pm 0.65$  kPa. The gas chromatograph (GC) with a thermal conductivity detector (TCD) (GC 1690, China) is used to analyze the compositions of the samples. The overall uncertainty in the measurement of the composition is estimated to be within  $\pm 0.0040$  mole fraction.

**2.3. Experimental Procedures.** The cell is evacuated at first to remove the inert gas and other impurities. At the same time, the system is cooled down to near 90 K. Then a specified mass of  $\text{C}_2\text{H}_6$  and  $\text{CH}_4$  is added into the cell. Because of the large difference of temperature between the cell and its surroundings (almost 200 K), it spends about 10 h to charge the samples. After charging the samples, the temperature is set at the required experimental temperature. Most likely, after about 5 h the system arrives at equilibrium. When the desired equilibrium temperature is obtained, the pressure in the

Table 2. Purities and Providers of the Gases

name	purity	provider
CH <sub>4</sub>	≥ 0.9999 (mass fraction)	Zhejiang Minxing Industrial and Trading Co., Ltd.
C <sub>2</sub> H <sub>6</sub>	≥ 0.999 (mass fraction)	Dalian Anruiheng special gas Chemical Co., Ltd.

Table 3. Experimental VLE Results for the Binary Mixture (CH<sub>4</sub> (1) + C<sub>2</sub>H<sub>6</sub> (2)) at the Temperature Range of (126.01 to 140.01) K

$x_1$	$y_1$	$p/\text{kPa}$	$x_1$	$y_1$	$p/\text{kPa}$
$T = 126.01 \text{ K}$			$T = 127.99 \text{ K}$		
0.5922	0.9968	191.62	0.4498	0.9960	164.99
0.6722	0.9971	212.34	0.5578	0.9971	198.31
0.7855	0.9983	240.07	0.6089	0.9974	213.65
0.8724	0.999	260.94	0.6986	0.9977	238.52
0.9852	0.9999	284.09	0.7486	0.9979	251.53
1	1	286.85	0.8057	0.9985	272.20
			0.8427	0.9988	286.31
			1	1	324.94
$T = 130.02 \text{ K}$			$T = 132.01 \text{ K}$		
0.3527	0.9933	148.12	0.3248	0.9921	159.00
0.4021	0.9942	166.00	0.4098	0.9938	191.21
0.4489	0.9951	183.00	0.4901	0.9951	222.02
0.5488	0.9966	217.19	0.6249	0.9966	272.00
0.6485	0.9972	248.32	0.7059	0.9975	302.05
0.7152	0.9976	268.52	0.7986	0.9981	337.82
0.8476	0.9987	318.72	0.8814	0.9986	368.04
0.9801	0.9996	366.31	0.9948	0.9999	410.97
1	1	367.76	1	1	413.65
$T = 133.98 \text{ K}$			$T = 135.99 \text{ K}$		
0.3368	0.9911	188.70	0.2578	0.9869	186.02
0.4268	0.9933	225.67	0.3308	0.9901	217.36
0.5287	0.9949	270.82	0.4219	0.9926	255.89
0.6059	0.9961	300.14	0.5253	0.9946	299.01
0.6996	0.9969	339.46	0.6054	0.9955	335.10
0.8019	0.9982	384.86	0.6437	0.996	354.61
0.9278	0.999	432.07	0.7501	0.997	400.78
1	1	463.11	0.8097	0.9976	430.66
			0.9328	0.9989	484.07
			1	1	517.90
$T = 137.97 \text{ K}$			$T = 140.01 \text{ K}$		
0.3128	0.9881	244.00	0.3388	0.9877	287.88
0.3974	0.9909	278.03	0.4537	0.9912	338.42
0.4538	0.9923	300.12	0.5345	0.9934	370.99
0.5098	0.9936	324.03	0.6098	0.9942	414.97
0.6583	0.9959	397.10	0.6853	0.9954	445.90
0.7428	0.9967	444.10	0.7482	0.9965	493.09
0.8018	0.9972	476.22	0.8907	0.9983	570.83
0.8807	0.9983	511.15	0.9646	0.9991	618.12
1	1	576.38	1	1	641.51

<sup>a</sup> $u(T) = 0.001 \text{ K}$ ,  $u(p) = 0.65 \text{ kPa}$ , and  $u(x_1) = u(y_1) = 0.0040$ .

equilibrium cell is recorded, and the vapor–liquid samples are withdrawn from the cell and measured by GC online.

**2.4. Experimental Data.** In this work, reliable VLE data of the mixture (C<sub>2</sub>H<sub>6</sub> + CH<sub>4</sub>) are measured from (126.01 to 140.01) K and in the concentration range from mole fractions of (0.2 to 1) of methane. The experimental results are listed in Table 3.

Table 4. Critical Parameters and Acentric Factors for CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub><sup>26</sup>

substance	molecular formula	molecular weight	$T_c/\text{K}$	$p_c/\text{MPa}$	$\omega$
CH <sub>4</sub>	CH <sub>4</sub>	16.043	190.56	4.5992	0.0114
C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>6</sub>	30.070	305.33	4.8718	0.0993

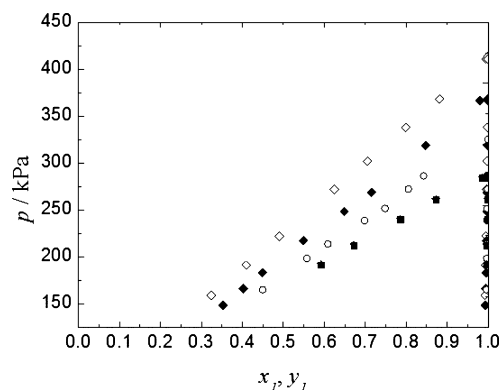


Figure 2. Pressure–composition phase diagram for the binary mixture (CH<sub>4</sub> (1) + C<sub>2</sub>H<sub>6</sub> (2)). Experimental data in this work: ■, 126.01 K; ○, 127.99 K; ◆, 130.02 K; ◇, 132.01 K.

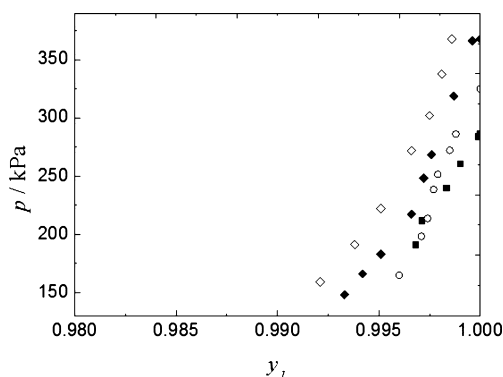


Figure 3. Local pressure–composition phase enlarged diagram for the binary mixture (CH<sub>4</sub> (1) + C<sub>2</sub>H<sub>6</sub> (2)) at the composition ranges of (0.98 to 1.0) from Figure 2. Experimental data in this work: ■, 126.01 K; ○, 127.99 K; ◆, 130.02 K; ◇, 132.01 K.

### 3. RESULTS AND DISCUSSION

The correlation of the VLE data for the mixture (C<sub>2</sub>H<sub>6</sub> and CH<sub>4</sub>) was conducted using the Peng–Robinson (PR)<sup>23</sup> equation of state (EoS) with the first modified Huron–Vidal mixing rule (MHV1).<sup>24</sup>

The excess Gibbs energy  $G^E$  used in MHV1 mixing rule is calculated by the Wilson model<sup>25</sup>

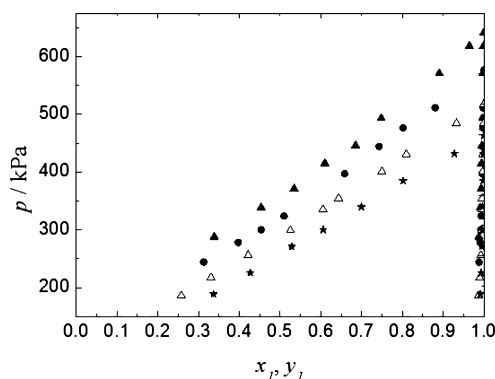
$$\frac{G_{(T,P)}^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(\Lambda_{21}x_1 + x_2) \quad (1)$$

where  $\Lambda_{12}$  and  $\Lambda_{21}$  are adjustable parameters.

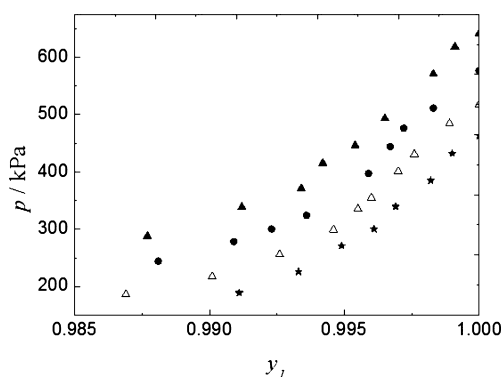
The activity coefficients can be calculated as

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + \beta x_2 \quad (2)$$

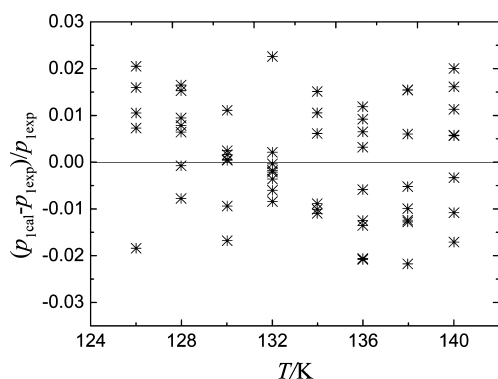
$$\ln \gamma_2 = -\ln(\Lambda_{21}x_1 + x_2) - \beta x_1 \quad (3)$$



**Figure 4.** Pressure–composition phase diagram for the binary mixture ( $\text{CH}_4$  (1) +  $\text{C}_2\text{H}_6$  (2)). Experimental data in this work: ★, 133.98 K; △, 135.99 K; ●, 137.97 K; ▲, 140.01 K.



**Figure 5.** Local pressure–composition phase enlarged diagram for the binary mixture ( $\text{CH}_4$  (1) +  $\text{C}_2\text{H}_6$  (2)) at the composition ranges of (0.98 to 1.0) from Figure 4. Experimental data in this work: ★, 133.98 K; △, 135.99 K; ●, 137.97 K; ▲, 140.01 K.



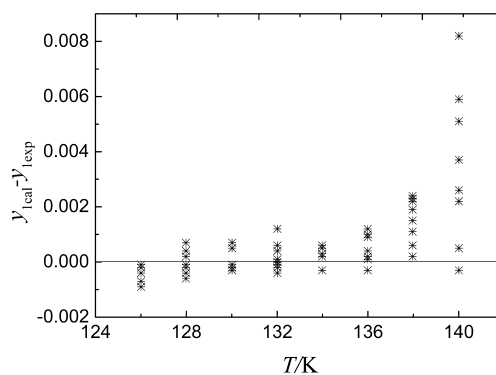
**Figure 6.** Deviations of pressure for the binary mixture ( $\text{CH}_4$  (1) +  $\text{C}_2\text{H}_6$  (2)) from the PR + MHV1 + Wilson model.

where

$$\beta = \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \quad (4)$$

To take the effect of temperature into account,  $\Lambda_{12}$  and  $\Lambda_{21}$  are written as follows

$$\Lambda_{12} = \frac{\Lambda_{12}^{(0)} + \Lambda_{12}^{(1)} \ln(T)}{RT} \quad (5)$$



**Figure 7.** Deviations of vapor composition for the binary mixture ( $\text{CH}_4$  (1) +  $\text{C}_2\text{H}_6$  (2)) from the PR + MHV1 + Wilson model.

**Table 5. Correlated Results of VLE Data for the Binary Mixture ( $\text{CH}_4$  (1) +  $\text{C}_2\text{H}_6$  (2)) at Different Temperatures Using the PR + MHV1 + Wilson Model**

		PR + MHV1 + Wilson model			
$T/\text{K}$	$N_p$	$ y_{\text{cal}} - y_{\text{exp}} $	$\max  y_{\text{cal}} - y_{\text{exp}} $	$\delta p^a/\%$	$\max 100( p_{\text{exp}} - p_{\text{cal}} /p_{\text{exp}})/\%$
$\text{CH}_4/\text{C}_2\text{H}_6$					
126.01	6	0.0005	0.0009	1.45	2.05
127.99	8	0.0004	0.0007	0.92	1.65
130.02	9	0.0004	0.0007	0.43	1.68
132.01	9	0.0004	0.0120	0.41	0.84
133.98	8	0.0004	0.0006	1.03	1.51
135.99	10	0.0007	0.0012	1.16	2.08
137.97	9	0.0015	0.0024	1.24	2.18
140.01	9	0.0036	0.0082	1.13	2.00

$$^a \delta p = 100 \sum_{i=1}^{N_p} (|p_{\text{cal}} - p_{\text{exp}}|/p_{\text{exp}})(1/N_p).$$

**Table 6. Constant Values Derived by Fitting the Experimental Data**

model	constant values				experimental data ranges	
	$a_0$	$a_1$	$b_0$	$b_1$	T/K	mole fraction of $\text{CH}_4$
Wilson	81.86	−16.59	−49.50	10.30	127.01–140.01	0.2–1

$$\Lambda_{21} = \frac{\Lambda_{21}^{(0)} + \Lambda_{21}^{(1)} \ln(T)}{RT} \quad (6)$$

To correlate the experimental data, a computer program has been developed, applying the least-square method for fitting an objective function as follows

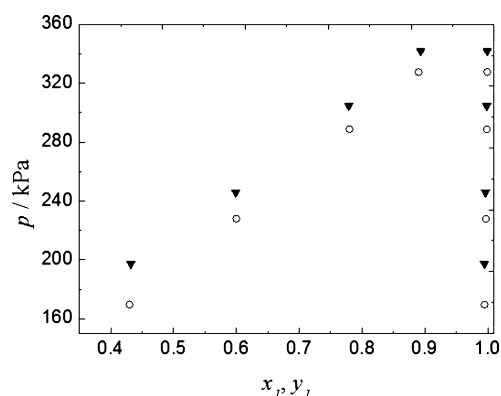
$$\text{OF} = \frac{1}{N_p} \sum_{N_p} \left\{ 0.5 \left( \frac{p_{\text{exp}} - p_{\text{cal}}}{p_{\text{exp}}} \right)^2 + 0.5 ((y_{1,\text{exp}} - y_{1,\text{cal}})_j^2 + (y_{2,\text{exp}} - y_{2,\text{cal}})_j^2) \right\} \quad (7)$$

where  $N_p$  is the number of experimental points, the subscripts exp and cal denote the calculated and experimental data, respectively, and  $j$  denotes the  $j$ th experimental point.

In the process of calculating, the basic properties of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  are listed in Table 4.

The experimental data and calculated results are shown in Figures 2 to 7 and Table 5; it can be seen that the calculated results reveal a good agreement with the existing experimental





**Figure 8.** Comparison of experimental data at 130.37 K between our work and ref 13. O, the values in this work; ▼, the values in the ref 13.

data. The average and maximum relative derivations of pressure are within 1.45 % and 2.25 %, respectively; the average and maximum derivations of vapor mole composition are within 0.0010 and 0.0120. The regressed parameters are listed in Table 6. Also, it can be seen from Figure 2 that the mixture ( $\text{CH}_4 + \text{C}_2\text{H}_6$ ) has a slightly positive deviation from Roule's law. In addition, the comparison of experimental data at 130.37 K between our work and ref 13 (in most conditions, our experimental data have no repetition in the temperature range with other cited references) was conducted, shown in Figure 8. From Figure 8, the relative pressure deviation between both is usually within 5 %, and the composition deviation between both is usually within 0.01.

#### 4. CONCLUSIONS

In this paper, vapor–liquid equilibrium data for the binary mixture  $\text{CH}_4 + \text{C}_2\text{H}_6$  reported in the temperature range from (126.01 to 140.01) K are given in Table 2 and Figures 2 to 4. The experimental data are correlated by using the PR equation of state, combined with the MHV1 mixing rule and Wilson model. The obtained results are in good agreement with the experimental data. The average and maximum relative deviations of pressure are within 1.45 % and 2.25 %, respectively; and the average and maximum derivations of vapor mole composition are within 0.0010 and 0.0120. The regressed parameters are given in Table 6. The VLE presented herein will be used in the near future by the LNG industry.

#### AUTHOR INFORMATION

##### Corresponding Author

\*Tel.: +86 571 8795 2446. Fax: +86 571 8795 2446. E-mail: xuejzhang@zju.edu.cn.

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##### Notes

The authors declare no competing financial interest.

#### REFERENCES

- (1) Zhu, Z. Q.; Yao, J. S.; Jin, Z. L. *Fluid phase equilibrium principle and application*; Zhejiang University Press: Hangzhou, 1990; p 377.
- (2) Qiao, G. F.; Li, Y. X.; Zhang, K. M.; Li, D. J. Uniting atmospheric pressure containers and high-pressure containers to store liquefied natural gas. *Oil Gas Sci. Technol.* **2005**, *24* (4), 29–31.
- (3) Gu, A. Z. *LNG Technical Manual*; Mechanical Industry Press: Beijing, 2010.

- (4) Guter, M.; Newitt, D. M.; Ruhemann, M. Two-Phase Equilibrium in Binary and Ternary Systems. II. The System Methane-Ethylene. *Proc. R. Soc. London* **1940**, A176, 140.
- (5) Levitskaya, E. P. Study of the liquid-vapor equilibria of the ternary system ethane-methane-hydrogen (in Russian). *Zh. Tekh. Fiz.* **1941**, *11*, 197.
- (6) Bloomer, O. T.; Gami, D. C.; Parent, J. D. Physical-chemical properties of methane-ethane mixtures. *Inst. Gas Technol. Chicago Res. Bull.* **1953**, 22.
- (7) Moran, D. W. Low Temperature Equilibria in Binary System. Ph.D. Thesis, University of London, London, U.K., 1959.
- (8) Price, A. R.; Kobayashi, R. Low Temperature Vapor-Liquid Equilibrium in Light Hydrocarbon Mixtures: Methane-Ethane-Propane System. *J. Chem. Eng. Data* **1959**, *4* (1), 40–52.
- (9) Ellington, R. T.; Eakin, B. E.; Parent, J. D. *Thermodynamic and Transport Properties of Gases, Liquids, and Solids*; McGraw Hill: New York, 1959; p 180.
- (10) Chang, S. D.; Lu, B. C. Y. Vapor-liquid equilibria in the nitrogen-methane-ethane system. *Chem. Eng. Progr. Symp. Ser.* **1967**, *63* (81), 18–27.
- (11) Skripka, V. G.; Nikitina, I. E.; Zhdanovich, L. A.; Sirotnin, A. G.; Benyaminovich, O. A. Liquid-vapor phase equilibria at low temperatures in binary systems formed by components of nature gas. *Gazov. Prom.* **1970**, *15* (12), 35.
- (12) Hsi, C.; Lu, B. C. Y. Vapor-liquid equilibria in the methane-ethylene-ethane system. *Can. J. Chem. Eng.* **1971**, *49* (1), 140.
- (13) Wichterle, I.; Kobayashi, R. Liquid-Vapor equilibrium of methane+ ethane system at low temperatures and high pressures. *J. Chem. Eng. Data* **1972**, *17* (1), 9–12.
- (14) Wilson, G. M.; Vapor-liquid equilibria of nitrogen, methane, ethane, and propane binary mixtures at LNG temperatures from total pressure measurements. In *Advances in Cryogenic Engineering*, Vol. 20; Timmerhaus, K. D., Ed.; Plenum Press: New York, 1975. *Mater. Sci. Eng.*, **1976**, *22*, 281.
- (15) Davalos, J.; Anderson, W. R. Liquid-Vapor equilibrium at 250.00K for system containing methane, ethane, and carbon dioxide. *J. Chem. Eng. Data* **1976**, *21* (1), 81–84.
- (16) Miller, R. C.; Staveley, L. A. K. In *Advances in Cryogenic Engineering*, Vol. 21; Timmerhaus, K. D., Weitzel, D. H., Eds.; Plenum Press: New York, 1976; p 493.
- (17) Miller, R. C.; Kidnay, A. J.; Hiza, M. J. Liquid-Vapor equilibrium in methane + ethane and in methane + nitrogen from 150.00–190.00 K. *J. Chem. Thermodyn.* **1977**, *9*, 167–178.
- (18) Gupta, M. K.; Gardner, G. C.; Hegarty, M. J.; Kidnay, A. J. Liquid-Vapor equilibrium  $\text{N}_2 + \text{CH}_4 + \text{C}_2\text{H}_6$  system from 160–280 K. *J. Chem. Eng. Data* **1980**, *25* (4), 313–318.
- (19) Gomes De Azevedo, E. J. S.; Calado, J. C. G. Thermodynamics of liquid methane+ethane. *Fluid Phase Equilib.* **1989**, *49*, 21–34.
- (20) Raabe, G.; Janisch, J.; Koehler, J. Experimental studies of phase equilibria in mixtures relevant for the description of natural gases. *Fluid Phase Equilib.* **2001**, *185* (1–2), 199–208.
- (21) Janisch, J.; Raabe, G.; Köhler, J. Vapor–Liquid Equilibria and Saturated Liquid Densities in Binary Mixtures of Nitrogen, Methane, and Ethane and Their Correlation Using the VTPR and PSRK GCEOS. *J. Chem. Eng. Data* **2007**, *52* (5), 1897–1903.
- (22) Han, X. H.; Zhang, Y. J.; Gao, Z. J. Vapor-liquid equilibrium for the mixture Nitrogen ( $\text{N}_2$ ) + Methane ( $\text{CH}_4$ ) at the temperature ranges of (110 to 130) K. *J. Chem. Eng. Data* **2012**, *57* (5), 1621–1626.
- (23) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.
- (24) Michelsen, M. L. A modified Huron-Vidal mixing rule for cubic equations of state. *Fluid Phase Equilib.* **1990**, *60*, 213–219.
- (25) Wilson, G. M. Vapor-liquid equilibrium. XI: A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.
- (26) Lemmon, E. W.; Huber, M. L.; McLinden, M. O. *NIST Reference Fluid Thermodynamic and Transport Properties Database - REFPROP*, Version 7.0; National Institute of Standards and Technology: Gaithersburg, MD, 2002.