

## Vapor-liquid equilibria for the binary mixtures of methanol+ cyclopentyl methyl ether (CPME)

Wan Ju Jeong, Hang-kyu Cho, and Jong Sung Lim<sup>†</sup>

Department of Chemical and Biomolecular Engineering, Sogang University, C. P. O. Box 1142, Seoul 04107, Korea

(Received 13 February 2016 • accepted 30 May 2016)

**Abstract**—VLE data for binary systems of methanol (1)+cyclopentyl methyl ether (2) were measured at five equal-spaced temperatures between 313.15 and 353.15 K using a circulation-type equilibrium apparatus with on-line gas chromatography analysis. This binary system shows strong positive deviation from Raoult's law and forms an azeotrope at each temperature. The experimental data were correlated with the Peng-Robinson equation of state using the Wong-Sandler mixing rule combined with the NRTL excess Gibbs free energy model. The overall average relative deviations of pressure (ARD-P (%)) and vapor phase compositions (ARD-y (%)) between experimental and calculated values through the temperature range from 313.15 to 353.15 K were 0.298 and 0.499%, respectively. In the range of experimental temperature, azeotropic compositions showed a linear relationship with temperature and were correlated by the empirical equation of  $x_{azeo}=0.001\ T/K+0.617$ .

**Keywords:** Vapor Liquid Equilibria, Cyclopentyl Methyl Ether (CPME), Peng-Robinson Equation of State (PR-EoS), Wong-Sandler Mixing Rule

### INTRODUCTION

The demand for greener solvents in chemical processes in the pharmaceutical and other manufacturing industries has increased greatly. Among them, cyclopentyl methyl ether (CPME) has attracted much attention as a greener solvent alternative to other ethereal solvents such as tetrahydrofuran (THF), 2-methyl tetrahydrofuran (2-MeTHF), dioxane, and 1,2-dimethoxyethane (DME), as it is less toxic, less hazardous, and safer than other organic solvents. In comparison with other ethereal solvents, CPME also has distinct advantages. In particular, it has a high boiling point and high hydrophobicity, and does not generate significant amounts of peroxides, allowing it to be used as reaction, extraction, and crystallization solvent. Furthermore, owing to its great stability, it has been used as a reaction medium under either basic or acidic conditions [1-5].

Various methods are available for the synthesis of CPME: (1) methylation of cyclopentanol with dimethyl sulfate, (2) a two-step reaction between cyclopentanol and sodium hydroxide, and (3) an addition reaction of methanol to cyclopentene. Reactions (1) and (2), however, suffer from some drawbacks since dimethyl sulfate and methyl iodide, which are the reactants used in the corresponding reactions, are carcinogenic and mutagenic to the human body. On the other hand, reaction (3) is favorable from an environmental point of view, and it is also industrially effective due to the high yields obtained. The reaction is carried out in a tightly closable reaction vessel for 6-8 hours. Methanol, cyclopentene, and an acidic ion-exchange resin are involved in this reaction at different temperatures and pressures [1,6]. As part of a study on the

phase behavior of binary systems under various conditions, vapor-liquid equilibrium (VLE) data of the materials employed in this method are necessary for determining the optimal reaction conditions and designing an optimum separation process.

In this work, isothermal VLE data for the binary mixture composed of MeOH (1)+CPME (2), at five equally spaced temperatures in the range from 313.15 to 353.15 K, were measured using a circulation-type equilibrium apparatus in which both phases were continuously recirculated. The experimental data were correlated with the Peng-Robinson equation of state [7], using the Wong-Sandler mixing rule [8] combined with the NRTL excess Gibbs free energy model [9,10]. In addition, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were represented, and the relevant parameters were determined.

### EXPERIMENTAL

#### 1. Chemicals

High-grade chemicals of MeOH and CPME were used for the VLE measurement. CPME was purchased from Dae-Jung Chemicals & Metals CO., LTD. (KOREA) (greater than 99.9 mass%), and CPME was purchased from Sigma Aldrich (USA) (greater than 99.9 mass%). These two chemicals were analyzed with a gas chromatograph (GC) and the resulting purities of both MeOH and CPME were higher than 99.9 mass%. So, they were used without any further purification. The purity data and properties of these components are shown in Table 1.

#### 2. Experimental Apparatus

The vapor-liquid equilibrium apparatus used in this work was a circulation-type one in which both liquid and vapor phases were recirculated continuously. A schematic diagram of this apparatus is

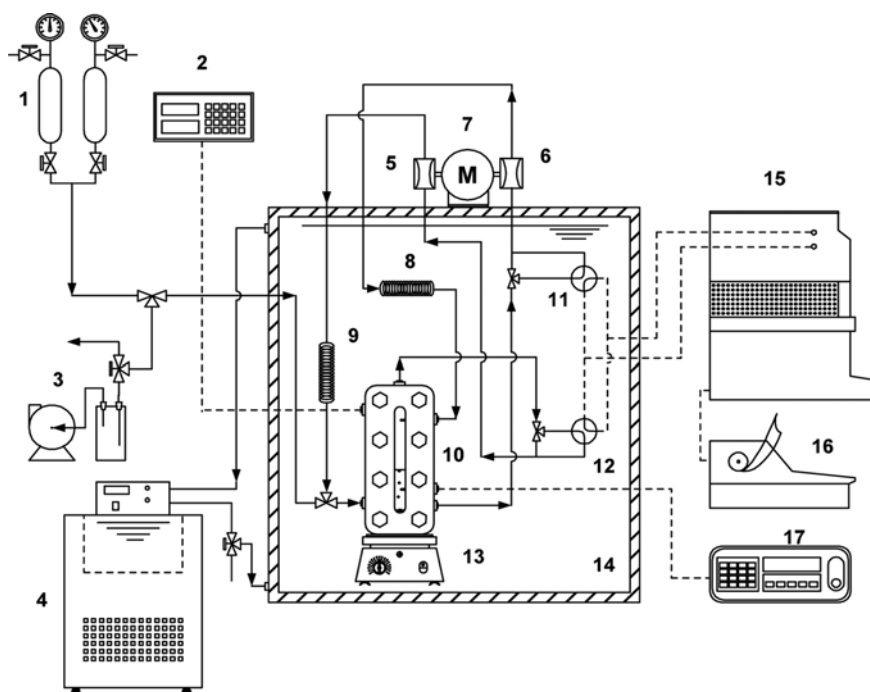
<sup>†</sup>To whom correspondence should be addressed.

E-mail: limjs@sogang.ac.kr

Copyright by The Korean Institute of Chemical Engineers.

**Table 1. Thermodynamic properties of components [18]**

Chemical	Chemical formula	$T_c/K$	$P_c/MPa$	$\omega$	Purities/mass %
Methanol (1)	$CH_3O$	513.00	7.954	0.5520	99.9
Cyclopentyl methyl ether (2)	$C_6H_{12}O$	576.00	3.807	0.2868	99.9

**Fig. 1. Schematic diagram of the experimental apparatus.**

- |                           |                                 |                                  |                           |
|---------------------------|---------------------------------|----------------------------------|---------------------------|
| 1. Sample reservoir       | 6. Liquid circulation pump      | 11. Liquid auto-sampler          | 16. Computing integrator  |
| 2. Pressure indicator     | 7. Electric motor               | 12. Vapor auto-sampler           | 17. Temperature indicator |
| 3. Vacuum pump            | 8. Liquid/liquid heat exchanger | 13. Magnetic stirrer             |                           |
| 4. Bath circulator        | 9. Gas/liquid heat exchanger    | 14. Bath containing heat carrier |                           |
| 5. Vapor circulation pump | 10. Equilibrium cell            | 15. Gas chromatograph            |                           |

illustrated in Fig. 1. Detailed explanations can be found in our previous work [11–15], and it is only briefly described here. The equilibrium cell was made of type-316 stainless steel with an inner volume of about 85 cm<sup>3</sup>, equipped with a pair of Pyrex glass windows in front and back side of the cell. The temperature in the cell was measured with a platinum resistance sensor connected to a digital temperature indicator (F250 precision thermometer, Automatic Systems Laboratories, Ltd., U.K.). They were calibrated by the NAMAS accredited calibration laboratory. The combined expanded uncertainty in temperature measurements is estimated to be within  $\pm 0.01$  K. The pressure was measured with a pressure transducer (model XPM60) and a digital pressure calibrator (PC106, Beamax, Finland). Pressure calibrations are traceable to National Standards (Center for Metrology and Accreditation Cert. No. M-95P077, 14.11.1995, M-M 730, 16.11.1995, and M-95P078, 16.11.1995), the calibrator uncertainty was  $\pm 0.0001$  MPa and the sensor uncertainty was  $\pm 0.0001$  MPa. Thus, the combined expanded uncertainty of the pressure measurement is estimated to be within  $\pm 0.0002$  MPa.

### 3. Experimental Procedure

Experiments to measure VLE data for the binary system of (MeOH (1)+CPME (2)) were performed by the following proce-

dures. First, the system was evacuated with a vacuum pump to remove all inert gases. A certain amount of CPME (less volatile than MeOH) was supplied to the cell, and then the temperature of the entire system was maintained constant by controlling the temperature of the water bath. When the system temperature reached the desired one, the vapor pressure of the pure CPME was measured. Then, a targeted amount of MeOH was introduced into the cell from a sample reservoir. Both the vapor and liquid phases were recirculated by a dual-head circulation pump until equilibrium was established. Two hours were sufficient to obtain thermal equilibrium between the mixture in the cell and the thermostatic bath as well as between the vapor and liquid phases. After phase equilibrium was reached, the equilibrium pressure of the binary system was measured, and then the equilibrium vapor and liquid compositions were measured by using the vapor and liquid sampling valves which were connected online to the GC. The GC was calibrated with the gas mixtures of known composition that were prepared gravimetrically. At least five analyses were performed for each phase, and the average values were considered to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we estimated an overall uncertainty of 0.002 in the measurements

of the mole fraction for both the liquid and the vapor phases.

## THERMODYNAMIC CORRELATION

### 1. Correlation with the PR-EoS using the W-S Mixing Rule

The experimental VLE data were correlated with the Peng-Robinson equation of state (PR-EoS) combined with the Wong-Sandler mixing rule [8]. The PR-EoS [7] is expressed by

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

$$a(T) = 0.457235 \frac{R^2 T_C^2}{P_C} \alpha(T) \quad (2)$$

$$b = 0.077796 \frac{RT_C}{P_C} \quad (3)$$

$$\alpha(T) = [1 + k(1 - \sqrt{T/T_C})]^2 \quad (4)$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where the parameter  $a$  is a function of temperature,  $b$  is constant,  $k$  is a constant characteristic of each substance,  $\omega$  is the acentric factor,  $P$  and  $P_C$  (MPa) are the absolute and critical pressures, respectively,  $T$  and  $T_C$  (K) is the absolute and critical temperature, respectively, and  $v_M$  is the molar volume.

The Wong-Sandler mixing rule [8] was used to obtain equation-of-state parameters for a mixture from those of the pure components. This mixing rule for a cubic equation is expressed by

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A_\infty^E/CRT - \sum_i x_i a_i/RTb_i)} \quad (6)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2} [(b - a/RT)_i + (b - a/RT)_j] (1 - k_{ij}) \quad (7)$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \quad (8)$$

where  $C$  is a numerical constant equal to  $\ln(\sqrt{2}-1)/\sqrt{2}$  for the Peng-Robinson EoS used in this work. The single adjustable parameter ( $k_{ij}$ ) for each binary pair is referred to the Wong-Sandler mixing rule parameter. Also,  $A_\infty^E$  is an excess Helmholtz free energy model at infinite pressure and it can be equated to a low-pressure excess Gibbs energy model [9]. The nonrandom two-liquid (NRTL) model [10] was used and is given in the following equations:

$$\frac{A_\infty^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_r x_r G_{ri}} \quad (9)$$

with

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad \text{and} \quad \tau_{ji} = (g_{ji} - g_{ii})/RT \quad (10)$$

where  $G_{ji}$  is the local composition factor for the NRTL model,  $\tau_{ji}$  is the NRTL model binary interaction parameter,  $\alpha_{ji}$  is a nonrandomness parameter, and  $R$  is the universal gas constant ( $8.3144 \text{ J K}^{-1} \text{ mol}^{-1}$ ). We set the non-randomness parameter,  $\alpha_{ij}$  equal to a fixed value of 0.3 for the binary mixture studied here. Pure component parameters  $T_C$ ,  $P_C$ , and  $\omega$  necessary for calculating the  $a$  and  $b$  values of the pure components of interest in this study, are shown in Table 1.

### 2. Azeotrope Point

If a gaseous phase and liquid phase are in equilibrium, the fundamental equation of phase equilibria can be expressed as follow [16];

$$P y_i \phi_i = x_i \gamma_i P_i^{sat} \quad (11)$$

where  $P_i^{sat}$  is the saturated vapor pressure,  $\gamma_i$  is the activity coefficient and  $\phi_i$  is the fugacity coefficient:

$$P = y_1 P + y_2 P = x_1 \gamma_1 P_1^{sat} + x_2 \gamma_2 P_2^{sat} \quad (12)$$

We assumed that the vapor phase behaves ideally, and NRTL model was used to obtain activity coefficients:

$$\ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (13)$$

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \quad (14)$$

Table 2. Comparison of the measured pure component vapor pressures with literature data [18]

Component	T/K	$P_{v,exp}$ /MPa	$P_{v,ref}$ /MPa	$^a \Delta P_v $	$ \Delta P_v /P_{v,exp}$
Methanol (1)	313.15	0.0354	0.0354	0.0000	0.0009
	323.15	0.0555	0.0556	0.0001	0.0016
	333.15	0.0845	0.0846	0.0001	0.0015
	343.15	0.1249	0.1254	0.0005	0.0038
	353.15	0.1815	0.1812	0.0003	0.0017
	Average			0.0003	0.0019
Cyclopentyl methyl ether (2)	313.15	0.0097	0.0097	0.0000	0.0000
	323.15	0.0149	0.0147	0.0001	0.0097
	333.15	0.0221	0.0218	0.0002	0.0106
	343.15	0.0321	0.0318	0.0003	0.0088
	353.15	0.0457	0.0455	0.0002	0.0044
	Average			0.0002	0.0067

$$^a|\Delta P_v| = |P_{v,exp} - P_{v,ref}|$$

$$\tau_{12} = \frac{g_{12} - g_{21}}{RT} \quad (15)$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12}) \quad (16)$$

where  $g_{12}$ ,  $g_{21}$  are the parameters of interaction between components 1 and 2, and  $\alpha_{12}$  is nonrandomness parameter and is set 0.3. Eq. (17) was obtained by combining Eqs. (12)-(14):

$$P = x_1 P_1^{sat} \exp \left[ (1-x_1)^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right] \right] + (1-x_1) P_2^{sat} \exp x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right] \quad (17)$$

or azeotropic composition we have

$$\frac{dP}{dx} = 0 \quad (18)$$

The azeotropic compositions and pressures can be obtained from Eqs. (17) and (18).

## RESULTS AND DISCUSSION

The isothermal VLE data for the MeOH (1)+CPME (2) binary systems were measured at five equally spaced temperatures from

**Table 3. Vapor-liquid equilibrium measurements for MeOH (1)+CPME (2) system**

Experimental data			PR EoS (W-S MR)			
$P_{exp}/$ MPa	$x_{1,exp}$	$y_{1,exp}$	$P_{cal}/$ MPa	$y_{1,cal}$	$^a \Delta P/P/$ (%)	$^b \Delta y/y/$ (%)
T=313.15 K						
0.0097	0.000	0.000	0.0097	0.000	0.000	0.000
0.0160	0.060	0.426	0.0160	0.423	0.000	0.704
0.0200	0.112	0.563	0.0200	0.558	0.000	0.888
0.0214	0.134	0.600	0.0214	0.594	0.000	1.000
0.0255	0.215	0.684	0.0255	0.678	0.000	0.877
0.0308	0.395	0.768	0.0307	0.765	0.325	0.391
0.0340	0.664	0.820	0.0344	0.830	1.176	1.220
0.0350	0.752	0.842	0.0351	0.849	0.286	0.831
0.0359	0.881	0.892	0.0356	0.889	0.836	0.336
0.0357	0.950	0.943	0.0354	0.933	0.840	1.060
0.0354	1.000	1.000	0.0354	1.000	0.000	0.000
T=323.15 K						
0.0149	0.000	0.000	0.0149	0.000	0.000	0.000
0.0221	0.038	0.352	0.0223	0.352	0.905	0.000
0.0310	0.096	0.556	0.0307	0.549	0.968	1.259
0.0405	0.207	0.685	0.0404	0.682	0.247	0.438
0.0458	0.323	0.737	0.0459	0.740	0.218	0.407
0.0492	0.435	0.769	0.0493	0.773	0.203	0.520
0.0528	0.627	0.814	0.0529	0.816	0.189	0.246
0.0544	0.742	0.851	0.0545	0.844	0.184	0.823
0.0558	0.858	0.890	0.0556	0.884	0.358	0.674
0.0562	0.950	0.946	0.0557	0.943	0.890	0.317
0.0555	1.000	1.000	0.0555	1.000	0.000	0.000

313.15 to 353.15 K at 10 K intervals. Comparisons of measured saturated vapor pressures ( $P_{v,exp}$ ) of pure MeOH and CPME with the literature values ( $P_{v,ref}$ ) from NIST Standard Reference Database 103b [18] are listed in Table 2. The result illustrates that the

**Table 3. Continued**

Experimental data			PR EoS (W-S MR)			
$P_{exp}/$ MPa	$x_{1,exp}$	$y_{1,exp}$	$P_{cal}/$ MPa	$y_{1,cal}$	$^a \Delta P/P/$ (%)	$^b \Delta y/y/$ (%)
T=333.15 K						
0.0221	0.000	0.000	0.0221	0.000	0.000	0.000
0.0353	0.048	0.399	0.0353	0.392	0.000	1.754
0.0473	0.111	0.571	0.0472	0.565	0.211	1.051
0.0618	0.244	0.702	0.0618	0.695	0.000	0.997
0.0720	0.421	0.768	0.0719	0.766	0.139	0.260
0.0775	0.580	0.811	0.0776	0.809	0.129	0.247
0.0800	0.672	0.834	0.0802	0.833	0.250	0.120
0.0836	0.824	0.880	0.0836	0.881	0.000	0.114
0.0850	0.887	0.905	0.0846	0.909	0.471	0.442
0.0851	0.947	0.945	0.0851	0.948	0.000	0.317
0.0845	1.000	1.000	0.0845	1.000	0.000	0.000
T=343.15 K						
0.0321	0.000	0.000	0.0321	0.000	0.000	0.000
0.0517	0.085	0.421	0.0516	0.416	0.193	1.188
0.0656	0.174	0.582	0.0659	0.578	0.457	0.687
0.0782	0.265	0.681	0.0782	0.674	0.000	1.028
0.0875	0.338	0.735	0.0869	0.728	0.686	0.952
0.1044	0.531	0.821	0.1051	0.821	0.670	0.000
0.1120	0.641	0.854	0.1121	0.855	0.089	0.117
0.1186	0.770	0.887	0.1182	0.890	0.337	0.338
0.1237	0.890	0.924	0.1230	0.932	0.566	0.866
0.1255	0.951	0.959	0.1251	0.964	0.319	0.521
0.1249	1.000	1.000	0.1249	1.000	0.000	0.000
T=353.15 K						
0.0457	0.000	0.000	0.0457	0.000	0.000	0.000
0.0602	0.057	0.284	0.0607	0.283	0.831	0.352
0.0745	0.112	0.454	0.0750	0.451	0.671	0.661
0.0917	0.174	0.580	0.0907	0.576	1.091	0.690
0.1154	0.275	0.709	0.1147	0.702	0.607	0.987
0.1390	0.401	0.790	0.1397	0.790	0.504	0.000
0.1630	0.586	0.853	0.1634	0.855	0.245	0.234
0.1742	0.752	0.883	0.1740	0.889	0.115	0.680
0.1780	0.839	0.906	0.1782	0.909	0.112	0.331
0.1827	0.950	0.954	0.1828	0.959	0.055	0.524
0.1815	1.000	1.000	0.1815	1.000	0.000	0.000

$$^a \Delta P/P (\%) = |(P_{exp} - P_{cal})/P_{exp}| \times 100$$

$$^b \Delta y/y (\%) = |(y_{exp} - y_{cal})/y_{exp}| \times 100$$

Combined expanded uncertainty of the temperature is within  $\pm 0.01$  K

Combined expanded uncertainty of the pressure is within  $\pm 0.001$  MPa

Overall uncertainty of liquid and vapor phase mole fraction is within 0.002

absolute deviation of vapor pressure ( $|\Delta P_v|$ ) between experimental and cited data was less than 0.0005 MPa for MeOH and 0.0003 MPa for CPME, and that the average relative deviation ( $\sum |\Delta P_v/P_{v,exp}|/N$ ) was 0.0019 and 0.0067 for MeOH and CPME, respectively. All values are low and acceptable.

The measured and calculated VLE data for the binary mixture MeOH (1)+CPME (2) at 313.15, 323.15, 333.15, 343.15, and 353.15 K are presented in Table 3. Before doing correlation, all the experimental VLE data were performed consistency tests for the verification of data. The resulting average absolute values of residuals  $\delta \ln (\gamma_1/\gamma_2)$  were 0.0325, 0.0520, 0.0578, 0.0579 and 0.0461 for 313.15, 323.15, 333.15, 343.15 and 353.15 K, respectively. All the values were relatively small and considered to be acceptable [17]. Table 3 contains the measured equilibrium pressure and mole fractions of the vapor and liquid phases for each temperature and the calculated pressure and mole fraction of the vapor composition. In addition,

**Table 4. Values of binary parameters and average relative deviations of P and y**

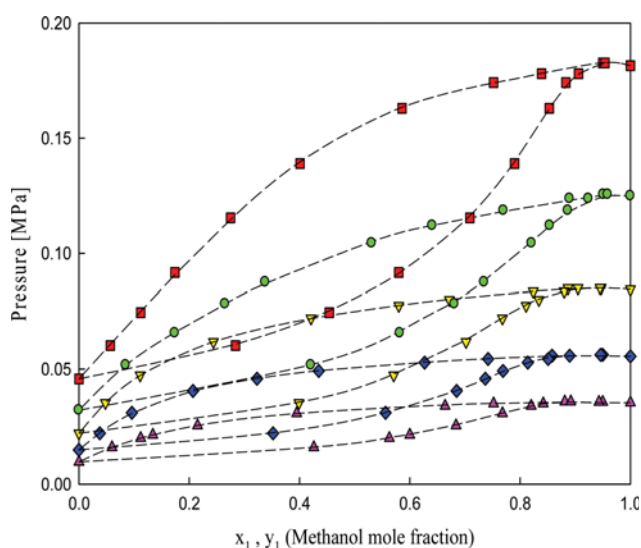
T/K	PR EoS (W-S MR)				
	$^a k_{12}$	$^b \tau_{12}$	$^b \tau_{21}$	$^c \text{ARD-P}$ (%)	$^d \text{ARD-y}$ (%)
313.15	-0.0782	1.0784	0.9014	0.315	0.664
323.15	0.0118	1.1853	2.1018	0.378	0.426
333.15	-0.1087	1.3101	2.4968	0.109	0.482
343.15	0.4780	2.1653	-1.0179	0.302	0.518
353.15	0.4858	-0.3549	0.7420	0.385	0.405
Overall				0.298	0.499

$^a k_{12}$  is dimensionless

$^b \text{NRTL: } \tau_{12} = (g_{12} - g_{22})/RT, \tau_{21} = (g_{21} - g_{11})/RT$

$^c \text{ARD-P} (\%) = (1/N) \sum |(P_{exp} - P_{cal})/P_{exp}| \times 100$

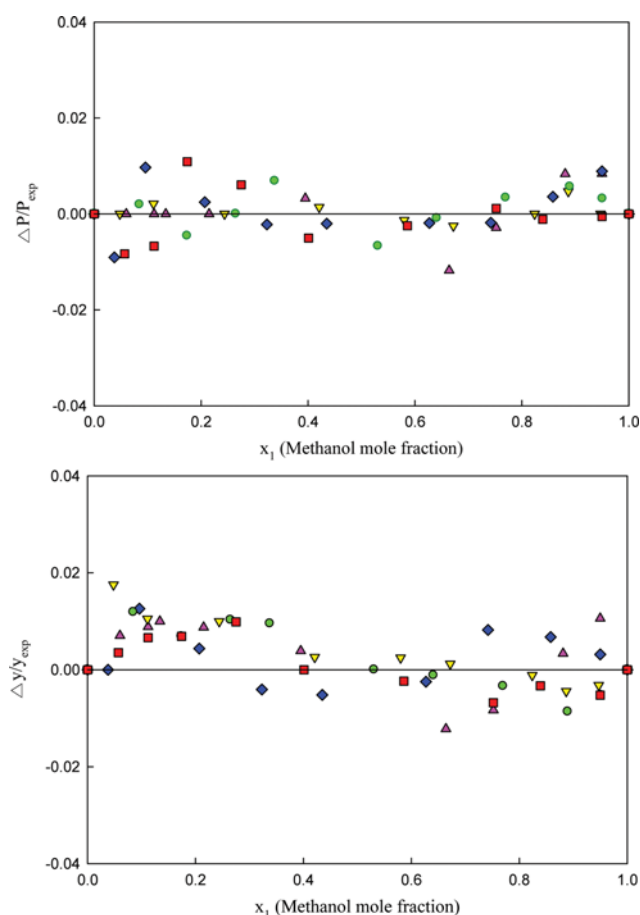
$^d \text{ARD-y} (\%) = (1/N) \sum |(y_{exp} - y_{cal})/y_{exp}| \times 100$



**Fig. 2.  $P$ - $x$ - $y$  diagram for the MeOH (1)+CPME (2) system. Experimental data at various temperatures: ▲, 313.15 K; ◆, 323.15 K; ▼, 333.15 K; ●, 343.15 K; ■, 353.15 K; ---, calculated with the PR EoS using W-S mixing rule.**

tion, relative deviations between measured and calculated pressures ( $|\Delta P/P_{exp}|$ ) and vapor compositions ( $|\Delta y/y_{exp}|$ ) are represented. The results of correlation including all the values of determined  $k_{12}$ , the NRTL parameters and , and the average relative deviation in pressure (ARD-P (%)) and vapor phase composition (ARD-y (%)) between calculated and experimental data for this binary mixture are reported in Table 4. The overall average values of ARD-P (%) and ARD-y (%) through the temperature range from 313.15 to 353.15 K were 0.298 and 0.499%, respectively. The  $P$ - $x$ - $y$  diagrams for this system are shown in Fig. 2, where the experimental data are presented as symbols and the dashed lines represent the calculated values by PR-EoS. Both experimental and calculated diagrams clearly illustrate that the mixture MeOH (1)+CPME (2) exhibits strong positive deviation from Raoult's law and it forms an azeotrope in the temperature ranges studied here.

Fig. 2 shows a comparison of the measured and calculated values with the PR-EoS using the W-S mixing rule for the binary system of MeOH (1)+CPME (2) at various temperatures 313.15, 323.15, 333.15, 343.15 and 353.15 K. As can be seen, the calculated values were in close accordance with the experimental data. In Fig. 3, the relative deviations of pressure ( $\Delta P/P_{exp}$ ) and the vapor phase compositions ( $\Delta y/y_{exp}$ ) for the PR-EoS using the W-S mixing rule are



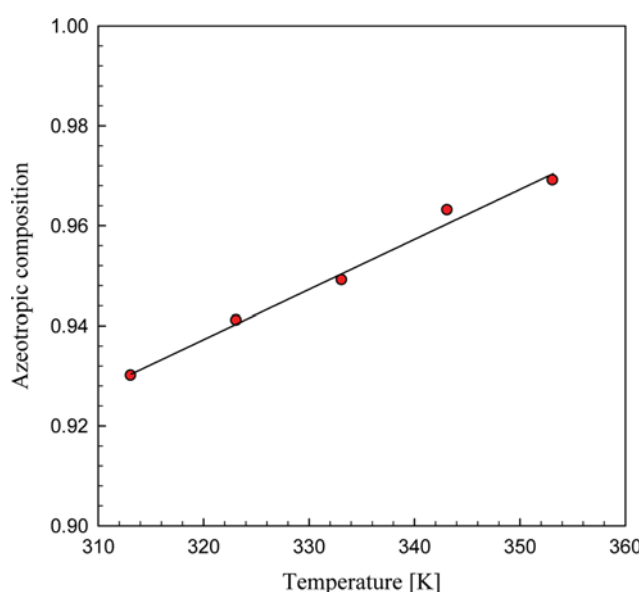
**Fig. 3. Deviation of pressure and vapor composition for the system of MeOH (1)+CPME (2) from the PR-EoS using WS mixing rule: ▲, 313.15 K; ◆, 323.15 K; ▼, 333.15 K; ●, 343.15 K; ■, 353.15 K.**

**Table 5. Azeotropic compositions and pressures of MeOH (1)+CPME (2) system**

T/K	Azeotropic composition					
	$x_{exp}$	$x_{cal}$	$P_{exp}/$ MPa	$P_{cal}/$ MPa	$\Delta x^a$	$\Delta P/P /$ (%)
313.15	0.930	0.938	0.0359	0.0356	0.008	0.836
323.15	0.941	0.943	0.0563	0.0559	0.002	0.710
333.15	0.949	0.953	0.0854	0.0852	0.004	0.234
343.15	0.963	0.971	0.1255	0.1253	0.008	0.159
353.15	0.969	0.968	0.1831	0.1830	0.001	0.055

$$^a \Delta x = |x_{exp} - x_{cal}|$$

$$^b \Delta|P/P| = \left| \frac{P_{exp} - P_{cal}}{P_{exp}} \right| \times 100$$

**Fig. 4. Azeotropic composition ( $x_{azeo}$ ) of MeOH(1)+CPME (2) system as a function of temperature. The equation of the fitting line is  $x_{azeo}=0.001 T/K+0.617$ .**

plotted with the liquid phase compositions ( $x_i$ ), point by point.

In Table 5, azeotropic compositions of MeOH (1)+CPME (2) mixture are reported, and plotted with temperature in Fig. 4. In the range of experimental temperature, azeotropic compositions showed linear relationship with temperature, and were correlated with temperature by the empirical equation:  $x_{azeo}=0.001 T/K+0.617$ .

## CONCLUSION

The isothermal VLE data for binary systems of methanol (1)+cyclopentyl methyl ether (2) were measured at five equal-spaced temperatures between 313.15 and 353.15 K using a circulation-type equilibrium apparatus. All the experimental VLE data were performed consistency tests for the verification of data. The resulting average absolute values of residuals  $\delta \ln (\gamma_1/\gamma_2)$  were 0.0325, 0.0520, 0.0578, 0.0579 and 0.0461 for 313.13, 323.15, 333.15, 343.15 and 353.15 K, respectively. All the values were relatively small and con-

sidered to be acceptable. The experimental data were correlated with the Peng-Robinson equation of state using the Wong-Sandler mixing rule combined with the NRTL excess Gibbs free energy model. As a result, this binary system showed strong positive deviation from Raoult's law and formed azeotropes at each temperature. In the range of experimental temperature, azeotropic compositions showed linear relationship and were correlated by the empirical equation:  $x_{azeo}=0.001 T/K+0.617$ . The calculated data with the PR-EoS using the Wong-Sandler mixing rule showed good agreement with the experimental data.

## NOMENCLATURE

- $a(T)$  : attraction parameter (temperature dependent) [MPa·cm<sup>6</sup>·mol<sup>-2</sup>]  
 $b$  : molecular volume parameter [cm<sup>3</sup>·mol<sup>-1</sup>]  
 $P, P_C$  : pressure, critical pressure [MPa]  
 $R$  : gas constant 8.3144 [J·mol<sup>-1</sup>·K<sup>-1</sup>]  
 $k_{ij}$  : interaction parameter  
 $T, T_C$  : absolute temperature, critical temperature [K]  
 $v_M$  : molar volume [cm<sup>3</sup>·mol<sup>-1</sup>]  
 $x$  : liquid mole fraction  
 $y$  : vapor mole fraction  
 $A_\infty^E$  : excess Helmholtz free energy at infinite pressure [J·mol<sup>-1</sup>]  
 $G, g$  : excess Gibbs energy [J·mol<sup>-1</sup>]

## Greek Letters

- $\omega$  : acentric factor  
 $\alpha$  : non-randomness parameter

## Subscripts

- $c$  : critical property  
 $cal$  : calculated  
 $exp$  : experimental  
 $i, j$  :  $i$  th,  $j$  th component of the mixture  
 $r$  : reduced property

## REFERENCES

1. K. Watanabe, N. Yamagiwa and Y. Torisawa, *Org. Process Res. Dev.*, **11**, 251 (2007).
2. K. Watanabe, *Molecules*, **18**, 3183 (2013).
3. R. K. Henderson, C. J. Gonzalez, D. J. C. Constable, S. R. Alston, G. G. A. Inglis, G. Fisher, J. Sherwood, S. P. Blinks and A. D. Curzons, *Green Chem.*, **13**, 854 (2011).
4. H. Zhang, *Fluid Phase Equilib.*, **403**, 23 (2015).
5. H. Zhang, *J. Chem. Eng. Data*, **60**, 1371 (2015).
6. I. Kin, G. Ohta, K. Teraishi and K. Watanabe, Process for Production of Cycloalkyl Alkyl Ethers, US Patent No. 8017813 (2011).
7. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
8. D. S. H. Wong and S. I. Sandler, *AIChE J.*, **38**, 671 (1992).
9. D. S. Abrams and J. M. Prausnitz, *AIChE J.*, **21**, 116 (1975).
10. H. Renon and J. M. Prausnitz, *AIChE J.*, **14**, 135 (1968).
11. W. J. Jeong and J. S. Lim, *Korean J. Chem. Eng.*, **33**, 248 (2016).
12. H. Cho and J. S. Lim, *Fluid Phase Equilib.*, **379**, 52 (2014).

13. H. Cho, J. H. Yim and J. S. Lim, *J. Supercrit. Fluids*, **81**, 7 (2013).
14. M. H. Lee, J. H. Yim and J. S. Lim, *Korean J. Chem. Eng.*, **29**, 1418 (2012).
15. S. A. Kim, J. H. Yim, H. S. Byun and J. S. Lim, *Korean J. Chem. Eng.*, **28**, 2324 (2011).
16. J. Y. Park, J. S. Lim and B. G. Lee, *Fluid Phase Equilib.*, **194**, 981 (2002).
17. J. M. Smith, H. C. Van Ness and M. M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 7<sup>th</sup> Ed., 441-444, McGraw-Hill, New York (2005).
18. M. Frenkel, R. D. Chirico, V. Diky, C. D. Muzny and A. F. Kazakov, NIST ThermoData Engine, NIST Standard Reference Database 103b-Pure Compounds, Binary Mixtures, and Chemical Reactions, Version 5.0, Standard Reference Data Program, National Institute of Standards and Technology, Gaithersburg, MD (2010).