

Measurement and correlation of the isothermal VLE data for the binary mixtures of cyclopentene (CPEN)+cyclopentyl methyl ether (CPME)

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Abstract—The isothermal vapor-liquid equilibrium data for the binary systems of cyclopentene (1)+cyclopentyl methyl ether (2) were measured at 313.15, 323.15, 333.15, 343.15 and 353.15 K using a dynamic-type equilibrium apparatus and online gas chromatography analysis. For all the measured VLE data consistency tests were performed for the verification of data using Barker's method and the ASPEN PLUS Area Test method. All the resulting average absolute values of residuals $[\delta \ln (\gamma_1/\gamma_2)]$ for Barker's method and D values for the ASPEN PLUS area test method were comparatively small. So, the VLE data reported in this study are considered to be acceptable. This binary system shows negative deviation from Raoult's law and does not exhibit azeotropic behavior at whole temperature ranges studied here. The measured data were correlated with the P-R EoS using the Wong-Sandler mixing rule. The overall average relative deviation of pressure (ARD- P (%)) between experimental and calculated values was 0.078% and that of vapor phase compositions (ARD- y (%)) was 0.452%.

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

INTRODUCTION

Ethers are widely used in organic chemistry and biochemistry. Ethers do not react with oxidizing agents, reducing agents, bases, dilute acids and active metals, so they are considered as stable chemical compounds. Therefore, they have been used as greener solvents in many organic reactions [1]. Among them, cyclopentyl methyl ether (CPME), recently, has received attraction in many chemical and pharmaceutical processes. CPME has many desirable properties, including a high boiling point, relatively low solubility in water, narrow explosive range, and stability under both acidic and basic conditions [2-5]. In addition, CPME does not present skin sensitization, genotoxicity and mutagenicity, and it is approved by the Toxic Substances Control Act (TSCA) and the European List of Notified Chemical Substances (ELINCS) [6-8]. CPME can be used as an alternative of other ether solvents such as tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), dioxane or 2-methyl tetrahydrofuran (2-MeTHF) [9,10]. Because of its advantages, CPME has been used as a green solvent in organic synthesis processes. Yet, CPME still has a problem associated with the low auto-ignition point (180 °C); however, this risk can be managed in most industrial facilities [2].

There are several methods for synthesis of CPME: a methylation reaction of cyclopentanol by dimethyl sulphate is the first, a two-step reaction between cyclopentanol and sodium hydroxide is the second, and an addition reaction of methanol (MeOH) to cyclopentene (CPEN) is the third [2,11]. The first and second reactions,

however, have some disadvantages because they use dimethyl sulfate and methyl iodide as a reactant, respectively, which are mutagenic and carcinogenic to the human body. However, the third reaction is favorable from an environmental point of view, because it does not contain harmful compounds such as dimethyl sulphate and methyl iodide. It has also industrial advantages due to its high productivity. This reaction includes methanol, CPEN, and acidic ion-exchange resin and is carried out at various temperatures and pressures. To determine the optimal reaction conditions and to design an optimum separation process, vapor liquid equilibrium (VLE) data between product and reactant materials related in this method, those are MeOH, CPEN, and CPME, are necessary. In this work, the isothermal VLE data for the binary mixture of CPEN (1)+CPME (2) was measured at five equally spaced temperatures between 313.15 and 353.15 K. This work was performed as the consecutive study of the measurement of isothermal VLE data for the binary mixture of MeOH (1)+CPME (2), reported in our previous work [12]. We correlated the measured VLE data by using the Peng-Robinson equation of state (PR-EoS) [13] with the Wong-Sandler mixing rule [14] combined with the nonrandom two-liquid (NRTL) excess Gibbs free energy model [15,16] and the relevant binary parameters were suggested.

EXPERIMENTAL

1. Chemicals

High-grade chemicals of CPEN and CPME were used for this study. CPEN was purchased from Tokyo Chemistry Industry CO., LTD. (JAPAN) (greater than 98.0 mass%) and CPME was purchased from Sigma Aldrich (USA) (greater than 99.9 mass%) We analyzed these two pure components with a gas chromatography (GC), and

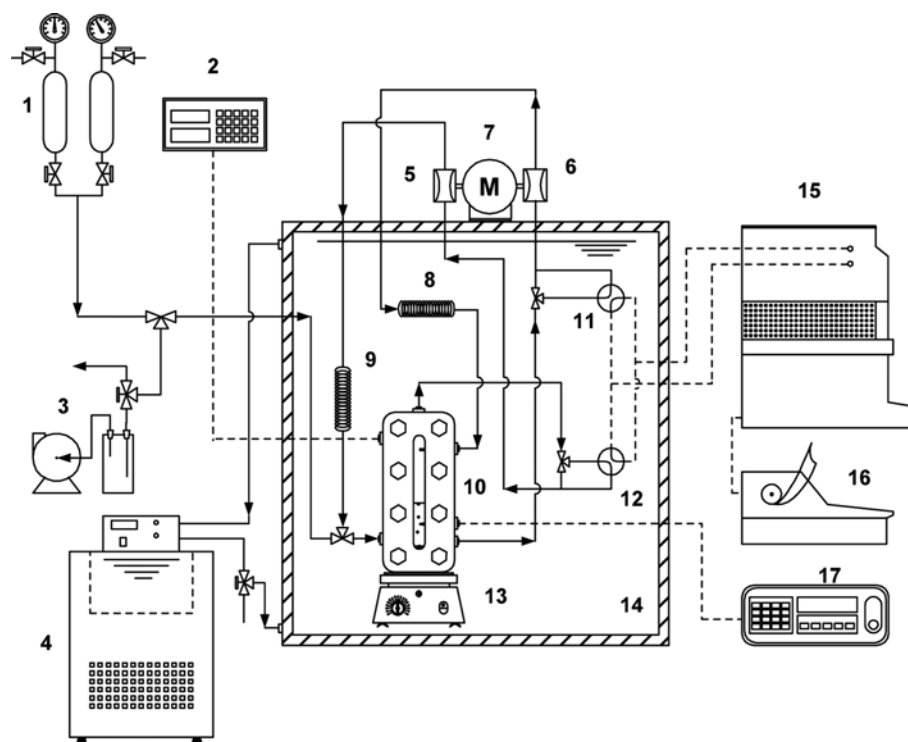
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Table 1. Thermodynamic properties of components

Chemical	Chemical formula	T_c/K [22]	P_c/MPa [22]	ω [22]	Purities/mass%
Cyclopentene (1)	C_5H_8	506.08	4.784	0.1995	98.0
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 | |

the resulting purity of cyclopentene was higher than 98.0 mass%, and CPME was higher than 99.9 mass%. So, we used these materials without any further purification. The purity and property data of both components are shown in Table 1.

2. Experimental Apparatus and Procedure

A schematic diagram of the vapor-liquid equilibrium apparatus used in this work is shown in Fig. 1, but a more detailed description can be obtained in our previous studies [12,17–21], and only brief explanation was made here. It is a dynamic-type isothermal equilibrium apparatus in which both vapor and liquid phases were continuously recirculated by a dual-head high pressure pump. The system was first evacuated to remove all the inert gases. The temperature of the equilibrium cell in the water bath was maintained by a circulator (Haake AC150, Thermo Fisher Scientific Ltd., USA). When the system reached a desired temperature, the vapor pressures of the pure components were measured. The system temperature was measured with a 1/8 inch (O.D) platinum-resistance sensor inserted into the equilibrium cell and connected to a digital temperature indicator (F250 precision thermometer, Automatic

Systems Laboratories, Ltd., UK). The temperature sensor and indicator were calibrated by the NAMAS accredited calibration laboratory. The combined expanded uncertainty in temperature measurements was estimated to be within ± 0.01 K. The pressure was measured with a pressure transducer (XPM60, Beamex, Finland) which was connected to a digital pressure calibrator (PC106, Beamex, 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 sensor uncertainty was ± 0.1 KPa and the calibrator uncertainty was ± 0.1 KPa. Thus, the combined expanded uncertainty of the pressure measurement was estimated to be within ± 0.2 KPa. After the vapor pressures of pure components were measured, a targeted amount of both components were introduced into the cell from a sample reservoir. After equilibrium was reached, the composition of the vapor and liquid samples was analyzed by a GC (YL6100, Young-Lin Instrument Co., Korea), which was connected online to the VLE cell. We estimated an overall uncertainty in measuring the mole fractions of both phases was 0.002.

Table 2. Comparison of the measured pure component vapor pressures with literature data [22]

Component	T/K	$P_{v,exp}/\text{MPa}$	$P_{v,ref}/\text{MPa}$	$^a \Delta P_v $	$ \Delta P_v /P_{v,exp}$
Cyclopentene	313.15	0.0880	0.0878	0.0002	0.0025
	323.15	0.1230	0.1225	0.0005	0.0038
	333.15	0.1672	0.1672	0.0000	0.0000
	343.15	0.2236	0.2236	0.0000	0.0002
	353.15	0.2926	0.2935	0.0009	0.0030
	Ave			0.0003	0.0019
Cyclopentyl methyl ether	313.15	0.0097	0.0097	0.0000	0.0000
	323.15	0.0149	0.0147	0.0002	0.0134
	333.15	0.0221	0.0218	0.0003	0.0136
	343.15	0.0321	0.0318	0.0003	0.0093
	353.15	0.0457	0.0455	0.0002	0.0044
	Ave			0.0002	0.0081

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

THERMODYNAMIC CORRELATION

The experimental VLE data were correlated with the PR-EoS [13], which is one of the most popular EoS for practical applications, combined with the Wong-Sandler mixing rules [14]. Detailed description can be found in our previous studies [12,17-21], and only briefly explained here.

The PR-EoS [13] is expressed as follows:

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

We calculated the binary mixture parameters from the following Wong-Sandler mixing rules [14]:

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A_\infty^E/CRT - \sum_i x_i a_i/RTb_i)} \quad (2)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2}[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \quad (3)$$

and

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \quad (4)$$

where C is equal to $\ln(\sqrt{2}-1)/\sqrt{2}$ for the Peng-Robinson EoS and k_{ij} is the adjustable parameter for each binary pair. A_∞^E , an excess Helmholtz free energy at infinite pressure, can be equated to a low-pressure excess Gibbs energy model [15]. In this study, the NRTL excess Gibbs energy model [16] was used as follows:

$$\frac{A_\infty^E}{RT} = \sum_i \sum_j x_i x_j \frac{G_{ji} \tau_{ji}}{\sum_r x_r G_{ri}} \quad (5)$$

The binary interaction parameters (k_{ij}) were obtained to minimize the following objective function in this study:

$$F = \sum_{i=1}^N \frac{|P_i^{exp} - P_i^{calc}|}{P_i^{exp}} \quad (6)$$

RESULTS AND DISCUSSION

The isothermal vapor-liquid equilibrium data for the binary system of CPEN (1)+CPME (2) were measured at five equally spaced temperatures from 313.15 to 353.15 K. In Table 2, the measured pure component vapor pressures ($P_{v,exp}$) of CPEN and CPME were compared with the literature data ($P_{v,ref}$) cited from the NIST Standard Reference Database 103b [22], which is considered to be reliable and consistent data. As can be seen in this table, the absolute deviations of vapor pressures ($|\Delta P_v|$) between the experimental and the reference data [22] were less than 0.9 KPa for CPEN and 0.3 KPa for CPME, and the average relative deviations ($\sum |\Delta P/P|/N$) were 0.0019 and 0.0081 for CPEN and CPME, respectively. All values are considered to be small and acceptable.

Fig. 2 shows an isothermal P - x - y diagrams and comparisons between the measured data (symbols) and calculated values by the PR-EoS using the W-S mixing rule (dashed lines) at various tem-

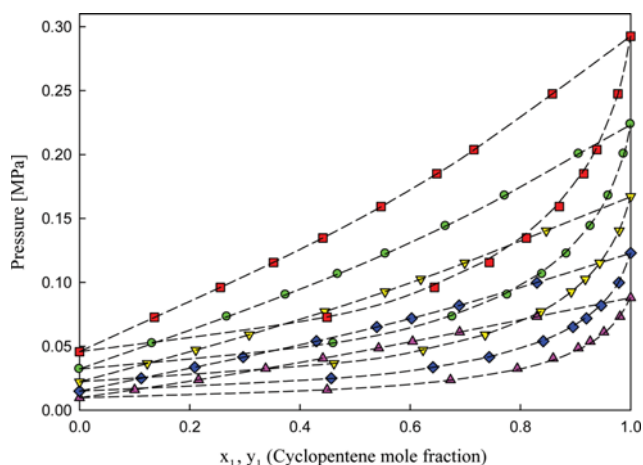


Fig. 2. P - x - y diagram for the CPEN (1)+CPME (2) system. Experimental data at various temperatures: \blacktriangle , 313.15 K; \blacklozenge , 323.15 K; \blacktriangledown , 333.15 K; \bullet , 343.15 K; \blacksquare , 353.15 K; $---$, calculated with the PR EoS using the W-S mixing rule.

peratures 313.15, 323.15, 333.15, 343.15 and 353.15 K. For the verification of our experimental data, we performed consistency tests before doing correlation using Barker's method [23] and the ASPEN PLUS program (area test method). As a result, the average absolute values of residuals $[\delta \ln (\gamma_1/\gamma_2)]$ for Barker's method were 0.0346, 0.0392, 0.0763, 0.0779 and 0.0805 and the D values for the ASPEN PLUS area test method were 2.853, 1.531, 4.171, 3.365 and 1.252

for 313.15, 323.15, 333.15, 343.15 and 353.15 K, respectively. For the consistency test of VLE data, it is known to be acceptable when the $[\delta \ln (\gamma_1/\gamma_2)]$ values are less than 0.1 for Barker's method [23] and the D values are less than 5 for the ASPEN PLUS area test method. All the values meet the criteria of the consistency tests and so they are considered to be acceptable. As represented in this diagram, the calculated values fit well with the experimental data, and the

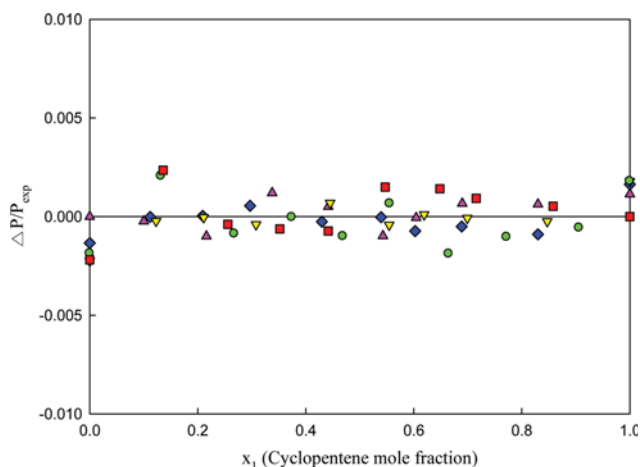


Fig. 3. Deviation of pressure for the system of CPEN (1)+CPME (2) from the PR-EoS using the WS mixing rule: \blacktriangle , 313.15 K; \blacklozenge , 323.15 K; \blacktriangledown , 333.15 K; \bullet , 343.15 K; \blacksquare , 353.15 K, where $\Delta P/P_{exp} = (P_{exp} - P_{cal})/P_{exp}$

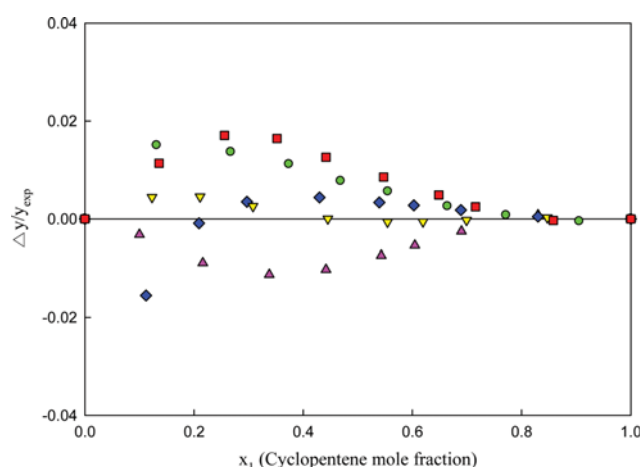


Fig. 4. Deviation of vapor composition for the system of CPEN (1)+CPME (2) from the PR-EoS using the WS mixing rule: \blacktriangle , 313.15 K; \blacklozenge , 323.15 K; \blacktriangledown , 333.15 K; \bullet , 343.15 K; \blacksquare , 353.15 K, where $\Delta y/y_{exp} = (y_{exp} - y_{cal})/y_{exp}$

Table 3. Vapor-liquid equilibrium measurements for CPEN (1)+CPME (2) system at 313.15 to 353.15 K

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	0.100	0.449	0.0160	0.451	0.023	0.318
0.0238	0.216	0.673	0.0238	0.679	0.099	0.888
0.0326	0.338	0.794	0.0326	0.803	0.120	1.124
0.0406	0.442	0.859	0.0405	0.868	0.051	1.024
0.0486	0.543	0.905	0.0487	0.912	0.098	0.739
0.0538	0.605	0.927	0.0538	0.932	0.006	0.537
0.0611	0.690	0.952	0.0610	0.954	0.066	0.250
0.0733	0.830	0.981	0.0732	0.980	0.063	0.081
0.0880	1.000	1.000	0.0879	1.000	0.114	0.000
T=323.15 K						
0.0149	0.000	0.000	0.0149	0.000	0.134	0.000
0.0250	0.112	0.457	0.0250	0.464	0.002	1.552
0.0336	0.209	0.641	0.0336	0.642	0.004	0.087
0.0415	0.297	0.743	0.0415	0.741	0.055	0.349
0.0539	0.430	0.842	0.0539	0.838	0.026	0.439
0.0650	0.539	0.896	0.0650	0.893	0.003	0.336
0.0718	0.603	0.920	0.0719	0.917	0.073	0.277
0.0818	0.689	0.947	0.0819	0.945	0.050	0.182
0.0998	0.830	0.979	0.0999	0.978	0.090	0.048
0.1230	1.000	1.000	0.1228	1.000	0.163	0.000

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	0.0222	0.000	0.226	0.000
0.0365	0.123	0.462	0.0365	0.460	0.023	0.443
0.0470	0.211	0.623	0.0470	0.621	0.004	0.453
0.0590	0.308	0.736	0.0590	0.734	0.040	0.257
0.0772	0.445	0.837	0.0771	0.837	0.069	0.003
0.0926	0.554	0.892	0.0927	0.893	0.043	0.063
0.1025	0.619	0.918	0.1025	0.918	0.010	0.057
0.1152	0.699	0.944	0.1152	0.944	0.008	0.025
0.1404	0.847	0.979	0.1404	0.979	0.024	0.024
0.1672	1.000	1.000	0.1669	1.000	0.179	0.000
T=343.15 K						
0.0321	0.000	0.000	0.0322	0.000	0.187	0.000
0.0522	0.132	0.461	0.0521	0.454	0.206	1.502
0.0730	0.268	0.677	0.0731	0.668	0.087	1.363
0.0902	0.374	0.777	0.0902	0.768	0.003	1.114
0.1063	0.469	0.840	0.1065	0.833	0.100	0.773
0.1223	0.555	0.884	0.1222	0.879	0.066	0.559
0.1439	0.665	0.928	0.1442	0.925	0.188	0.254
0.1677	0.772	0.960	0.1679	0.959	0.104	0.073
0.2004	0.906	0.988	0.2005	0.988	0.057	0.052
0.2236	1.000	1.000	0.2232	1.000	0.179	0.000
T=353.15 K						
0.0457	0.000	0.000	0.0458	0.000	0.219	0.000
0.0727	0.136	0.449	0.0725	0.444	0.236	1.138
0.0961	0.256	0.644	0.0961	0.633	0.039	1.707
0.1155	0.352	0.744	0.1156	0.731	0.062	1.642
0.1347	0.442	0.811	0.1348	0.801	0.073	1.261
0.1593	0.547	0.871	0.1590	0.863	0.150	0.855
0.1850	0.648	0.915	0.1847	0.911	0.141	0.489
0.2038	0.716	0.939	0.2037	0.937	0.093	0.249
0.2475	0.858	0.977	0.2474	0.977	0.052	0.032
0.2926	1.000	1.000	0.2926	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 ± 0.01 K

Combined expanded uncertainty of the pressure is within ± 0.2 KPa

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

system showed slightly negative deviation from Raoult's law. In Figs. 3 and 4, the relative deviations of experimental pressures ($\Delta P/P_{exp}$) and the vapor phase compositions ($\Delta y_1/y_{1,exp}$) from the PR-EoS using the W-S mixing rule were plotted with the liquid phase compositions (x_1).

The experimental vapor-liquid equilibrium data and the calculated data are illustrated in Table 3. This table lists the measured equilibrium pressures (P_{exp}) and mole fractions of both vapor ($y_{1,exp}$) and liquid ($x_{1,exp}$) phases along with the calculated equilibrium pressures (P_{cal}) and mole fractions of the vapor composition ($y_{1,cal}$) for each temperature. Additionally, the absolute values of the relative

deviations between measured and calculated pressures ($|\Delta P/P_{exp}|$) and vapor compositions ($|\Delta y/y|$) for each measured data point were represented.

The adjustable binary parameters (k_{ij}), the interaction parameters (τ_{ij}), the average relative deviations of the pressure (ARD-P (%)), and the average relative deviations of the vapor-phase composition (ARD-y (%)) are summarized in Table 4. The parameters did not show relevance each other, and the overall average values of ARD-P (%) and ARD-y (%) were 0.078% and 0.452%, respectively. From these results, it could be concluded that the PR-EoS using the W-S mixing rule model can provide a good correlation

Table 4. Values of binary parameters and average relative deviations of P and y for CPEN (1)+CPME (2) system

T/K	PR EoS (W-S)				
	^a k ₁₂	^b τ ₁₂	^b τ ₂₁	^c ARD-P (%)	^d ARD-y (%)
313.15	-0.0201	-0.0522	-0.0575	0.064	0.496
323.15	-0.2790	0.3512	0.1676	0.050	0.327
333.15	-0.1827	0.0593	0.2092	0.063	0.132
343.15	-0.3119	0.1308	0.4441	0.118	0.569
353.15	-0.3048	0.3594	0.2152	0.093	0.737
Overall				0.078	0.452

^ak₁₂ is dimensionless^bNRTL: τ₁₂=(g₁₂-g₂₂)/RT, τ₂₁=(g₂₁-g₁₁)/RT^cARD-P (%)=(1/N)Σ|(P_{exp}-P_{cal})/P_{exp}|×100^dARD-y (%)=(1/N)Σ|(y_{exp}-y_{cal})/y_{exp}|×100

for the binary system of CPEN (1)+CPME (2).

CONCLUSION

The isothermal vapor-liquid equilibrium data for the binary system of cyclopentene (CPEN)+cyclopentyl methyl ether (CPME) were studied in the temperature range from 313.15 to 353.15 K. The equilibrium data of the two-phase region were measured by using a continuous circulation-type equilibrium apparatus and analyzed by gas chromatography. The system showed slightly negative deviation from the Raoult's law and no azeotropic behavior at whole temperature ranges studied here. The phase equilibrium data were correlated with the PR-EoS combined with the Wong-Sandler mixing rules. The calculated results showed a relatively good agreement with the experimental data. So, it is concluded that this model could provide feasible data for predicting phase equilibrium behavior of this binary system.

NOMENCLATURE

a(T) : attraction parameter (temperature dependent) [MPa·cm⁶·mol⁻²]b : molecular volume parameter [cm³·mol⁻¹]P, P_C : pressure, critical pressure [MPa]R : gas constant 8.3144 [J·mol⁻¹·K⁻¹]k_{ij} : interaction parameterT, T_C : absolute temperature, critical temperature [K]v_M : molar volume [cm³·mol⁻¹]

x : liquid mole fraction

y : vapor mole fraction

A_∞^E : excess Helmholtz free energy at infinite pressure [J·mol⁻¹]G, g : excess Gibbs energy [J·mol⁻¹]

Greek Letters

ω : acentric factor

α : non-randomness parameter

Subscripts

c : critical property

cal : calculated

exp : experimental

i, j : i th, j th component of the mixture

r : reduced property

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