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Vapor–Liquid Equilibria for Propane (R290) + *n*-Butane (R600) at Various Temperatures

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Isothermal vapor–liquid equilibrium data for the binary mixture of propane (R290) + normal butane (R600) were measured at (273.15, 283.15, 293.15, 303.15, 313.15, and 323.15) K, respectively. The experiments were carried out using a continuous circulation-type equilibrium apparatus to measure temperature, pressure, and the compositions of the liquid and vapor phases. The experimental data were correlated with the Peng–Robinson equation of state (PR-EOS) using the Wong–Sandler mixing rule. The calculated results showed good agreement with experimental data. This system showed slightly negative deviation from Raoult's law and no azeotropes for all the temperature ranges studied here.

Introduction

In recent years, the utilization of light hydrocarbons such as propane, *n*-butane, isobutane, propylene, and so forth as effective refrigerants is believed to be an alternative solution for CFCs and HFCs because these hydrocarbons are environmentally benign chemicals (zero ODPs and near zero WGP) and have many outstanding properties. Moreover, they are common components of natural gas, so they are cheap and plentiful. Their flammability has caused some concerns, but all tests done so far indicated that they are quite safe in small applications such as domestic refrigeration and car air-conditioning, due to the very small amounts involved.^{1,2}

Generally, hydrocarbons can be used as refrigerants in the form of a single component or as a multicomponent mixture. In the case of the second form, vapor–liquid equilibrium data are very important basic information in evaluating the performance of refrigeration cycles and in determining the optimal composition of a mixture.² For the mixture of propane (R-290) + *n*-butane (R-600), vapor–liquid equilibrium (VLE) data were previously reported by some authors. However, most of the data were measured several decades ago and were not in detail.

In this work, isothermal VLE data for a binary mixture of propane + butane at six equally spaced temperatures between (273.15 and 323.15) 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 (PR-EOS)³ using the Wong–Sandler mixing rule⁴ combined with the NRTL excess Gibbs free energy model. In the range of experimental temperatures, the average absolute deviations of pressure and vapor phase compositions between experimental and calculated values were determined, and the relevant parameters were presented.

Experimental

Chemicals. High-quality chemicals of propane and butane were used for VLE measurement. Propane (R290) and butane (R600) were supplied by MG Industry (UK) with a guaranteed purity in mass fraction higher than 0.995. Furthermore, we also analyzed these two pure components with a gas chromatograph.

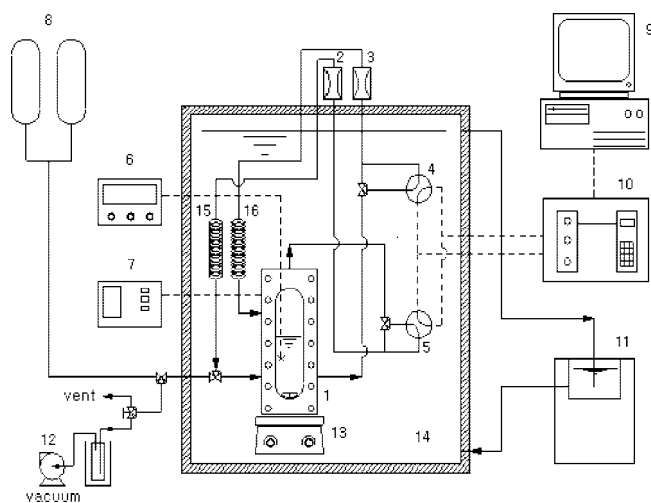


Figure 1. Schematic diagram of the experimental apparatus: 1, Equilibrium cell; 2, Vapor circulation pump; 3, Liquid circulation pump; 4, Liquid sample valve; 5, Vapor sample valve; 6, Temperature indicator; 7, Pressure indicator; 8, Sample reservoir; 9, Computer; 10, Gas chromatograph; 11, Circulator; 12, Vacuum pump; 13, Magnetic stirrer; 14, Constant temperature water bath; 15, Vapor phase heat exchanger; 16, Liquid phase heat exchanger.

The resulted mass fraction purities of propane and butane were higher than 0.999. So, they were used without any further purification.

Experimental Apparatus. A schematic diagram of the experimental apparatus for measuring the VLE is given in Figure 1. Since the vapor–liquid equilibrium apparatus used in this work was the same as that used in our previous work,^{5–8} only a brief description is given here. It was a circulation-type in which both liquid and vapor phases were recirculated continuously. The equilibrium cell was a type-316 stainless steel vessel within an inner volume of about 85 cm³. In its middle part, two Pyrex glass windows of 20 mm thickness were installed before and behind so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed by a back light during operation. A stirrer, rotated at variable speeds by

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an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases.

The temperature of the equilibrium cell in the water bath was maintained by a circulator from Jeio Tech, Korea. The temperature in the cell was measured with a platinum-resistance sensor and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems Laboratories, Ltd., United Kingdom. They were calibrated by the National Measurement Accreditation Service accredited calibration laboratory. The total uncertainty in temperature measurements is estimated to be within 0.01 K, including sensor uncertainty, 0.001 K, temperature resolution, 0.001 K, and measurement uncertainty, 0.001 K. The pressure was measured with a pressure transducer, model XPM60, and a digital pressure calibrator, model PC106, from 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 0.0005 MPa, the sensor uncertainty was 0.0001 MPa, and measurement uncertainty was 0.0001 MPa. Therefore, the total uncertainty of the pressure measurement is estimated to be within 0.001 MPa.

The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump (Milton Roy Company) to reach the equilibrium state rapidly in the cell. The composition of the phases was determined by means of a gas chromatograph (Gow-Mac model 550P) connected online to the VLE cell. The response of the thermal conductivity detector (TCD) was carefully calibrated using the mixture prepared gravimetrically and the gas chromatographs (GC) with a Porapak Q column from Alltech-Company. Data derived from gas chromatography were treated with a computer program (Autochro-WIN from Young-Lin Instrument Co., Ltd.). The uncertainty for the GC measurement and calibration is estimated to be within 0.001 in area fraction.

Experimental Procedures. Experiments to measure VLE data for the binary system of propane (1) + butane (2) at various temperatures were performed by the following procedures. At first, the system was evacuated to remove all inert gases. A certain amount of butane was supplied to the cell, and then the temperature of the entire system was held constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A certain amount of propane was introduced into the cell from a sample reservoir. The mixture in the cell was stirred continuously with the magnetic stirrer for over 1 h. Both the vapor and liquid phases were recirculated by the dual-head circulation pump until an equilibrium state was established. According to our experimental experiences, 1 h or more was sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath as well as the vapor and liquid phases. After equilibration, the pressure in the equilibrium cell was measured, and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to the vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least five analyses were performed for each phase, and the average values were considered to correspond to the equilibrium values. Considering the margin of error and the reproducibility of the GC, we generally estimated an overall

uncertainty in the measurements of the composition of 0.002 in mole fraction for both the liquid and the vapor phases.

Correlation

In this work, the experimental VLE data were correlated with the Peng–Robinson equation of state (PR-EOS).³

PR-EOS.

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

with

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c}\right) \alpha(T) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

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

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

where the parameter a is a function of temperature; b is constant; k is a constant characteristic of each substance; ω is the acentric factor; P (MPa) is the pressure; P_c (MPa) is the critical pressure; T (K) is the absolute temperature; T_c (K) is the critical temperature; and v_M is the molar volume.

The Wong–Sandler mixing rules⁴ were used in this work to obtain EOS parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

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

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 PR-EOS used in this work. The single adjustable parameter (k_{ij}) for each binary pair is referred to as the Wong–Sandler mixing rule parameter. Also, A_∞^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs energy model.⁹ In this study, we used the nonrandom two-liquid (NRTL) model¹⁰ given by

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

with

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

where

$$A_{ij} = (g_{ij} - g_{jj}) \quad (11)$$

The critical temperature (T_c), critical pressure (P_c), and acentric factor (ω) for both propane and butane that were used

Table 1. Characteristic Properties of the Chemicals (Critical Temperature T_c , Critical Pressure P_c , Acentric Factor ω) from Database REFPROP 6.01¹¹

component	chemical formula	molecular weight	T_c /K	P_c /MPa	ω
propane (1)	C ₃ H ₈	42.08	369.85	4.248	0.1524
butane (2)	C ₄ H ₁₀	58.12	425.16	3.796	0.1995

Table 2. Comparison of the Measured Pure Component Vapor Pressures P with Reference Vapor Pressures P_{REF} from the Database REFPROP 6.01¹¹

T /K	P /MPa	P_{REF} /MPa	ΔP^a /MPa	$^b \Delta P/P $
Butane				
273.15	0.104	0.103	0.001	0.010
283.15	0.150	0.149	0.001	0.007
293.15	0.208	0.208	0.000	0.000
303.15	0.284	0.284	0.000	0.000
313.15	0.378	0.379	-0.001	0.003
323.15	0.494	0.497	-0.003	0.006
Average value				0.004
Propane				
273.15	0.476	0.474	0.002	0.004
283.15	0.632	0.636	-0.004	0.006
293.15	0.833	0.836	-0.003	0.004
303.15	1.079	1.079	0.000	0.000
313.15	1.366	1.369	-0.003	0.002
323.15	1.709	1.713	-0.004	0.002
Average value				0.003

$$^a \Delta P = P - P_{\text{REF}}, \quad ^b |\Delta P/P| = |(P_{\text{exptl}} - P_{\text{cal}})/P_{\text{exptl}}|.$$

to calculate the parameters for the PR-EOS are provided in Table 1. A_{ij} and A_{ji} are the adjusted parameters from the NRTL model, and they are listed in Table 4. We also have set the nonrandomness parameter, α_{ij} , equal to a fixed value of 0.3 for all of the binary mixtures studied here. The parameter of the PR-EOS was obtained by minimizing the following objective function

$$\text{objective function} = \frac{1}{N} \sum_j \left[\left(\frac{P_{j,\text{exptl}} - P_{j,\text{cal}}}{P_{j,\text{exp}}} \right)^2 \right] \quad (12)$$

Results and Discussion

Table 2 shows the comparison of measured vapor pressures of pure propane and butane with those calculated from the database REFPROP 6.01,¹¹ which is considered to be reliable for the pure compounds considered and consistent with other literature data. As can be seen in this table, the average values of relative deviations of P ($\Delta P/P$) between measured and calculated values were 0.004 for propane and 0.003 for butane. The experimental data of isothermal VLE for the binary system of propane (1) + butane (2) are listed in Table 3. These tables list the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium.

Figure 2 shows the comparison of measured and calculated values with the PR-EOS for the binary system of propane (1) + butane (2) at various temperatures. As can be seen in this figure, this system showed slightly negative deviation from Raoult's law and no azeotropes for all the temperature ranges studied here. Also, the calculated values were well matched with experimental data. The interaction parameters of the binary mixtures for each isotherm, the binary parameters k_{ij} , and the absolute average relative deviations of pressure (AARD- P) and average absolute deviation of vapor-phase composition (AAD- y) between measured and calculated values are reported in Table 4. The binary parameter, k_{ij} , has been shown in Figure 3. These parameters are temperature dependent. The average values of AARD- P and AAD- y for all six temperatures were 0.004 and

Table 3. Vapor–Liquid Equilibrium Measurements for the Propane (1) + Butane (2) System at (273.15 to 323.15) K

Experimental data					
P /MPa	x_1	y_1	P /MPa	x_1	y_1
$T = 273.15$ K			$T = 283.15$ K		
0.103	0.000	0.000	0.149	0.000	0.000
0.126	0.060	0.172	0.180	0.065	0.182
0.144	0.113	0.300	0.216	0.146	0.322
0.188	0.228	0.504	0.260	0.242	0.492
0.203	0.270	0.563	0.374	0.476	0.717
0.302	0.543	0.773	0.413	0.552	0.774
0.337	0.638	0.839	0.456	0.643	0.838
0.370	0.727	0.887	0.509	0.745	0.893
0.395	0.792	0.915	0.546	0.819	0.925
0.442	0.912	0.970	0.578	0.882	0.956
0.450	0.933	0.978	0.601	0.931	0.974
0.462	0.963	0.989	0.620	0.965	0.988
0.476	1.000	1.000	0.633	1.000	1.000
$T = 293.15$ K			$T = 303.15$ K		
0.208	0.000	0.000	0.284	0.000	0.000
0.242	0.058	0.152	0.324	0.054	0.132
0.272	0.108	0.245	0.364	0.113	0.266
0.326	0.201	0.421	0.456	0.235	0.464
0.388	0.304	0.564	0.529	0.330	0.582
0.460	0.419	0.679	0.611	0.436	0.686
0.530	0.532	0.769	0.693	0.543	0.768
0.579	0.606	0.812	0.775	0.641	0.826
0.624	0.679	0.854	0.856	0.736	0.882
0.649	0.714	0.872	0.910	0.802	0.916
0.726	0.833	0.933	0.966	0.866	0.945
0.771	0.900	0.961	1.010	0.919	0.966
0.820	0.971	0.991	1.049	0.964	0.986
0.833	1.000	1.000	1.079	1.000	1.000
$T = 313.15$ K			$T = 323.15$ K		
0.378	0.000	0.000	0.493	0.000	0.000
0.429	0.063	0.164	0.557	0.054	0.139
0.510	0.148	0.323	0.618	0.112	0.254
0.574	0.217	0.432	0.743	0.226	0.432
0.683	0.335	0.580	0.878	0.334	0.563
0.777	0.434	0.671	0.971	0.426	0.651
0.882	0.540	0.754	1.101	0.535	0.732
0.988	0.640	0.819	1.222	0.634	0.804
1.077	0.729	0.872	1.324	0.714	0.853
1.151	0.802	0.907	1.448	0.808	0.906
1.212	0.859	0.938	1.564	0.895	0.950
1.269	0.911	0.963	1.602	0.922	0.964
1.323	0.959	0.983	1.643	0.951	0.978
1.366	1.000	1.000	1.709	1.000	1.000

Table 4. Optimal Values of the Binary Parameter k_{12} , Adjustable Parameters for the NRTL Model τ_{21} and τ_{12} , and Absolute Average Relative Deviations of P (AARD- P) and Average Absolute Deviation of y (AAD- y)

T /K	PR-EOS				
	$^a k_{12}$	$^b \tau_{21}$	$^b \tau_{12}$	$^c \text{AARD-}P$	$^d \text{AAD-}y$
273.15	0.1062	-0.3478	0.1987	0.005	0.027
283.15	0.0963	-0.3465	0.2071	0.004	0.024
293.15	0.0840	-0.3763	0.2809	0.003	0.023
303.15	0.0704	-0.3545	0.2855	0.002	0.016
313.15	0.0614	-0.3448	0.3096	0.003	0.011
323.15	0.0485	-0.3155	0.3248	0.005	0.008
Average values				0.004	0.018
270.00 ¹⁰	0.1726	0.9327	-1.1130	0.003	0.007
280.00 ¹⁰	0.1626	1.0431	-1.1746	0.001	0.003
290.00 ¹⁰	0.1117	-0.2181	0.0220	0.002	0.002
300.00 ¹⁰	0.6894	-1.6885	-0.5608	0.010	0.060
Average values				0.004	0.018

^a k_{12} is the interaction parameter. ^b τ_{ij} is adjustable parameters for the NRTL model, dimensionless. ^c $\text{AARD-}P = 1/N \sum |(P_{\text{exptl}} - P_{\text{cal}})/P_{\text{exptl}}|$. ^d $\text{AAD-}y = 1/N \sum |y_{\text{exptl}} - y_{\text{cal}}|$.

0.018 for the PR-EOS. To compare with reference data, we calculated Yohei's data¹² with the Peng–Robinson EOS includ-

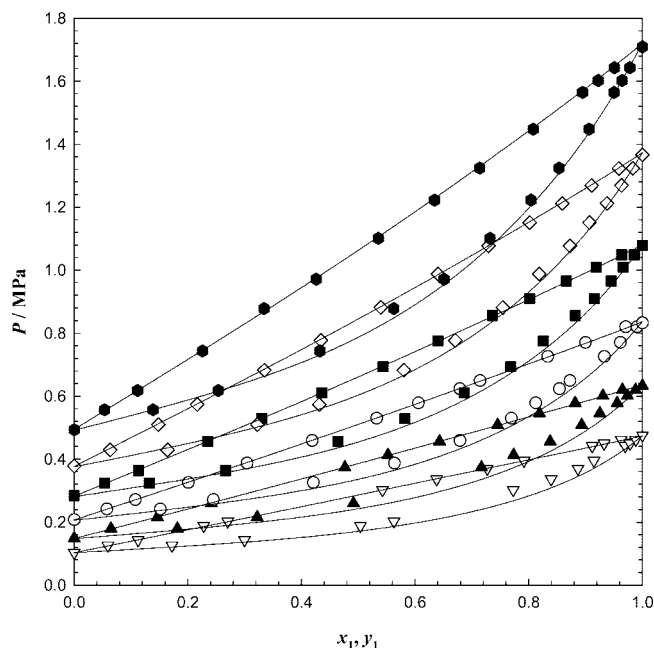


Figure 2. P – x – y diagram for propane (1) + butane (2). Experimental data at \square , 273.15 K; \blacktriangle , 283.15 K; \circ , 293.15 K; \blacksquare , 303.15 K; \diamond , 313.15 K; \bullet , 323.15 K; and —, calculated with the PR-EOS using W–S mixing.

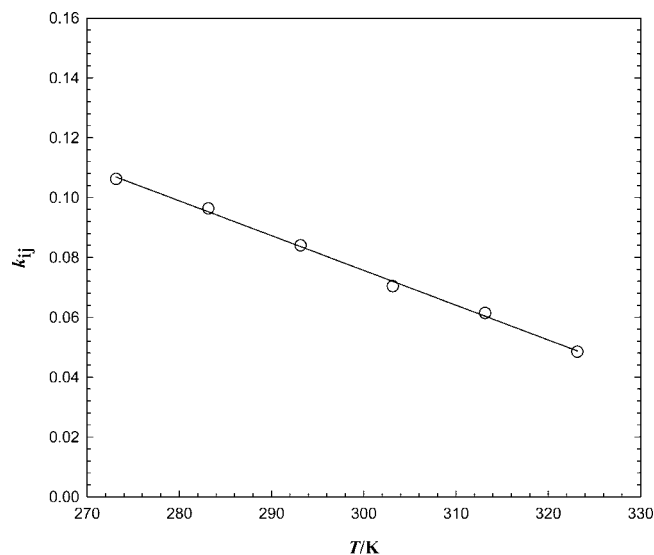


Figure 3. Parameter k_{ij} obtained by using the PR-EOS with the W–S mixing rule. The equation of the fitting line is $k_{ij} = -0.0012T/K + 0.4244$ ($323.15 \text{ K} \geq T \geq 273.15 \text{ K}$).

ing the Wong–Sandler mixing rule. Since Yohei’s data¹² have few experimental data compared with ours, it was difficult to

find any temperature dependency of the binary interaction factor. However, the values of AARD- P and AAD- y were good enough.

Conclusions

VLE data for binary systems of propane (1) + butane (2) were measured at five equally spaced temperatures between (273.15 and 323.15) K using a circulation-type equilibrium apparatus. The experimental data were correlated with the PR-EOS using the Wong–Sandler mixing rules. Calculated results with these equations have given satisfactory results in comparison with the experimental data. These results indicate that the Peng–Robinson equation of state with the Wong–Sandler mixing rules can be used to estimate pressures and compositions for the mixture of propane + n -butane in the range of experimental temperatures. This system exhibits no azeotropes.

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