[Regular Paper]

Measurements and Correlation of Saturated Vapor Pressure of a New Sulfur-free Odorant for Liquefied Petroleum Gas, 2-Hexyne, and Bubble Point Pressure for Three Binaries, Ehtane–2-Hexyne, Propane–2-Hexyne, and Butane–2-Hexyne

Tomoya Tsuji* [†1, †2], Peck Loo Kiew [†1], Hiroaki Matsukawa [†3], Taka-aki Hoshina [†4], and Katsuto Otake [†3]

[†1] Dept. of Chemical and Environmental Engineering, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, Kuala Lumpur 54100, MALAYSIA

[†2] Div. of Mechanical Engineering, Osaka Metropolitan University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, JAPAN

[†3] Dept. of Industrial Chemistry, Faculty of Engineering, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, JAPAN

[†4] Dept. of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, 1-2-1 Izumicho, Narashino, Chiba 275-8575, JAPAN

2-Hexyne is a potential sulfur-free odorant for liquefied petroleum gas (LPG). In this study, saturated vapor pressure of 2-hexyne at 273.14-313.14 K, and bubble point pressure for three binaries, ethane–2-hexyne, propane–2-hexyne and butane–2-hexyne were measured using a static apparatus at 273.15, 303.15 and 313.15 K. The attractive parameter in the Peng–Robinson (PR) equation of state was re-determined for 2-hexyne using the saturated vapor pressure data. The attractive parameters and the excluded volumes in the PR equation were also re-determined for ethane, propane and butane using the saturated vapor pressure and liquid density data. The binary parameters were evaluated by fitting the bubble point pressure data for the three binaries. Quaternary vapor-liquid equilibrium was estimated for 45.00 kg of LPG, with the mass ratio of ethane : propane : butane = 0.6000 : 97.07 : 1.700 containing 50.00 ppm of 2-hexyne, in a household LPG cylinder with inner volume of 117.50 L. The mole fraction of 2-hexyne was evaluated as 3.939×10^{-9} in the vapor phase at 273.15 K, and increased by 2.49 times and 3.40 times at 303.15 K and 313.15 K, respectively.

1. Introduction

Liquefied petroleum gas (LPG) is a mixture mainly consisting of propane and lesser amounts of other light hydrocarbons, such as ethane and butane, and is widely used as a transportation and heating fuel. The mixing ratio is used to control the bubble point pressure considering the seasonal outside temperature in Japan. According to the Japan LP Gas Association[1], the annual consumption of LPG was 12,857,000 tons in FY 2022, 46 % was household gas delivered in gas cylinders, 23 % was fuel for industrial boilers, 8.5 % was additives for city gas to increase the heat of combustion, and 4.6 % was fuel for taxis. Therefore, about 80 % of the total consumption of LPG is used as various fuels.

Sulfur compounds, such as dimethyl sulfide (DMS) and *t*-butyl mercaptane (TBM), are also added within 50 ppm by mass to LPG as odorants to give warning of any gas leakage. DMS and TBM are converted to toxic sulfur monoxide or dioxide (SO_x) after combustion, so alternative sulfur-free odorants for LPG have been proposed[2]~[6]. The normal boiling points of DMS and TBM are 310.48 K and 337.37 K[7], respectively, which are close to those of pentane and hexane, 309.22 K and 341.88 K[7]. However, these sulfur compounds, DMS and TBM, are strongly adsorbed on the metal catalysts required for fuel cells. Consequently, 1-pentyne and 2-hexyne have been proposed as new sulfur-free odorants[3],[4]. These compounds have strong smells similar to the rotten onion odor of DMS and TBM. Recently, residential fuel cell systems, named 'Ene・farm,' have been promoted by the Fuel Cell Commercialization Conference of Japan. The 'Ene・farm' project has developed small scale fuel cells suitable for

Table 1 Chemicals Used in This Study

	CAS No.	Supplier	Grade	Molecular weight M_w [-]	Purity [a]
Ethane	74-84-0	Takachiho Chemical Industrial Co., Ltd., Japan	Research	30.070	99.9 vol%
Propane	98-74-98	Takachiho Chemical Industrial Co., Ltd., Japan	Research	44.097	99.9 vol%
Butane	106-97-8	Takachiho Chemical Industrial Co., Ltd., Japan	Research	58.123	99.8 vol%
2-Hexyne	764-35-2	Sigma-Aidrich U.S.		82.145	99 mass%
Heptane	142-82-5	Wako Pure Chemical Industries, Ltd., Japan	Special	100.204	99.0 mass%

a) Stated by supplier.

installation in private residences which directly supply both heat and supplemental electric power, and the hydrogen fuel is obtained by the catalytic reforming reaction of city gas or LPG[8),9]. Therefore, these sulfur-free odorants are important to avoid the catalytic deactivation caused by adsorption of DMS and TBM on the metal catalysts.

Formulation of LPG containing an adequate amount of sulfur-free odorant requires knowledge of the bubble point pressure or the vapor-liquid equilibrium (VLE) for light hydrocarbon mixtures with sulfur-free odorants. In addition, the volume ratio of liquid must be less than 85 % in the LPG container such as a cylinder. The pressure-molar volume-temperature (PVT) relationship and saturated vapor pressure have been reported for 1-pentyne together with the bubble point pressure for propene–1-pentyne[6]. However, little data are available for 2-hexyne. A review of the thermodynamic properties for mixtures containing alkynes[10] included the bubble point pressure data for propane–2-hexyne only at 303.15 K, partly derived from our presentations[11]. The data were previously published together with the boiling point of 2-hexyne at atmospheric pressure[5]. The saturated vapor pressure for 2-hexyne at 273.15-363.15 K[12], and the VLE for 2-hexyne–octane at 263.15-343.15 K[13] were also reported. Excess molar enthalpy for 2-hexyne–tetracosane was reported at 349.15 K[14]. These are the known data for the binaries of gasoline, kerosene and additives with 2-hexyne.

In this study, the saturated vapor pressure for 2-hexyne were measured at 273.14-313.14 K, and the saturated vapor pressure for heptane at 273.15-313.15 K was also measured to verify the experimental data. The bubble point pressure was measured for the three binaries, ethane–2-hexyne, propane–2-hexane and butane–2-hexyne, at 273.15, 303.15 and 313.15 K. The experimental temperature, 313.15 K, corresponds to the highest temperature for the usage of household LPG. Two experimental temperatures, 273.15 K and 303.15 K, correspond to the references for winter and summer, respectively. The experimental data were correlated with the Peng-Robinson (PR)[15] equation of state which was modified to estimate the partition coefficients of 2-hexyne between the vapor and liquid phases. Then, the two constants in the PR equation were re-deter-

mined for ethane, propane and butane, by using the standard data of saturated liquid densities provided by the U.S. National Institute of Standards and Technology (NIST)[16], because the volume of the liquid should be accurately predicted in the gas cylinder. Only the attractive parameter in PR equation was also re-determined for 2-hexyne using the experimental data for the saturated vapor pressure.

2. Experimental Section

2. 1. Materials

Table 1 lists the chemicals used in this study. All chemicals were used as supplied without further purifications. However, 2-hexyne and heptane were used after degassing. Ethane, propane and butane were loaded in the sample cell by distillation from the cylinder to the sample cell as required. The degassing and distillation procedure will be described later.

2. 2. Measurement of Saturated Vapor and Bubble Point Pressure

The saturated vapor pressure was measured for 2-hexyne and heptane at 273.14-313.15 K. **Figure 1** shows a schematic diagram of the apparatus, as used in the previous study[5], and based on a static method[5),6),17)~19]. This apparatus was also used for the bubble point pressure measurements. The constant temperature bath (part 3 in **Fig. 1**) had an inner volume of 32 L (TRL-101FEZ, Thomas Co., Ltd., Tokyo), and filled with an aqueous solution of ethylene glycol (35 mass%). The built-in heater and refrigerator controlled the set temperature within 0.01 K. The sample cell (part 4) was made of Pyrex glass with an inner volume of about 36 cm³. The dimensions of the cell are also shown in **Fig. 1**. The previous study found the maximum safe pressure was up to 4.5 MPa at 298 K[5),6),17)~19], which is slightly lower than the critical pressure of ethane, 4.87976 MPa[20]. Consequently, another cell was employed for pressures higher than 4.5 MPa, which was made from a double-ended sample cylinder (304-HDF-2-40, Swagelok, Solon, U.S.) made of stainless steel 304. Stainless steel tube with a diameter of 1/4" was used to connect the valve and the cylinder, and the overall length of the cell was the same as that of the glass cell, 315 mm. The inner volume of the cell was about
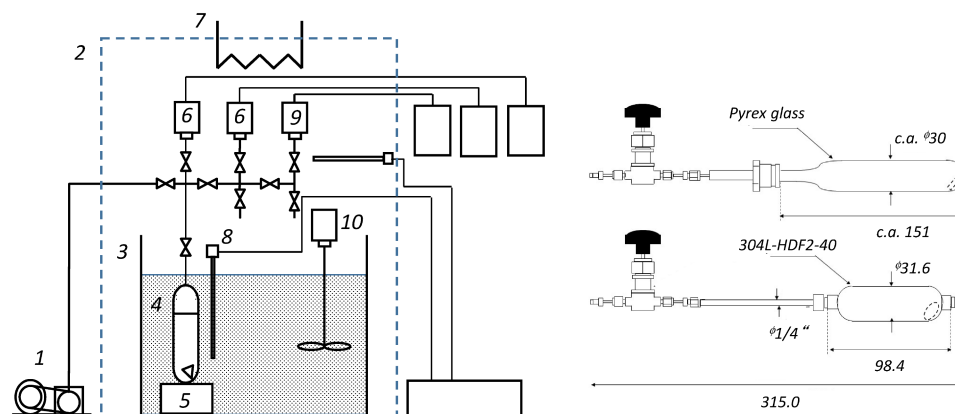
1: vacuum pump; 2: air chamber; 3: constant temperature bath; 4: sample cell; 5: water-proof magnetic stirrer; 6: pressure sensor (maximum capacity of 10 MPa and 1 MPa); 7: heater for air chamber; 8: thermistor thermometer; 9: absolute pressure sensor (maximum capacity of 200 kPa absolute); 10: agitator.

Fig. 1 Schematic Diagram of Static Apparatus and Dimension of Cells for Saturated Vapor and Bubble Point Pressure Measurements

40 cm^3, and the maximum safe pressure was 12.4 MPa up to 310 K. Two pressure sensors (part 6) were equipped (PG-100KU and PG-10KU, Kyowa Electrronic Instruments Co., Ltd., Tokyo) with maximum in the gauge pressure of 10 MPa and 1 MPa, respectively. An absolute pressure sensor (part 9) was also equipped (PHS-2KA, Kyowa Electronic Instruments Co., Ltd.) with a maximum pressure of 200 kPa. The sensors were connected to signal conditioners (WGA-800B-23AC, Kyowa Electronic Instruments Co., Ltd.). The resolutions were 0.01 MPa for PG-10KU and PHS-200KA, and 0.1 MPa for PG-100KU. The valves (SS-0RS2, Swagelok) were equipped with sensors to switch the pressure range: sensor PHS-200KA was used in the pressure range lower than 200 kPa, sensor PG-10KU in the range from 200 kPa to 1 MPa, and sensor PG-100KU in the range higher than 1 MPa. The temperature in the air chamber (part 2) was maintained at 313 K by a heater (part 7) to avoid the condensation of the vapor phase. The temperatures in the air chamber and the bath were accurately measured by two thermistor thermometers (part 8, D461, Techno Seven Co., Ltd., Yokohama, Japan). The mole fraction was determined by weighting method similar to that of the previous studies[5),6),17)〜19)]. A direct reading balance (AV1581, Exact Inc., Kamagaya, Japan) was used to evaluate the overall mole fraction of the binaries in the cell. The capacity and the sensitivity were 1 kg and 0.1 mg, respectively. The uncertainties for the pressure measurements were $u(p) = 0.4$, 2.5 and 15 kPa for sensors PHS-200KA, PG-10KU and PG-100KU, respectively. The uncertainty of the temperature was $u(T) = 0.05$ K. The uncertainties for the mass and the mole fraction were $u(w) = 2.0$ mg and $u(x_i) = 0.0004$, respectively.

The procedure for the sample preparation was previously described[5),6)]. 2-Hexyne or heptane was heated in the closed cell until the pressure reached 200 kPa. After ensuring the pressure or the corresponding temperature, one quarter of the sample was released into the air by opening the valve with the cell, then the valve was closed again. Thus, the degassed sample was prepared in the cell. For sample preparation for the bubble point pressure measurements, ethane, propane or butane was directly loaded into the cell from the cylinder. Then, the cell was cooled using methanol with added dry ice, so the sample gas was distilled and purified during loading. The mass of the cell was measured with the direct reading balance after loading. Subsequently, 2-hexyne was loaded into the cell through an HPLC pump (LC-6A, Shimadzu Corp., Kyoto, Japan). Prior to the loading, dissolved gas was removed from the 2-hexyne by the same procedure used for the saturated vapor pressure measurements. The mass was measured again to determine the overall mole fraction. The cell was then placed in the constant temperature bath. The mole fraction in the liquid phase was assumed to be the overall mole fraction because the density of the vapor was far lower than that of the liquid phase.

2. 3. Equation of State, α-Function, β-Function and Mixing Rules

Experimental data were correlated with the PR equation of state with some modifications (mod. PR):

$$p = \frac{RT}{v - b_c\beta} - \frac{a_c\alpha}{v^2 + 2b_c\beta v - (b_c\beta)^2} \qquad (1)$$

where the two parameters, a_c and b_c, are given by applying the critical condition for pure compound, $(\partial p/\partial v)|_{T_c} = (\partial^2 p/\partial v^2)|_{T_c} = 0$ [15),20)]. The temperature dependences, α- and β-functions, in the original PR equation[15)] are given by:

Table 2 Critical Properties Used for Estimating Parameters in the PR Equation

	Critical temperature T_c [K]	Critical pressure p_c [-]	Acentric factor ω [-]	Parameter by Stryjek and Vera κ_1 [-]
Ethane [a]	305.43	4.87976	0.09781	0.02669
Propane [a]	369.82	4.24953	0.15416	0.03136
Butane [a]	425.16	3.79661	0.20096	0.03443
2-Hexyne [b]	552.99	3.7454	0.22962	-
Heptane [a]	540.10	2.73575	0.350022	

a) Stryjek and Vara[20]. b) Tsuji et al.[5]
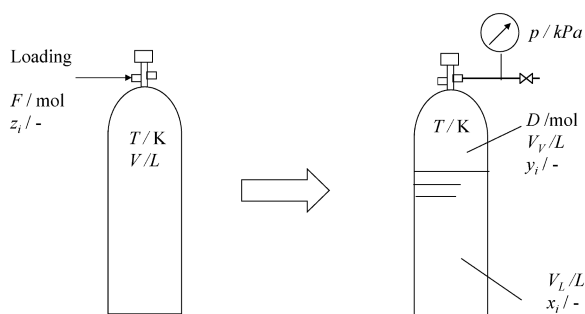
Fig. 2 Flush Calculation for a Household LPG Cylinder

$$\alpha = \alpha_{PR}\left(T/T_c, \omega\right) \tag{2}$$

$$\beta = 1 \tag{3}$$

whereas those of Stryjek and Vera[20] are given by:

$$\alpha = \alpha_{SV}\left(T/T_c, \omega, \kappa_1\right) \tag{4}$$

$$\beta = 1 \tag{3}$$

where κ_1 is an additional parameter. Considering the actual use conditions of household LPG cylinders, the liquid volume should be precisely evaluated in the cylinder. The PR equation is well known to not provide the liquid density with high accuracy. So, the following modifications were proposed for ethane, propane and butane:

$$\alpha = \alpha_{SV}\left[\alpha_0 + \alpha_1\left(1 - \frac{T}{T_c}\right) + \alpha_2\left(1 - \frac{T}{T_c}\right)^2\right]$$
$$(T_c > T) \tag{5}$$

$$\alpha = \alpha_{SV}\alpha_0 \quad (T \geq T_c) \tag{6}$$

$$\beta = \beta_0 + \beta_1\left(1 - \frac{T}{T_c}\right) + \beta_2\left(1 - \frac{T}{T_c}\right)^2 \quad (T_c > T) \tag{7}$$

$$\beta = \beta_0 \quad (T \geq T_c) \tag{8}$$

where α_0, α_1, α_2, β_0, β_1 and β_2 were determined by the experimental data or the standard data of saturated vapor pressure and liquid density[16]. Although the methods are similar to those reported[21], Eqs. (5) to (8) were newly proposed in this study. On the other hand, for 2-hexyne and heptane, only α_0, α_1 and α_2 were de-

termined by using the experimental data of saturated vapor pressure:

$$\alpha = \alpha_{PR}\left[\alpha_0 + \alpha_1\left(1 - \frac{T}{T_c}\right) + \alpha_2\left(1 - \frac{T}{T_c}\right)^2\right]$$
$$(T_c > T) \tag{5'}$$

$$\alpha = \alpha_{PR}\alpha_0 \quad (T \geq T_c) \tag{6'}$$

$$\beta = 1 \tag{3}$$

The detailed determinations for α_0, α_1, α_2, β_0, β_1 and β_2 are described later. **Table 2** lists the critical properties used for evaluating the parameters in the PR equation[15],[20]. Various values for the critical temperature and pressure have been reported for 2-hexyne[5],[7],[10]. In this study, $T_c = 552.99$ K, $p_c = 3.7455$ MPa and $\omega = 0.22962$ were employed for 2-hexyne. In the previous study[5], the bubble point pressure data were correlated by mixing rules with simple function forms. So, the following mixing rules were employed:

$$\alpha_c\alpha = \sum_i \sum_j x_i x_j (1 - k_{ij})\left[(\alpha_{c,i}\alpha_i)(\alpha_{c,j}\alpha_j)\right]^{1/2} \tag{9}$$

$$b_c\beta = \sum_i x_i (b_{c,i}\beta_i) \tag{10}$$

where k_{ij} is a binary interaction parameter, and its value was evaluated by fitting the experimental data to the minimum by the following objective function:

$$O.F. = \sum\left[x_{i,\exp(j)} - x_{i,\text{calc}(j)}\right] \quad (i = 1, 2, 3) \tag{11}$$

where $x_{i,\exp(j)}$ and $x_{i,\text{calc}(j)}$ are the j-th experimental and calculated values of x_i, respectively. $i = 1, 2$ and 3 indicate ethane, propane and butane, respectively. Also, $i = 4$ indicates 2-hexyne.

2. 4. Calculation of Partition Coefficient

The liquid volume in the cylinder and the partition coefficient of 2-hexyne were evaluated by calculating the quaternary VLE in an LPG cylinder. **Figure 2** shows an image of the calculation procedure. A quaternary mixture, consisting of ethane, propane and butane with a small amount of 2-hexyne, was loaded into the cylinder with the inner volume of V. Then, the total number of moles was set to be F, and the mole fraction of each component was z_i. The loaded LPG would be separated into two phases, liquid and vapor,

Table 3 Saturated Vapor Pressure 2-Hexyne and Heptane

Measured		Standard [a]		mod. PR equation	
Temperature [b] T [K]	Saturated vapor pressure [c] p^s [kPa]	Saturated vapor pressure p^s_{NIST} [kPa]	ARD $|\delta p^s_{NIST}|$ [%]	Saturated vapor pressure p^s_{cal} [kPa]	ARD $|\delta p^s|$ [%]
2-Hexyne					
273.14	2.75			2.74	0.311
274.18	2.99			2.90	2.866
276.19	3.31			3.25	1.936
278.05	3.65			3.59	1.593
283.16	4.78			4.71	1.529
288.15	6.15			6.06	1.391
293.25	7.64			7.78	1.798
298.15	9.73			9.79	0.585
303.14	12.40			12.26	1.131
308.27	15.56			15.32	1.540
313.14	19.00			18.78	1.138
				(average)	1.438
Heptane					
273.15	1.57	1.53	2.866	1.56	0.692
293.15	4.85	4.73	2.482	4.75	2.135
298.10	6.20	6.08	1.860	6.09	1.835
303.25	7.69	7.83	1.756	7.80	1.479
308.21	9.64	9.87	2.435	9.82	1.904
313.15	12.1	12.34	1.983	12.25	1.240
		(average)	2.230	(average)	1.548

a) Reported by NIST[16].   b) $u(T) = 0.05$ K.   c) Measured by PHS-200KA, $u(p) = 0.40$ kPa.

with the mole fractions of x_i and y_i ($i = 1, 2, 3$ and 4), respectively.   Then, the number of moles was set to be D in the vapor phase.   The mass balance was given by:

$$z_i F = x_i(F - D) + y_i D \tag{12}$$

The partition coefficient was given by:

$$K_i = \frac{y_i}{x_i} \tag{13}$$

The partition coefficient is sometimes called the K-value in VLE.   From Eqs. (12) and (13), the mole fractions in the liquid and vapor phases were given by:

$$x_i = \frac{z_i}{1 + (K_i - 1)(D/F)} \tag{14}$$

$$y_i = K_i x_i \tag{15}$$

At given temperature and pressure, the mole fractions, x_i and y_i, can be calculated by finding (D/F) to satisfy the following constraint conditions:

$$\sum_i x_i = 1.0000 \tag{16}$$

$$\sum_i y_i = 1.0000 \tag{17}$$

In this study, using the molar volume for the liquid and vapor phases, v_L and v_V, the final value of the pressure was determined to satisfy the following other constraint conditions:

$$F\left(1 - \frac{D}{F}\right)v_L + Dv_V = V_L + V_V = V \tag{18}$$

As shown in Eqs. (12)-(18), the calculation procedure was based on a flush VLE calculation where the sum of the liquid and the vapor volumes equaled the inner volume of the cylinder.

3. Experimental Results

3. 1. Saturated Vapor Pressure for Ethane, Butane, 2-Hexyne and Heptane

Firstly, the saturated vapor pressure was measured for heptane to verify the experimental data, as shown in **Table 3** and **Fig. 3**.   The standard saturated vapor pressure data, provided by NIST[16], are also listed in **Table 3**.   The relative deviation (RD) and the absolute relative deviation (ARD) were calculated by:

$$\delta p^s_{NIST} = \frac{p^s_{NIST} - p^s}{p^s} \times 100 \tag{19}$$

$$\left|\delta p^s_{NIST}\right| = \frac{\left|p^s_{NIST} - p^s\right|}{p^s} \times 100 \tag{20}$$

The ARDs are shown in **Table 3**, and the RDs in **Fig. 4**.   The average ARD was 2.230 % for the whole range of the experimental temperature.   Average ARD lower than 0.3 % is generally required for the saturated vapor pressure measurements.   The average ARD did not attain this value.   However, the experimental data was thought to be acceptable because measurements were obtained using the absolute pressure sensor with uncertainty, $u(p) = 0.4$ kPa.
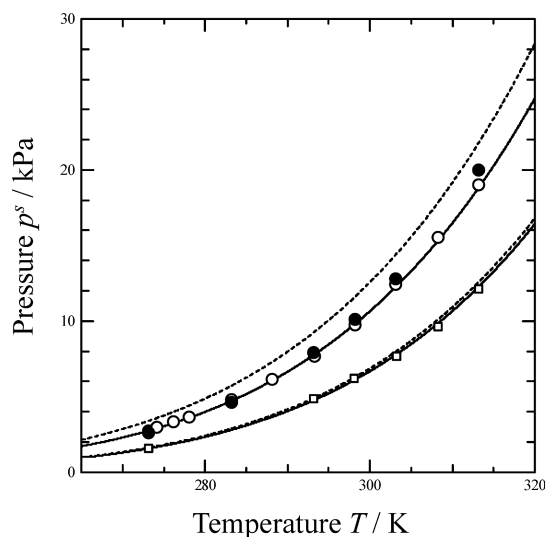
(○): this study, 2-hexyne; (●): Negadi et al.[12], 2-hexyne; (□): this study, heptane; (------): PR equation[15]; (——): mod. PR equation.
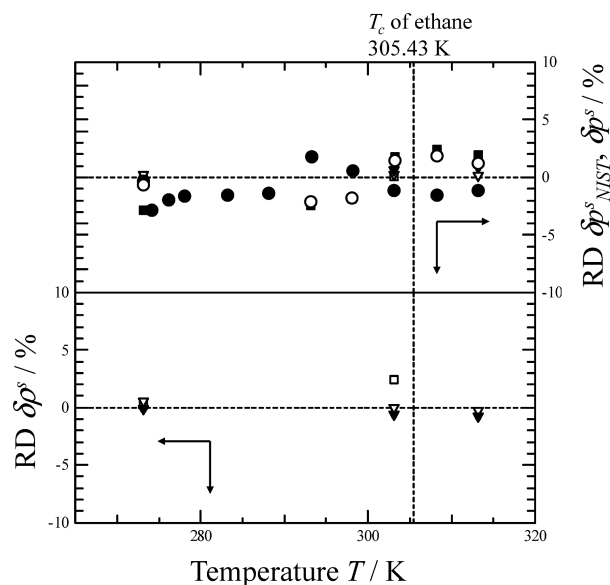
Fig. 3 Saturated Vapor Pressure of 2-Hexyne and Heptane

(■): heptane for NIST standard data[16]; (□): ethane for mod. PR equation; (▽): NIST standard data of propane[16] for mod. PR equation; (▼): butane for mod. PR equation; (●): 2-hexyne for mod. PR equation; (○): heptane for mod. PR equation.

Fig. 4 RDs of Saturated Vapor Pressure and Saturated Liquid Density

Table 3 lists the experimental data of the saturated vapor pressure of 2-hexyne, and Fig. 3 compares the experimental and previous data[12]. In the previous study[5], the boiling point was reported to be 357.59 K at atmospheric pressure, 101.11 kPa. Saturated vapor pressure was also measured up to 363.15 K[12]. The comparison is shown only in the temperature range lower than 320 K. The experimental data agreed well with previous data[12]. Although the average ARD for heptane was not always acceptable, the reliability was confirmed by the experimental data for 2-hexyne.

3. 2. Bubble Point Pressures for Three Binaries, Ethane (1)–2-Hexyne (4), Propane (2)–2-Hexyne (4) and Butane (3)–2-Hexyne (4)

Table 4 lists the experimental data of the bubble point pressure for ethane (1)–2-hexyne (4), propane (2)–2-hexyne (4) and butane (3)–2-hexyne (4) at 273.15, 303.15 and 313.15 K. The data, at $x_i = 1.0000$ ($i = 1$ and 3), are also listed in the Table 4. The pressure, at $x_1 = 1.0000$ and 303.15 K, was higher than 4.5 MPa. Therefore, the stainless steel cell was employed for the measurements. Similarly, the sample, at $x_1 = 0.8388$ for ethane (2)–2-hexyne (4), tended to exceed 4.5 MPa at 313.15 K. Then, the measurements were carried out only at 273.15 K and 303.15 K. The sample, at $x_2 = 0.2982$ for propane (2)–2-hexyne (4), was found to leak from the cell after measurement at 273.15 K. Then, a sample at $x_2 = 0.3343$ was newly prepared and the bubble point pressure measured at 303.15 K and 313.15 K. Similar re-preparations were also carried out for the samples at $x_3 = 0.3967$, 0.5227, 0.7276 and 0.7820 for butane (3)–2-hexyne (4).

Figure 5 compares the bubble point pressure for the three binaries. The pressure ranges of the vertical axis were different for the three binaries, so the dashed lines, colored with red, are drawn to indicate the corresponding pressure. The data, shown in Fig. 5, include the saturated vapor pressure for 2-hexyne at 273.14, 303.14 and 313.14 K. Figure 5 also shows the previous data for propane (2)–2-hexyne (4) at 303.15 K[5]. The experimental data obtained in this study agreed well with the previous data at 303.15 K. Although the saturated vapor pressure was not measured for propane, the reliability of the data could be verified using the previous data. Similar tendencies were observed in the mole fraction dependence of the bubble point pressures. The bubble point pressure which approximately followed Henry's Law was observed for the three binaries at 313.15 K. For the mole fraction close to $x_i = 0.0000$ ($i = 1$, 2 and 3) at 273.15 K and 303.15 K, the dependences seemed to be slightly different between the three binaries. The results suggested that the interactions in ethane (2)–2-hexyne (4) are not different from those in propane (2)–2-hexyne (4) and butane (3)–2-hexyne (4) in the high temperature range.

3. 3. Determination of the α-Function and β-Function

The parameters, α_0, α_1, α_2, β_0, β_1 and β_2 were determined for ethane and butane from the experimental pressure at $x_i = 0.0000$ ($i = 1$ and 3) and the saturated liquid densities cited from standard data of NIST[16], and for propane from the saturated vapor pressure and the

Table 4 Bubble Point Pressure for Ethane (1)–2-Hexyne (4), Propane (2)–2-Hexyne (4) and Butane (3)–2-Hexyne (4)

Measured			mod. PR equation			
Temperature [a]	Mole fraction [b]	Pressure	Mole fraction	ARD	Pressure	ARD
T [K]	x_i [-]	p [kPa]	$x_{i,cal}$ [-]	$|\delta x_i|$	p_{cal} [kPa]	$|\delta p|$
		Ethane (1)–2-Hexyne (4) ($i = 1$)				
273.15	0.2216	620.00 [c]	0.2347	5.917	586.07	5.472
	0.3178	849.68 [c]	0.3247	2.167	832.32	2.043
	0.4396	1131.9 [d]	0.4394	0.041	1132.33	0.038
	0.5122	1289.0 [d]	0.5062	1.162	1302.69	1.062
	0.6683	1620.3 [d]	0.6575	1.609	1642.51	1.371
	0.7231	1729.9 [d]	0.7114	1.623	1753.33	1.354
	0.7257	1738.4 [d]	0.7156	1.390	1758.55	1.159
	0.8388	1954.2 [d]	0.8253	1.605	1980.95	1.369
	1.0000	2395.9 [d]			2391.15	0.198
			(average)	1.939	(average)	1.734
303.15	0.2216	1015.4 [d]	0.2356	6.316	954.43	6.005
	0.3178	1410.9 [d]	0.3257	2.478	1376.13	2.464
	0.4396	1915.9 [d]	0.4395	0.019	1916.28	0.020
	0.5122	2212.4 [d]	0.5062	1.172	2239.07	1.205
	0.6683	2856.0 [d]	0.6521	2.418	2926.46	2.467
	0.7231	3083.8 [d]	0.7045	2.567	3164.11	2.604
	0.7257	3101.9 [d]	0.7087	2.340	3175.35	2.368
	0.8388	3560.7 [d]	0.8148	2.867	3666.57	2.973
	1.0000	4655.0 [d]			4657.93	0.063
			(average)	2.522	(average)	2.241
313.15	0.2216	1168.3 [d]	0.2363	6.636	1094.33	6.331
	0.3178	1628.5 [d]	0.3265	2.741	1583.59	2.758
	0.4396	2219.0 [d]	0.4396	0.011	2219.25	0.011
	0.5122	2569.3 [d]	0.5055	1.298	2604.77	1.380
	0.6683	3348.4 [d]	0.6509	2.609	3442.16	2.800
	0.7231	3625.4 [d]	0.7024	2.868	3737.00	3.078
	0.7257	3649.1 [d]	0.7068	2.609	3751.00	2.793
			(average)	2.681	(average)	2.736
		Propane (2)–2-Hexyne (4) ($i = 2$)				
273.15	0.0902	57.56 [e]	0.0914	1.285	56.89	1.171
	0.2982	168.46 [e]	0.2969	0.424	169.09	0.374
	0.4525	241.38 [c]	0.4522	0.063	241.51	0.052
	0.7074	344.82 [c]	0.7033	0.585	346.45	0.472
	0.7349	354.81 [c]	0.7286	0.852	357.28	0.695
	0.8891	419.29 [c]	0.8868	0.254	420.27	0.235
	0.9097	427.67 [c]	0.9059	0.421	429.38	0.400
			(average)	0.509	(average)	0.444
303.15	0.0902	121.87 [e]	0.0920	2.036	119.72	1.766
	0.3343	392.31 [c]	0.3341	0.057	392.51	0.051
	0.4525	514.62 [c]	0.4523	0.040	514.80	0.035
	0.7074	756.94 [c]	0.7017	0.803	762.37	0.717
	0.7349	781.54 [c]	0.7274	1.014	788.69	0.915
	0.8891	939.20 [c]	0.8851	0.446	943.46	0.454
	0.9097	961.26 [c]	0.9054	0.474	966.05	0.498
			(average)	0.696	(average)	0.634
313.15	0.0902	151.67 [e]	0.0915	1.433	149.82	1.223
	0.3343	485.95 [c]	0.3333	0.295	487.26	0.269
	0.4525	638.92 [c]	0.4509	0.361	641.01	0.327
	0.7074	948.39 [c]	0.7004	0.992	957.02	0.910
	0.7349	981.69 [c]	0.7274	1.020	990.97	0.945
	0.9097	1210.9 [d]	0.9025	0.797	1221.41	0.868
			(average)	0.816	(average)	0.757

(continued from previous page)

Measured			mod. PR equation			
Temperature [a] T [K]	Mole fraction [b] x_i [-]	Pressure p [kPa]	Mole fraction $x_{i,cal}$ [-]	ARD $|\delta x_i|$	Pressure p_{cal} [kPa]	ARD $|\delta p|$
		Butane (3)–2-Hexyne (4) ($i = 3$)				
273.15	0.2884	38.02 [e]	0.2872	0.426	38.15	0.338
	0.4198	51.03 [e]	0.4183	0.366	51.17	0.282
	0.5174	59.92 [e]	0.5160	0.278	60.05	0.212
	0.6999	75.65 [e]	0.6994	0.066	75.69	0.052
	0.8628	90.17 [e]	0.8673	0.525	89.77	0.441
	1.0000	103.36 [e]			102.89	0.455
			(average)	0.332	(average)	0.297
303.15	0.2884	102.56 [e]	0.2898	0.470	102.18	0.369
	0.3967	131.12 [e]	0.3956	0.280	131.41	0.221
	0.5727	174.94 [e]	0.5699	0.482	175.61	0.385
	0.7276	212.41 [c]	0.7248	0.384	213.09	0.319
	0.7820	225.18 [c]	0.7771	0.627	226.39	0.536
	0.8653	246.57 [c]	0.8624	0.337	247.32	0.303
	1.0000	282.06 [c]			283.90	0.652
			(average)	0.430	(average)	0.398
313.15	0.2884	136.21 [e]	0.2890	0.202	136.00	0.157
	0.3967	173.77 [e]	0.3943	0.597	174.59	0.472
	0.5727	233.24 [c]	0.5723	0.074	233.38	0.059
	0.7276	283.79 [c]	0.7284	0.107	283.54	0.090
	0.7820	298.59 [c]	0.7735	1.082	301.39	0.937
	0.8653	326.75 [c]	0.8573	0.929	329.51	0.846
	1.0000	375.60 [c]			378.81	0.855
			(average)	0.499	(average)	0.488

a) $u(T) = 0.05$ K.   b) $u(x_i) = 0.0004$ ($i = 1$, 2 and 3).   c) PG-10KU, $u(p) = 2.50$ kPa.   d) Measured by PG-100KU, $u(p) = 15.0$ kPa.   e) PHS-200KA, $u(p) = 0.40$ kPa.
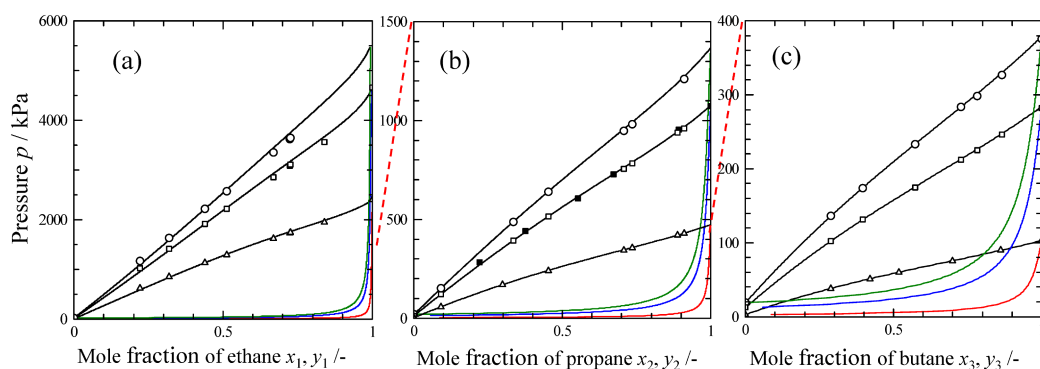
($\bigcirc$): this study, 273.15 K; ($\square$) this study, 303.15 K; ($\blacksquare$): Tsuji et al.[5], 303.15 K; ($\triangle$): this study, 313.15 K; (——): bubble lines correlated by mod. PR equation; (——, ——, ——): dew lines predicted by mod. PR equation.

Fig. 5   VLE for (a) Ethane (1)–2-Hexyne (4), (b) Propane (2)–2-Hexyne (4) and (c) Butane (3)–2-Hexyne (4) at 273.15, 303.15 and 313.15 K

saturated liquid density cited from the standard data of NIST[16]. Only α_0, α_1 and α_2 were determined for 2-hexyne and heptane from the experimental data of the saturated vapor pressure data. **Figure 6** shows α/α_{PR}, α/α_{SV} and β. Although the ranges of $(1 - T/T_c)$ were not the same for ethane, propane and butane, the temperature dependencies of α/α_{SV} and β showed common tendencies given by the convex shape functions with

temperature. Ethane, propane and butane are linear aliphatic compounds, with 2, 3 and 4 carbon atoms, respectively. Therefore, the corresponding state theory seems to be applicable for both the α-function and the β-function. On the other hand, the experimental ranges of $(1 - T/T_c)$ were not different for 2-hexyne and heptane. However, the α/α_{PR} for 2-hexyne was different from that for heptane. The $(1 - T/T_c)$ dependences
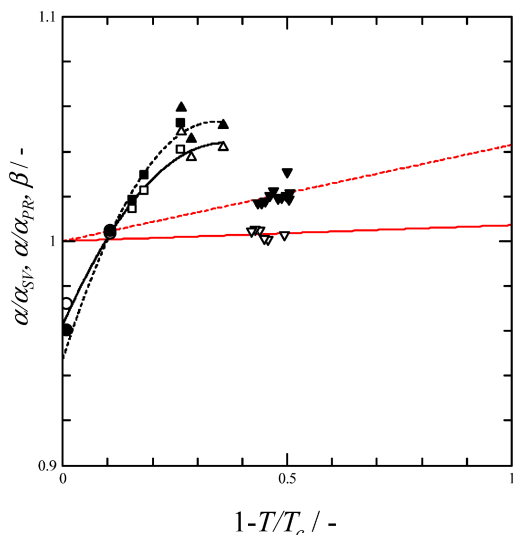
(○): α/α_{SV}, ethane; (□): α/α_{SV}, propane; (△): α/α_{SV}, butane ; (▼): α/α_{PR}, 2-hexyne ; (▽): α/α_{PR}, heptane; (●): β, ethane; (■): β, propane; (▲); β, butane; (——): Eq. (5); (------): Eq. (7); (------): Eq. (5') for 2-hexyne; (——): Eq. (5') for heptane.

Fig. 6 Temperature Dependence of α/α_{PR}, α/α_{SV} and β, in mod. PR Equation

Table 5 Value of Correction Factors, α' and β', for Parameters in the mod. PR Equation

	α_0 [-]	α_1 [-]	α_2 [-]
Ethane, propane, butane	0.962863	0.449277	−0.623757
2-Hexyne	1	0.042917	0.000000
Heptane	1	0.007117	0.000000
	β_0 [-]	β_1 [-]	β_2 [-]
Ethane, propane, butane	0.947555	0.624657	−0.923640

Table 6 Binary Parameters in the mod. PR Equation

Temperature T [K]	Binary parameter k_{ij} [-]		
	Ethane (1)– 2-Hexyne (4)	Propane (2)– 2-Hexyne (4)	Butane (1)– 2-Hexyne (4)
273.15	0.023	0.017	0.016
303.15	0.019	0.014	0.013
313.15	0.016	0.014	0.013

were not clear for 2-hexyne and heptane. Therefore, the first order linear $(1 - T/T_c)$ dependences, with the intercept with $\alpha_0 = 1$, were separately assumed for 2-hexyne and heptane. **Table 5** lists the values of α_0, α_1, α_2, β_0, β_1 and β_2, and **Fig. 6** shows the correlations using these values. The corrections of the constants sometimes provide an abnormal critical point in cubic equations of states, so the critical point was for ethane to be 308.36 K and 5.17371 MPa from the mod. PR equation. These values are slightly larger than the reported values of 305.43 K and 4.87976 MPa[20]. However, the differences were not thought to be serious for the bubble point pressure of the binary at 313.15 K. The RDs and the ARDs for the saturated vapor pressure and the saturated liquid density were evaluated as follows:

$$\delta p^s = \frac{p^s_{cal} - p^s}{p^s} \times 100 \qquad (21)$$

$$\left| \delta p^s \right| = \frac{\left| p^s_{cal} - p^s \right|}{p^s} \times 100 \qquad (22)$$

$$\delta \rho^s = \frac{\rho^s_{cal} - \rho^s_{NIST}}{\rho^s_{NIST}} \times 100 \qquad (23)$$

$$\left| \delta \rho^s \right| = \frac{\left| \rho^s_{cal} - \rho^s_{NIST} \right|}{\rho^s_{NIST}} \times 100 \qquad (24)$$

The ARDs for the saturated vapor pressure are listed in **Tables 3** and **4**. **Figure 4** shows the RDs for the saturated vapor pressure and the saturated liquid density.

3. 4. Correlations for the Three Binaries and the Binary Interaction Parameters Fitted with the Experimental Data
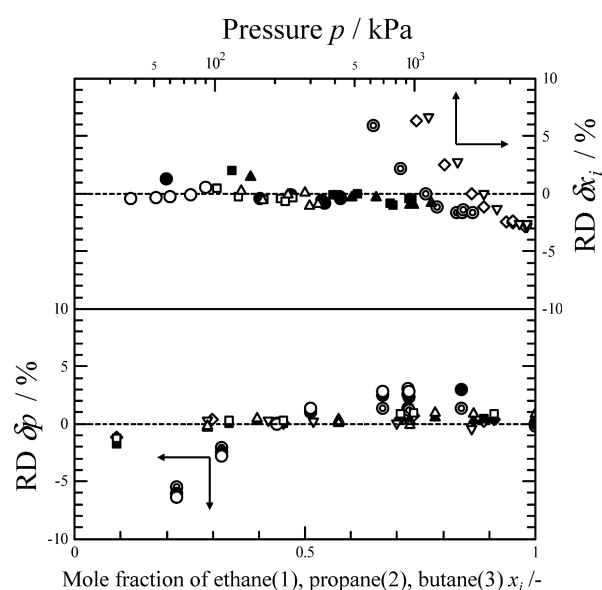
The bubble point pressure data were correlated with the mod. PR equation as shown in **Table 4**. The binary parameters, fitted with the experimental data, are listed in **Table 6**. **Figure 5** also compares the calculation results and the experimental data for the three binaries. The dew point pressure can be predicted by the correlation of the experimental data, so the predicted dew lines are also shown in **Fig. 5**. The calculated bubble point pressure agreed well with the experimental data for the three binaries. The binary critical point of ethane (1)–2-hexyne (4) was evaluated as $x_1 = 0.9940$ and $p = 5.4690$ MPa at 313.15 K. **Table 6** shows the binary interaction parameters tended to decrease with higher temperature. The calculations were also carried out using the PR equation without any modifications[15),20)] and showed reproducibility similar to that obtained by the mod. PR equation. However, the binary interaction parameters had slightly larger values than those from the mod. PR equation. For example, the binary parameters at 273.15 K were $k_{ij} = 0.025$, 0.023 and 0.020 for ethane (1)–2-hexyne (4), propane (2)–2-hexyne (4) and butane (3)–2-hexyne (4), respectively. On the other hand, the binary parameters were $k_{ij} = 0.016$ and 0.013 for ethane (1)–2-hexane (3) at 303.15 K and 313.15 K, respectively. Only these two values were smaller than those from the mod. PR equation. These deviations are due to the modification by the α- and β-functions. The α- and β-functions contributed to the correlations with small values of the binary interaction parameters because of the liquid density corrections. Otherwise, the α- and β-functions

were also thought to provide the higher critical temperature and pressure for ethane than those from the original PR equation. The RD and the ARD were evaluated for the pressure and the mole faction as follows:

$$\delta p = \frac{p_{cal} - p}{p} \times 100 \qquad (25)$$

$$|\delta p| = \frac{|p_{cal} - p|}{p} \times 100 \qquad (26)$$

$$\delta x_i = \frac{x_{i,cal} - x_i}{x_i} \times 100 \qquad (27)$$

$$|\delta x_i| = \frac{|x_{i,cal} - x_i|}{x_i} \times 100 \qquad (28)$$

The ARDs for the pressure and the mole fraction are listed in **Table 4**, and the RDs are shown in **Fig. 7**. The average ARDs were not larger than 2.681 % in ethane (1)–2-hexyne (4) for the mole fraction, and 2.736 % for the pressure in ethane (1)–2-hexyne (4), respectively. The large average ARDs were due to the values at the mole fraction close to zero in ethane (1)–2-hexyne (4). The ARDs for the mole fraction and the pressure for propane (2)–2-hexyne (4) were 1.443 % and 1.233 %, respectively. The large ARDs were thought to originate from the poor estimates and data quality for the saturated vapor pressure of 2-hexyne.

3. 5. Estimation of 2-Hexyne in Household LPG Cylinder

The partition coefficients of 2-hexyne were estimated in a household LPG cylinder using the calculated results for the bubble and dew point pressure. Based on information from The High Pressure Gas Safety Institute of Japan[22], the evaluations were carried out under the following conditions:

1) LPG composition
ethane: 0.6000 mass %; propane: 97.70 mass%; butane: 1.700 mass% with 2-hexyne 50.00 ppm (mass basis)
2) Inner volume of cylinder; 117.50 L
3) Loading amount of LPG; 45.00 kg

The mole fraction and the partition coefficient of 2-hexyne were calculated at the initial loading. Then, the vapor volume and the liquid volume were also evaluated in the LPG cylinder. The binary interaction parameters between the three light hydrocarbons were set to be zero, $k_{12} = k_{23} = k_{31} = 0.000$.

Table 7 lists the calculation results. The liquid volume was increased with higher temperature. However, the volume ratio of the liquid was 80.80 % even at 313.15 K, which is acceptable for the safety regulations. The initial mole fraction of 2-hexyne in the vapor phase increased from 3.939×10^{-9} to 13.39×10^{-9} with increased temperature from 273.15 to 313.15 K,

($\circledcirc$): ethane (1)–2-hexyne (4), 273.15 K; ($\bullet$): ethane (1)–2-hexyne (4), 303.15 K; ($\bigcirc$): ethane (1)–2-hexyne (4), 313.15 K; ($\diamondsuit$): propane (2)–2-hexyne (4), 273.15 K; ($\blacksquare$): propane (2)–2-hexyne (4), 303.15 K; ($\square$): propane (2)–2-hexyne (4), 313.15 K; ($\triangledown$): butane (3)–2-hexyne (4), 273.15 K; ($\blacktriangle$): butane (3)–2-hexyne (4), 303.15 K; ($\triangle$): butane (3)–2-hexyne (4), 313.15 K.

Fig. 7 RDs of Bubble Point Pressure Data for mod. PR Equation

Table 7 Calculation Results for Quaternary VLE in the LPG Gas Cylinder with Inner Volume of 117.50 L

Temperature T [K]	Pressure p [kPa]	Liquid phase				Vapor phase				
		Mole fraction			Volume V_L [L]	Mole fraction				Volume V_V [L]
		x_1 [-]	x_2 [-]	x_3 [-]		y_1 [-]	y_2 [-]	y_3 [-]	y_4 [-]	
273.15	481.55	8.619×10^{-3}	0.9784	1.299×10^{-2}	83.92_2	3.287×10^{-2}	0.9638	3.290×10^{-3}	3.939×10^{-9} ($K_4 = 0.0145$)	33.57_8
303.15	1087.1	8.593×10^{-3}	0.9784	1.303×10^{-2}	91.53_3	2.440×10^{-2}	0.9711	4.563×10^{-3}	9.802×10^{-9} ($K_4 = 0.0360$)	25.96_7
313.15	1378.4	8.601×10^{-3}	0.9784	1.304×10^{-2}	94.93_8	2.219×10^{-2}	0.9728	5.018×10^{-3}	13.39×10^{-9} ($K_4 = 0.0491$)	22.56_2

LPG 45.00 kg loading, ethane : propane : butane = 0.6 : 97.7 : 1.7 (mass %) with 50 ppm (mass basis) of 2-hexyne.

respectively. The partition coefficient at 273.15 K was $K_4 = 0.0145$, and increased at higher temperature. Therefore, the partition coefficient at 313.15 K was $K_4 = 0.0491$, which was 3.39 times that at 273.15 K. These results suggested that the odor strength will be increased at high temperatures. According to the Japan Association on Odor Environment[23], the mole fractions of the odor threshold are reported to be 3×10^{-9} and 2.9×10^{-11} for DMS and TBM, respectively. If the odor threshold of 2-hexane is clarified, the optimum amount of 2-hexyne can be determined by using the method proposed in this study.

4. Conclusion

Saturated vapor pressure was measured for 2-hexyne, which is a potential sulfur-free odorant for LPG, with a static apparatus in the temperature range from 273.14 to 313.14 K. The measurements were also carried out for heptane, and the results verified by comparison with the standard data. The bubble point pressure was measured for ethane–2-hexyne, propane–2-hexyne and butane–2-hexyne using the static apparatus at 273.15, 303.15 and 313.15 K. The α- and β-function in the PR equation were determined for ethane, propane and butane using the saturated vapor pressure and the saturated liquid density. Only the α-function was determined for 2-hexyne using the saturated vapor pressure. The three binary interaction parameters in the mod. PR equation were determined by fitting the experimental data of the bubble point pressure for ethane–2-hexyne, propane–2-hexyne and butane–2-hexyne. The other binary interaction parameters between ethane, propane and butane were assumed to be zero. The 2-hexyne concentration was evaluated in LPG (ethane : propane : butane = 0.6000 : 97.70 : 1.700, mass basis) with 50.00 ppm mass of 2-hexyne in a cylinder with the inner volume of 117.50 L. The initial mole fraction of 2-hexyne in the vapor phase increased from 3.939×10^{-9} to 13.39×10^{-9} with higher temperature from 273.15 to 313.15 K, respectively. These data and the calculation methods will allow calculation of the optimum amount of 2-hexyne for the various compositions of LPG.

Nomenclatures

a_c:	attractive parameter in the PR equation at the critical point
b_c:	excluded volume parameter in the PR equation at the critical point
D:	initial mole number of vapor in the LPG cylinder
F:	mole number of loading in the LPG cylinder
K_i:	partition coefficient of component i
k_{ij}:	binary interaction parameter in the mixing rule of the PR equation
p:	pressure
p_c:	critical pressure
p_{cal}:	calculated bubble point pressure
p^s:	saturated vapor pressure
p^s_{cal}:	calculated saturated vapor pressure
p^s_{NIST}:	saturated vapor pressure reported by the NIST
δp:	relative deviation for pressure
$|\delta p|$:	absolute relative deviation for pressure
δp^s:	relative deviation for saturated vapor pressure
$|\delta p^s|$:	absolute relative deviation for saturated vapor pressure
δp^s_{NIST}:	relative deviation for saturated vapor pressure from NIST data
$|\delta p^s_{NIST}|$:	absolute relative deviation for saturated vapor pressure from NIST data
R:	gas constant
T:	temperature
T_c:	critical temperature
$u(X)$:	uncertainty for physical properties X
V:	inner volume of the LPG cylinder
v:	molar volume
V_L:	liquid volume in the LPG cylinder
v_L:	saturated molar volume of vapor
V_V:	liquid volume in the LPG cylinder
v_V:	saturated molar volume of liquid
w:	mass
x_i:	mole fraction of component i in the liquid phase
$x_{i,cal}$:	calculated mole fraction of component i in the liquid phase
δx_i:	relative deviation for mole fraction of component i in the liquid phase
$|\delta x_i|$:	absolute relative deviation for mole fraction of component i in the liquid phase
y_i:	mole fraction of component i in the vapor phase

〈Greeks〉

α:	α-function in the mod. PR equation
α_i:	i-th coefficient of α-function used in the mod. PR equation
α_{PR}:	α-function in the PR equation
α_{SV}:	α-function in the PR equation corrected by Stryjek and Vera
β:	β-function in the PR equation
β:	i-th coefficient of β-function used in the mod. PR equation
ρ^s_{cal}:	calculated saturated liquid density
ρ^s_{NIST}:	saturated liquid density reported by the NIST
$\delta\rho^s$:	relative deviation for saturated liquid density
$|\delta\rho^s|$:	absolute relative deviation for saturated liquid density
ω:	acentric factor

〈superscript〉

s:	saturated

〈subscripts〉

cal:	calculated
exp:	experimental
NIST:	NIST standard
1, 2, 3, 4:	ethane, propane, butane, 2-hexyne

References

1) https://www.j-lpgas.gr.jp/stat/geppou/, data accessed May 11, 2022.
2) Graf, F., Kroger, K., Reimert, R., *Energy & Fuels*, **21**, 3322 (2007).
3) Takabe, K., Mase, N., Hisanaga, Y., Takahashi, M., Miyamoto, T., Kondoh, T., Uematsu, R., Kanabe, T., Namba, M., *Nioi · Kaorikankyo Gakkaishi* (*J. Japan Association on Odor Environment*), **40**, 248 (2009).
4) Oka, Y., Yoshida, T., Knodo, T., Ito, S., Kato, K., *J. Therm. Anal. Calorim.*, **99**, 9 (2010).
5) Tsuji, T., Sato, T., Hoshina, T., Oba, S., *J. Jpn. Petrol. Inst.*, **64**, (2), 92 (2021).
6) Tsuji, T., Hoshina, T., Kinoshita, S., Yoshida, A., *J. Jpn. Petrol. Inst.*, **65**, (3), 97 (2022).
7) Yaws, C. L., "Chemical Properties Handbook," McGraw-Hill, New York (1999), pp.1-29.
8) Recupero, V., Pino, L., Vita, A., Cipiti, F., Cordaro, M., Lagana, M., *Int. J. Hydrogen Energy*, **30**, 963 (2005).
9) Gokaliler, F., Caglayan, B. S., Onsan, Z. I., Aksoylu, A. E., *Int. J. Hydrogen Energy*, **33**, 1383 (2008).
10) Xu, X., Jaubert, J.-N., Privat, R., Arpentiner, P., *Ind. Eng. Chem. Res.*, **56**, 8143 (2017).
11) Tsuji, T., Sato, T., Kondo, T., Uematsu, R., Hiaki, T., Namba, M., 18th European Conference on Thermophysical Properties, Pau, France, Sept. 2008, Abstr.
12) Negadi, L., Kaci, A. A., Negadi, A., Jose, J., *Fluid Phase Equilib.*, **300**, 135 (2010).
13) Boukais-Belaribi, G., Belaribi, B. F., Ait-Kaci, A., Jose, J., *Fluid Phase Equilib.*, **167**, 83 (2000).
14) Mayer, E. F., Zielinski, W. M., *J. Chem. Thermodynamics*, **14**, 403 (1982).
15) Peng, D.-Y., Robinson, D. B., *Ind. Eng. Chem. Fundam.*, **15**, 59 (1976).
16) https://webbook.nist.gov/chemistry/fluid/, data accessed May 11, 2022.
17) Nakazawa, M., Tsuji, T., Lai, A. J. X., Zaini, N., Hoshina, T., Otake, K., Yoshida, A., *Fluid Phase Equilib.*, **522**, 112764 (2020).
18) Tsuji, T., Hoshina, T., Takagi, T., *J. Jpn. Petrol. Inst.*, **63**, (1), 107 (2020).
19) Tsuji, T., Shigeru, M., Hoshina, T., Yoneda, K., Funazukuri, T., Morad, N. A., *Fluid Phase Equilib.*, **441**, 9 (2017).
20) Stryjek, R., Vera, J. H., *Can. J. Chem. Eng.*, **64**, 323 (1986).
21) Moshfeghian, M., Shariat, A., Maddox, R. N., *Chem. Eng. Comm.*, **73**, 205 (1988).
22) Kondo, T., Uematsu, R., Namba, M., personal communication.
23) https://orea.or.jp/gijutsu/kyuukakusokuteihou/odor-threshold-values/, data accessed Dec. 3, 2022.

………………………………………………….

要　　　旨

液化石油ガス用非硫黄系新規着臭剤2-ヘキシンの飽和蒸気圧とエタン–2-ヘキシン，プロパン–2-ヘキシンおよびブタン–2-ヘキシンの沸点の測定と相関

辻　　智也[†1),†2)]，邱　　必馨[†1)]，松川　博亮[†3)]，保科　貴亮[†4)]，大竹　勝人[†3)]

[†1)] マレーシア工科大学マレーシア日本国際工科院，Off Jalan Sultan Yahya Petra, Kuala Lumpur 54100, MALAYSIA

[†2)] 大阪公立大学工学部，599-8531　大阪府堺市中区学園町1-1

[†3)] 東京理科大学工学部，125-8585　東京都葛飾区新宿6-3-1

[†4)] 日本大学生産工学部，275-8575　千葉県習志野市泉町1-2-1

　液化石油ガス（LPG）の非硫黄系着臭剤候補として期待される2-ヘキシンについて静置型装置により273.14～313.14 Kにおける飽和蒸気圧および273.15，303.15，313.15 Kにおけるエタン，プロパン，ブタンとの2成分混合系の沸点圧を測定した。2-ヘキシンについては飽和蒸気圧データを用いてPeng・Robinson（PR）状態方程式の引力定数を，エタン，プロパン，ブタンについては飽和蒸気圧および飽和液密度データを用いてPR状態方程式の引力定数と排除体積を再決定した。さらに，2成分混合系の沸点圧実測値から，PR状態方程式混合則中の2成分系パラメーターを決定した。これらを用いてエタン：プロパン：ブタンの質量比が0.6000：97.70：1.700のLPG 45.00 kgに50.00 ppmの2-ヘキシンを添加した際の117.50 L容器内での気液平衡関係を推算した。273.15 Kにおける気相中の2-ヘキシンのモル分率推算値は3.939×10^{-9}であり，313.15 Kに温度が上昇すると3.40倍になることが分かった。

………………………………………………….