[Regular Paper]

Boiling Point of Five New Sulfur-free Odorants for LPG, 1-Pentyne, Cyclopentene, 1-Hexyne, 2-Hexyne and 1,5-Cyclooctadiene, and Bubble Point Pressures of Binaries with Propane

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Boiling point and bubble point pressure in binaries with propane were measured for five compounds, 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne, and 1,5-cyclooctadiene, new sulfur-free odorants for liquefied petroleum gas. The boiling point was measured with an ebulliometer under atmospheric pressure. The experimental boiling points were 313.51, 313.76, 344.53, 357.59 and 424.02 K for 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne, and 1,5-cyclooctadiene, respectively. The bubble point pressures were measured with a static apparatus at 303.15 K. The pressure was also measured by a synthetic apparatus at 303.15 K for propane–1-hexyne. The experimental boiling points were used for estimation of critical temperature, critical pressure and acentric factor by Lydersen's group contribution method to evaluate the two constants in the Peng-Robinson equation of state. The Peng-Robinson equation could correlate the bubble point pressure to the mole fraction of propane with absolute relative deviation of less than 2.556 %. The data will be useful in the development of fuel cells with reformers for liquefied petroleum gas.

1. Introduction

Sulfur compounds, such as *t*-butyl mercaptane, dimethyl sulfide and tetrahydrothiophene, are widely used as odorants for liquefied petroleum gas (LPG) to warn of gas leaks[1)]. However, these compounds react with oxygen and form sulfur oxide during the combustion of LPG. LPG is expected to become a hydrogen source for fuel cell applications[2)~6)]. Light hydrocarbons in LPG are converted to hydrogen by reforming reactions over catalysts. However, the catalysts are sometimes damaged by any sulfur compounds, because of the strong absorption of sulfur compounds on transition metals in the catalysts. Consequently, various compounds have been considered for use as sulfur free odorants of natural gas and LPG[7)]. The High Pressure Gas Safety Institute of Japan has already selected 37 oxidized, 42 non-branched/branched aliphatic and 31

alicyclic hydrocarbons as potential compounds for sulfur-free odorants[1),8)]. These compounds have strong odors and boiling points similar to those of conventional odorants. Subsequently, 1-pentyne and 2-hexyne were selected as the most suitable candidates for sulfur-free odorants[1)]. However, cyclopentene, 1-hexyne and 1,5-cyclooctadinene have attractive commercial prices, so are also potential sulfur-free odorants from the economical view point[9)]. Further knowledges of both the type and strength of odors as well as the vapor-liquid equilibrium (VLE), chemical stabilities and toxicities, are essential for the development and usage of these odorants.

The present study investigated the VLE for the five binary systems of propane containing 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne and 1,5-cyclooctadinene at 303.15 K. **Figure 1** shows the chemical structures of these compounds.

Little VLE data for hydrocarbons is available in the literature. VLE have been reported for 2-heyxyne-octane and 3-hexyne-octane[10)], cyclopentene–ethanol[11)], 1-hexyne–2-methoxy-2-methylpropane (MTBE)[12)], and

2-hexyne–MTBE[12], and bubble point pressure for 1-hexyne–ethanol[13], 2-hexyne–ethanol[14], and 3-hexyne–ethanol[15]. VLE and enthalpy changes on mixing were reviewed for 84 binaries containing alkynes and other hydrocarbons[16]. The data were correlated with the E-PPR78 model, which is based on the Peng-Robinson (PR) equation of state[17]. The bubble point pressure data for propane–1-pentane, propane–1-hexyne and propane–2-hexyne were also includeded[16]. However, the data from our unpublished study were presented at a conference[18]. This study partly includes the data presented at the conference[18], but also the boiling points under atmospheric pressure and the bubble point pressures with propane at 303.15 K for the five compounds. The experimental data were correlated with the original and revised versions of the PR equations.[17),19]

2. Experimental Section

2. 1. Materials

Table 1 lists the chemicals employed in this study.

1: propane; 2: 1-pentyne; 3: cyclopentene; 4: 1-hexyne; 5: 2-hexyne; 6: 1,5-cyclooctadiene.
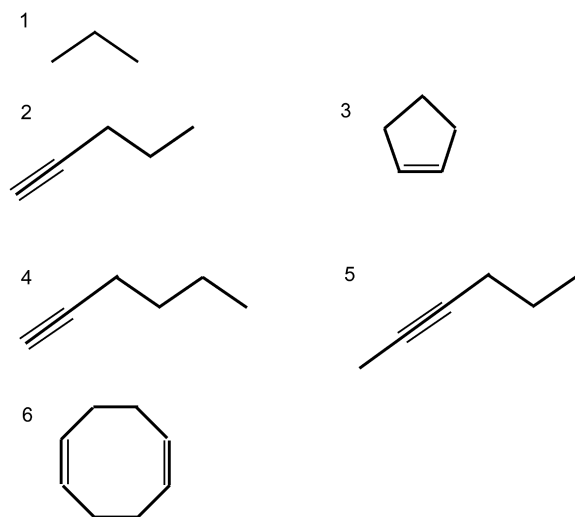
Fig. 1   Chemical Structures of Propane and Candidate Sulfur-free Odorants

Pentane was used as a standard to check the reliability of boiling point data. All chemicals were used without further purifications.

2. 2. Measurement of Boiling Point under Atmospheric Pressure

Precise data for the saturated vapor pressure of propane have been already reported. However, little data are available for 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne and 1,5-cyclooctadiene. Data seem to be variable even for the normal boiling point. Therefore, the boiling points were measured for 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne and 1,5-cyclooctadinene using an ebulliometer under atmospheric pressure.

Figure 2 shows the dimensions of the ebulliometer. The ebulliometer was made of Pyrex glass, and specially designed by Hiaki and Kawai[20] to measure the boiling point and vapor-liquid equilibrium (VLE) under atmospheric pressure for newly synthesized compounds using a small volume of only 38 cm^3. The main parts of the apparatus were covered with a heat insulating material to accurately measure the experimental temperatures.

Before starting the measurements, the ebulliometer was set in a ventilator to avoid the strong odors of the odorants. The liquid sample was loaded into the ebulliometer *via* a loading and sampling port (part 7 in **Fig. 2**). The liquid sample was heated in a boiling flask (part 10) using a cartridge heater (part 11). After the sample reached the boiling condition, the vapor and the liquid were sent together to the flush drum (part 9). The vapor was passed through a heating zone (part 6), and liquefied in the condenser (part 1). The liquefied vapor was dropped into a chamber with an observation window (part 4) and sent to a sampling port (part 2). The sample port was for obtaining the liquefied vapor to analyze the mole fraction of the vapor phase, so was not used for the measurements of boiling point. Otherwise, the liquid from the flush drum was passed down to the loading and sampling port, and returned to the boiling flask together with the liquefied vapor. Constant flow of the liquefied vapor was monitored from the observation window, and the equilibrium temperature and the atmospheric pressure were recorded. The temperature was measured with a Pt resistance thermometer (part 8, ASL F250MkII, Croydon, U. K.), cali-

Table 1   Chemical Reagents Employed in This Study

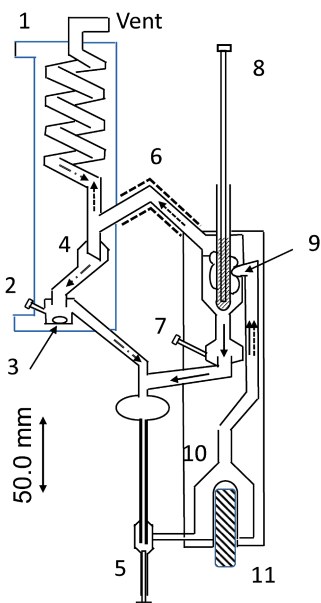|	Supplier	Grade	Purity
propane	Takachiho Chemical Industrial Co., Ltd., Japan	Research	99.9 vol%
pentane	Wako Pure Chemical Industries, Ltd., Japan	Special	98 mass%
1-pentyne	Sigma-Aldrich, U. S.		99 mass%
cyclopentene	Sigma-Aldrich, U. S.		96 mass%
1-hexyne	Wako Pure Chemical Industries, Ltd., Japan		97 mass%
2-hexyne	Sigma-Aldrich, U. S.		99 mass%
1,5-cyclooctadiene	Sigma-Aldrich, U. S.		99 mass%

1: condenser; 2: sampling port; 3: magnetic stirrer bar; 4: observation window to count drop of liquid; 5: drain; 6: heating zone; 7: loading and sampling port; 8: Pt-resistance thermometer; 9: flush drum; 10: boiling flask; 11: cartridge heater; (——▶): liquid flow; (- - ▶): vapor flow; (—·▶): liquefied vapor flow.

Fig. 2　Diagram of the Ebulliometer Employed

1: vacuum pump; 2: air chamber; 3: constant temperature bath; 4: glass cell; 5: water-proof magnetic stirrer; 6: pressure gauge; 7: heater; 8: thermistor thermometer; 9: absolute pressure sensor; 10: agitator.

Fig. 3　Diagram of the Static Apparatus Employed

brated with a standard Pt resistance thermometer (R800-2, Chino Co., Tokyo). The atmospheric pressure was measured with a Fortin mercury barometer (T60, Tokyoseisakusho Co., Ltd., Tokyo). The uncertainties of temperature and pressure measurements were $u(T) = 0.05$ K and $u(p) = 0.03$ kPa, respectively.

2. 3. Measurement of Bubble Point Pressure for Binanries

Bubble point pressures were measured for the five binaries, propane containing 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne and 1,5-cyclooctadinene using a static apparatus at 303.15 K. To ensure the reliability of the experimental data, bubble point pressure was also measured for propane–1-hexyne by a different method, a synthetic apparatus, at 303.15 K.

2. 3. 1. Sample Preparation

Samples were prepared in a pressure resistance glass cell. The glass cell was used in both the static and synthetic apparatus. The cell was made of Pyrex glass with inner volume of 37 cm^3 and safe pressure up to 4.5 MPa[21]~[24]. A magnetic stirrer bar was placed in the glass cell to agitate the sample. The mole fraction of the sample was determined by the weights before and after loading. Therefore, propane was loaded into the glass cell from the gas cylinder, and then the glass cell was cooled with methanol with added dry ice. After weighing the glass cell with a direct reading balance (AV1581, Exact Co., Kamagaya, Japan), the other component was loaded into the glass cell through an
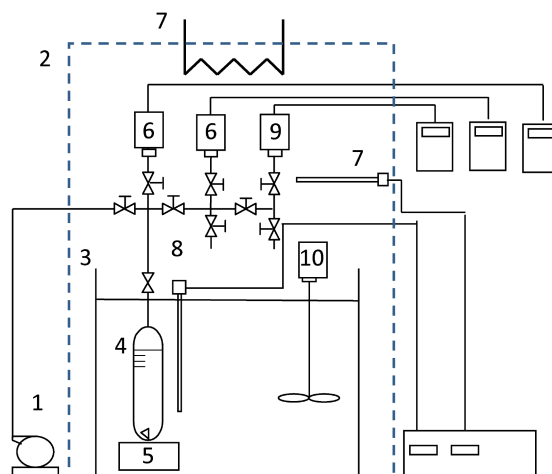
HPLC pump (PU713, GL Sciences Inc., Tokyo). The glass cell was weighed again and the mole fraction was determined. The maximum capacity and the minimum resolution of the balance were 6 kg and 1 mg, respectively.

2. 3. 2. Static Apparatus

Figure 3 shows a schematic diagram of the static apparatus. The apparatus was similar to that of Nakazawa *et al.*[21] and Tsuji *et al.*[22],[23]. After preparation of the sample, the glass cell (part 4 in **Fig. 3**) was set in a constant temperature bath (part 3, TRL-101FEZ, Thomas Kagaku Co., Ltd., Tokyo). The mole fraction in the liquid phase was assumed to be that at preparation because the density of the vapor was far lower than that of the liquid phase. The validity was checked by comparison with the data from the synthetic apparatus as described later. Three sensors were employed for the pressure measurements. The two pressure gauges (part 6, PG-10KU and PG-100KU, Kyowa Electronic Instruments Co., Ltd., Tokyo) had capacities of 1 MPa and 10 MPa, respectively. The absolute pressure sensor (part 9, PHS-2KA, Kyowa Electronic Instruments Co., Ltd., Tokyo) had a capacity of 200 kPa. The absolute pressure sensor was used at the pressures from 50 kPa up to atmospheric pressure. The PG-10KU was calibrated with the saturated vapor pressure of propane at 298.20 K, as evaluated by a standard data table[25]. The PG-100KU was calibrated with a dead weight tester (PD-22, Nagano Keiki Co., Ltd., Tokyo) at 4.8060 MPa. The PHS-2KA was calibrated by admitting atmospheric pressure to the conditioner before measurement. The temperature was measured with a thermistor thermometer (part 8, SXA-33, Technoseven Co., Ltd., Yokohama, Japan). The uncertainties for the
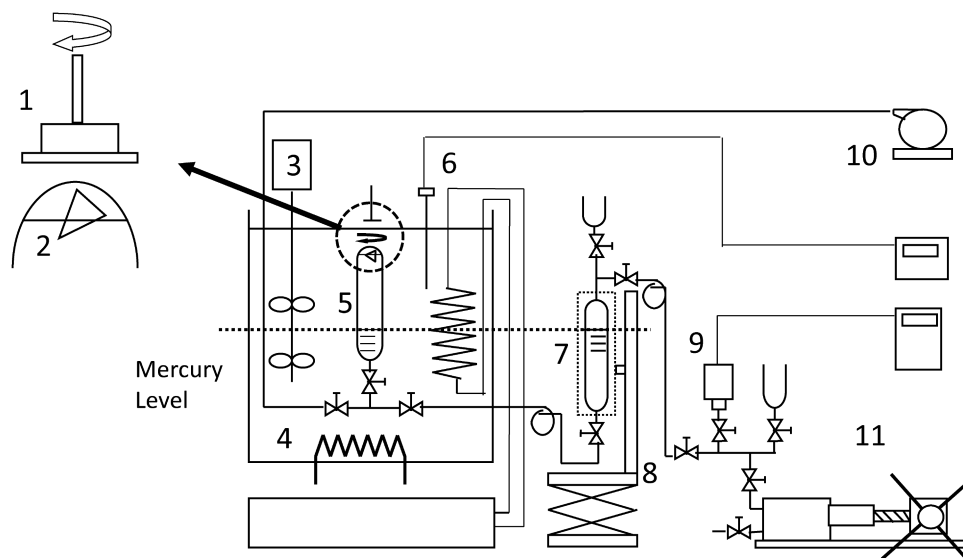
1: stirrer using rare earth magnet; 2: magnetic stirrer bar 3: agitator; 4: constant temperature bath; 5: glass cell; 6: thermistor thermometer; 7: mercury manometer/reservoir; 8: z-axis slider; 9: pressure gauge; 10: vacuum pump; 11: pressure generator.

Fig. 4 Diagram of the Synthetic Apparatus Employed

pressure were $u(p) = 0.2$, 2.5 and 15 kPa and for the PHS-200KA, PG-10KU and PG-100KU, respectively. The uncertainties for the temperature and mole fraction were $u(T) = 0.05$ K and $u(x_1) = 0.0004$, respectively.

2. 3. 3. Synthetic Apparatus

Figure 4 shows a schematic diagram of the synthetic apparatus. The details were described in our previous reports[24],[26]. The glass cell (part 5) was useful to observe the appearance/disappearance of bubbles in the solution. The apparatus measures the actual bubble point pressure, so provides a comparison with the data from the static apparatus. The glass cell was placed in a constant temperature bath (part 4, T-104TS, Thomas Kagaku Co., Ltd., Tokyo), and connected with a pressurizing line. The pressure resistance glass tube (part 7, HPG-10-5, Taiatsu Techno Co., Tokyo) was connected with the pressurizing line to separate mercury and the pressurizing medium, silicone oil. The level of mercury was adjusted with a z-axis slider (part 8). Using a pressure generator (part 11, H020201, Tama Seiki Ind. Co., Ltd., Tokyo), the mercury was injected into the glass cell until the bubble was reduced to a small size. The interface between the vapor and liquid phases was then agitated with a magnetic stirrer bar (part 2) powered by a stirrer equipped with a rare-earth magnet (part 1). Consequently, the bubble was rapidly dissolved in the solution. The solution was pressurized again until the bubble had disappeared. Controlling the mercury level, the solution was slowly depressurized. The experimental pressure was measured as the bubble was appeared again in the solution with a pressure gauge (part 9, PH-200KB, Kyowa Electronic Instruments Co., Ltd., Tokyo). The pressure gauge was calibrated with the saturated vapor pressure of ethane at 297.13 K, and also evaluated with the standard data table[25]. The experimental temperature was measured with a thermistor thermometer (part 6, SXA-33, Technoseven Co., Ltd., Yokohama, Japan). The uncertainties of the temperature, pressure and mole fraction were estimated as $u(T) = 0.05$ K, $u(p) = 6$ kPa, $u(x_1) = 0.0002$, respectively.

2. 4. Equation of State and Its Mixing Rules

Experimental data were correlated with the PR equation of state[17]:

$$p = \frac{RT}{v-b} - \frac{a}{v^2 + 2bv - b^2} \tag{1}$$

where the two parameters for propane, a and b, were evaluated from the relationships in Peng-Robinson-Stryjek-Vera (PRSV) equation of state[19] for propane, and parameters for the other five compounds were evaluated from the relationships in the original PR equation. **Table 2** lists the critical properties used for evaluating the parameters in the PR/PRSV equation. The PRSV equation requires an additional parameter, κ_1, which is available only for propane. Different values of the critical properties have been reported for the other five compounds[16],[27]. The following group contribution method[28] was also applied for the five compounds:

$$T_c/T_b = \frac{1}{0.584 + 0.965 \sum_k N_k(tc_k) - \left[\sum_k N_k(tc_k)\right]^2} \tag{2}$$

Table 2 Critical Properties Employed for Evaluation of Parameters in PR/PRSV Equation

	Critical temperature T_c [K]	Critical pressure p_c [MPa]	Acentric factor ω [-]	PRSV parameter κ_1 [-]	Critical temperature T_c [K]	Critical pressure p_c [MPa]	Acentric factor ω [-]
	(Stryjek and Vera[19])				(Xu et al.[16])		
propane	369.82	4.24593	0.15416	0.03136			
1-pentyne					498.40	4.24169	0.16828
cyclopentene							
1-hexyne					533.50	4.33557	0.26261
2-hexyne					575.10	6.15723	0.24563
1,5-cyclooctadiene							
	(Yaws[27])				(experimental data and Eqs. (2)-(4))		
1-pentyne	481.20	4.170	0.290		493.39	4.1623	0.20527
cyclopentene	507.00	4.790	0.195		506.46	4.7628	0.20270
1-hexyne	516.20	3.620	0.333		529.10	3.6910	0.24911
2-hexyne	549.00	3.530	0.221		552.99	3.7454	0.22962
1,5-cyclooctadiene	645.00	3.900	0.286		653.39	3.7823	0.25000

$$p_c / bar = \frac{1}{\left[0.113 - \sum_k N_k(pc_k) - 0.0032 N_{atoms} \right]^2} \quad (3)$$

where T_b is normal boiling point, N_k number of group, N_{atoms} total numbers of atoms in a molecule, and tc_k and pc_k group parameters of group, k. The acentric factor was evaluated from the following approximation[29]:

$$\omega = \frac{3T_b/T_c}{7[1 - T_b/T_c]} \log_{10}(p_c/bar) - 1.000 \quad (4)$$

The group parameters, tc_k and pc_k, are available in the literature[28]. The experimental boiling point was employed instead of the normal boiling point, T_b. The parameters are discussed later.

The mixing rules used in the PR/PRSV equation were from the van der Waals one fluid model:

$$a = \sum_i \sum_j x_i x_j (1 - k_{ij})(a_i a_j)^{1/2} \quad (5)$$

$$b = \sum_i x_i b_i \quad (6)$$

where k_{ij} is a binary interaction parameter determined from fitting of experimental data at given pressure using the following objective function:

$$\text{O.F.} = \sum (x_{1,exp} - x_{1,cal}) \quad (7)$$

3. Results and Discussion

3. 1. Boiling Point and Saturated Vapor Pressure of 1-Pentyne, Cyclopentene, 1-Hexyne, 2-Hexyne and 1, 5-Cyclooctadiene

The boiling point of pentane was measured to ensure the reliability of experimental data, shown in **Table 3**. The boiling point depends on the atmospheric pressure and is slightly different from the normal boiling point at standard atmospheric pressure, 101.325 kPa. Therefore, using the Chemistry Webbook, SRD 69[30] provided by the National Institute of Standards and Technology (NIST), the saturated vapor pressure was evaluated as 101.73 kPa at the experimental temperature, 309.33 K. The relative deviation (RD) was calculated from:

$$\frac{\delta p^s}{p^s_{exp}} = \frac{p^s_{cal} - p^s_{exp}}{p^s_{exp}} \quad (8)$$

The RD was $\delta p^s/p^s_{exp} = 0.029$ % for pentane.

Table 3 lists the boiling points of 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne and 1,5-cyclooctadiene under atmospheric pressure, and **Fig. 5** shows the experimental results. The saturated vapor pressures of cyclopentene[31], and 1-hexyne and 2-hexyne[32] have been reported. The literature data are also shown in **Fig. 5**. Isomers of alkynes have different boiling points. Alkanes and alkenes with symmetric molecular structure have the lower normal boiling point than those with asymmetric structure because of the molecular polarity. However, alkynes with symmetric structure have the higher boiling point than those with asymmetric structure. The saturated vapor pressures were also measured for 1-pentyne and cyclopentene using the static apparatus at 303.15 K. These two compounds have lower boiling point than the other three compounds. The data for the saturated vapor pressure are shown in **Table 3**. These data were used not only for ensuring the reliability of the data but also for investigating the reproducibility of the PR equation. The parameters of the PR equation were evaluated by using the three different critical properties. **Figure 5** shows the calculation results for the PR equation, and the RDs are listed in **Table 3**. The RDs were no larger than 2.887 % for the PR equation, for the parameters evaluated from the experimental boiling point and Eqs. (2)-(4). Therefore, these parameters were employed for

Table 3 Saturated Vapor Pressure, Measured and Calculated

	Measured		Calculated							
			PRSV equation		PR equation[a)]		PR equation[b)]		PR equaton[c)]	
	Temperature T[d)] [K]	Pressure p^s [kPa]	Pressure p^s_{cal} [kPa]	$\delta p^s/p^s_{exp}$ [%]	Pressure p^s_{cal} [kPa]	$\delta p^s/p^s_{exp}$ [%]	Pressure p^s_{cal} [kPa]	$\delta p^s/p^s_{exp}$ [%]	Pressure p^s_{cal} [kPa]	$\delta p^s/p^s_{exp}$ [%]
propane	303.15	1074.0[e)]	1079.0	0.466						
pentane	309.33	101.70[f)]								
1-pentyne	303.15	69.2[g)]			72.6$_6$	5.000	68.33	−1.257	69.28	0.116
	313.51	101.09[f)]			103.10	1.988	99.86	−1.217	99.26	−1.810
cyclopentene	303.15	60.8[g)]					61.4	0.954	59.9	−1.480
	317.36	100.96[f)]					100.98	0.020	98.89	−2.050
1-hexyne	344.53	101.13[f)]			102.42	1.276	100.24	−0.880	99.32	−1.790
2-hexyne	357.59[e)]	101.11[f)]			101.20	0.089	103.67	2.532	99.36	−1.731
1,5-cyclooctadiene	424.02[e)]	100.80[f)]					104.28	3.452	9.789	−2.887

a) using T_c, p_c, ω of Xu *et al.*[16)].　b) using T_c, p_c, ω of Yaws[27)].　c) using T_c, p_c, ω from experimental data and Eqs. (2)-(4).　d) $u(T) = 0.05$ K.
e) pressure gauge PG-100KU, $u(p) = 15$ kPa.　f) barometer T60, $u(p) = 0.03$ kPa.　g) absolute pressure sensor PHS-2KA, $u(p) = 0.2$ kPa.
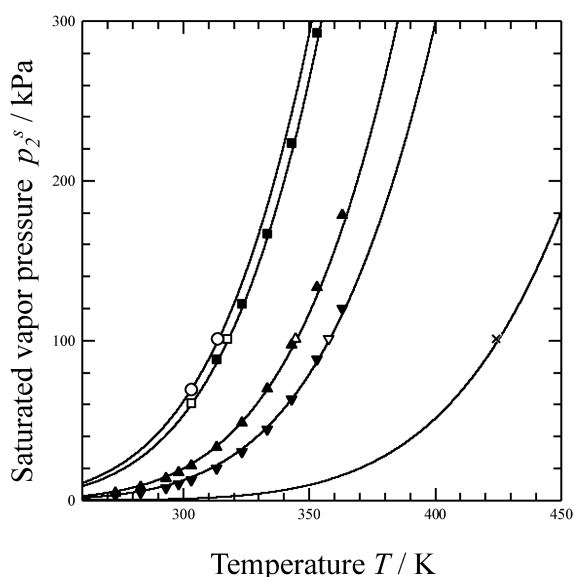
(○): this work, 1-pentyne; (□): this work, cyclopentene; (■): Jeong and Lim[31)], cyclopentene; (△): this work, 1-hexyne; (▲): Negadi *et al.*[32)], 1-hexyne; (▽): this work, 2-hexyne; (▼): Negadi *et al.*[32)], 1-hexyne; (×): this work, 1,5-cyclooctadiene; (−): PR/PRSV equation.

Fig. 5 Saturated Vapor Pressure of 1-Pentyne, Cyclopentene, 1-Hexyne, 2-Hexyne and 1,5-Cyclooctadiene

the correlation of bubble point pressure.

3. 2. Bubble Point Pressure of Five Binaries with Propane

The absolute pressure sensor, PHS-2KA, was checked by measuring the saturated vapor pressure for 1-pentyne and cyclopentene at 303.15 K. The other pressure gauge, PG-100KU, was checked by measuring the saturated vapor pressure for propane at 303.15 K. The saturated vapor pressure of propane is listed in **Table 3**. According to the NIST Chemistry Webbook, SRD 69[30)], the saturated vapor pressure of propane is

1079.1 kPa at 303.15 K. Then, the RD was evaluated as $\delta p^s/p^s_{exp} = 0.475$ %. The reliability of the experimental data measured by the other pressure gauge, PG-10KU, was ensured by comparison with the data from the static and synthetic apparatuses. The mole fraction at bubble point pressure was exactly the same as that at the preparation in the synthetic apparatus. The mole fraction at the bubble point pressure was assumed to be the same as that at the preparation in the static apparatus. However, alkynes and alkadienes are well known to react with elemental mercury[33)]. In particular, 1,5-cyclooctadiene is a well-known ligands for various metal ions[34)]. Mercury was used as a pressurizing medium in the synthetic apparatus. Therefore, prior to measurements, 1-hexyne and 1.5-cyclooctadiene were mixed with elemental mercury and maintained for a day at room temperature. A trace of reaction was observed on the mercury with 1,5-cyclooctadiene, as the surface of the mercury had become blackened. No changes were seen with 1-hexyne. Therefore, the static and synthetic apparatuses were used only for the propane (1)−1-hexyne (2) binary to ensure the reliability of the bubble point pressure data at 303.15 K.

Table 4 lists the experimental data, and **Fig. 6** shows the comparison of the data from the two apparatuses. The data from the synthetic apparatus seemed to show somewhat higher values than those from the static apparatus. The maximum capacities of the pressure sensors were 20 MPa in the synthetic apparatus and 1 MPa in the static apparatus, respectively. The data from static apparatus tended to give slightly lower bubble point pressure because the composition was assumed to be that at preparation. However, the data seemed to agree well. Therefore, the static apparatus was mainly employed for investigation of the other four binaries.

Figure 7 shows the boiling points for propane (1)−1-pentyne (2), propane (1)−1-cyclopentene (2), pro-

Table 4 Bubble Point Pressure of Propane with 1-Pentyne, Cyclopentene, 1-Hexyne, 2-Hexyne, 1,5-Cyclooctadiene at 303.15 K

Measured[a]		Calculated			
Mole fraction of propane x_1[b] [-]	Bubble point pressure p[c] [kPa]	Mole fraction of propane x_1 [-]	$\delta x_1/x_{1,\,\mathrm{exp}}$ [%]	Bubble point pressure p [kPa]	$\delta p/p_{\mathrm{exp}}$ [%]
propane (1)–1-pentyne (2)					
0.0000[d]	69.2[d]			69.3	0.116
0.2177	334.0	0.2172	−0.244	334.6	0.175
0.3256	447.4	0.3252	−0.129	447.8	0.094
0.5768	678.5	0.5756	−0.202	679.5	0.149
0.7184	801.5	0.7179	−0.068	802.0	0.065
1.0000[d]	1074[d]			1079	0.466
propane (1)–cyclopentene (2)					
0.0000[d]	60.8[d]			59.9	−1.480
0.3019	382.0	0.3029	0.321	381.0	−0.254
0.4335	509.9	0.4336	0.028	509.8	−0.023
0.6579	721.8	0.6574	−0.076	722.3	0.065
0.8941	964.0	0.9016	0.843	957.2	−0.701
1.0000[d]	1074[d]			1079	0.466
propane (1)–1-hexyne (2) by static apparatus					
0.2188	286.9	0.2201	0.573	285.5	−0.493
0.3513	426.9	0.3490	−0.642	429.3	0.551
0.4653	541.3	0.4622	−0.675	544.4	0.568
0.6401	706.9	0.6371	−0.466	709.7	0.390
0.7653	830.9	0.7706	0.693	825.9	−0.604
0.8571	916.4	0.8579	0.097	915.6	−0.092
1.0000[d]	1074[d]			1079	0.466
propane (1)–1-hexyne (2) by synthetic apparatus					
0.6731[e]	753.0[f]	0.6871	2.075	740.1	−1.712
0.6778[e]	759.2[f]	0.6938	2.358	744.4	−1.944
0.7578[e]	834.8[f]	0.7747	2.232	818.8	−1.915
0.8221[e]	890.1[f]	0.8318	1.177	880.5	−1.074
0.8782[e]	942.8[f]	0.8834	0.592	937.3	−0.579
propane (1)–2-hexyne (2)					
0.2215	282.2	0.2272	2.556	275.8	−2.251
0.3751	441.2	0.3742	−0.241	442.1	0.213
0.5528	606.7	0.5390	−2.501	620.1	2.206
0.6733	729.0	0.6672	−0.908	734.8	0.792
0.8933	953.0	0.8948	0.168	951.4	−0.213
1.0000[d]	1074[d]			1079	0.466
propane (1)–1,5-cyclooctadiene (2)					
0.2371	336.7	0.2377	0.274	335.9	−0.247
0.3727	507	0.3801	1.973	498.8	−1.616
0.5248	652.9	0.5227	−0.399	654.9	0.300
0.6451	744.4	0.6261	−2.939	760.1	2.110
0.7871	863.7	0.7762	−1.383	872.2	0.986
0.8884	969.9	0.9033	1.677	956.2	−1.416
1.0000[e]	1074[e]			1079	0.466

a) $u(T) = 0.05$ K.　b) $u(x_1) = 0.0004$ (except for data by synthetic apparatus).　c) pressure gauge PG-10KU, $u(p) = 2.5$ kPa (except for data by synthetic apparatus).　d) data already listed in Table 3.　e) $u(x_1) = 0.0002$.　f) pressure gauge PG-200KU, $u(p) = 2.5$ kPa.

pane (1)–2-hexyne (2) and propane (1)–1,5-cyclooctadiene (2) at 303.15 K, and **Table 4** lists the experimental data. The bubble point pressures, except for propane (1)–1,5-cyclooctadiene (2), showed linear dependences with the mole fraction, and Raoult's law was approximately acceptable at the experimental temperature. The tendency was common with that for propane (1)–1-hexyne (2). Even for propane (1)–1,5-cyclooctadiene (2), the non-ideality was not so large.

The experimental data were correlated with the PR/PRSV equation. **Table 5** lists the binary parameters for the five binaries. **Figures 6** and **7** show the results of the correlation. All data were well correlated with the PR/PRSV equation. The reproducibility was evaluated by the following two RDs:

$$\frac{\delta x_1}{x_{1,\mathrm{exp}}} = \frac{x_{1,\mathrm{cal}} - x_{1,\mathrm{exp}}}{x_{1,\mathrm{exp}}} \tag{9}$$
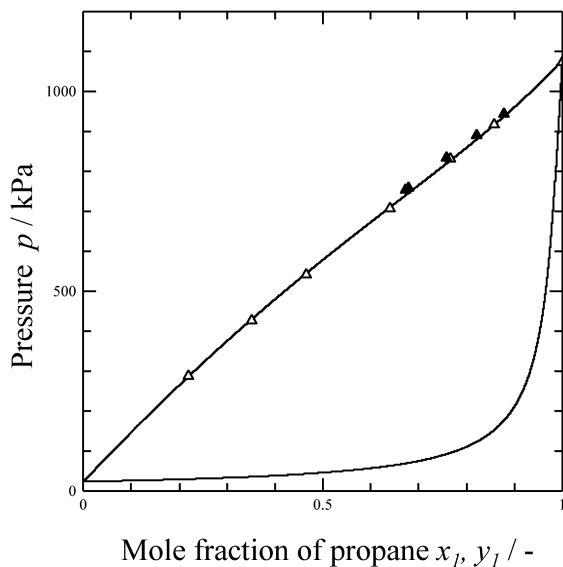
(△): this work, static apparatus; (▲): this work, synthetic apparatus;
(−): PR/PRSV equation.

Fig. 6　VLE for Propane (1)–1-Hexyne (2) at 303.15 K

$$\frac{\delta p}{p_{exp}} = \frac{p_{cal} - p_{exp}}{p_{exp}} \qquad (10)$$

Table 4 lists the RDs, $\delta x_1/x_{1,exp}$ and $\delta p/p_{exp}$ for the five binaries. **Figure 8** shows the distribution of the RDs with experimental pressure and mole fraction of propane. In **Fig. 8**, the upper horizontal axis indicates reduced pressure, where the bubble point pressure was divided by the saturated vapor pressure of propane. The RDs were no larger than 2.939 % and 2.251 % for the mole fraction of propane and the bubble point pressure, respectively. In the correlation of the bubble point pressure, VLE or dew point pressure was predict-

Table 5　Binary Parameters in PR/PRSV Equation at 303.15 K

	Binary parameter k_{ij} [-]
propane (1)–1-pentyne (2)	0.035
propane (1)–cyclopentene (2)	0.003
propane (1)–1-hexyne (2)	0.028
propane (1)–2-hexyne (2)	0.021
propane (1)–1,5-cyclooctadiene (2)	0.028
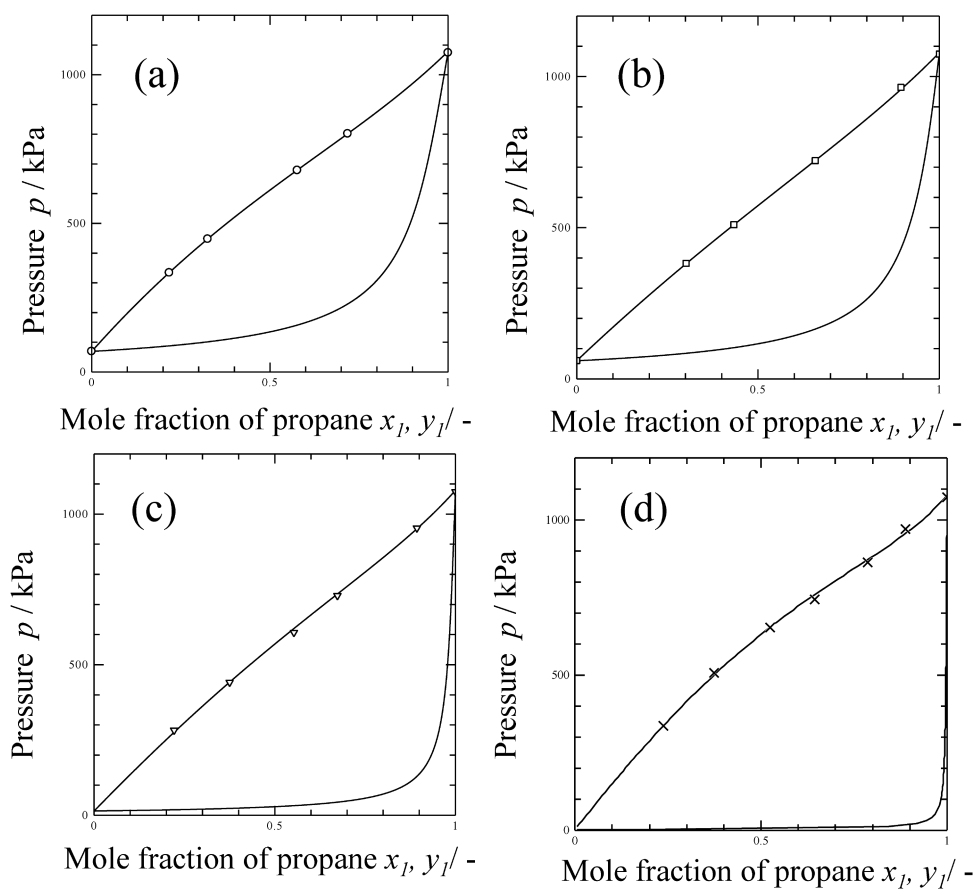
(a) (○): this work, propane (1)–1-pentyne (2); (b) (□): this work, propane (1)–cyclopentene (2); (c) (▽): this work, propane (1)–2-hexyne (2); (d) (×): this work, propane (1)–1,5-cyclooctadiene (2); (−): PR/PRSV equation.

Fig. 7　VLE for Propane with 1-Pentyne, Cyclopentene, 2-Hexyne or 1,5-Cyclooctadiene at 303.15 K

Reduced pressure p / p_1^s / -
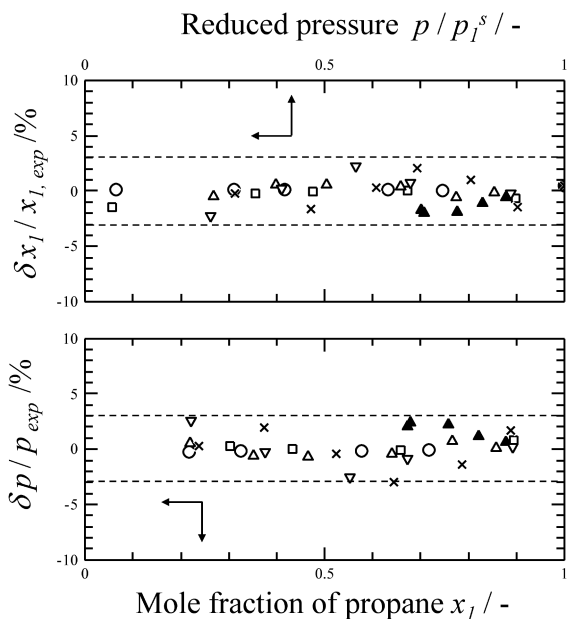
($\bigcirc$): propane (1)–1-pentyne (2); ($\square$): propane (1)–cyclopentene (2); ($\triangle$): propane (1)–1-hexyne (2) by static apparatus; ($\blacktriangle$): propane (1)–1-hexyne (2) by synthetic apparatus; ($\triangledown$):propane (1)–2-hexyne (2); ($\times$): propane (1)–1,5-cyclooctadiene (2).

Fig. 8 Deviation from the PR/PRSV Equation of Bubble Point Pressures and Mole Fractions of Propane

Table 6 Calculated Concentrations of Odorant for 1000 ppm (mole base) in Propane at 303.15 K

	Calculated pressure p_{cal} [kPa]	Concentration of odorant C_2 [ppm (mole base)]
1-pentyne	1077.8	165.6
cyclopentene	1077.8	120.5
1-hexyne	1077.7	63.00
2-hexyne	1077.7	42.08
1,5-cyclooctadiene	1077.6	9.457

303.15 K. The PR/PRSV equation reliably correlated the bubble point pressures for the five binaries, and described the concentrations of the five compounds in the vapor phase. The experimental data of the bubble point pressure and boiling point under atmospheric pressure will be useful in the development of a new sulfur-free odorants for LPG.

Acknowledgment

Nomenclatures

a	: parameter in the PR/PRSV equation
b	: parameter in the PR/PRSV equation
C_2	: mole basis concentration of odorant in vapor phase
k_{ij}	: binary interaction parameter in the mixing rule
N_{atoms}	: number of atoms in a molecule
N_k	: number of group k
p	: pressure
p_c	: critical pressure
pc_k	: group parameter of critical temperature for group k
p^s	: saturated vapor pressure
R	: gas constant
T	: temperature
T_b	: normal boiling point
T_c	: critical temperature
tc_k	: group parameter of critical temperature for group k
$u(X)$	: uncertainty for X
v	: molar volume
x_i	: mole fraction of component i in liquid phase
y_i	: mole fraction of component i in vapor phase

$<$Greeks$>$

δX	: difference between calculation and experimental datum for X
κ_1	: parameter for the PRSV equation
ω	: acentric factor

$<$Subscripts$>$

1, 2	: component 1 and 2
exp, cal	: experimental and calculated

ed automatically. The VLEs are also shown in **Figs. 6** and **7**. The objective of this research was to assess the volatility of the five compounds from the liquid phase of LPG. The concentration in vapor phase was estimated at the concentration of 1000 ppm in liquefied propane on the mole basis. **Table 6** lists the calculation results. The concentration seems to depend on the boiling point or the saturated vapor pressure. As listed in **Table 3**, the saturated vapor pressures of 1-pentyne and cyclopentene at 303.15 K were 69.2 kPa and 60.8 kPa, respectively. The saturated vapor pressure of 1-hexyne, 2-hexyne and 1,5-cyclooctadine at 303.15 K were estimated to be 22.7, 14.4 and 1.11 kPa, respectively, using the PR equation. However, no linear relationship of the saturated vapor pressure was found with the concentration.

4. Conclusion

Boiling points, under atmospheric pressure, were measured for 1-pentyne, cyclopentene, 1-hexyne, 2-hexyne, and 1,5-cyclooctadiene, which are potential sulfur-free odorants for LPG. The experimental boiling points were used for the evaluation of parameters in the PR equation by applying a group contribution method for critical temperature and pressure, and approximation for the acentric factor. Bubble point pressures were measured for the five binaries with propane at

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要　　旨

5種類の液化ガス用新規非硫黄系着臭剤候補物質1-ペンチン，シクロペンテン，1-ヘキシン，2-ヘキシン，1,5-シクロオクタジエンおよびプロパンとの混合系の沸点測定

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液化石油ガスの新規非硫黄系着集剤候補物質として期待される5種類の化合物，1-ペンチン，シクロペンテン，1-ヘキシン，2-ヘキシン，および1,5-シクロオクタジエンの大気圧下の沸点をエブリオメーターで測定したところ313.51，313.76，344.53，357.59および424.02 K であった。また，これらの化合物にプロパンを加えた2成分系の303.15 K における沸点圧力を静置型装置で測定した。プロパン–1-ヘキシンについては同一温度でシンセチック装置でも測定し，データの健全性も確認した。純物質の沸点実測値と Lydersen のグループ寄与法によって臨界温度，臨界圧力および偏心因子から Peng-Robinson 状態方程式のパラメーターを求めた。この値を使用することにより，純物質および混合系の沸点は，それぞれ絶対相対偏差2.887 % および2.251 % 内で一致した。

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