$p\rho Tx$-Property Measurements Near Saturation in the Gaseous Phase for Propane + Isobutane

Atsushi Yamaguchi, Mitsuru Mukoubayashi, Tae Matsunami, and Haruki Sato*

Graduate School of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

$p\rho Tx$-property measurements near saturation in the gaseous phase for propane (1) + isobutane (2) at x_1 = 0.25 (w_1 = 20.19 %), x_1 = 0.5 (w_1 = 43.14 %), and x_1 = 0.80 (w_1 = 75.22 %) are reported. The data near saturation in the gaseous phase are important information for deriving reliable property values such as specific heats near saturation or for determining the second and third virial coefficients. The measurements were performed using a magnetic suspension densimeter. 154 $p\rho Tx$ values for propane + isobutane mixtures were obtained at the temperatures of (303.15 and 323.15) K and for pressures up to 980 kPa. The experimental uncertainties are estimated to be 10 mK for temperature, 0.45 kPa for pressure, (0.03 % + 0.005 $kg \cdot m^{-3}$) for density, and 0.31 % in mass fraction (0.32 % in mole fraction). The purities of propane and isobutane were both 99.99 % in mass fraction according to the report from the manufacturer. The measurements are used for assessing the reliability of existing equations of state.

Introduction

For the development of energy-conversion systems, accurate thermodynamic properties of the working fluid are required. These properties are calculated from a thermodynamic equation of state. To develop the equations of state which accurately represent the gaseous thermodynamic surfaces of interest, reliable measurements of the thermodynamic properties must be available near saturation.

When the $p\rho Tx$-properties are not reported in the region near saturation in the gaseous phase, there is a possibility to have more than 5 % of uncertainty in the specific heat at saturation as we have found for R-143a.[1]

$p\rho Tx$-properties of a system composed of propane + isobutane in the gaseous phase including in the region near saturation were measured with a magnetic suspension densimeter.

Experimental Apparatus

An experimental apparatus which has two densimeters with a magnetic suspension balance was used for density measurements. The apparatus and the principle used here were reported by Wagner et al. in detail in a publication.[2]

Pressure was measured by a quartz digital pressure gauge, which was calibrated by using a dead-weight pressure gauge (model 5201, DH Instruments). The density measurement system consists of two magnetic suspension densimeters. The reliability was confirmed by the measurements of Argon density to be within (0.03 % + 0.005 $kg \cdot m^{-3}$) as reported in a previous publication.[3] The temperature was measured using a standard platinum-resistance thermometer. The temperature values were processed in accordance with the ITS-90. The thermometer was installed in the middle between the two cells of the A and B densimeters in the thermostatic bath.

The sample purities of propane and isobutane were better than 99.99 % in mass fraction according to the report from the manufacturer. Each sample was cooled by using liquid nitrogen and then degassed once or twice using a vacuum pump. The weight of sample gases was measured by using a chemical balance.

The expanded uncertainties with a coverage factor of 2 having a level of confidence of 95 % were estimated to be not greater than 10 mK for temperature measurements, not greater than 0.45 kPa for pressure measurements, and not greater than (0.03 % + 0.005 $kg \cdot m^{-3}$) in density measurements. The composition measurement uncertainties were not greater than 0.31 % in mass fraction (0.32 % in mole fraction). Tables 1 and 2 show the details of the uncertainties in temperature and pressure measure-

Table 1. Details of Temperature Uncertainty

factor	uncertainty/mK
standard platinum resistance	1.0
thermometer bridge	0.27
temperature stability in the isothermal bath	3.0
temperature distribution in the isothermal bath	4.0
reproducibility of correlating equation by ITS-90	0.13
combined standard uncertainty	5.1
expanded uncertainty	10

Table 2. Details of Pressure Uncertainty

factor	uncertainty/kPa
quartz digital pressure gauge	0.098
variation of zero point	0.017
standard deviation of correlating equation	0.12
atmosphere pressure gauge	0.015
dead-weight pressure gauge	0.15
variation in measurements	0.06
pressure difference from head difference	0.033
combined standard uncertainty	0.23
expanded uncertainty	0.45

Table 3. Filled Mass for Each Composition

	filled mass/g	
mole fraction of propane	propane	isobutane
0.244	0.995	4.051
0.249	1.014	4.030
0.499	2.615	3.455
0.503	1.563	2.034
0.799	3.522	1.165

* To whom correspondence should be addressed. E-mail: hsato@sd.keio.ac.jp.

10.1021/je900244c CCC: $40.75
Published on Web 06/15/2009

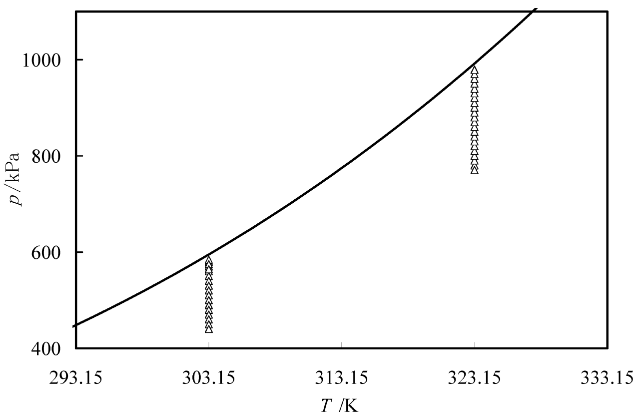

Figure 1. Experimental data points for propane + isobutane mixtures at x_1 = 0.5. Δ, This work. The line is the saturation curve calculated from ref 6.

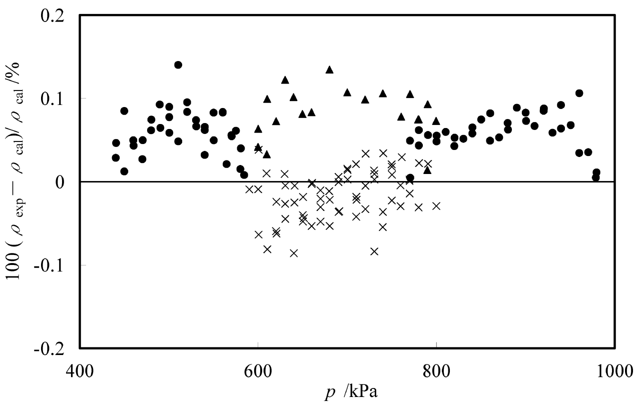

Figure 2. Relative deviation of the experimental density ρ_{exp} of propane + isobutane mixtures from values ρ_{cal} calculated from the equation of state developed by Kunz et al.[6] ×, This work (x_1 = 0.25); ●, This work (x_1 = 0.5); ▲, This work (x_1 = 0.80).

Table 4. Details of Composition Uncertainty

mole fraction of propane	from purity of 99.99 % propane	from purity of 99.99 % isobutane	mass measurement	residual mass in filling process	combined standard uncertainty	expanded uncertainty	expanded uncertainty
	g	g	g	g	mass fraction	mass fraction	mole fraction
0.244	0.0001	0.0004	0.006	0.005	0.0013	0.0026	0.0030
0.249	0.0001	0.0004			0.0013	0.0026	0.0030
0.499	0.0003	0.0004			0.0009	0.0018	0.0019
0.503	0.0002	0.0002			0.0015	0.0031	0.0032
0.799	0.0004	0.0001			0.0013	0.0026	0.0023

ments, respectively. Tables 3 and 4 show the filled mass of each composition and the details of composition measurement uncertainties, respectively.

Experimental Results

The $p\rho Tx$-properties for propane + isobutane at x_1 = 0.25 (65 points), x_1 = 0.5 (69 points), and x_1 = 0.80 (20 points) were represented along two different isotherms near saturation at temperatures of (303.15 and 323.15) K with pressures up to 980 kPa. The measured data for the mixture system of propane + isobutane are listed in Table 5. The data distribution exemplified at x_1 = 0.5 is represented on a pressure−temperature plot in Figure 1. Our data were measured at every 10 kPa in the region near saturation. The reproducibility was confirmed by the data given at exactly the same state conditions.

Discussion

An equation of state for propane has been developed by Lemmon et al.[4] and for isobutane by Buecker and Wagner.[5]

Table 5. Experimental $p\rho Tx$-Properties of Propane + Isobutane at x_1 = 0.25, 0.5, and 0.80

x_1	T/K	p/kPa	ρ/kg·m^{-3}	x_1	T/K	p/kPa	ρ/kg·m^{-3}
0.244	323.15	590.1	13.582	0.249	323.15	650.1	15.168
0.244	323.15	600.1	13.847	0.249	323.15	660.0	15.436
0.244	323.15	609.5	14.100	0.249	323.15	660.1	15.447
0.244	323.15	620.5	14.391	0.249	323.15	670.0	15.714
0.244	323.15	629.7	14.643	0.249	323.15	670.1	15.719
0.244	323.15	630.5	14.658	0.249	323.15	680.3	15.998
0.244	323.15	640.7	14.937	0.249	323.15	680.4	16.006
0.244	323.15	650.3	15.201	0.249	323.15	690.2	16.277
0.244	323.15	651.3	15.223	0.249	323.15	690.2	16.285
0.244	323.15	660.6	15.487	0.249	323.15	700.3	16.571
0.244	323.15	670.0	15.744	0.249	323.15	700.4	16.571
0.244	323.15	670.0	15.744	0.249	323.15	710.0	16.835
0.244	323.15	679.7	16.015	0.249	323.15	710.1	16.843
0.244	323.15	690.2	16.310	0.249	323.15	720.3	17.129
0.244	323.15	691.1	16.328	0.249	323.15	720.4	17.137
0.244	323.15	700.1	16.592	0.249	323.15	730.0	17.416
0.244	323.15	709.8	16.868	0.249	323.15	730.3	17.408
0.244	323.15	710.3	16.875	0.249	323.15	739.8	17.687
0.244	323.15	720.6	17.177	0.249	323.15	740.0	17.697
0.244	323.15	730.4	17.456	0.249	323.15	750.0	17.989
0.244	323.15	730.5	17.456	0.249	323.15	750.0	17.996
0.244	323.15	740.4	17.750	0.249	323.15	759.7	18.276
0.244	323.15	749.8	18.022	0.249	323.15	759.9	18.276
0.244	323.15	750.2	18.029	0.249	323.15	769.9	18.577
0.244	323.15	761.2	18.357	0.249	323.15	770.0	18.577
0.244	323.15	769.7	18.602	0.249	323.15	780.0	18.871
0.244	323.15	790.6	19.228	0.249	323.15	780.5	18.894
0.249	323.15	600.6	13.833	0.249	323.15	799.9	19.467
0.249	323.15	600.7	13.848	0.499	323.15	770.4	16.983
0.249	323.15	610.4	14.090	0.499	323.15	770.7	16.982
0.249	323.15	620.1	14.354	0.499	323.15	780.2	17.239
0.249	323.15	620.7	14.369	0.499	323.15	780.3	17.244
0.249	323.15	630.3	14.633	0.499	323.15	790.6	17.513
0.249	323.15	630.5	14.640	0.499	323.15	800.2	17.765
0.249	323.15	640.1	14.889	0.499	323.15	800.2	17.769
0.249	323.15	640.9	14.923	0.499	323.15	810.5	18.042
0.249	323.15	650.1	15.168	0.499	323.15	820.2	18.299
0.499	323.15	820.4	18.307	0.503	303.15	510.3	11.608
0.499	323.15	830.3	18.572	0.503	303.15	510.5	11.600
0.499	323.15	840.3	18.844	0.503	303.15	520.4	11.861
0.499	323.15	840.4	18.848	0.503	303.15	520.4	11.864
0.499	323.15	850.3	19.121	0.503	303.15	530.4	12.121
0.499	323.15	860.2	19.387	0.503	303.15	530.7	12.129
0.499	323.15	860.4	19.398	0.503	303.15	540.1	12.370
0.499	323.15	870.4	19.669	0.503	303.15	540.2	12.378
0.499	323.15	879.9	19.938	0.503	303.15	540.2	12.378
0.499	323.15	880.4	19.948	0.503	303.15	550.1	12.642
0.499	323.15	890.2	20.228	0.503	303.15	550.3	12.642
0.499	323.15	900.1	20.506	0.503	303.15	560.3	12.914
0.499	323.15	900.6	20.517	0.503	303.15	560.3	12.914
0.499	323.15	910.1	20.784	0.503	303.15	564.6	13.019
0.499	323.15	920.3	21.078	0.503	303.15	570.1	13.170
0.499	323.15	920.6	21.087	0.503	303.15	570.4	13.178
0.499	323.15	930.3	21.359	0.503	303.15	575.1	13.306
0.499	323.15	939.7	21.637	0.503	303.15	580.1	13.434
0.499	323.15	939.8	21.635	0.503	303.15	580.7	13.453
0.499	323.15	950.6	21.949	0.503	303.15	584.3	13.548
0.499	323.15	960.2	22.222	0.799	303.15	599.9	12.550
0.499	323.15	960.3	22.242	0.799	303.15	600.1	12.557
0.499	323.15	970.3	22.521	0.799	303.15	609.7	12.784
0.499	323.15	978.9	22.767	0.799	303.15	610.2	12.802
0.499	323.15	979.6	22.791	0.799	303.15	620.2	13.040
0.503	303.15	440.3	9.824	0.799	303.15	630.2	13.289
0.503	303.15	440.7	9.834	0.799	303.15	639.7	13.516
0.503	303.15	449.9	10.061	0.799	303.15	649.7	13.757
0.503	303.15	450.0	10.069	0.799	303.15	659.8	14.006
0.503	303.15	460.0	10.317	0.799	303.15	680.1	14.516
0.503	303.15	460.4	10.325	0.799	303.15	700.0	15.010
0.503	303.15	470.2	10.570	0.799	303.15	720.0	15.515
0.503	303.15	470.5	10.581	0.799	303.15	739.9	16.028
0.503	303.15	480.0	10.823	0.799	303.15	760.5	16.557
0.503	303.15	480.3	10.830	0.799	303.15	770.4	16.821
0.503	303.15	489.7	11.072	0.799	303.15	779.5	17.055
0.503	303.15	490.4	11.087	0.799	303.15	780.1	17.073
0.503	303.15	500.3	11.344	0.799	303.15	789.8	17.319
0.503	303.15	500.4	11.344	0.799	303.15	790.1	17.342
0.503	303.15	500.4	11.344	0.799	303.15	799.6	17.590

The equation of state for the properties of the mixture developed by Kunz et al.[6] is applied, and the relative deviations of the experimental data of this work from the calculated values are presented in Figure 2. As shown in Figure 2, the discrepancy between our data and the equation of state developed by Kunz et al. is between (−0.1 and 0.15) % depending on the composition.

Conclusions

The $p\rho Tx$-properties of propane (1) and isobutane (2) mixtures in the gaseous phase including values near saturation were measured with a magnetic suspension densimeter. A total of 154 $p\rho Tx$-values at $x_1 = 0.25$, 0.5, and 0.80 with an uncertainty of ($0.03\ \% + 0.005\ \mathrm{kg\cdot m^{-3}}$) in density were obtained. In the near future, reliable values of the virial coefficient values and of other thermodynamic properties such as specific heats, sound speed, etc. including those near saturation conditions or at very low pressures, where measurements are not easily performed, will be calculated on the basis of the present data.

Literature Cited

(1) Ichikura, K.; Kano, Y.; Sato, H. Importance of Third Virial Coefficients for Representing the Gaseous Phase Based on Measuring PVT-Properties of 1,1,1-Trifluoroethane (R143a). *Int. J. Thermophys.* **2006**, *27*, 23–38.

(2) Wagner, W.; Brachthäuser, K.; Kleinrahm, R.; Lösch, H. W. A New, Accurate Single-Sinker Densitometer for Temperatures from 233 to 523 K at Pressures up to 30 MPa. *Int. J. Thermophys.* **1995**, *16*, 399–411.

(3) Mukoubayashi, M.; Ichikura, K.; Kano, Y.; Sato, H. PVT-Property Measurements for R143a, R125, and R32 in the Gaseous Phase. *J. Chem. Eng. Data* **2007**, *52*, 1925–1929.

(4) Lemmon, E. W.; McLinden, M. O.; Wagner, W. NIST Standard Reference Database 23. *NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)*, ver. 8.0; The National Institute of Standards and Technology: Boulder, USA, 2008.

(5) Buecker, D.; Wagner, W. Reference Equations of State for the Thermodynamic Properties of Fluid Phase n-Butane and Isobutane. *J. Phys. Chem. Ref. Data* **2006**, *35*, 929–1019.

(6) Kunz, O.; Klimeck, R., Wagner, W.; Jaeschke, M. *The GERG-2004 Wide-Range Reference Equation of State for Natural Gases and Other Mixtures*. GERG Technical Monograph 15 2007. Fortschr.-Ber. VDI, 6, No. 557, VDI Verlag: Düsseldorf, 2007.

Received for review March 7, 2009. Accepted June 1, 2009. We are grateful to MAYEKAWA MFG. CO., LTD. and IWATANI INDUSTRIAL GASES CORPORATION for a part of the financial support. This work was supported in part by a Grant in Aid for the Global Center of Excellence Program for “Center for Education and Research of Symbiotic, Safe and Secure System Design” from the Ministry of Education, Culture, Sport, and Technology in Japan.

JE900244C