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Isochoric Heat Capacities of Propane + Isobutane Mixtures at Temperatures from 280 to 420 K and at Pressures to 30 MPa[1]

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The isochoric heat capacity (c_v) and pressure–volume–temperature-composition ($pvTx$) properties were measured for propane + isobutane mixtures in the liquid phase and in the supercritical region. The expanded uncertainty ($k = 2$) of temperature measurements is estimated to be ±13 mK, and that of pressure measurements is ±8 kPa. The expanded relative uncertainty for c_v is ±3.2% for the liquid phase, increasing to ±4.8% for near-critical densities. The expanded uncertainty for density is estimated to be ±0.16%. The present measurements for $\{xC_3H_8 + (1-x)i\text{-}C_4H_{10}\}$ with $x = 0.0$, 0.498, 0.756, and 1.0, were obtained at 659 state points at temperatures from 270 to 420 K and at pressures up to 30 MPa. The experimental data were compared with a published equation of state.

KEY WORDS: critical region; density; heat capacity; isobutane; mixtures; propane; *pvTx* property.

1. INTRODUCTION

Recently, refrigerant substances found in nature have attracted renewed attention due to their mild impact on the environment. Hydrocarbons and their mixtures are considered to be leading candidates for alternative refrigerants because they have zero ozone depletion potential (ODP)

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values and negligible global warming potential (GWP) values. Reliable equations of state for these working fluids are necessary to evaluate the cycle performance of refrigeration systems.

In order to develop a reliable equation of state for a fluid, various thermodynamic property measurements of the fluid are required. Among them, isochoric heat capacity (c_v) measurements provide a very useful check for calculations of the second derivative of the pressure with respect to temperature, which is essential information to develop equations of state but is challenging to measure accurately. For $\{xC_3H_8 + (1-x)i\text{-}C_4H_{10}\}$ in the compressed liquid phase, earlier measurements of c_v have been reported by Duarte-Garza and Magee [1] in a temperature range from 202 to 342 K. To extend them to higher temperatures, heat capacities of the mixtures up to near the critical region were measured in this study. The present measurements were compared with c_v measurements in the liquid phase reported by Goodwin [2] for propane and by Miyamoto et al. [3] for isobutane.

In this work, we report c_v and pvT property measurements for $\{xC_3H_8 + (1-x)i\text{-}C_4H_{10}\}$ with $x = 0.0$, 0.498, 0.756, and 1.0 at temperatures from 270 to 420 K, and at pressures up to 30 MPa and evaluate them with a reliable equation of state. The reported density measurements are in the single-phase region and covered a range $\rho > 0.273\,\mathrm{g \cdot cm^{-3}}$.

2. MEASUREMENTS

2.1. Experimental Procedures

A twin-cell-type adiabatic calorimeter was used for these measurements; it has been described previously in detail by Kuroki et al. [4]. A spherical cell (approximately 33 cm^3) contains a sample, and a second identical cell serves as a reference. A resistive heater wire is firmly attached to each cell surface to heat the sample. The heater wires are capable of reaching 470 K. Part of the heating energy is released to the surroundings via low-resistance lead wires of the heater wire. In an earlier paper [5], the actual electric energy supplied to each cell was determined to be 94.0% of the supplied energy to the heater wire during apparatus validation measurements on distilled water. For the heat capacity measurement, precisely measured electrical energy (Q) is applied and the resulting temperature rise ($\Delta T = T_2 - T_1$) is measured. c_v is obtained from

$$c_v = \left(\frac{\partial U}{\partial T}\right)_V \cong \frac{\alpha\,(\Delta Q - \Delta Q_0) - W_{PV}}{m \Delta T} \tag{1}$$

where U is the internal energy, ΔQ_0 is the energy difference between the sample cell and reference cell when both cells are empty, ΔQ refers to the energy added during an experiment with a sample in the sample cell and a blank (vacuum) in the reference cell, W_{PV} is the change-of-volume work due to the slight dilation of the cell, α is the coefficient of the available electrical energy supplied to the heater wire, and m is the mass of sample in the sample cell.

2.2. Materials

High-purity samples of propane (C_3H_8) and isobutane (i-C_4H_{10}) were obtained to prepare the mixtures. The C_3H_8 and i-C_4H_{10} were each certified by manufacturer to have a minimum purity of 0.9999 mol fraction by gas chromatographic analysis. The two mixtures of this study were prepared inside the calorimeter cell. A quantity of each pure component was filled into its own lightweight cylinder (75 cm^3) and was accurately weighed with a digital balance having a 0.1 mg uncertainty. After both components of the mixture were introduced into the cell from its cylinder, the cell was cooled below 278 K by a minicooler. The remaining mass in each cylinder was weighed, and the composition of the sample in the cell was calculated from the masses charged to the cell. To ensure complete homogenization prior to measurements, the sample temperature was rapidly increased until the sample pressure reached 20 MPa, then it was cooled, and this process was repeated.

2.3. Assessment of Uncertainties

The experimental expanded uncertainty (with a coverage factor $k = 2$) of the absolute temperature measurement is ±13 mK, by considering the calibration report of the PRTs (±2 mK), temperature distribution in the cell, and the accuracy of each instrument. That of the pressure measurement is ±8 kPa, based on the pressure transducer's specifications and the accuracy of the instruments. The standard uncertainty of the inner volume of the cell is 0.025 cm^3, estimated by calibration with distilled water, and that of the mass measurement is 0.15 mg, based on the balance's specifications. The expanded uncertainty of the sample mole fraction composition is ±0.1%. The estimated expanded uncertainty of density is ±0.16%, as derived from the standard uncertainties of the inner volume of the cell and the mass measurement. The expanded uncertainty of c_v is estimated from a combination of the standard uncertainty of the elapsed time required for a 1 K temperature rise (0.65%), that of the change-of-volume work (20%) which contributes 0.3% to the uncertainty of c_v, the experimental standard deviation of α of 0.6%, the uncertainty of the density, and the temperature fluctuation of adiabatic shields which contributes an amount 0.4/(m c_v) $\mathrm{J \cdot g^{-1} \cdot K^{-1}}$ to the uncertainty of c_v. The resulting expanded uncertainty of c_v is ±3.2% in the liquid phase and ±4.8% in the supercritical region.

3. RESULTS

Figure 1 shows the p-T diagram of these measurements and the published c_v data for propane, isobutane, and their mixtures. The experimental c_v and $pvTx$ results at temperature intervals of 5 K for $\{xC_3H_8 + (1-x)i\text{-}C_4H_{10}\}$ with $x = 0.0$, 0.498, 0.756, and 1.0 are presented in Table I.

Figure 2 shows the density deviations for the pvT measurements from an equation of state (EOS) developed by Miyamoto [6]. The model represents published $pvTx$ data of the mixtures ($x = 0.3$ and 0.7) that were measured with an isochoric apparatus by Duarte-Garza and Magee [1]; they show deviations of from −0.09 to 0.06% of the density. The present data are represented within ±0.2% except $x = 0.498$ at temperatures ranging from 270 to 310 K where the absolute deviations slightly grow to 0.3%. The explanation for this is unknown, but we may speculate that a vapor + liquid coexistence condition existed within the sample containment volume during this series. Good agreement of ±0.2% was noted for both pure components in the entire temperature range.

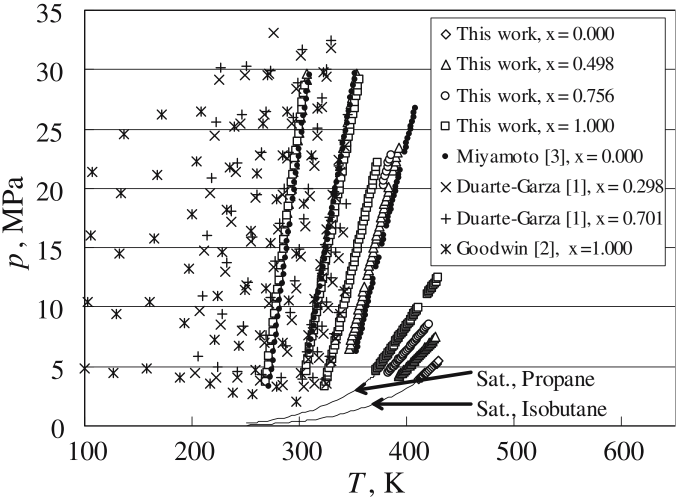

Fig. 1. Range of experimental measurements for this work.

Table I. Experimental c_v and pvT Properties for $x\mathrm{C_3H_8}$ + $(1-x)i$-$\mathrm{C_4H_{10}}$ Mixtures

$T(K)$	p (MPa)	ρ ($\mathrm{g \cdot cm^{-3}}$)	c_v ($\mathrm{J \cdot g^{-1} \cdot K^{-1}}$)	$T(K)$	p (MPa)	ρ ($\mathrm{g \cdot cm^{-3}}$)	c_v ($\mathrm{J \cdot g^{-1} \cdot K^{-1}}$)
$x = 0.000$ (Isobutane)							
415.15	4.254	0.2738	3.821	415.15	4.254	0.2738	3.971
420.15	4.664	0.2737	3.487	420.15	4.665	0.2738	3.492
425.15	5.082	0.2737	3.201	425.15	5.083	0.2737	3.219
$x = 0.498$							
270.15	4.579	0.5668	1.619	350.15	7.962	0.4717	1.836
275.15	8.198	0.5663	1.596	355.15	9.814	0.4714	1.833
280.15	11.759	0.5659	1.619	360.15	11.663	0.4712	1.833
285.15	15.256	0.5655	1.648	365.15	13.509	0.4709	1.823
290.15	18.687	0.5651	1.665	370.15	15.351	0.4707	1.852
295.15	22.038	0.5648	1.678	375.15	17.187	0.4705	1.842
300.15	25.302	0.5645	1.715	380.15	19.017	0.4702	1.859
305.15	28.471	0.5642	1.753	390.15	22.647	0.4698	1.910
315.15	9.748	0.5243	1.748	395.15	4.489	0.2741	3.597
320.15	12.415	0.5239	1.784	400.15	4.949	0.2740	3.129
325.15	15.069	0.5236	1.806	405.15	5.419	0.2739	2.827
330.15	17.709	0.5233	1.797	410.15	5.896	0.2738	2.575
335.15	20.336	0.5230	1.820	415.15	6.379	0.2737	2.431
340.15	22.950	0.5228	1.812	420.15	6.865	0.2736	2.251
345.15	25.550	0.5225	1.807	425.15	7.354	0.2736	2.135
350.15	28.136	0.5223	1.823				
$x = 0.756$							
380.15	20.994	0.4586	1.860	400.15	6.290	0.2796	2.227
385.15	22.824	0.4584	1.909	405.15	6.830	0.2796	2.133
385.15	4.713	0.2799	3.164	410.15	7.375	0.2795	2.028
390.15	5.229	0.2798	2.692	415.15	7.922	0.2794	1.962
395.15	5.756	0.2797	2.454	420.15	8.472	0.2793	1.912
$x = 1.000$ (Propane)							
270.15	4.427	0.5399	1.627	330.15	5.594	0.4546	1.786
275.15	7.953	0.5396	1.616	335.15	7.530	0.4543	1.776
280.15	11.458	0.5393	1.617	340.15	9.468	0.4541	1.762
285.15	14.939	0.5390	1.647	345.15	11.404	0.4539	1.752
290.15	18.398	0.5387	1.666	350.15	13.339	0.4537	1.802
295.15	21.836	0.5384	1.691	355.15	15.273	0.4535	1.755
300.15	25.251	0.5381	1.692	360.15	17.203	0.4533	1.763
305.15	28.640	0.5378	1.686	365.15	19.126	0.4531	1.783
310.15	6.561	0.4903	1.691	370.15	21.044	0.4529	1.795
315.15	9.049	0.4901	1.706	375.15	5.095	0.3011	2.236
320.15	11.532	0.4898	1.727	380.15	5.744	0.3010	2.110
325.15	14.008	0.4896	1.732	385.15	6.404	0.3009	2.032
330.15	16.475	0.4893	1.738	390.15	7.072	0.3008	1.952
335.15	18.934	0.4891	1.744	395.15	7.746	0.3007	1.924

Table I. (*Continued*)

$T(K)$	p (MPa)	ρ $(\mathrm{g \cdot cm^{-3}})$	c_v $(\mathrm{J \cdot g^{-1} \cdot K^{-1}})$	$T(K)$	p (MPa)	ρ $(\mathrm{g \cdot cm^{-3}})$	c_v $(\mathrm{J \cdot g^{-1} \cdot K^{-1}})$
340.15	21.386	0.4889	1.751	400.15	8.425	0.3006	1.824
345.15	23.827	0.4886	1.731	405.15	9.109	0.3005	1.788
350.15	26.253	0.4884	1.758	410.15	9.795	0.3004	1.814
355.15	28.668	0.4882	1.756	420.15	11.176	0.3002	1.810
325.15	3.660	0.4548	1.768	425.15	11.869	0.3001	1.854

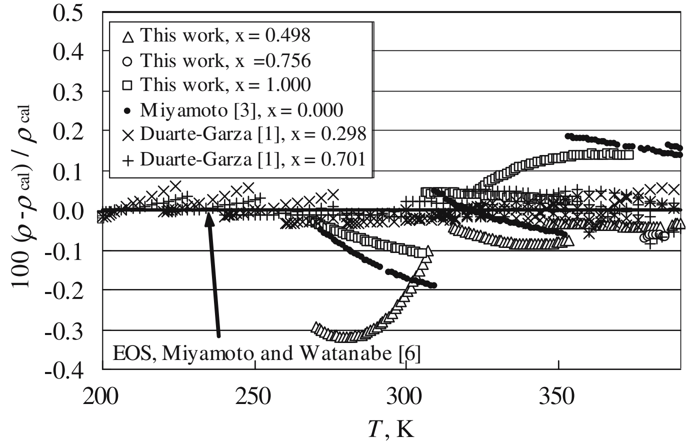

Fig. 2. Deviations of measured densities for propane, isobutane, and propane + isobutane mixtures from calculations with an EOS by Miyamoto and Watanabe [6].

Figure 3 shows the present c_v data and that reported by others [1–3] in the entire temperature range including that near the critical point. At temperatures just above the critical temperature, the enhancement of c_v that is due to critical fluctuations decreases rapidly with increasing temperature, as expected. Near the locus of critical temperatures, the c_v data of propane show less critical enhancement than that of either isobutane or the propane + isobutane binary mixtures. This behavior is observed since the density data of propane go slightly further away from the critical density (ρ_c) and its reduced density (ρ/ρ_c) is 1.31 compared to 1.20, 1.16, and 1.19 for $x = 0.000$, 0.498, and 0.756, respectively, for $x\mathrm{C_3H_8}$ + $(1-x)i$-$\mathrm{C_4H_{10}}$ mixtures. Published data of Goodwin [2] for liquid propane and Duarte-Garza and Magee [1] for liquid propane + isobutane mixtures show almost the same behavior in their overlapping temperature range. It

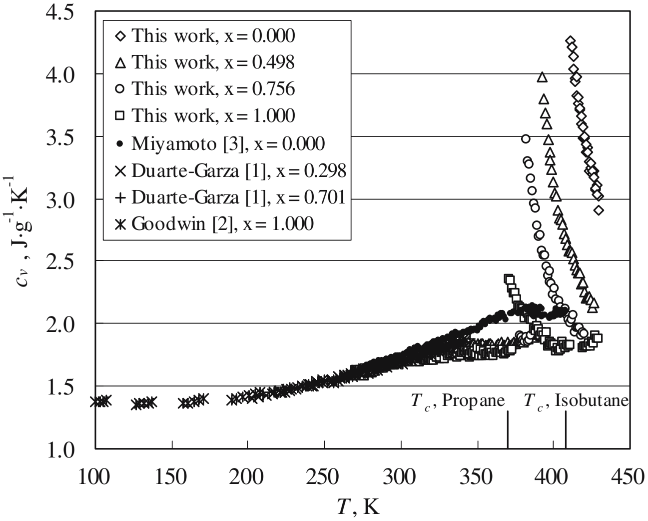

Fig. 3. Isochoric heat capacities for propane, isobutane, and propane + isobutane mixtures.

was noted that the c_v measurements for liquid isobutane [3] are higher than those of liquid propane.

Comparisons of the c_v measurements were made with values calculated with the EOS developed by Miyamoto and Watanabe [6], who did not have access to the present measurements. Figures 4 and 5 show the relative deviations of the c_v data in the full temperature range and the limited range of the liquid phase, respectively. In a range of temperatures up to 300 K, agreement is good, while in the critical region deviations up to 80% are noted, as shown in Fig. 4. This behavior would be expected of an analytic equation of state. In Figure 5, the horizontal axis represents reduced temperature by each critical temperature [7]. This figure shows systematic deviations increasing to +5% at $T/T_c = 0.9$ and decreasing to −4% at $T/T_c = 1$ for isobutane. For both propane and the binary mixtures, a systematic trend, shifting slightly and decreasing to −9% at $T/T_c = 1$, is shown in Fig. 5. The same trend for propane was confirmed during another series of propane + difluoromethane measurements [8]. Figure 6 depicts the expected linear behavior of c_v, for the pure components and binary mixtures, when plotted versus the logarithm of a departure function that is a measure of a relative temperature deviation from the critical point.

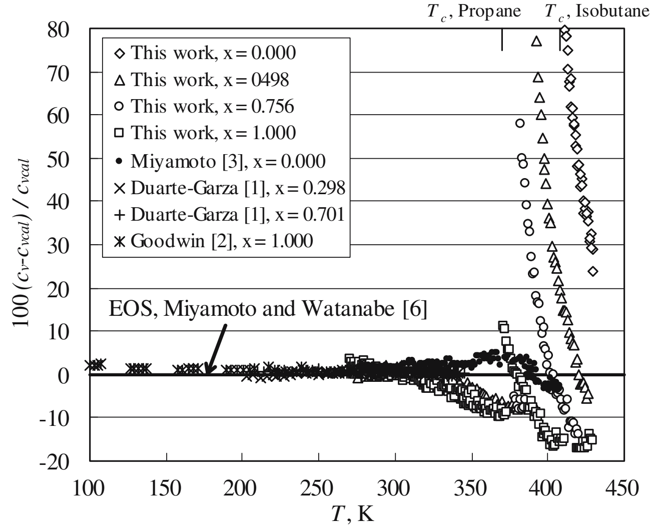

Fig. 4. Deviations of measured c_v for propane, isobutane, and propane + isobutane mixtures from calculations with an EOS by Miyamoto and Watanabe [6].

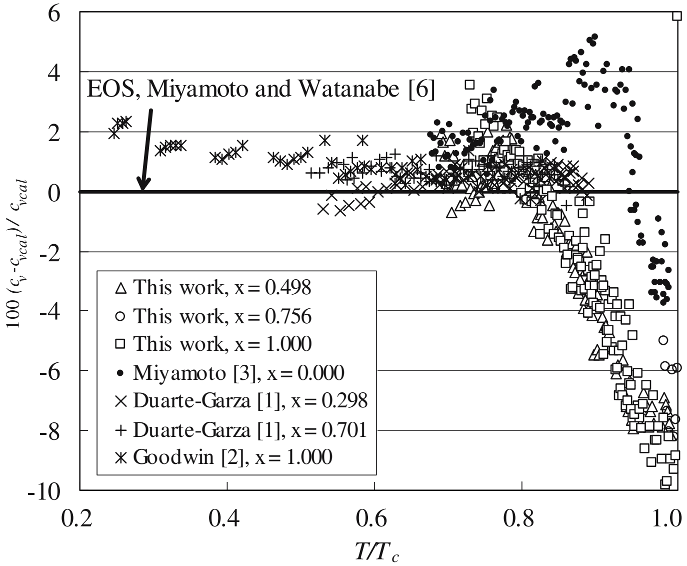

Fig. 5. Deviations of measured c_v for propane, isobutane, and propane + isobutane mixtures from calculations with an EOS by Miyamoto and Watanabe [6] for liquid-phase states.

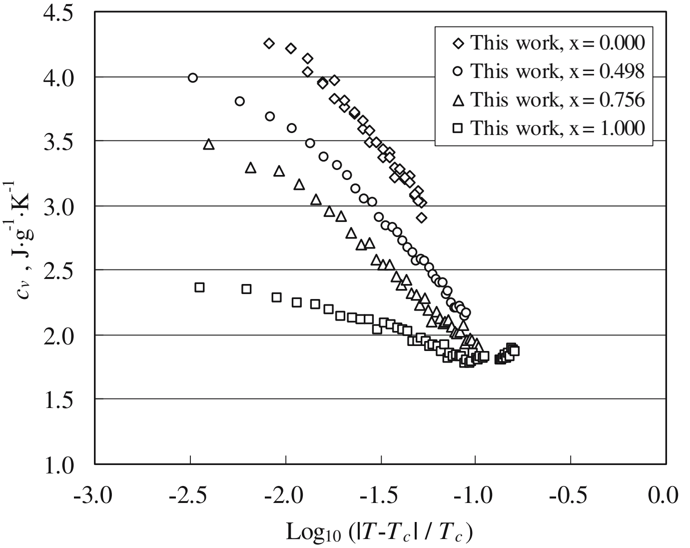

Fig. 6. Representation of c_v in the supercritical region as a function of $\log_{10}(T-T_c)/T_c$.

4. CONCLUSIONS

Measurements of c_v and $pvTx$ properties were reported for $\{xC_3H_8 + (1-x)i\text{-}C_4H_{10}\}$ with $x = 0.0$, 0.498, 0.756, and 1.0 in the liquid phase and supercritical region. The published EOS represents the observed behavior at most conditions with the exception of c_v near the critical point. At temperatures near the critical locus, the EOS calculations deviate from the c_v measurements by −10 to +6%. These data will be essential to develop accurate models to represent thermodynamic properties of this binary mixture near the critical region.

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