Helmholtz-Type Equations of State for Hydrocarbon Refrigerant Mixtures of Propane/*n*-Butane, Propane/Isobutane, *n*-Butane/Isobutane, and Propane/*n*-Butane/Isobutane

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Highly accurate thermodynamic property models for binary and ternary hydrocarbon mixtures containing propane, *n*-butane, and isobutane have been developed. In the present model, reliable equations of state explicit in Helmholtz free energy for these three hydrocarbons that have already been developed by the present authors have been adapted. The excess term used to represent the contribution of mixing was optimized for each binary mixture by using the available experimental thermodynamic property data including $P\rho Tx$, isochoric heat capacity, and saturation properties (bubble-point pressures, mole fractions in the vapor phase, and saturated vapor- and liquid-densities) as input data. A generalized correction for the three binary mixtures, besides the ideal mixing, consists of only four terms in its functional form, the structure of which was determined by simultaneous optimization to the input data for the three binary mixtures by employing a stepwise regression analysis. The "bank of terms," that is a matrix of candidate terms applied for the regression, was carefully prepared through detailed observation of the nonideal mixing representation of the experimental data of the three binary mixtures. No additional adjustable parameters were used in the present model for the ternary propane/*n*-butane/isobutane mixture. Based on comparisons with the available experimental data and values from the developed equations of state, the present models for the three binary and the ternary hydrocarbon mixtures accurately represent most of the reliable experimental data. In addition, the graphical tests of the derived thermodynamic properties show that the models, including that for the ternary

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mixture, provide a physically sound representation of all the thermodynamic properties over the entire fluid phase.

1. INTRODUCTION

Among the alternative refrigerants proposed, hydrocarbons, including propane, n-butane, isobutane, and their binary and ternary mixtures, are considered promising candidates for refrigeration and/or heat-pump systems due to their negligible impacts on global warming. These natural working fluids are also considered as drop-in refrigerants because of their excellent lubricant solubility in the existing equipment. For cycle performance evaluation and optimum design of components contained in refrigeration and heat-pump systems, reliable thermodynamic property models are required for the aforementioned substances. Recently, for hydrocarbon mixtures, the accurate equations of state developed by Lemmon and Jacobsen [1] have been widely used in various applications including REFPROP (Ver. 6.01) [2]. Their models employ a 10-term universal function, which is valid for 22 different binary mixtures of hydrocarbons and simple inorganics, and only one additional parameter pertinent to each binary mixture is required aside from the functions for the pseudo-critical temperature and density. The equations of state for propane, n-butane, and isobutane used in the mixture models of Lemmon and Jacobsen were, however, developed by Younglove and Ely [3] in the mid-1980s based upon the IPTS-68 temperature scale. Recently, new and highly accurate Helmholtz-type equations of state for propane, n-butane, and isobutane have been developed by the present authors [4–6] for the fluid phase region including the vapor phase, liquid phase, supercritical, and saturation regions. Additionally, for hydrocarbon mixtures, accurate experimental thermodynamic property information such as $P\rho Tx$ properties, isochoric heat capacities, and saturation properties have been published over the last decade, especially for the liquid phase. It becomes feasible, therefore, to describe the mixing contribution for mixtures of these typical hydrocarbons accurately. This is essential not only for the development of accurate equation of state for each mixture but also as an effective baseline for further improvement in modeling other mixtures, such as hydrocarbon mixtures with hydrofluorocarbon (HFC) refrigerants.

Taking such background into account, we aimed to formulate accurate Helmholtz-type equations of state for the fluid phase of binary and ternary

hydrocarbon mixtures containing propane, n-butane, and isobutane by applying the necessary and sufficient number of terms as accurately as the representation of the Lemmon and Jacobsen models, but on the basis of the ITS-90. For our model, the available experimental data for these mixtures were collected. Through our detailed evaluation of the experimental data and calculated values from ideal mixing (which is introduced only by the equations of state for the pure fluids), a generalized correction consisting of only four terms in its functional form for the three binary mixtures was developed to represent the contribution of mixing as accurately as possible. No additional adjustable parameters were needed in the present model for the ternary propane/n-butane/isobutane mixture. The present study confirmed the physically sound behavior of the derived thermodynamic properties from the present models for the three binary and the ternary mixtures over the entire fluid-phase region.

2. AVAILABLE EXPERIMENTAL DATA FOR MIXTURES

We compiled about 2800 experimental thermodynamic property data for these hydrocarbon mixtures. A summary of the data in the single-phase region, such as $P\rho Tx$ and isochoric heat capacity, C_V, measurements for the three binary mixtures, is given in Table I, while the data in the saturation region, such as bubble-point pressures, P_{bub}, mole fractions in the vapor phase, y, saturated liquid densities, ρ', and saturated vapor densities, ρ'', are listed in Table II. The two sets of available experimental $P\rho Tx$ and P_{bub} data for the ternary mixture are also listed in Table III. For our modeling process, the temperature values of all experimental data were converted to ITS-90. The distribution of the $P\rho Tx$ property data on a pressure-temperature plane for each binary mixture is shown in Figs. 1–3, while the experimental C_V data for propane/isobutane are plotted on a pressure-temperature plane as shown in Fig. 4. It is clear from these four figures that single-phase experimental data exist only in the liquid phase, except for a set by Holcomb and Outcalt [14] for the propane/isobutane binary mixture. It seems important to carry out new reliable measurements in the vapor phase for more detailed and quantitative testing of the present models.

Considering the claimed accuracy of each set of measurements and the continuity of available sets of data in the single-phase region summarized in Table I, we selected three sets of $P\rho Tx$ property data by Kahre [7], Parrish [11], and Magee [13] for propane/n-butane, two sets by Kahre [7] and Duarte-Garza and Magee [15] for propane/isobutane, and a set by Kahre [7] for n-butane/isobutane, as input data sets for the present models. For propane/n-butane, as shown in Fig. 1, the data by Parrish [11] are widely distributed, and the accuracy of these data is comparatively

Table I. Sources of Experimental Thermodynamic Property Data for Binary Hydrocarbon Mixtures in the Single-Phase Region

First author	Ref.	Property	No. of data	x_1 Range (mol%)	x_1 δx_1 (mol%)	P Range (MPa)	P δP (kPa)	ρ Range (mol·m⁻³)	ρ $\delta\rho$ (%)	T Range (K)	T δT (mK)
						propane(1)/n-butane(2)					
Kahre[a]	[7]	$P\rho Tx$	20	15–84	n.a.	0.3–1.6	n.a.	9390–11283	n.a.	289–328	100
Acosta	[8]	$P\rho Tx$	12	25–76	n.a.	3.4–14	n.a.	9999–11113	n.a.	311	n.a.
Thompson	[9]	$P\rho Tx$	4	90–95	n.a.	0.1–0.2	0.1%	12999–13128	0.2	228–228	100
Luo	[10]	$P\rho Tx$	1	89	n.a.	0.8	0.3	11338	0.2	289	100
Parrish[a]	[11]	$P\rho Tx$	513	10–75	0.02	0.3–9.7	13	9229–11626	0.2	283–333	100
Holcomb	[12]	$P\rho Tx$	23	61	0.3	1.8–7.5	5	8058–9860	1.8 mg·cm⁻³	339–374	50
Magee[a]	[13]	$P\rho Tx$	106	61	0.004	2.6–35	0.7	9044–12081	0.05	244–400	30
						propane(1)/isobutane(2)					
Kahre[a]	[7]	$P\rho Tx$	19	14–84	n.a.	0.3–1.7	n.a.	8973–11191	n.a.	289–328	100
Thompson	[9]	$P\rho Tx$	4	91–95	n.a.	0.1–0.1	0.1%	12963–13114	0.2	228–228	100
Holcomb	[14]	$P\rho Tx$	109	0–100	n.a.	0.1–3.7	n.a.	28–12682	n.a.	250–395	n.a.
Duarte-Garza[a]	[15]	$P\rho Tx$	341	30,70	0.02	1.2–35	0.05%	7687–13096	0.05	200–400	30
Duarte-Garza[a]	[15]	C_v	135	30,70	0.002	3.3–33	0.05%	9408–13059	0.15	203–345	30
						n-butane(1)/isobutane(2)					
Kahre[a]	[7]	$P\rho Tx$	16	20–79	n.a.	0.20–0.71	n.a.	8885–9969	n.a.	289–328	100

[a] Data used as input data.

Table II. Sources of Experimental Thermodynamic Property Data for Binary Hydrocarbon Mixtures in the Saturation Region

First author	Ref.	Property	No. of data	x_1 Range (mol%)	δx_1 (mol%)	P Range (MPa)	δP (kPa)	ρ Range (mol·m⁻³)	$\delta \rho$ %	T Range (K)	δT (mK)
						propane(1)/n-butane(2)					
Nysewander	[16]	P_bub	32	20–85	1.5	0.56–4.2	n.a.	—	—	311–411	111
Barber	[17]	P_bub	83	15–93	n.a.	1.6–4.3	n.a.	—	—	344–419	n.a.
Hirata	[18]	P_bub	35	0–100	n.a.	0.0–0.2	5	—	—	237–249	100
Kay	[19]	P_bub	129	0–100	0.5	1.6–4.3	14	—	—	332–425	500
Skripka	[20]	P_bub	24	0–100	n.a.	0.05–0.5	n.a.	—	—	253–273	n.a.
Beranek	[21]	P_bub	29	6–91	1.5	0.4–3.4	1	—	—	303–363	10
Kaminishi	[22]	P_bub	17	20–80	n.a.	0.2–1.4	2	—	—	273–323	20
Clark	[23]	P_bub	30	0–100	2.0	0.1–0.6	1	—	—	260–280	10
Holcomb	[12]	P_bub	69	15–83	0.3	0.1–3.9	5	—	—	237–414	50
Nysewander	[16]	y	16	20–85	1.5	1.1–4.1	n.a.	—	—	344–411	111
Barber	[17]	y	87	15–93	n.a.	1.4–4.3	n.a.	—	—	340–419	n.a.
Hirata	[18]	y	35	0–100	n.a.	0.0–0.2	5	—	—	237–249	100
Kay	[19]	y	128	0–100	0.5	1.6–4.3	14	—	—	332–425	500
Skripka	[20]	y	24	0–100	n.a.	0.05–0.5	n.a.	—	—	253–273	n.a.
Beranek	[21]	y	29	12–96	1.5	0.4–3.4	1	—	—	303–363	10
Clark	[23]	y	30	0–100	2	0.1–0.6	1	—	—	260–280	10
Holcomb	[12]	y	69	18–94	0.3	0.1–3.9	5	—	—	237–414	50
Nysewander	[16]	ρ'	30	20–85	1.5	—	—	3848–10684	3	311–411	111
Barber	[17]	ρ'	83	15–93	n.a.	—	—	4003–9142	n.a.	344–419	n.a.
Kay	[19]	ρ'	63	15–93	0.5	—	—	4666–9180	1 mg·cm⁻³	343–418	500
Hiza	[24]	ρ'	8	59–61	0.016	—	—	13935–14684	0.16	110–150	30
Holcomb	[12]	ρ'	69	15–83	0.3	—	—	5542–19601	1.8 mg·cm⁻³	237–414	50
Nysewander	[16]	ρ''	15	20–85	1.5	—	—	604–3227	3	344–411	111
Barber	[17]	ρ''	87	15–93	n.a.	—	—	622–4530	n.a.	340–419	n.a.
Kay	[19]	ρ''	66	15–93	0.5	—	—	681–4123	0.1 mg·cm⁻³	346–419	500
Holcomb	[12]	ρ''	60	18–94	0.3	—	—	124–2722	1.8 mg·cm⁻³	269–414	50

Table II. *(Continued)*

First author	Ref.	Property	No. of data	x_1 Range (mol%)	δx_1 (mol%)	P Range (MPa)	δP (kPa)	ρ Range (mol·m⁻³)	$\delta\rho$ %	T Range (K)	δT (mK)
						propane(1)/isobutane(2)					
Hipkin	[25]	P_{bub}	86	0–100	n.a.	0.1–4.2	n.a.	–	–	267–394	n.a.
Hirata	[18]	P_{bub}	37	0–100	n.a.	0.04–0.2	5	–	–	237–249	100
Hirata	[26]	P_{bub}	14	5–99	n.a.	1.1–2.4	n.a.	–	–	340	n.a.
Skripka	[20]	P_{bub}	24	0–100	n.a.	0.07–0.5	n.a.	–	–	253–273	n.a.
Kaminishi	[22]	P_{bub}	23	17–80	n.a.	0.21–1.5	2	–	–	273–323	20
Higashi	[27]	P_{bub}	18	17–80	0.4	0.3–1.1	5	–	–	283–313	10
Holcomb	[14]	P_{bub}	55	0–100	n.a.	0.06–3.7	n.a.	–	–	250–395	n.a.
Hipkin	[25]	y	86	0–100	n.a.	0.1–4.2	n.a.	–	–	267–394	n.a.
Hirata	[18]	y	37	0–100	n.a.	0.04–0.2	5	–	–	237–249	100
Hirata	[26]	y	14	9–99	n.a.	1.1–2.4	n.a.	–	–	340	n.a.
Skripka	[20]	y	24	0–100	n.a.	0.07–0.5	n.a.	–	–	253–273	n.a.
Higashi	[27]	y	18	29–89	0.4	0.3–1.1	5	–	–	283–313	10
Holcomb	[14]	y	54	0–100	n.a.	0.06–3.7	n.a.	–	–	250–395	n.a.
Legatski	[28]	ρ'	3	53	n.a.	–	–	9956–11117	n.a.	266–311	n.a.
Hiza	[24]	ρ'	8	49–50	0.016	–	–	13834–14308	0.16	105–130	30
						n-butane(1)/isobutane(2)					
Connolly	[29]	P_{bub}	15	25–75	n.a.	0.9–3.4	n.a.	–	–	344–407	n.a.
Hirata	[30]	P_{bub}	24	7–91	n.a.	0.1–0.2	n.a.	–	–	273.15	n.a.
Hirata	[18]	P_{bub}	33	0–100	n.a.	0.7–2.0	5	–	–	334–374	100
Yokoyama	[31]	P_{bub}	38	4–95	n.a.	1.0–2.0	n.a.	–	–	347–373	n.a.
Martinez-Ortiz	[32]	P_{bub}	30	25–75	0.01	0.0–1.0	0.14	–	–	278–344	11
Connolly	[29]	y	15	25–75	n.a.	0.9–3.4	n.a.	–	–	344–407	n.a.
Hirata	[30]	y	24	5–89	n.a.	0.1–0.2	n.a.	–	–	273.15	n.a.
Hirata	[18]	y	33	0–100	n.a.	0.7–2.0	5	–	–	334–374	100
Yokoyama	[31]	y	38	3–94	n.a.	1.0–2.0	n.a.	–	–	347–373	n.a.
Hiza	[24]	ρ'	4	53	0.016	–	–	12445–12694	0.16	125–140	30

Table III. Sources of Experimental Thermodynamic Property Data for the Ternary Propane/n-Butane/Isobutane Mixture

First author	Ref.	Property	No. of data	x Range x_1 (mol%) x_2 (mol%) x_3 (mol%)	δx (mol%)	P Range (MPa)	δP (kPa)	ρ Range (mol·m⁻³)	$\delta\rho$ %	T Range (K)	δT (mK)
				propane(1)/n-butane(2)/isobutane(3)							
Luo	[10]	$P\rho Tx$	2	49, 71 25, 14 26, 15 25, 94	n.a.	0.1–0.2	0.3	11985–12486	0.2	228–228	100
Kaminishi	[22]	P_{bub}	24	3–60 3–29	n.a.	0.2–1.6	2	—	—	273–323	20
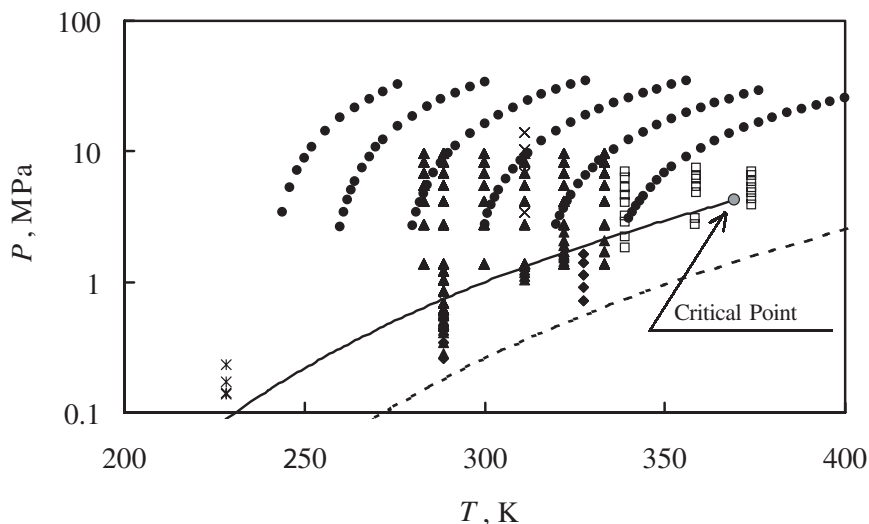
Fig. 1. Distribution of experimental $P\rho Tx$ property data for the binary propane/n-butane mixture. (♦) Kahre [7], (×) Acosta and Swift [8]; (∗) Thompson and Miller [9]; (◇) Luo and Miller [10]; (▲) Parrish [11], (□) Holcomb et al. [12], (●) Magee [13]; (–) Vapor pressure curve for propane, (---) Vapor pressure curve for n-butane.
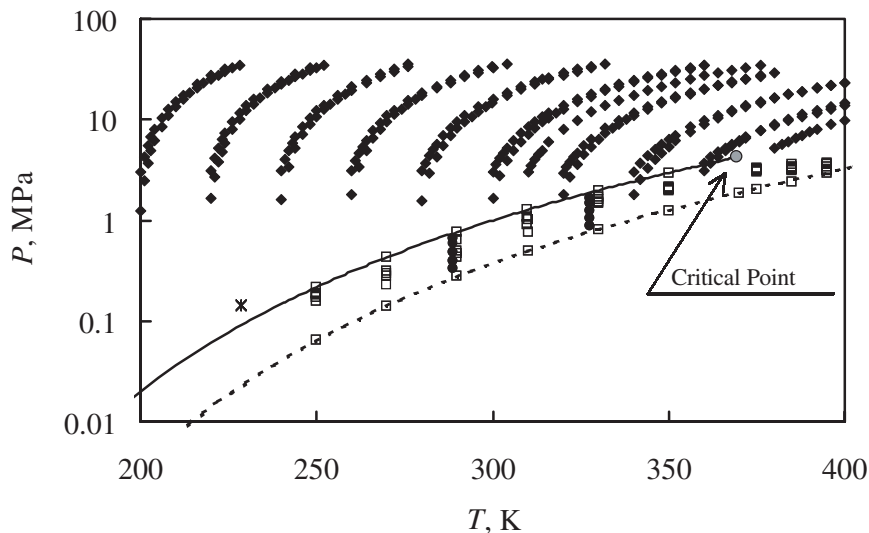
Fig. 2. Distribution of experimental $P\rho Tx$ property data for the binary propane/isobutane mixture. (●) Kahre [7]; (∗) Thompson and Miller [9]; (□) Holcomb and Outcalt [14]; (♦) Duarte-Garza and Magee [15]; (–) Vapor pressure curve for propane; (---) Vapor pressure curve for isobutane.
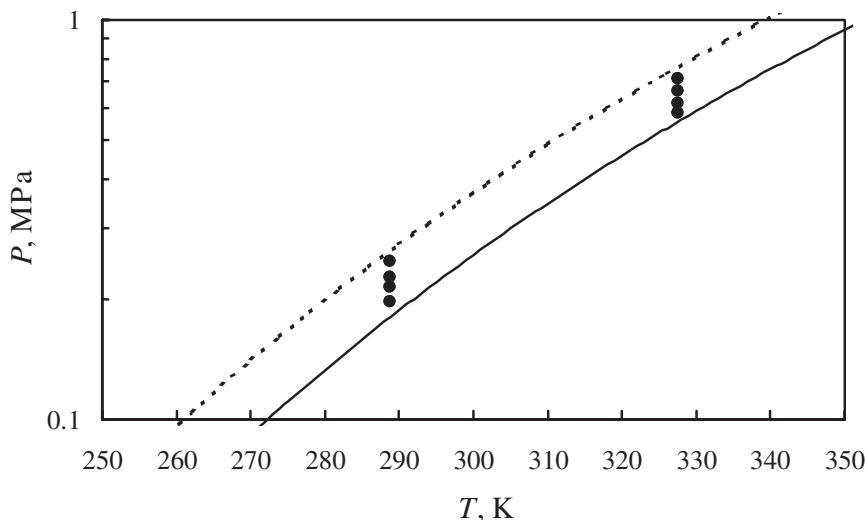
Fig. 3. Distribution of experimental $P\rho Tx$ property data for the binary n-butane/isobutane mixture. (●) Kahre [7]; (–) Vapor pressure curve for n-butane; (---) Vapor pressure curve for isobutane.

good. The $P\rho Tx$ property measurements by Magee [13] using an isochoric method agree with the data by Parrish [11]. For propane/isobutane, as shown in Fig. 2, the data by Duarte-Garza and Magee [15] exist over a wide range of temperatures down to 200 K and pressures up to 35 MPa at two different compositions of 70/30 mol% and 30/70 mol%. They also reported 135 data points of C_V measurements [15] at the same compositions by using the same single-cell type adiabatic isochoric calorimeter, as summarized in Table I and shown in Fig. 4. It should be noted that the C_V data of Duarte-Garza and Magee are key information for determining the structure and combination of excess terms of the present Helmholtz-type models for mixtures aside from the ideal mixing as mentioned below. For n-butane/isobutane, as shown in Table I and Fig. 3, we face a difficult situation for reliable modeling to cover the entire fluid-phase region, since a single data set reported by Kahre [7] covers a very limited range of temperatures, pressures, and compositions in the single-phase region.

The saturation property measurements for the three binary mixtures exist over a wide range of temperatures and compositions as summarized in Table II. For propane/n-butane, the experimental bubble-point pressures by Kay [19] are in good agreement, mostly within $\pm 1.0\%$ in pressure at temperatures from 332 to 425 K, with the calculated values from the
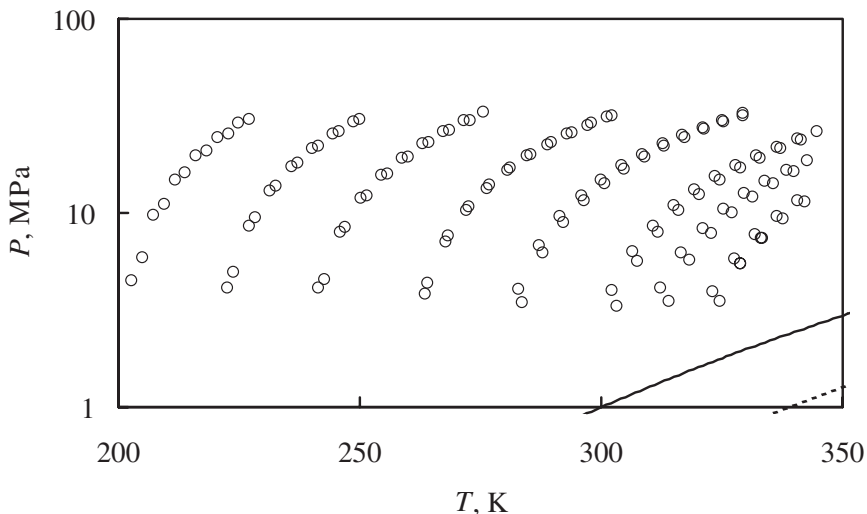
Fig. 4. Distribution of experimental C_V data for the binary propane/isobutane mixture. (○) Duarte-Garza and Magee [15]; (–) Vapor pressure curve for propane; (---) Vapor pressure curve for isobutane.

ideal mixing applied to the Helmholtz-type models for propane [4] and *n*-butane [5], except several data points that exhibit more scattered deviations with each other. The bubble-point pressure data for propane/ *n*-butane by Hirata et al. [18], Beranek and Wichterle [21], Clark and Stead [23], and the data by Holcomb et al. [12] at temperatures above 290 K also show comparatively similar behavior to each other. Five of the sets of experimental P_{bub} data mentioned above coincide mostly within ± 5.0% in relative pressure deviations. The exact temperature dependence of bubble-point pressures for propane/*n*-butane, however, are not as well described by ideal mixing and show larger scattered deviations. Under such circumstances, we concluded that the representation regarding the bubble-point pressures for propane/*n*-butane by ideal mixing was satisfactory enough and should be maintained throughout the present modeling. Similar requirements are also found in the present observations with respect to the available experimental mole fraction data in the vapor phase, saturated vapor- and liquid-densities, and for other binary mixtures containing propane/isobutane and *n*-butane/isobutane, as summarized in Table II.

For the ternary propane/*n*-butane/isobutane mixture, as listed in Table III, the available experimental data are far more limited than those

for the three binary mixtures. Only two points of experimental $P\rho Tx$ property data by Luo and Miller [10] exist in the liquid phase near 228 K and 0.1 MPa.

3. EQUATIONS OF STATE FOR MIXTURES

In general, the Helmholtz-type equation of state for mixtures is described as the sum of contributions from the ideal gas, the real gas, and the excess from mixing. The contributions from the ideal and real gas can be viewed as ideal mixing, and the latter excess part can be used to accurately represent the available experimental data for each binary/ternary mixture. Experimental information for the hydrocarbon mixtures is, however, limited as mentioned above. Hence, in the present study, we developed generalized functional forms for the excess part for hydrocarbon mixtures of interest here, by using the necessary but minimum number of terms.

The dimensionless Helmholtz free energy, ϕ_{mix}, models for the three binary and the ternary hydrocarbon mixtures of present interest are given by Eq. (1),

$$\phi_{\mathrm{mix}} = \frac{f_{\mathrm{m}}}{R_{\mathrm{m}}T} = \phi_{\mathrm{mix}}^0(\tau_i^{\mathrm{pure}}, \delta_i^{\mathrm{pure}}, x_i) + \phi_{\mathrm{mix}}^{\mathrm{r}}(\tau, \delta, x_i) \qquad (i = 1, 2, 3) \quad (1)$$

In the present models, f_{m} is the molar Helmholtz free energy and $R_{\mathrm{m}} = 8.314472 \ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ [33] is the universal gas constant. The ideal-gas part of the mixture model is given by a combination of the ideal-gas parts of the equations of state for pure components as follows:

$$\phi_{\mathrm{mix}}^0(\tau_i^{\mathrm{pure}}, \delta_i^{\mathrm{pure}}, x_i) = \sum_{i=1}^{N} x_i \phi_i^0(\tau_i^{\mathrm{pure}}, \delta_i^{\mathrm{pure}}) + \sum_{i=1}^{N} x_i \ln x_i \quad (2)$$

where N denotes the number of components and x_i is the mole fraction of component i. The second sum in Eq. (2) describes the entropy increase of the ideal-gas mixture, and the dimensionless variables, $\tau_i^{\mathrm{pure}} = T_{\mathrm{C},i}^{\mathrm{pure}}/T$ and $\delta_i^{\mathrm{pure}} = \rho/\rho_{\mathrm{C},i}^{\mathrm{pure}}$, used to evaluate the ideal-gas function for the pure components are different from each other due to the reducing parameters, $T_{\mathrm{C},i}^{\mathrm{pure}}$ and $\rho_{\mathrm{C},i}^{\mathrm{pure}}$, given in the equations of state for the pure fluids.

The residual real-fluid contribution of the dimensionless Helmholtz free-energy of a mixture is expressed by Eq. (3).

$$\phi_{\mathrm{mix}}^{\mathrm{r}}(\tau, \delta, x_i) = \sum_{i=1}^{N} x_i \phi_i^{\mathrm{r}}(\tau, \delta) + \sum_{i=1}^{N} \sum_{j=i+1}^{N} x_i x_j \, \Delta\phi_{ij}^{\mathrm{r}}(\tau, \delta) \quad (3)$$

The dimensionless variables are $\tau = T_{C,\text{mix}}/T$ and $\delta = \rho/\rho_{C,\text{mix}}$, while the pseudo-critical temperature $T_{C,\text{mix}}$ and density $\rho_{C,\text{mix}}$ are defined as follows:

$$T_{C,\text{mix}} = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j T_{C,ij} \tag{4}$$

$$1/\rho_{C,\text{mix}} = v_{C,\text{mix}} = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j v_{C,ij} \tag{5}$$

The cross-terms in the sums of Eqs. (4) and (5) are defined as

$$T_{C,ij,i \neq j} = \frac{T_{C,i} + T_{C,j}}{2} k_{T,ij} \tag{6}$$

$$v_{C,ij,i \neq j} = \frac{v_{C,i} + v_{C,j}}{2} k_{V,ij} \tag{7}$$

where $k_{T,ij}$ and $k_{V,ij}$ are the interaction parameters in the cross terms for temperature and molar volume, respectively.

The second sum of Eq. (3) consists of excess terms for the binary mixtures in addition to the ideal mixing of the residual part. The structure of $\Delta\phi_{ij}^{r}(\tau, \delta)$ is determined by employing Wagner's stepwise regression analysis [34]. For this procedure, the aforementioned "bank of terms" has been prepared with a total of 30 terms through our detailed evaluation regarding the deviations between the available experimental data and the calculated thermodynamic property values from ideal mixing. The dimensionless values, that were introduced in terms of the thermodynamic relation with experimental $P\rho Tx$ property data for the three binary mixtures, have simultaneously been used as input data for the present regression procedure. The generalized excess term for the three binary mixtures was then determined as follows:

$$\Delta\phi_{ij}^{r}(\tau, \delta) = a_1\delta^2 + a_2\tau\delta^4 + a_3\delta^{12}\exp(-\delta) + a_4\tau\delta^5\exp(-\delta) \tag{8}$$

For each binary mixture, the values of the coefficients a_i of Eq. (8) and the interaction parameters, $k_{T,ij}$ and $k_{V,ij}$, of Eqs. (6) and (7) were adjusted to the experimental data by using a nonlinear fitting process [35]. The coefficients for each binary mixture are listed in Table IV. For the ternary propane/n-butane/isobutane mixture, no additional adjustable parameters were needed, and the residual part of the present model consists of equations of state for the three respective binary mixtures by Eqs. (3) to (5). The present equations of state for the binary and the ternary mixtures have

Table IV. Numerical Constants in Eqs. (6)–(8) for Binary Hydrocarbon Mixtures

	propane/n-butane	propane/isobutane	n-butane/isobutane
$k_{V, ij}$	0.9993065	1.000812	1.020212
$k_{T, ij}$	1.007890	0.9963851	0.9817304
a_1	-3.777189×10^{-3}	-3.702259×10^{-2}	-4.681355×10^{-2}
a_2	-7.349850×10^{-3}	-1.051534×10^{-2}	-8.751766×10^{-3}
a_3	1.612372×10^{-5}	1.983604×10^{-5}	9.443666×10^{-6}
a_4	3.382925×10^{-2}	5.806764×10^{-2}	4.414370×10^{-2}

been developed on the basis of ITS-90, and are valid over the entire fluid-phase region except in the vicinity of the mixture critical points. The effective temperature, pressure, and density ranges of the present models are: $228 \text{ K} \leqslant T \leqslant 589 \text{ K}$, $P \leqslant 69 \text{ MPa}$, and $\rho \leqslant 19600 \text{ mol} \cdot \text{m}^{-3}$ for propane/n-butane; $203 \text{ K} \leqslant T \leqslant 573 \text{ K}$, $P \leqslant 35 \text{ MPa}$, and $\rho \leqslant 13100 \text{ mol} \cdot \text{m}^{-3}$ for propane/isobutane; $273 \text{ K} \leqslant T \leqslant 573 \text{ K}$, $P \leqslant 35 \text{ MPa}$, and $\rho \leqslant 12800 \text{ mol} \cdot \text{m}^{-3}$ for n-butane/isobutane and propane/n-butane/isobutane, respectively.

4. COMPARISON WITH EXPERIMENTAL DATA

Figures 5 and 6 show the density deviations of experimental $P\rho T x$ property measurements in different temperature ranges from the present model for propane/n-butane and propane/isobutane, respectively. In the present paper, however, we only discuss the representation for propane/isobutane mixture, for which the most recent experimental $P\rho T x$ property data are available. In the wide range of temperatures from 200 to 400 K, the reliable measurements by Duarte-Garza and Magee [15] are satisfactorily represented within $\pm 0.09\%$ in density. These deviations are outside the reported uncertainty in density, 0.05%; however, the statistical results including the absolute average deviation "AAD," the bias "BIAS," the standard deviation "SDV," and the root-mean-square deviation "RMS" with respect to the data set of Duarte-Garza and Magee are less than 0.03%. In the liquid phase near the saturation boundary, the $P\rho T x$ property data by Kahre [7] agree with Eq. (1) within $\pm 0.27\%$ in density. The maximum deviation of the data by Holcomb and Outcalt [14] is off-scaled from Fig. 6, however, the liquid-phase experimental data included in this set of measurements agree with the present model within $\pm 1.7\%$ in density. At lower pressures below 0.2 MPa, the data of Thompson and Miller [9], which were not used as input data, are represented within $\pm 0.14\%$ in density as shown in Fig. 6. The satisfactory representations of the present
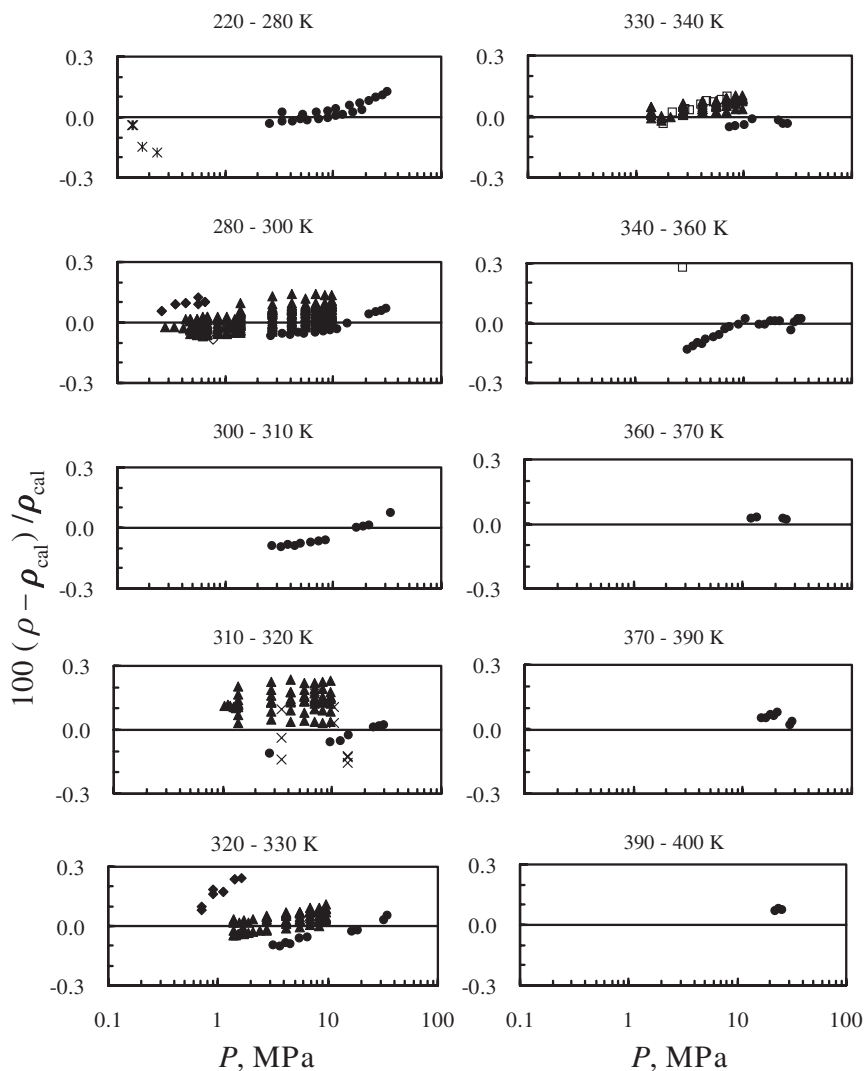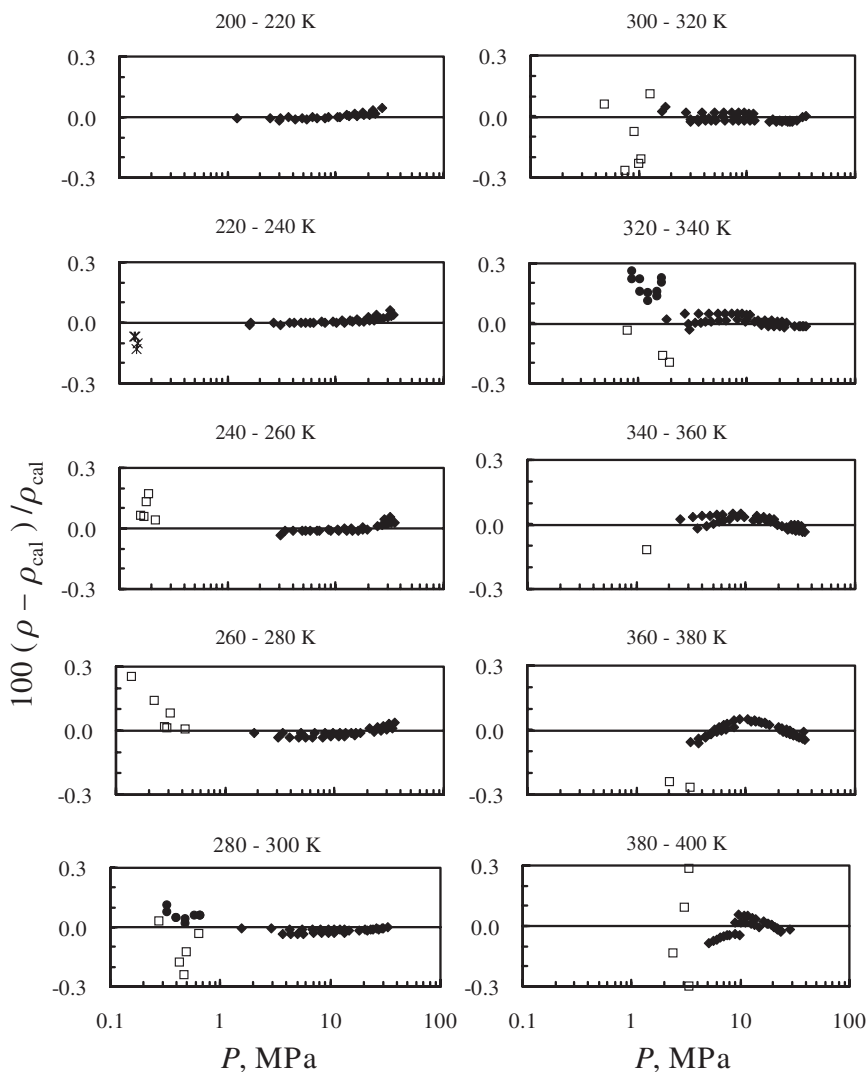
Fig. 5. Density deviations of $P\rho Tx$ property data for the binary propane/n-butane mixture from the present model. ($\blacklozenge$) Kahre [7]; ($\times$) Acosta and Swift [8], ($*$) Thompson and Miller [9]; ($\diamondsuit$) Luo and Miller [10]; ($\blacktriangle$) Parrish [11]; ($\square$) Holcomb et al. [12]; ($\bullet$) Magee [13].

Fig. 6. Density deviations of $P\rho Tx$ property data for the binary propane/isobutane mixture from the present model. ($\bullet$) Kahre [7]; ($*$) Thompson and Miller [9]; ($\square$) Holcomb and Outcalt [14], ($\blacklozenge$) Duarte-Garza and Magee [15].

models regarding $P\rho Tx$ property data for propane/n-butane and n-butane/isobutane are also confirmed in the present study, as summarized in Section 6.

Figure 7 illustrates the relative deviations of experimental C_V data for propane/isobutane from Eq. (1). Only a single set of C_V measurements by Duarte-Garza and Magee [15] is available for the hydrocarbon mixtures studied in this work, and is well represented within $\pm 1.17\%$ for temperatures from 203 to 345 K, as shown in Fig. 7. The representation regarding the C_V data of Duarte-Garza and Magee is almost the same as for the ideal mixing, and the AAD, BIAS, SDV, and RMS are less than the reported uncertainty of C_V, 0.7%.
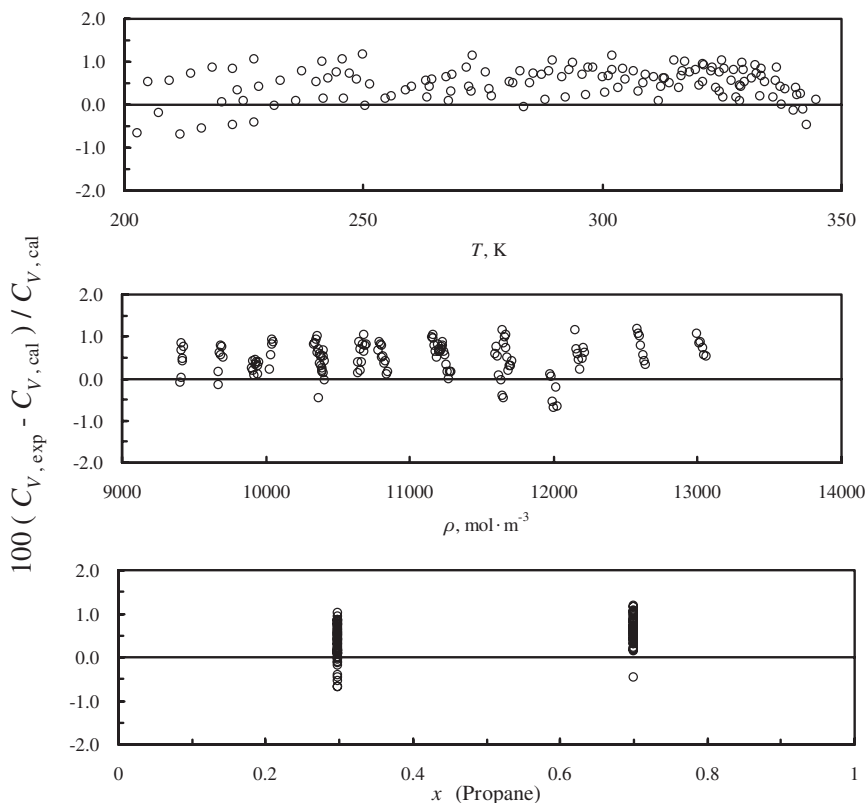

Fig. 7. Relative deviations of isochoric heat capacity data for the binary propane/isobutane mixture from the present model (Note that the horizontal axis of each graph denotes temperature, density, and mole fraction for propane). (○) Duarte-Garza and Magee [15].

Regarding the saturation properties, somewhat larger deviations for each data set are found, especially for the bubble-point pressures. For example, Fig. 8 shows the relative pressure deviations of experimental P_{bub} data for propane/isobutane. The experimental data by Hipkin [25] are represented within $\pm 3.3\%$ in pressure except for a single datum at 394 K, whereas the data by Hirata et al. [18], Hirata et al. [26], and Higashi et al. [27] agree with the present model within $\pm 4.3\%$, $\pm 2.5\%$, and $\pm 6.7\%$, respectively. It should be noted, however, that such representation by Eq. (1) is almost the same as those for the ideal mixing. Similar situations are also observed for propane/n-butane and n-butane/isobutane. It is reasonable, therefore, to conclude that the present model succeeded in representing the available experimental data in the saturation region, although considerable scatter existed among them.

For the ternary propane/n-butane/isobutane mixture, only a set of experimental $P\rho Tx$ property data by Luo and Miller [10] is available in the single-phase region. Although no additional adjustable parameters are used in the model for the ternary mixture, the data of Luo and Miller are satisfactorily represented by the present model within $\pm 0.05\%$ in density.
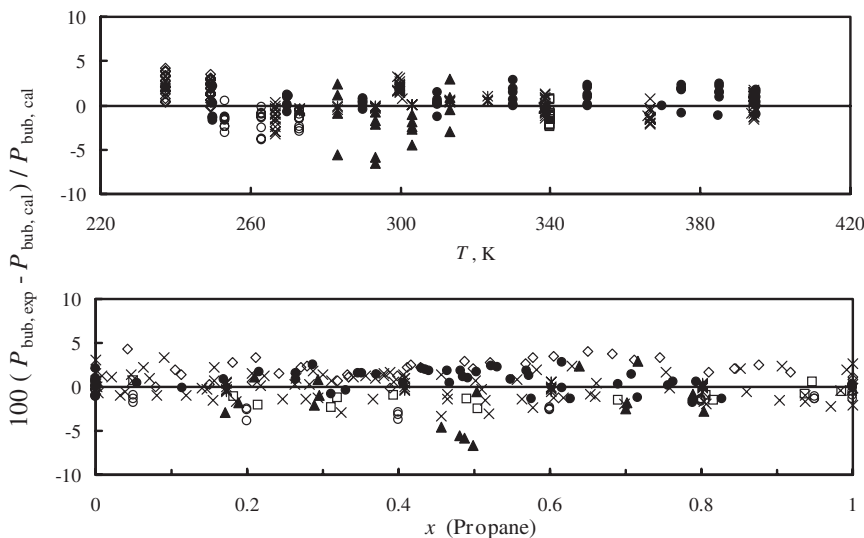
Fig. 8. Deviations of bubble point pressure data for the binary propane/isobutane mixture from the present model. ($\times$) Hipkin [25]; ($\diamond$) Hirata et al. [18]; ($\square$) Hirata et al. [26]; ($\bigcirc$) Skripka et al. [20]; ($\ast$) Kaminishi et al. [22]; ($\blacktriangle$) Higashi et al. [27]; ($\bullet$) Holcomb and Outcalt [14].

Through our detailed examinations mentioned above, we estimated that the uncertainties of properties calculated by our models are: 0.2% in densities, 1% in heat capacities, 2% in bubble-point pressures, 2% in saturated vapor-densities, and 0.5% in saturated liquid-densities, except in the critical region.

5. DERIVED PROPERTIES

As one of the most important tests for the accuracy of the thermodynamic models, the behavior of the calculated derived thermodynamic properties have been examined in the present study over an extended range of temperatures and pressures. For example, Fig. 9 shows isobars of the isobaric heat capacity, C_P, from Eq. (1) for propane/isobutane [50/50 mol%] at 1–6, 10, 20, and 50 MPa at temperatures extending up to 600 K in order to examine the extrapolation behavior of the present model. The ideal-gas heat capacities and calculated values on the saturation boundaries are also included in this figure. The calculated C_P values along different isobars behave very smoothly and they exhibit physically sound behavior over the entire fluid phase. Similar thermodynamic consistencies are also found for different compositions, in other derived properties such
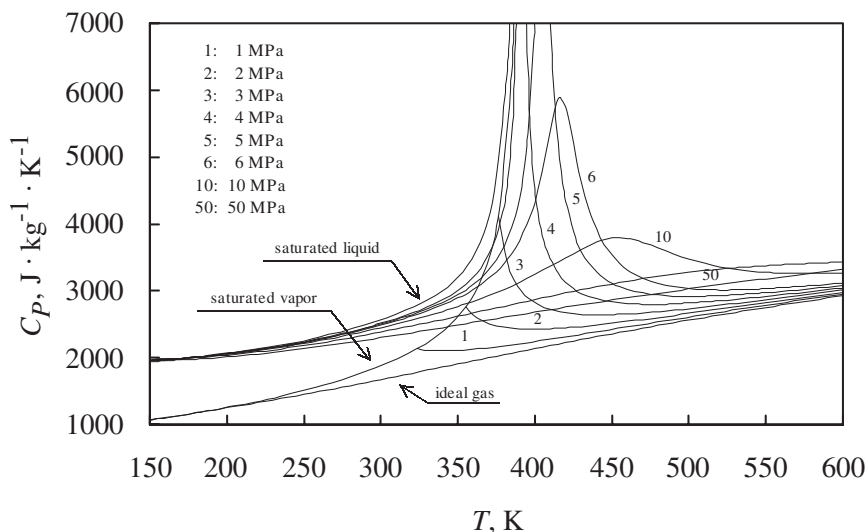

Fig. 9. Calculated isobaric heat capacity values along isobars of the binary propane/isobutane [50/50 mol%] mixture from the present model.
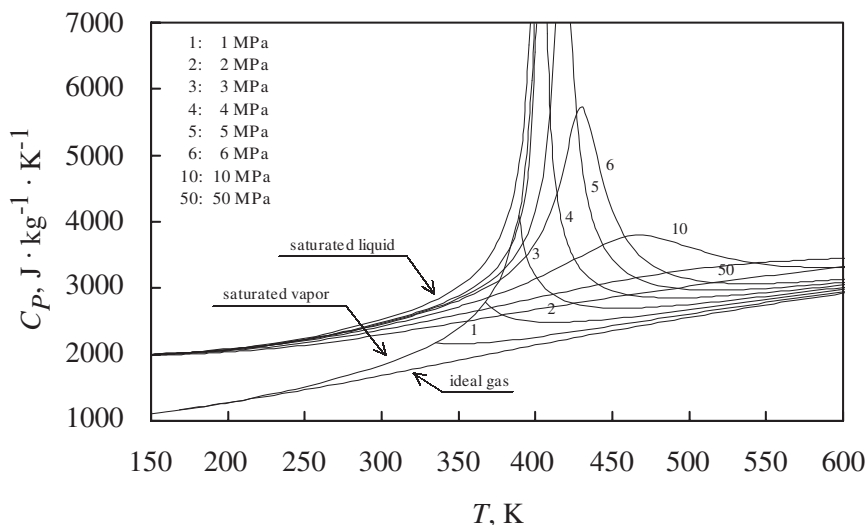
Fig. 10. Calculated isobaric heat capacity values along isobars of the ternary propane/ *n*-butane/isobutane [33/33/34 mol%] mixture from the present model.

as isochoric heat capacities, speeds of sound, and the Joule–Thomson coefficients, and in the present models for propane/*n*-butane and *n*-butane/ isobutane. Moreover, Fig. 10 shows isobars of C_P values for propane/ *n*-butane/isobutane [33/33/34 mol%] for temperatures up to 600 K and pressures up to 50 MPa calculated from the present model. The isobars of C_P are physically correct over the range of interest, although no additional adjustable parameters were introduced in the present model for the ternary mixture.

6. COMPARISON WITH EXISTING MODEL

In this section, we compare the present models for propane/*n*-butane, propane/isobutane, *n*-butane/isobutane, and propane/*n*-butane/isobutane with the aforementioned existing equations of state by Lemmon and Jacobsen [1] so as to confirm their reliability. We used subroutines given in the source program of REFPROP (Ver. 6.01) [2] for comparing the Lemmon and Jacobsen model with experimental data. The accuracy of each model for the three binary and the ternary mixtures was statistically examined in terms of AAD, BIAS, SDV, RMS, and the maximum percentage deviation "MAX%" with respect to each data set for the single-phase and saturation regions as summarized in Tables V and VI, respectively.

The statistical values in Table V show that the present equations of state reproduce the $P\rho Tx$ property data as well as the models by Lemmon

Table V. Statistical Percentage Deviations for Experimental Thermodynamic Property Data in the Single-Phase Region

First author	Ref.	Property	No. of data	Present Model					Lemmon and Jacobsen Model [1]				
				AAD	BIAS	SDV	RMS	MAX%	AAD	BIAS	SDV	RMS	MAX%
				propane/n-butane									
Kahre	[7]	$PρTx$	20	0.14	0.14	0.08	0.16	0.38	0.26	0.26	0.14	0.29	0.55
Acosta	[8]	$PρTx$	12	0.14	0.05	0.17	0.17	0.42	0.16	0.08	0.18	0.19	0.45
Thompson	[9]	$PρTx$	4	0.10	−0.10	0.07	0.12	−0.18	0.07	−0.07	0.07	0.09	−0.14
Parrish	[11]	$PρTx$	513	0.06	0.04	0.06	0.07	0.23	0.11	0.11	0.06	0.12	0.34
Holcomb	[12]	$PρTx$	23	0.29	0.29	0.21	0.35	0.59	0.47	0.47	0.21	0.51	0.70
Magee	[13]	$PρTx$	106	0.05	−0.01	0.06	0.06	−0.14	0.03	−0.01	0.03	0.03	−0.09
				propane/isobutane[a]									
Kahre	[7]	$PρTx$	19	0.12	0.12	0.08	0.14	0.26	0.13	0.13	0.08	0.15	0.29
Thompson	[9]	$PρTx$	4	0.09	−0.09	0.03	0.10	−0.13	0.04	−0.04	0.03	0.05	−0.08
Holcomb	[14]	$PρTx$	109	1.68	−0.94	2.92	3.05	19.81	0.55	−0.43	0.80	0.90	−3.23
Duarte-Garza	[15]	$PρTx$	341	0.02	0.00	0.03	0.02	−0.09	0.03	0.02	0.03	0.04	0.12
Duarte-Garza	[15]	C_v	135	0.55	0.49	0.38	0.62	1.17	0.38	0.00	0.47	0.47	−1.30
				n-butane/isobutane									
Kahre	[7]	$PρTx$	16	0.02	0.00	0.04	0.04	0.09	0.02	0.00	0.02	0.02	0.04
				propane/n-butane/isobutane									
Luo	[10]	$PρTx$	2	0.03	−0.02	0.05	0.04	−0.05	0.04	−0.04	0.01	0.04	−0.05

[a] Note that 54 data points by Holcomb and Outcalt [14] were not used for the calculation of statistical values from the Lemmon and Jacobsen model, since these data deviate by more than 25% from the model.

Table VI. Statistical Percentage Deviations for Experimental Thermodynamic Property Data along the Saturation Curves

First author	Ref.	Property	No. of data	Present Model					Lemmon and Jacobsen Model [1]				
				AAD	BIAS	SDV	RMS	MAX%	AAD	BIAS	SDV	RMS	MAX%
						propane/n-butane[a]								
Nysewander	[16]	P_{bub}	32	2.79	2.40	2.01	3.11	4.92	2.86	2.43	2.01	3.13	4.91
Barber	[17]	P_{bub}	83	0.73	0.72	0.71	1.01	4.54	1.27	-0.13	1.79	1.79	4.94
Hirata	[18]	P_{bub}	35	2.79	2.73	1.80	3.26	6.73	2.30	2.21	1.64	2.73	6.13
Kay	[19]	P_{bub}	129	0.90	0.81	2.21	2.35	13.89	0.93	0.16	1.70	1.70	10.70
Skripka	[20]	P_{bub}	24	1.81	-1.81	1.31	2.22	-4.45	2.01	-2.01	1.50	2.49	-4.84
Beranek	[21]	P_{bub}	29	0.92	-0.85	0.83	1.17	-2.79	1.06	-1.03	0.82	1.31	-3.05
Kaminishi	[22]	P_{bub}	17	0.32	0.32	0.18	0.36	0.87	0.15	0.01	0.17	0.17	-0.35
Clark	[23]	P_{bub}	30	1.37	-1.01	1.46	1.76	-3.79	1.61	-1.23	1.57	1.97	-4.26
Holcomb	[12]	P_{bub}	69	2.83	2.52	4.73	5.33	18.12	2.97	2.54	5.23	5.79	21.59
Nysewander	[16]	ρ'	30	1.73	-1.20	2.12	2.41	-6.48	1.57	-1.08	2.15	2.38	-8.19
Barber	[17]	ρ'	83	2.77	1.42	3.78	4.01	14.00	4.70	-2.04	7.49	7.72	-22.57
Kay	[19]	ρ'	63	1.11	-0.38	1.43	1.47	-5.71	2.67	-1.62	4.78	5.02	-16.97
Holcomb	[12]	ρ'	69	0.56	0.35	1.05	1.10	5.09	0.72	0.56	1.52	1.61	11.29
Nysewander	[16]	ρ''	15	3.18	-3.18	3.60	4.71	-10.63	6.20	-6.12	6.44	8.73	-23.00
Barber	[17]	ρ''	87	0.94	-0.77	1.20	1.42	-4.54	7.45	-7.45	7.57	10.58	-24.28
Kay	[19]	ρ''	66	0.63	-0.62	1.77	1.87	-13.65	6.49	-6.15	8.15	10.15	-24.14
Holcomb	[12]	ρ''	60	2.15	0.27	2.97	2.95	8.11	2.43	-0.17	3.05	3.03	8.10

Table VI. *(Continued)*

First author	Ref.	Property	No. of data	Present Model					Lemmon and Jacobsen Model [1]				
				AAD	BIAS	SDV	RMS	MAX%	AAD	BIAS	SDV	RMS	MAX%
propane/isobutane													
Hipkin	[25]	P_{bub}	86	1.46	−0.12	2.45	2.44	−17.97	1.68	0.81	2.44	2.55	−14.85
Hirata	[18]	P_{bub}	37	2.01	2.00	1.17	2.31	4.25	5.00	5.00	2.01	5.37	8.52
Hirata	[26]	P_{bub}	14	1.31	−1.12	0.93	1.44	−2.48	0.61	−0.04	0.70	0.67	1.35
Skripka	[20]	P_{bub}	24	1.79	−1.75	1.10	2.05	−3.88	0.54	−0.16	0.66	0.66	1.51
Kaminishi	[22]	P_{bub}	23	0.36	0.04	0.44	0.43	0.98	1.91	1.91	0.72	2.04	3.06
Higashi	[27]	P_{bub}	18	2.61	−1.79	2.70	3.17	−6.61	2.03	0.22	2.58	2.51	4.32
Holcomb	[14]	P_{bub}	55	1.04	0.62	1.14	1.28	2.85	1.78	1.64	1.45	2.18	4.38
n-butane/isobutane													
Connolly	[29]	P_{bub}	15	0.43	0.43	0.16	0.46	0.76	0.26	0.25	0.13	0.28	0.39
Hirata	[30]	P_{bub}	24	0.27	0.15	0.31	0.34	0.67	0.57	0.57	0.27	0.63	1.15
Hirata	[18]	P_{bub}	33	1.03	−0.30	1.37	1.38	−3.02	0.98	−0.26	1.29	1.29	−2.80
Yokoyama	[31]	P_{bub}	38	0.38	−0.20	0.41	0.46	−1.01	0.36	−0.20	0.40	0.44	−0.93
Martinez-Ortiz	[32]	P_{bub}	30	0.06	0.02	0.08	0.08	0.19	0.27	0.27	0.17	0.32	0.62
propane/n-butane/isobutane													
Kaminishi	[22]	P_{bub}	24	0.36	0.15	0.50	0.51	−1.82	0.91	0.80	0.60	0.99	1.50

[a] Note that 3 data points by Barber [17] for saturated liquid densities were not used for the calculation of statistical values from the present model, while 14 data points by Barber [17], 10 data points by Kay [19], and 2 data points by Holcomb et al. [12] for saturated-vapor densities were not used for the calculation of statistical values from the Lemmon and Jacobsen model. These data deviate by more than 25% from each model.

and Jacobsen. For example, regarding the propane/n-butane mixture, the AAD, BIAS, SDV, and RMS from the present model for the data by Parrish [11] are within $\pm 0.07\%$, and the numerical differences among these statistical results are less than $\pm 0.07\%$ between the two models. The differences of the statistical values for the data by Magee [13] from both models are nearly zero, with the present model being slightly better. The statistical comparisons of experimental C_V data for propane/isobutane with both models are also presented in Table V. For the C_V data by Duarte-Garza and Magee [15], the Lemmon and Jacobsen model shows slightly smaller AAD, BIAS, and RMS, however, the SDV and MAX% from their model are larger than those from the present model. It could be confirmed therefore that the present models for the four hydrocarbon mixtures exhibit an almost equivalent representation compared to the Lemmon and Jacobsen models in the single-phase region.

The statistical results of comparison for the saturation property data with both models are presented in Table VI. For propane/n-butane, similar representations for the bubble-point pressure data and saturated vapor- and liquid-densities by Holcomb et al. [12] are found for the present model and the Lemmon and Jacobsen model. The bubble-point pressure data for propane/isobutane by Higashi et al. [27] are better represented by the Lemmon and Jacobsen model, however, the differences of the SDV from both models are negligible. In general, the differences among the statistical values calculated from the present models and the Lemmon and Jacobsen models for the three binary and the ternary mixtures are not very significant in the saturation region, although larger scatter in the deviations are observed from each set of data in the saturation region as described in Section 2. From the aforementioned comparisons, it is reasonable to conclude that the present models satisfactorily represent the available sets of saturation property data for propane/n-butane, propane/isobutane, n-butane/isobutane, and propane/n-butane/isobutane.

7. CONCLUSIONS

We developed Helmholtz-type equations of state for hydrocarbon mixtures of propane/n-butane, propane/isobutane, n-butane/isobutane, and propane/n-butane/isobutane. The present models were aimed at developing the mixture models exclusively on the basis of the models developed for each hydrocarbon of present interest [4–6]. The selected experimental data for $P\rho Tx$, isochoric heat capacity, and saturation properties were used as input data for optimizing the excess terms of the present models. The excess function regarding the contribution from mixing consists of only 4 terms in its functional form, which was the same form for

the three binary mixtures. No additional adjustable parameters were used in the present equation of state for the ternary propane/n-butane/isobutane mixture. The ranges of validity of the present models in temperature, pressure, and density are: $228\,K \leqslant T \leqslant 589\,K$, $P \leqslant 69\,MPa$, and $\rho \leqslant 19600\,mol \cdot m^{-3}$ for propane/n-butane; $203\,K \leqslant T \leqslant 573\,K$, $P \leqslant 35\,MPa$, and $\rho \leqslant 13100\,mol \cdot m^{-3}$ for propane/isobutane; $273\,K \leqslant T \leqslant 573\,K$, $P \leqslant 35\,MPa$, and $\rho \leqslant 12800\,mol \cdot m^{-3}$ for n-butane/isobutane and propane/n-butane/isobutane.

Through our detailed examination of the present models, a satisfactory representation regarding the available experimental thermodynamic property data for these mixtures both in the single-phase and in the saturation region was achieved in the present paper. The smooth behavior of derived properties has also been confirmed in the range of validity of the present models. The overall uncertainties of the present equations of state are estimated to be about 0.2% in densities, 1% in heat capacities, 2% in bubble point pressures, 2% in saturated vapor-densities, and 0.5% in saturated liquid-densities, except in the critical region.

In addition, we have also discussed the reliability of the model by Lemmon and Jacobsen in comparison with the present models. A statistical analysis has been extensively applied to compare both models for each binary and ternary mixture. The present models showed excellent thermodynamic consistency in representing the thermodynamic properties with almost similar results to the models by Lemmon and Jacobsen over the aforementioned range of validity.

We emphasize again that the available thermodynamic property data for binary and ternary mixtures of the present interest are scarce. It seems important to carry out new reliable measurements, especially in the vapor phase and in the saturation region, for more detailed and quantitative tests of the models including the present ones.

ACKNOWLEDGMENT

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