PρT Data for Hydrogen Sulfide + Propane from (263 to 363) K at Pressures up to 40 MPa

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Pressure, density, and temperature (*PρT*) data are presented for two compositions ($z_1 = 0.2227$ and 0.2691) of the hydrogen sulfide (1) + propane (2) binary mixture at three temperatures in vapor and liquid states from a vacuum up to 40 MPa. Experimental work was achieved thanks to a vibrating-tube densimeter using the forced path mechanical calibration model (FPMC). The Lee−Kesler−Plöcker model was chosen with one temperature-dependent binary interaction parameter to represent our experimental data. Observed deviations on liquid and vapor densities (between experimental and calculated data) are less than 2 % on both liquid and vapor phases except for data close to the critical point.

Introduction

This work is continuing part of several studies dealing with gas impurities (CO_2 and H_2S) into light hydrocarbons.[1−3] Experimental data are of great importance to develop a reliable model used for process engineering. Literature provides very few density data on the hydrogen sulfide (H_2S) + propane (C_3H_8) binary system. Only vapor−liquid equilibrium (VLE) data and saturating densities are found.[4,5]

The present work deals with pressure, density, and temperature (*PρT*) data sets for the H_2S (1) + C_3H_8 (2) system. Two compositions have been studied, $z_1 = 0.2227$ and 0.2691, at three temperatures for both mixtures. The Lee−Kesler[6] equation of state and Plöcker et al.[7] (LKP EoS) mixing rules are well-known for calculating volumetric properties and are already implemented in several process simulators such as PROSIM Plus.[8] Thus, we chose this model to check the coherence of our data and to provide modeling parameters.

Experimental Section

Materials. Propane was purchased from Messer (France) with a volume fraction certified purity higher than 99.95. Hydrogen sulfide was purchased from Alpha Gaz with a volume fraction certified purity higher than 99.5. Mixtures were prepared carefully[9] with a mass uncertainty estimated to $\pm\ 10^{-3}$ g.

Apparatus and Experimental Procedure. The apparatus is based on an Anton Paar DMA 512P cell. The vibrating-tube apparatus used for this work and the complete procedure has previously been described.[10] Briefly, the mixture is introduced into a loading and pressurizing cell and is maintained above its bubble pressure at ambient temperature. Vacuum is achieved with a vacuum pump working for several hours to obtain a reference vibrating period at very low pressures ($< 5 \cdot 10^{-4}$ MPa). Small amounts of fluid are then continuously introduced into the vibrating tube. The pressure increases continuously up to the dew point at a controlled rate of a maximum of 0.005 $\text{MPa} \cdot \text{s}^{-1}$. During this process the fluid is assumed to be in equilibrium, and the pressure, period, and temperature (*PτT*) are recorded every 0.3 s. After the dew point is reached, the fluid is fully condensed in the whole circuit by increasing pressure up to the maximum pressure studied (about 40 MPa in this work). The circuit content is homogeneized through partial purging to the event. The liquid phase is then measured from upper pressure down to the bubble point. The pressure decreases continuously by means of the regulating output valve.

The period of vibration of the vibrating tube is measured with an uncertainty estimated to $\pm\ 1 \cdot 10^{-8}$ s. The temperature of the vibrating tube is controlled by a regulated bath with a temperature stability of ± 0.01 K. The temperature is measured by two Pt100 probes, periodically calibrated against a 25 Ω reference thermometer (TINSLEY Precision Instrument) certified by the Laboratoire National d'Essais (Paris) following the 1990 International Temperature Scale protocol. The resulting uncertainty in the temperature is less than ± 0.01 K. The pressure is measured using three sensors with different operating ranges: (0 to 0.2) MPa, (0 to 5) MPa, and (0 to 40) MPa. These sensors are calibrated against a dead weight pressure balance (5202S model from Desgranges & Huot) for the range (0.3 to 40) MPa and against an electronic balance (Fundamental Digital Pressure Standard, model 24610 from Desgranges & Huot) for pressures below 0.3 MPa. Global uncertainties on pressures after calibration are (± 0.00015, ± 0.001, and ± 0.002) MPa, respectively, to sensor ranges. Real time data are recorded simultaneously by a computer.

Periods are converted into densities using the forced path mechanical calibration model (FPMC).[11] This semiempirical method is based on the study of the mechanical behavior of the vibrating-tube function of temperature and pressure. It contains two unknown parameters, which are estimated through only one reference fluid, while classical calibration procedures require the measurement of two references fluids for each temperature studied. In the present work periods of R134a were measured at several pressures and temperatures, and the dedicated equation of state of Tillner-Roth and Baehr[12] was used to estimate the two parameters of the FPMC model.

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Table 1. P, ρ, T Data for the Hydrogen Sulfide (1) + Propane (2) Binary System; $z_1 = 0.2227$

T/K = 263.11		T/K = 293.28		T/K = 333.22		T/K = 333.22	
P	ρ_{exp}	P	ρ_{exp}	P	ρ_{exp}	P	ρ_{exp}
MPa	$\mathrm{kg \cdot m^{-3}}$	MPa	$\mathrm{kg \cdot m^{-3}}$	MPa	$\mathrm{kg \cdot m^{-3}}$	MPa	$\mathrm{kg \cdot m^{-3}}$
0.008	0.1	0.014	0.2	0.050	0.8	8.351	472.3
0.159	3.1	0.186	3.3	0.260	4.1	8.992	475.5
0.298	6.1	0.350	6.3	0.470	7.5	9.907	479.8
0.438	9.1	0.509	9.4	0.671	10.9	10.643	482.8
0.707[a]	571.2[a]	0.665	12.6	0.838	13.9	11.360	485.8
2.357	574.3	0.804	15.6	0.995	16.9	12.135	488.8
4.057	577.3	0.932	18.7	1.186	20.5	12.959	491.9
5.814	580.3	1.050	21.9	1.363	24.1	13.811	495.0
7.697	583.3	3.770[a]	518.4[a]	1.512	27.2	14.817	498.4
9.735	586.4	4.686	521.6	1.663	30.6	15.868	501.8
11.879	589.5	5.576	524.8	1.805	33.9	16.856	504.8
14.087	592.6	6.556	527.8	1.931	37.0	17.893	507.8
16.300	595.6	7.610	530.9	2.048	40.0	18.975	510.8
18.708	598.6	8.755	534.1	2.176	43.6	20.100	513.8
21.118	601.6	9.941	537.3	2.300	47.2	21.435	517.2
23.736	604.6	11.195	540.5	2.398	50.2	22.830	520.5
26.466	607.7	12.466	543.5	2.551	55.6	24.120	523.5
29.282	610.8	13.825	546.6	2.630	59.1	25.466	526.5
32.290	613.9	15.156	549.6	2.722	62.4	26.959	529.7
35.311	616.9	16.605	552.6	2.778	65.4	28.465	532.7
38.486	620.0	18.128	555.6	3.571[a]	438.6[a]	30.160	536.0
41.881	623.1	19.790	558.8	3.861	441.9	31.961	539.4
		21.473	561.9	4.197	445.2	33.791	542.6
		23.224	564.9	4.915	450.2	35.752	546.0
		25.127	568.1	5.323	453.4	37.781	549.3
		27.137	571.3	5.731	456.4	39.778	552.5
		29.216	574.5	6.177	459.5		
		31.365	577.6	6.686	462.8		
		33.453	580.6	7.239	466.1		
		35.831	583.8	7.781	469.2		

[a] This footnote indicates the separation of liquid data from vapor data.

Table 2. P, ρ, T Data for the Hydrogen Sulfide (1) + Propane (2) Binary System; $z_1 = 0.2691$

T/K = 268.09		T/K = 313.21		T/K = 363.24		T/K = 363.24	
P	ρ_{exp}	P	ρ_{exp}	P	ρ_{exp}	P	ρ_{exp}
MPa	$\mathrm{kg \cdot m^{-3}}$	MPa	$\mathrm{kg \cdot m^{-3}}$	MPa	$\mathrm{kg \cdot m^{-3}}$	MPa	$\mathrm{kg \cdot m^{-3}}$
0.009	0.2	0.202	3.3	0.009	0.1	5.360	313.4
0.180	3.5	0.382	6.4	0.313	4.4	5.410	319.7
0.335	6.7	0.558	9.5	0.596	8.6	5.474	326.0
0.476	9.7	0.722	12.6	0.842	12.3	5.549	332.3
0.818[a]	570.0[a]	0.878	15.7	1.110	16.6	5.632	339.4
2.369	573.1	1.040	19.0	1.358	20.8	5.762	346.5
3.999	576.3	1.178	22.0	1.602	25.0	5.914	353.3
5.608	579.3	1.322	25.3	1.810	28.7	6.056	359.2
7.451	582.5	1.455	28.5	2.014	32.7	6.228	365.4
9.258	585.5	1.580	31.7	2.204	36.6	6.441	371.6
11.262	588.7	1.693	34.9	2.401	40.6	6.679	377.7
13.236	591.8	1.773	37.9	2.576	44.4	6.961	383.9
15.455	595.0	2.189[a]	491.5[a]	2.742	48.3	7.276	390.0
17.739	598.2	2.787	494.6	2.905	52.3	7.639	396.1
20.006	601.2	3.465	498.0	3.058	56.2	8.055	402.1
22.487	604.4	4.173	501.2	3.211	60.3	8.511	408.0
24.903	607.4	4.917	504.4	3.358	64.4	9.002	413.7
27.518	610.5	5.710	507.6	3.493	68.4	9.557	419.4
30.199	613.6	6.516	510.6	3.613	72.3	10.183	425.2
33.045	616.7	7.434	513.9	3.752	76.3	10.878	431.1
36.027	619.8	8.423	517.3	3.878	80.7	11.648	436.9
39.139	622.9	9.421	520.5	3.964	84.5	12.515	442.7
		10.495	523.7	4.056	88.4	13.444	448.5
		11.669	527.1	4.156	92.4	14.452	454.1
		12.933	530.5	4.237	96.3	15.616	460.1
		14.205	533.7	4.354	102.5	16.807	465.7
		15.491	536.9	4.468	108.5	18.163	471.5
		16.847	540.0	4.619	120.8	19.596	477.1
		18.303	543.3	4.747	132.2	20.717	481.2
		19.787	546.4	4.838	142.5	21.739	484.7
		21.354	549.6	4.877	152.9	22.936	488.7
		22.903	552.6	4.905	166.8	24.149	492.4
		24.556	555.7	4.932	180.1	25.434	496.2
		26.292	558.8	4.954	190.9	26.773	500.0
		28.082	561.8	4.982	203.7	28.220	503.8
		29.973	564.9	5.002	216.0	29.831	507.9
		32.005	568.1	5.021	229.7	31.352	511.5
		34.062	571.2	5.043	241.1	32.889	515.0
		36.163	574.3	5.101	254.0	34.710	519.0
		38.383	577.4	5.146	266.2		
				5.182	277.5		
				5.220	288.7		
				5.267	299.6		
				5.324	307.2		

[a] This footnote indicates the separation of liquid data from vapor data.

Experimental Data Points

Tables 1 and 2 and Figures 1 and 2 present experimental isothermal ($P\rho T$) data sets for both compositions of the H_2S (1) + C_3H_8 (2) binary system. Three isotherms in the (263 to 333) K range are studied for molar composition $z_1 = 0.2227$. For molar composition $z_1 = 0.2691$, three isotherms are studied in the (268 to 363) K range. We note that at 363.24 K no "vapor−liquid" transition is observed over the (0 to 35) MPa pressure range. Moreover, the flat behavior of $P\rho$ data observed in the range (200 to 300) $\mathrm{kg \cdot m^{-3}}$ indicates that the measurements were done close to the mixture critical point. This is confirmed by the data provided by Kay and Rambosek.[4] They present critical points along the whole composition range of the H_2S + C_3H_8 binary system as shown in Figure 3. Their data are smoothed to estimate the critical point coordinates for mixture molar composition $z_1 = 0.2691$. We find $T_c = 362.3$ K, $P_c = 5.16$ MPa, and $\rho_c = 243.9\ \mathrm{kg \cdot m^{-3}}$, which is in good agreement with this work. Kay and Rambosek provide also saturating densities. Data are graphically compared to ours in Figure 4 for the mixture with molar compositions $z_1 = 0.1633$ and 0.2986. In present work we could not estimate the phase boundaries precisely because of the instability on the vibrating period. However, our data close to the phase boundaries are all included in the area located between the boundaries of Kay and Rambosek for $z_1 = 0.1633$ and 0.2986.

Density Data Correlation

In this work, we estimate the coherence between a model and the experimental data through the following average and standard deviations:

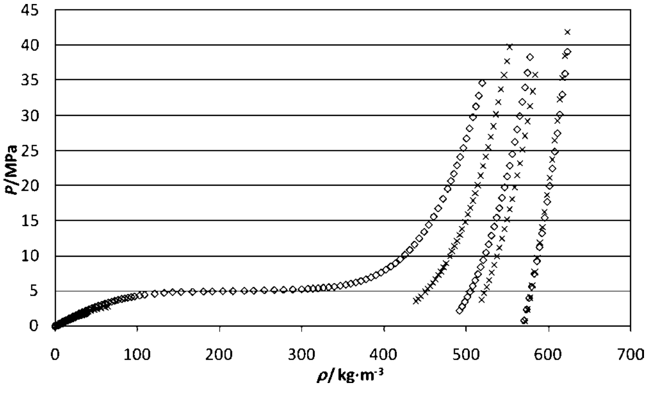

Figure 1. Experimental ($P\rho T$) data for the hydrogen sulfide (1) + propane (2) binary system: ×, $z_1 = 0.2227$ [(263, 293, and 333) K]; ◇, $z_1 = 0.2691$ [(268, 313, and 363) K].

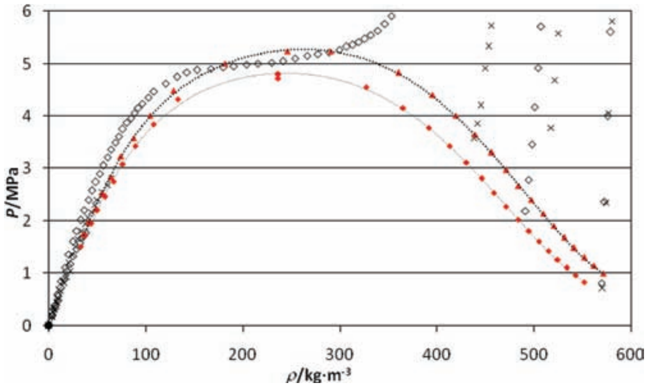

Figure 2. Experimental ($P\rho T$) data near VLE boundaries for the hydrogen sulfide (1) + propane (2) binary system: ×, $z_1 = 0.2227$ [(263, 293, and 333) K]; ◇, $z_1 = 0.2691$ [(268, 313, and 363) K]; ◆ (red), Kay and Rambosek phase boundaries at $z_1 = 0.1633$; ▲ (red), Kay and Rambosek phase boundaries at $z_1 = 0.2986$.

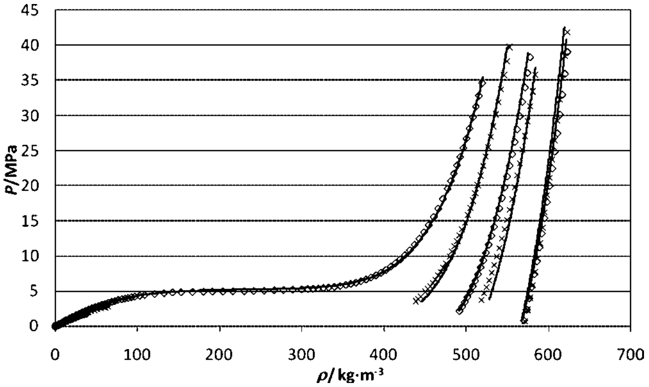

Figure 4. Experimental ($P\rho T$) data for the hydrogen sulfide (1) + propane (2) binary system: ×, $z_1 = 0.2227$ [(263.11, 293.28, and 333.22) K]; ◇, $z_1 = 0.2691$ [(268.09, 313.21, and 363.24) K]; —, LKP.

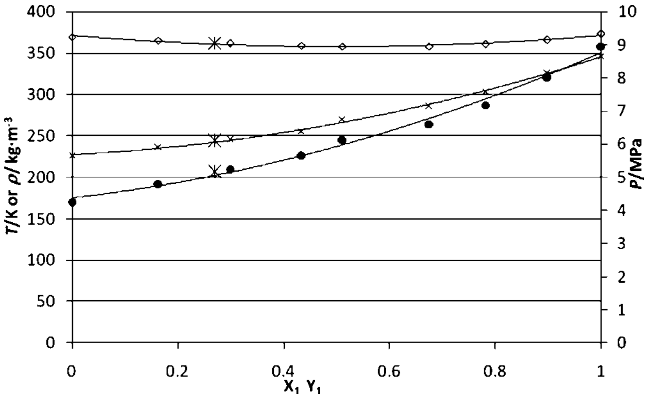

Figure 3. Critical point for the hydrogen sulfide (1) + propane (2) binary system: experimental data from Kay and Rambosek (1953). ×, critical density; ◇, critical temperature; ●, critical pressure; —, polynomial fitting; ∗, estimated critical data for $z_1 = 0.2691$ (243.9 kg·m^{-3}; 5.16 MPa and 362.3 K).

$$\text{average deviation: } \overline{\Delta\rho} = \frac{1}{N}\sum_N \Delta\rho$$

$$\text{where } \Delta\rho = (\rho_{\text{cal}} - \rho_{\text{exp}})$$

$$\text{sample standard deviation: } \sigma_{\Delta\rho} = \sqrt{\frac{\sum_N (\Delta\rho - \overline{\Delta\rho})^2}{N-1}}$$

In previous studies dealing with H_2S, CO_2, and light hydrocarbons,[1−3] several equations were used to represent experimental $P\rho T$ and VLE data. Benedict−Webb−Rubin−Starling's equation of state (BWRS EoS) was successfully applied to the H_2S/ethane[1] binary system with low deviations (± 2.5 kg·m^{-3}).

The 11 parameters of the BWRS EoS were fitted for each pure compound, and a binary interaction parameter was defined for mixture density data. However, the EoS was not suitable to estimate VLE boundaries (pressure, temperature). Cubic equations of state (cubic EoS), such as Peng−Robinson[13] or the Soave modification of Redlich−Kwong,[14] are well-known in VLE representation. In 1982 Péneloux and Rauzy[15] extend their ability to estimate liquid density with help of a volume translation method. More recently Laugier et al.[3] proposed a new method of volume translation based on neural network calculations. Authors successfully applied this method on $CO_2 + C_2H_6$ and $H_2S + C_2H_6$ binary systems with $\overline{\Delta\rho} < 3$ kg·m^{-3}. It has the great advantage not to require any binary interaction parameter. Weights of neural networks are only defined through pure component density data. Thus, such a method seems very promising for estimating volumetric properties of mixture data if it is coupled to a predictive equation of state like the predictive Peng−Robinson[16] for VLE phase boundaries.

In the present work we focus on the ability of the LKP EoS. The LKP model is based on the linearity of the compressibility factor Z thanks to two reference fluids, methane$^{(0)}$ and n-octane$^{(1)}$, and the acentric factor: $Z = Z^{(0)} + \omega Z^{(1)}$. The compressibility factor of reference fluids is calculated via the modified Benedict−Webb−Rubin[17] equation of state.

$$z = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{C^4}{T_r^3 V_r^5}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)$$

with

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^5},\quad C = c_1 - \frac{c_2}{T_r} - \frac{c_3}{T_r^3},\ \text{and}$$

$$D = d_1 - \frac{d_2}{T_r}$$

$$V_r = \frac{V}{V_c} \quad \text{and} \quad T_r = \frac{T}{T_c}$$

When dealing with mixtures, we used the following mixing rules involving the k_{ij} binary parameters from Plöcker et al.:

$$V_{cM} = \sum_i \sum_j z_i z_j V_{cij}$$

$$V_{cij} = \frac{1}{8}(V_{ci}^{\ 1/3} + V_{cj}^{\ 1/3})^3$$

$$V_{ci} = \frac{Z_{ci}RT_{ci}}{P_{ci}}$$

$$Z_{cM} = 0.2905 - 0.085\bar{\omega}_M$$

$$\bar{\omega}_{iM} = \sum_i z_i\bar{\omega}_i$$

$$T_{cM} = \frac{1}{V_{cM}}\sum_i \sum_j z_i z_j V_{cij} T_{cij}$$

$$T_{cij} = (T_{ci}T_{cj})^{0.5}K_{ij} \quad \text{with} \quad K_{ij} = K_{ji} \quad \text{and} \quad K_{ii} = 1$$

$$P_{cM} = \frac{RT_{cM}Z_{cM}}{V_{cM}}$$

Calculations are performed using Simulis Thermodynamics[8] coupled with Microsoft Excel. Parameters used for pure compound and reference fluids are gathered in Table 3. The temperature-dependent form $K_{ij} = K_{ij0} + K_{ijT}T$ was chosen. Parameters K_{ij0} and K_{ijT} are defined by fitting only VLE data from Brewer et al.[5] work at four pressures [(0.69, 1.38, 2.07, and 2.76) MPa] corresponding to the (258 to 344) K temperature range. An adjustment has been achieved using the Newton algorithm implemented into Microsoft Excel and the following objective function:

$$F = \frac{100}{N}\sqrt{\sum_i^N (T_{\text{exp}} - T_{\text{cal}})^2}$$

Parameters obtained are $K_{ij} = 0.8623 + 1.8805 \cdot 10^{-4}(T/\text{K})$. They lead to results with the following deviation in temperature: ± 0.85 K. Parameters are then applied to VLE data from Kay and Rambosek. Observed deviations in temperature, ± 0.31 K, are of the same order than previously, which confirmed the reliability of the parameters. Thus, the LKP EoS is then applied on $P\rho T$ for pure compounds and mixtures: Reamer et al.[18] data for H_2S between (278 and 444) K, Ihmels and Gmehling[19] data for H_2S between (250 and 550) K, Younglove and Ely[20] data for C_3H_8 between (250 and 370) K, Glos et al. data for C_3H_8[21] between (260 and 340) K, and present work data for mixtures between (263 and 363) K.

Table 3. Properties of Pure Compounds[8]

compound	M kg·mol^{-1}	P_c MPa	T_c K	V_c m^3·kmol^{-1}	ω
propane	0.0440956	4.248	369.83	0.2	0.152291
hydrogen sulfide	0.0340819	8.963	373.53	0.0985	0.0941677
methane	0.0160428	4.599	190.56	0.0986	0.0115478
n-octane	0.114231	2.490	568.70	0.486	0.399552

BWR EoS parameter	methane ($\omega = 0$)	*n*-octane ($\omega r = 0.3978$)
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0	0.016901
c_4	0.041724	0.041577
$d_1 \cdot 10^4$	0.155488	0.48736
$d_2 \cdot 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754

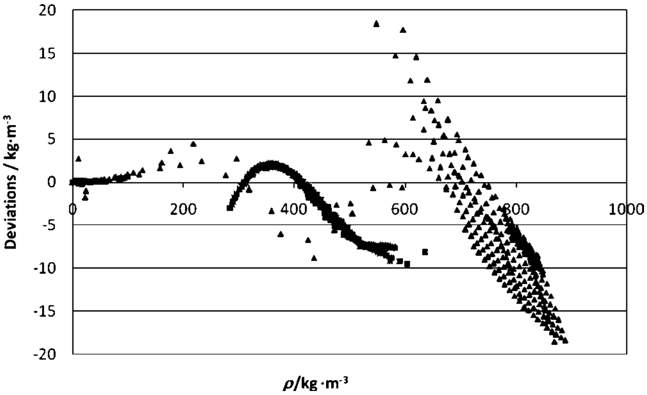

Figure 5. Absolute deviations for data of the pure compounds: hydrogen sulfide and propane: ▲, Reamer et al. and Ihmels et al. pure H_2S data [(250 to 550) K]; ■, Younglove et al. and Glos et al. pure C_3H_8 data [(250 to 370) K].

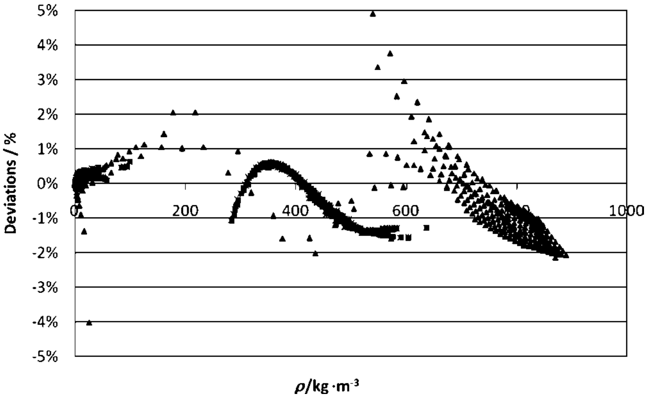

Figure 6. Relative deviations for data of the pure compounds: hydrogen sulfide and propane: ▲, Reamer et al. and Ihmels et al. pure H_2S data [(250 to 550) K]; ■, Younglove et al. and Glos et al. pure C_3H_8 data [(250 to 370) K].

We have to consider the two indicators $\overline{\Delta\rho}$ and $\sigma_{\Delta\rho}$ together to estimate the ability of the model. Thus, deviations between calculated and experimental data are presented in the form $\overline{\Delta\rho} \pm \sigma_{\Delta\rho}$; detailed deviations are plotted on Figures 5 and 6. Deviations for pure H_2S and C_3H_8 are respectively (−0.5 ± 1.7) % and (−0.5 ± 0.7) %. For mixtures, deviations are (−0.2 ± 3.1) kg·m^{-3}, less than 2 % for both liquid and vapor phases, excluding the data close to the critical region (cf. Figures 5 to 8). For the isotherm at 363.24 K, deviations up to 70 kg·m^{-3} are observed; a maximum deviation is obtained for the density of 241.13 kg·m^{-3}, which is very close to the critical density (243.9 kg·m^{-3} as estimated from Kay and Rambosek data). The LKP model represents well the experimental data of this work without any systematic deviation far from the critical region, and discrepancies are similar for pure compounds and mixtures.

Conclusion

Pressure, density, and temperature ($P\rho T$) data are presented for the hydrogen sulfide (1) + propane (2) binary system at two compositions (z_1 = 0.2227 and 0.2691) and various temperatures from vacuum up to 40 MPa. Experimental work was achieved using a vibrating-tube densimeter.

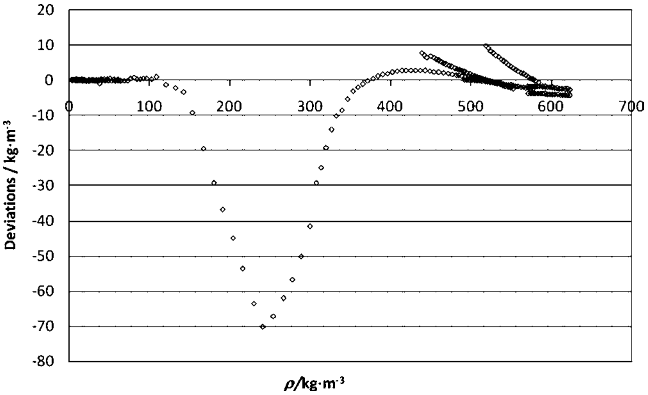

Figure 7. Absolute deviations for data of the hydrogen sulfide (1) + propane (2) binary system: ◇, $z_1 = 0.2227$ [(263.11, 293.28, and 333.22) K] and $z_1 = 0.2691$ [(268.09, 313.21, and 363.24) K].

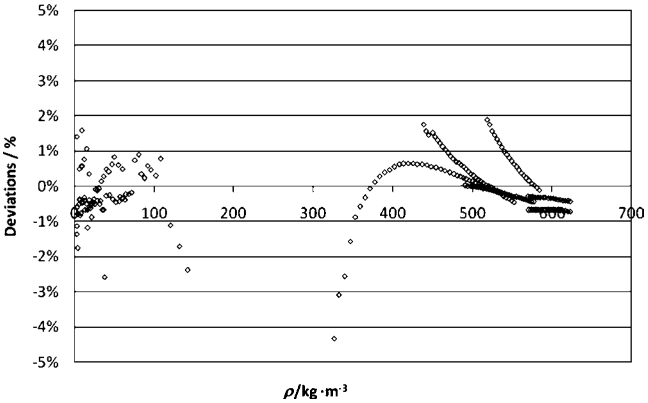

Figure 8. Relative deviations for data of the hydrogen sulfide (1) + propane (2) binary system: ◇, $z_1 = 0.2227$ [(263.11, 293.28, and 333.22) K] and $z_1 = 0.2691$ [(268.09, 313.21, and 363.24) K].

The LKP model was chosen to check consistency of experimental data. Density deviations are less than 2 % on liquid and vapor phases except for data close to critical point. Fluids present in general a specific behavior near a critical point, and if needed, we recommend the use of a more accurate model to resolve the discrepancies observed.[22]

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