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Experimental Densities of Hexane + Benzothiophene Mixtures from (313 to 363) K and up to 20 MPa

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Experimental densities of hexane and hexane + benzothiophene mixtures were obtained via a vibrating tube densimeter. Densities of hexane were measured from (313 to 363) K and pressures up to 25 MPa. For the case of hexane (1) + benzothiophene (2) mixtures, the experiments were performed at five compositions ($x_1 = 0.0629$, 0.2588, 0.4495, 0.7491, and 0.9432) in the same range of temperatures at pressures up to 20 MPa. Uncertainties for measured densities were estimated within 0.2 $\mathrm{kg \cdot m^{-3}}$. The obtained densities of hexane were compared with those values reported in the literature and with the results obtained by the Tait equation and the equation of state proposed by R. Span and W. Wagner (*Int. J. Thermophys.* **2003**, *24*, 1−39). These were also correlated with a modified five-parameter Toscani−Szwarc equation (MTS). Good agreement was found in all cases. Excess molar volumes for the mixtures, as well as isothermal compressibilities and isobaric thermal expansivities of hexane, were calculated using the reported parameters for the MTS equation.

Introduction

Sulfur content in fuels is regulated by international norms due to the contamination and acid rain they produce in the atmosphere. A possible way to eliminate the contamination is by extracting these compounds from fuels, particularly gasoline and diesel. For the design of this kind of process, basic information for the thermodynamical properties, such as phase equilibria, solubilities of sulfur compounds in some solvents, densities of liquid mixtures, etc., is required. However, scarce information concerning the properties for sulfur compounds or its mixtures is available in the literature.

Previous works to study the behavior of sulfur and aromatic compounds in supercritical CO_2 and in mixtures of CO_2 + cosolvents have been presented from our workgroup.[1−6] In this work, densities of mixtures of a sulfur compound and an alkane are used as basic information to simulate a fuel. Gasoline has compounds more important than hexane; however, this alkane was selected in this work as a first attempt to represent a fuel added to benzothiophene which was the model sulfur compound. Alkanes with a greater number of carbons will be tested in future works.

Hexane has been used mainly as a solvent in many applications such as, for instance, liquid−liquid extractions of seed oils, solvent in adhesives, and leather tanning. This alkane is a very important solvent in industry and research. Properties of hexane previously reported in the literature include measurements of densities and speeds of sound, calculations of isothermal compressibilities and isobaric thermal expansivities, and correlations of data.[7−9] On the other hand, experimental data for benzothiophene are scarce, and it is necessary to know its phase behavior in contact with alkanes for future extractions.

This work reports the experimental densities of hexane and five mixtures of hexane + benzothiophene, at temperatures from (313 to 363) K and pressures up to 25 MPa for hexane and 20 MPa for the mixtures. Densities of hexane were correlated with the modified five-parameter Toscani−Szwarc (MTS) equation,[6] and their optimal parameters were used to calculate densities and derivative properties, such as isothermal compressibilities and isobaric thermal expansivities. Excess molar volumes for hexane + benzothiophene mixtures were calculated by using reported densities and the five-parameter MTS equation[6] for the densities of pure compounds. The data for these mixtures have not been previously reported in the literature.

Experimental Section

Materials. Hexane (> 99.5 %) was supplied by Fluka (Germany); benzothiophene (99.0 %) and water (99.995 %) were obtained from Sigma-Aldrich (USA); and Air Products-Infra (Mexico) supplied the nitrogen (> 99.998 mol %). Liquid compounds were used without any further purification, except for careful degassing under vacuum before the measurements. Nitrogen was used as received.

Apparatus. The experimental apparatus has been previously described by Zúñiga-Moreno et al.[4−6] It is based on the static-synthetic method, with a sapphire tube feeding cell coupled to a vibrating tube densimeter (VTD).

The 10 cm^3 sapphire cell is placed inside an air bath. The temperature is maintained within ± 0.03 K and is monitored with a platinum probe (Specitec, model Pt100). The Pt100 probe is inserted at the top of the cell and connected to a digital indicator (Automatic Systems Laboratories, model F250). All the platinum probes used in this work were calibrated with a 25-Ω reference probe (Rosemount, model 162CE, uncertainty 0.005 K) coupled to a calibration system (Automatic Systems Laboratories, model F300S).

The pressure inside the measuring cell was registered by means of a pressure transducer (SEDEME, model 250) coupled to a digital multimeter (Hewlett-Packard, model 34401A). The transducer was calibrated against a dead weight balance (Desgranges & Huot, model 5304 Class S2, uncertainty 0.005 %). The total uncertainty was estimated to be within 0.008 MPa.

The mixture in the homogeneous phase is stirred inside the cell with the help of a magnetic rod and fed to the vibrating tube densimeter (Anton Paar, model DMA 512) made of Hastelloy C-276. The temperature of the VTD measured with a Pt100 probe is maintained within ± 0.03 K by means of a liquid bath (Polyscience, model 9510). The VTD was calibrated

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Table 1. Experimental Densities ρ of Hexane

T/K = 313.12		T/K = 323.05		T/K = 332.85		T/K = 342.73		T/K = 352.56		T/K = 362.40	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.019	642.2	1.030	633.0	1.020	623.5	1.010	613.9	1.017	604.0	1.029	593.8
1.010	613.9	1.017	604.0	1.029	593.8	2.010	615.5	2.028	605.8	2.020	595.8
2.044	643.5	2.010	634.3	2.021	625.0	3.011	617.1	3.030	607.6	3.028	597.6
3.023	644.6	3.021	635.6	3.022	626.5	4.010	618.6	4.024	609.2	4.029	599.5
4.018	645.8	4.018	636.9	4.020	627.8	5.005	620.0	5.022	610.9	5.040	601.3
5.016	647.0	5.014	638.1	5.011	629.2	6.031	621.6	6.024	612.5	6.026	602.9
6.012	648.1	6.007	639.4	6.016	630.6	7.020	623.0	7.027	614.0	7.026	604.7
7.016	649.2	7.010	640.6	7.012	631.9	8.009	624.4	8.021	615.5	8.004	606.3
8.016	650.3	8.012	641.8	8.025	633.3	9.015	625.7	9.022	617.0	9.007	607.9
9.020	651.4	9.020	643.0	9.012	634.5	10.012	627.0	10.020	618.4	10.009	609.4
10.018	652.5	10.008	644.1	10.010	635.7	11.006	628.4	11.023	619.9	11.009	610.9
11.020	653.5	11.021	645.2	11.012	636.9	12.014	629.7	12.003	621.2	12.010	612.5
12.004	654.6	12.011	646.4	12.019	638.1	13.011	630.9	13.021	622.6	13.000	614.0
13.007	655.6	13.007	647.4	13.007	639.2	14.014	632.2	14.012	623.9	14.028	615.5
14.015	656.6	14.007	648.5	14.021	640.4	15.008	633.4	15.007	625.2	15.017	616.8
15.006	657.6	15.035	649.6	15.014	641.6	16.006	634.6	16.016	626.5	16.014	618.1
16.023	658.6	16.011	650.6	16.025	642.8	17.021	635.7	17.012	627.7	17.004	619.5
17.015	659.6	17.021	651.6	17.011	643.8	18.016	636.9	18.015	629.0	18.002	620.9
18.011	660.5	18.020	652.7	18.035	644.9	19.025	638.0	19.003	630.2	18.988	622.1
19.009	661.4	19.013	653.7	19.014	646.0	20.037	639.2	20.040	631.4	20.027	623.4
20.016	662.4	20.001	654.6	20.011	647.1	21.025	640.3	21.005	632.5	21.002	624.7
20.995	663.3	21.028	655.6	21.015	648.1	22.016	641.3	22.035	633.8	22.018	625.9
22.018	664.2	22.004	656.6	22.000	649.1	23.010	642.5	23.002	634.8	23.013	627.1
23.018	665.1	23.010	657.5	23.012	650.1	24.023	643.5	24.039	636.0	24.001	628.4
24.013	666.0	24.021	658.5	24.022	651.2	25.006	644.5	25.000	637.1	25.000	629.5
25.002	666.8	25.018	659.4	25.030	652.2						

using water and nitrogen according to the classical method. The density of the mixture is given by[10]

$$\rho_F(p,T) = \rho_{H_2O}(p,T) + \frac{[\tau_F^2(p,T) - \tau_{H_2O}^2(p,T)][\rho_{H_2O}(p,T) - \rho_{N_2}(p,T)]}{\tau_{H_2O}^2(p,T) - \tau_{N_2}^2(p,T)} \tag{1}$$

where $\rho_F(p,T)$ is the studied fluid density; $\rho_{H_2O}(p,T)$ is the reference density of water; and $\rho_{N_2}(p,T)$ is that for nitrogen. These were calculated using the equations of state of Wagner and Pruss[11] and Span et al.,[12] respectively; $\tau(p,T)$ represents the vibrating period of each fluid.

Experimental Procedure. The first step is the sapphire cell loading. The empty cell is degassed and weighted. Then, the cell is again degassed containing a specific amount of benzothiophene. After that, the cell is weighted. The difference between the weight of the empty cell and the cell loaded with benzothiophene is the weight of this compound. Hexane is added to the cell. When a new weighting is performed, the amount of hexane is determined as well as the composition of the mixture. The mass measurements are done with a comparator balance (Sartorius, model MCA 1200), and the uncertainty of the mole fraction is within $1 \cdot 10^{-4}$.

The second step is setting up the experimental conditions. The air and liquid baths are turned on and set up to the lowest temperature of measurement (313 K). The mixture in the sapphire cell is pressurized using nitrogen. This gas enters at the bottom of the cell and pushes up the piston via a pressure generator. The mixture contained in the cell is loaded into the VTD by opening a feeding valve. When the desired temperature is reached and the vibrating period is constant, measurements can be performed.

The third step is recording the temperature and vibrating period at each pressure for the studied system. When the maximum pressure is reached, the temperature is changed to 323 K while the pressure is decreased to 1.0 MPa. This step is done for all of the measurement temperatures.

The experimental densities of hexane are presented in Table 1. The obtained densities for the hexane (1) + benzothiophene (2) mixtures measured at five compositions (x_1 = 0.0629, 0.2588, 0.4495, 0.7491, and 0.9432) are reported in Tables 2 to 6. The uncertainty for all measured densities is estimated to be 0.2 kg·m^{-3}.

Modeling. Experimental density data of hexane obtained in this work were correlated using the modified equation of Toscani−Szwarc (MTS) proposed by Zúñiga-Moreno et al.[6] It is expressed as follows

$$v = \frac{c_1 + c_2 p}{c_3 - (c_4/T + c_5/T^{1/3}) + p} \tag{2}$$

where v is the specific volume of the fluid at a specific p and T and c_i are the five parameters of the equation. The parameters of eq 2 were optimized by using the Marquardt−Levenberg method[13] and minimizing the objective function S

$$S = \sum_i [(v_i^{\text{exptl}} - v_i^{\text{calcd}})/v_i^{\text{exptl}}]^2 \tag{3}$$

The statistical values for the correlation were calculated with the following expressions:[4,14]

absolute average deviation

$$\text{AAD} = \frac{1}{n}\sum_{i=1}^{n} |\%\ \Delta v_i| \tag{4}$$

mean deviation

$$\text{bias} = \frac{1}{n}\sum_{i=1}^{n} (\%\ \Delta v_i) \tag{5}$$

standard deviation

$$\text{SDV} = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n} (\%\ \Delta v_i - \text{bias})^2} \tag{6}$$

Table 2. Experimental Densities ρ of the Hexane (1) + Benzothiophene (2) Mixture at $x_1 = 0.0629$

T/K = 313.00		T/K = 322.95		T/K = 332.77		T/K = 342.63		T/K = 352.41	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.011	1112.7	1.028	1103.4	1.019	1094.5	1.018	1085.6	1.015	1076.7
2.027	1113.3	2.021	1104.1	2.029	1095.3	2.039	1086.3	2.020	1077.4
3.046	1113.9	3.029	1104.7	3.030	1096.0	3.009	1087.0	3.016	1078.1
4.018	1114.5	4.021	1105.4	4.019	1096.7	4.022	1087.8	4.038	1078.8
5.014	1115.2	5.037	1106.1	5.026	1097.4	5.025	1088.5	5.000	1079.5
6.016	1115.7	6.021	1106.7	6.037	1098.1	5.925	1089.1	6.001	1080.4
7.014	1116.3	7.021	1107.4	7.035	1098.8	7.031	1089.9	7.017	1081.1
8.008	1116.9	8.029	1108.1	8.021	1099.5	8.009	1090.6	8.008	1082.0
9.013	1117.6	9.018	1108.7	9.012	1100.1	9.007	1091.3	9.017	1082.6
10.003	1118.1	10.003	1109.3	10.008	1100.8	10.024	1092.0	10.026	1083.4
11.005	1118.7	10.998	1109.9	11.026	1101.5	11.013	1092.7	11.018	1084.1
12.017	1119.3	12.016	1110.6	12.020	1102.2	12.012	1093.4	12.014	1084.7
13.017	1119.9	13.012	1111.2	13.012	1102.8	13.000	1094.1	13.014	1085.4
14.023	1120.5	14.019	1111.8	14.016	1103.4	14.019	1094.8	14.022	1086.2
15.024	1121.0	15.018	1112.5	15.015	1104.2	15.027	1095.4	15.028	1086.8
16.016	1121.6	16.018	1113.1	16.015	1104.7	16.019	1096.1	16.020	1087.6
17.014	1122.3	17.024	1113.7	17.020	1105.4	17.009	1096.8	17.023	1088.2
18.019	1122.8	18.018	1114.4	18.020	1106.1	18.015	1097.5	18.015	1088.8
19.014	1123.4	19.024	1115.0	19.022	1106.7	19.019	1098.2	19.016	1089.5
20.000	1124.0	20.012	1115.6	20.017	1107.3	20.018	1098.8	20.019	1090.2

Table 3. Experimental Densities ρ of the Hexane (1) + Benzothiophene (2) Mixture at $x_1 = 0.2588$

T/K = 312.99		T/K = 322.89		T/K = 332.66		T/K = 342.55		T/K = 352.33	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.009	1009.0	1.017	1000.0	1.020	991.1	1.028	982.2	1.030	973.2
2.023	1009.7	2.023	1000.8	2.021	991.9	2.013	983.1	2.012	973.9
3.016	1010.5	3.021	1001.5	3.022	992.7	3.013	983.8	3.021	974.8
4.029	1011.2	4.016	1002.3	4.018	993.5	4.017	984.7	4.018	975.8
5.004	1011.9	5.026	1003.1	5.021	994.3	5.024	985.5	5.020	976.6
6.021	1012.6	6.030	1003.8	6.012	995.0	6.012	986.3	6.024	977.6
7.031	1013.3	7.028	1004.6	7.018	995.8	7.004	987.1	7.016	978.5
8.005	1014.0	8.018	1005.3	8.005	996.6	8.017	987.9	8.000	979.3
9.022	1014.8	9.014	1006.0	9.012	997.3	9.012	988.7	9.020	980.2
10.016	1015.4	10.021	1006.7	10.011	998.2	10.016	989.5	10.010	981.0
11.004	1016.1	11.005	1007.5	11.013	998.9	11.015	990.4	11.018	981.9
12.015	1016.8	12.022	1008.2	12.006	999.7	12.022	991.2	12.012	982.7
13.015	1017.5	13.013	1008.9	13.011	1000.4	13.030	992.0	13.013	983.5
14.003	1018.2	14.012	1009.6	14.000	1001.2	14.011	992.8	14.007	984.3
15.011	1018.9	15.017	1010.3	15.025	1002.0	15.020	993.6	15.016	985.2
16.003	1019.5	16.016	1011.0	16.005	1002.6	16.020	994.3	16.012	986.0
17.010	1020.2	17.002	1011.7	17.000	1003.3	17.017	995.1	17.013	986.8
18.002	1020.9	18.014	1012.4	18.002	1004.1	18.008	995.8	18.003	987.6
19.029	1021.5	19.024	1013.1	19.009	1004.8	19.011	996.6	19.011	988.4
20.017	1022.2	20.016	1013.8	20.016	1005.5	20.013	997.4	20.014	989.1

root-mean-square

$$\mathrm{RMS} = \sqrt{\frac{1}{n}\sum_{i=1}^{n} (\%\ \Delta v_i)^2} \tag{7}$$

where $\%\ \Delta v_i = 100(v_i^{\mathrm{exptl}} - v_i^{\mathrm{calcd}})/v_i^{\mathrm{exptl}}$. n represents the number of correlated data. The parameters and statistical values for hexane for eq 2 are presented in Table 7.

Deviations between experimental and calculated densities with eq 2 are presented in Figure 1. As can be seen, densities of hexane are well represented for the equation in the studied range of pressures and temperatures. Almost all of the deviations showed in this figure are within the experimental uncertainty which is better than 0.035 %.

Derived Properties. Isothermal compressibilities and isobaric thermal expansivities of hexane were calculated according to

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{8}$$

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \tag{9}$$

Differentiation of eq 2 and substituting the results in eqs 8 and 9 leads to

$$\kappa_T = \frac{1}{c_3 - (c_4/T + c_5/T^{1/3}) + p} - \frac{c_2}{c_1 + c_2 p} \tag{10}$$

$$\alpha_p = -\left[\frac{c_4/T^2 + c_5/3T^{4/3}}{c_3 - (c_4/T + c_5/T^{1/3}) + p}\right] \tag{11}$$

The excess molar volume for a binary mixture is calculated with the expression

$$V^{\mathrm{E}} = \frac{M_{\mathrm{mix}}}{\rho_{\mathrm{mix}}} - \left(\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right) \tag{12}$$

In this equation, the excess molar volume V^{E} is calculated by using the density ρ, molecular weight M, and the mole fraction x. The subscripts 1 and 2 and mix denote hexane, benzothiophene, and the mixture, respectively.

In the calculation of excess molar volumes of hexane (1) + benzothiophene (2) mixtures, ρ_{mix} was taken from Tables 2 to 6 and ρ_1 and ρ_2 were calculated with eq 2 using the parameters

Table 4. Experimental Densities ρ of the Hexane (1) + Benzothiophene (2) Mixture at $x_1 = 0.4495$

T/K = 313.15		T/K = 322.05		T/K = 332.90		T/K = 342.79		T/K = 352.63		T/K = 362.50	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.025	910.7	1.026	901.9	1.028	892.5	1.022	883.3	1.037	874.2	1.028	864.8
2.010	911.5	2.020	902.8	2.010	893.2	2.032	884.3	2.029	875.3	2.025	866.0
3.028	912.4	3.015	903.7	3.021	894.1	3.024	885.3	3.026	876.4	3.020	867.1
4.011	913.2	4.003	904.5	4.018	895.3	4.029	886.4	4.032	877.5	4.000	868.2
5.013	914.0	5.014	905.4	5.018	896.2	5.019	887.3	5.015	878.5	5.045	869.3
6.021	914.8	6.021	906.3	6.008	897.0	6.019	888.3	6.024	879.5	6.017	870.4
7.010	915.6	7.015	907.2	7.019	897.9	7.035	889.3	7.028	880.5	7.018	871.5
8.033	916.4	8.009	908.0	8.016	898.8	8.022	890.2	8.017	881.5	8.013	872.5
9.029	917.2	9.028	908.9	9.023	899.8	9.016	891.1	9.003	882.5	9.024	873.6
10.015	918.0	10.013	909.7	10.018	900.7	10.010	892.0	10.022	883.5	10.011	874.6
11.018	918.8	11.021	910.5	11.007	901.6	11.010	893.0	11.024	884.5	11.008	875.6
12.012	919.5	12.023	911.3	12.010	902.4	12.024	893.9	12.013	885.4	12.025	876.6
13.010	920.3	13.008	912.1	13.019	903.3	13.001	894.8	13.038	886.4	13.004	877.6
14.022	921.0	14.021	913.0	14.015	904.2	14.017	895.7	14.000	887.3	14.014	878.6
15.019	921.8	15.012	913.7	15.019	905.0	15.021	896.6	15.021	888.2	15.011	879.6
16.008	922.6	16.018	914.5	16.002	905.9	16.020	897.4	16.012	889.1	16.027	880.6
17.018	923.3	17.012	915.3	17.014	906.7	17.009	898.3	17.010	890.0	17.017	881.5
18.027	924.1	18.012	916.1	18.017	907.5	18.009	899.2	18.015	890.9	18.030	882.5
19.006	924.8	19.007	916.9	19.023	908.3	19.011	900.0	19.022	891.8	19.022	883.4
20.006	925.5	20.015	917.7	20.028	909.1	20.011	900.9	20.005	892.7	20.002	884.3

Table 5. Experimental Densities ρ of the Hexane (1) + Benzothiophene (2) Mixture at $x_1 = 0.7491$

T/K = 313.13		T/K = 323.02		T/K = 332.86		T/K = 342.72		T/K = 352.53		T/K = 362.33	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.017	761.8	1.017	752.7	1.031	743.7	1.034	734.5	1.026	725.1	1.020	715.3
2.027	762.9	2.013	753.8	2.024	744.9	2.000	735.8	2.026	726.5	2.034	716.8
2.000	735.8	2.026	726.5	2.034	716.8	3.023	737.0	3.024	727.8	3.013	718.3
3.031	764.0	3.014	754.9	3.019	746.1	4.016	738.2	4.034	729.2	4.007	719.7
4.039	764.9	4.012	756.0	4.001	747.2	5.014	739.5	5.014	730.5	5.015	721.2
5.021	765.9	5.008	757.1	5.002	748.4	6.014	740.7	6.040	731.8	6.018	722.5
6.027	766.9	6.010	758.1	6.020	749.5	7.019	741.8	7.028	733.0	7.015	723.9
7.021	767.9	7.025	759.2	7.005	750.6	8.012	743.0	8.017	734.3	8.017	725.2
8.054	768.9	8.028	760.2	8.013	751.7	9.010	744.1	9.003	735.5	9.024	726.5
9.007	769.8	9.009	761.2	9.004	752.8	10.013	745.3	10.008	736.7	10.010	727.8
10.018	770.7	10.010	762.2	10.000	753.8	11.016	746.4	11.016	737.9	10.996	729.1
11.018	771.6	11.002	763.2	11.019	754.9	12.016	747.5	12.002	739.0	12.027	730.4
12.036	772.6	12.017	764.1	12.006	755.9	13.011	748.6	13.020	740.2	13.022	731.6
13.021	773.5	13.019	765.1	13.014	757.0	14.001	749.6	14.016	741.3	14.016	732.8
14.007	774.3	14.006	766.0	14.008	757.9	15.003	750.7	15.037	742.5	15.023	734.0
15.006	775.2	15.015	767.0	15.007	758.9	16.025	751.7	16.035	743.6	16.012	735.1
16.012	776.0	16.022	767.9	16.009	759.9	17.012	752.8	17.020	744.6	17.011	736.3
17.016	776.9	17.019	768.8	17.002	760.9	18.018	753.8	18.020	745.7	18.012	737.4
18.000	777.8	18.016	769.8	18.026	761.8	19.008	754.7	19.008	746.7	19.030	738.6
19.017	778.6	19.024	770.6	19.007	762.8	20.017	755.8	20.019	747.8	20.017	739.7
20.030	779.5	20.021	771.5	20.017	763.7						

obtained in this work for hexane and those reported by Jiménez-Gallegos[15] for benzothiophene (see Table 7) to have the same values of temperature and pressure for all mixtures. A typical behavior for the excess molar volumes of the studied mixtures can be observed in Figures 2 and 3. The uncertainty for calculated excess molar volumes in this work is estimated within 0.065 cm^3·mol^{-1}.

Results and Discussion

Experimental densities of hexane in this work were correlated with the five-parameter MTS and compared with those from the literature[7−9] and those calculated with the equation of state proposed by Span and Wagner.[16] A detailed procedure for calculation of densities with this equation is given in ref 16. Deviations between experimental and calculated densities of hexane are plotted in Figure 4. Good agreement is observed. Deviations were within −0.13 % and +0.04 %.

Densities of hexane were also compared with those calculated with the Tait equation using parameters reported by Cibulka[17] and Cibulka and Hnedkovský[18]

$$\rho = \rho_{\text{ref}}\left[1 - C_T \ln \frac{B_T + p}{B_T + p_{\text{ref}}}\right]^{-1} \qquad (13)$$

where ρ_{ref} is the reference density computed as

$$\rho_{\text{ref}} = \rho_{\text{C}}[1 + \sum_{i=1}^{N_{\text{A}}} a_{T_i}(1 - T/T_{\text{C}})^{(i/3)}] \qquad (14)$$

a_T are the adjusted parameters of the equation for a pure compound; N_{A} is the maximum number of parameters; ρ_{C} is the critical density; T is the system temperature; and T_{C} is the critical temperature of the substance. The values of B_T and C_T of eq 13 were calculated from

$$B_T = \sum_{i=0}^{N_{\text{B}}} b_{T_i}[(T - T_0)/100]^i \qquad (15)$$

$$C_T = \sum_{i=0}^{N_{\text{C}}} c_{T_i}[(T - T_0)/100]^i \qquad (16)$$

where b_T and c_T are the group of parameters reported by Cibulka and Hnedkovský[18] and N_{B} and N_{C} are the number of parameters. T_0 is a fixed temperature for hexane. p_{ref} is the reference pressure in eq 13 and is equal to 0.101325 MPa when the measurement temperature is under the normal boiling point of hexane;

Table 6. Experimental Densities ρ of the Hexane (1) + Benzothiophene (2) Mixture at $x_1 = 0.9432$

T/K = 313.11		T/K = 323.09		T/K = 332.82		T/K = 342.71		T/K = 352.53		T/K = 362.31	
p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}	p/MPa	ρ/kg·m^{-3}
1.023	669.0	1.017	659.3	1.026	650.1	1.025	640.4	1.025	630.4	1.028	620.3
2.023	670.0	2.024	660.6	2.016	651.4	2.014	641.8	2.023	632.1	2.031	622.2
3.037	671.0	3.024	661.9	3.016	652.8	3.011	643.3	3.030	633.8	3.031	624.0
4.019	672.2	4.016	663.1	4.023	654.1	4.027	644.8	4.018	635.4	4.012	625.7
5.025	673.3	5.024	664.2	5.004	655.4	5.014	646.2	5.021	637.0	5.026	627.4
6.058	674.4	6.021	665.5	6.016	656.7	6.027	647.6	6.018	638.5	6.013	629.1
7.008	675.5	7.018	666.6	7.012	658.0	7.019	649.0	7.010	639.9	7.022	630.7
8.047	676.6	8.020	667.8	8.018	659.2	8.015	650.3	8.018	641.4	8.014	632.3
9.025	677.6	9.019	668.9	9.014	660.5	9.010	651.6	9.044	642.8	9.000	633.7
10.040	678.6	10.010	670.0	10.014	661.6	10.003	652.9	10.011	644.2	10.011	635.3
11.000	679.6	11.012	671.1	11.009	662.8	11.017	654.2	11.022	645.5	11.007	636.7
12.016	680.7	12.013	672.2	12.005	664.0	12.006	655.4	12.013	646.9	12.007	638.2
13.019	681.6	13.021	673.3	13.020	665.1	13.024	656.7	13.005	648.2	13.008	639.6
14.016	682.6	14.023	674.3	14.007	666.3	14.021	657.8	14.000	649.5	14.024	640.9
15.029	683.6	15.015	675.3	15.005	667.3	15.006	659.0	15.021	650.8	15.002	642.3
16.024	684.5	16.001	676.3	16.012	668.4	16.015	660.2	16.022	652.0	16.016	643.6
17.011	685.5	17.028	677.3	17.015	669.5	17.016	661.3	17.001	653.2	17.000	644.9
18.015	686.4	18.003	678.3	18.010	670.6	18.000	662.4	18.013	654.4	18.008	646.3
19.046	687.4	19.001	679.3	19.000	671.6	19.034	663.6	19.007	655.6	19.018	647.5
20.016	688.2	20.017	680.3	20.001	672.6	20.012	664.6	20.039	656.7	20.028	648.8

otherwise, p_{ref} is the vapor pressure of hexane calculated with the equation

$$\log p_{\mathrm{ref}} = A_{\mathrm{vp}} - B_{\mathrm{vp}}/(T + C_{\mathrm{vp}} - 273.15) \qquad (17)$$

where $A_{\mathrm{vp}} = 4.00139$, $B_{\mathrm{vp}} = 1170.875$, and $C_{\mathrm{vp}} = 224.317$ were taken from ref 19.

Deviations between data reported in this work and those calculated with eq 13 are plotted in Figure 4. Good agreement can be seen with deviations better than 0.05 %, but it is greater at 362.40 K for some data points. Nevertheless, deviations in this isotherm are within 0.10 %, so the agreement is still good. Cibulka and Hnedkovský[18] reported the statistical values for their correlation as RMSD = 0.693 kg·m^{-3}, RMSDr = 0.112 %, and bias = −0.033 kg·m^{-3}. Following the same procedure, the statistics for this work are RMSD = 0.200 kg·m^{-3}, RMSDr = 0.032 %, and bias = 0.060 kg·m^{-3}.

Because temperatures and pressures in this work are not equal to the experimental data from the literature, the MTS equation was used for comparisons. Figure 5 shows the differences between densities of hexane calculated by using eq 2 and literature data. The deviations were slightly greater than those plotted in Figure 4.

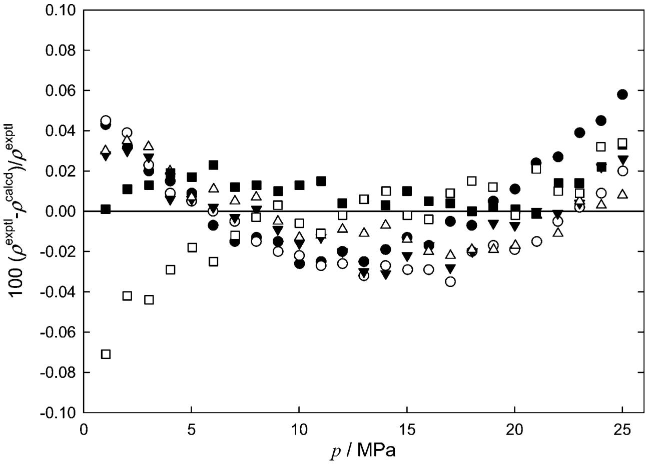

Figure 1. Deviations between experimental densities ρ^{exptl} of hexane with those calculated with eq 2, ρ^{calcd}, at: ●, 313.12 K; ○, 323.05 K; ▼, 332.85 K; △, 342.73 K; ■, 352.56 K; and □, 362.40 K.

Table 7. Parameters of the Five-Parameter MTS Equation[6] for Hexane and Benzothiophene

hexane		benzothiophene[a]	
c_1/MPa·kg^{-1}·m^3	0.1104	c_1/MPa·kg^{-1}·m^3	0.2442
c_2/kg^{-1}·m^3	1.3290·10^{-3}	c_2/kg^{-1}·m^3	7.3852·10^{-4}
c_3/MPa	−248.93	c_3/MPa	−2.6262
c_4/K·MPa	34929.44	c_4/K·MPa	9819.83
c_5/K$^{1/3}$·MPa	−2928.28	c_5/K$^{1/3}$·MPa	−2129.88
AAD/%	1.63·10^{-2}	AAD/%	7.33·10^{-3}
bias/%	−4.94·10^{-5}	bias/%	1.53·10^{-4}
SDV/%	2.05·10^{-2}	SDV/%	8.68·10^{-3}
RMS/%	2.04·10^{-2}	RMS/%	8.64·10^{-3}
T_{min}/K	313.12	T_{min}/K	314.04
T_{max}/K	362.40	T_{max}/K	352.80
p_{min}/MPa	1.010	p_{min}/MPa	1.010
p_{max}/MPa	25.030	p_{max}/MPa	20.020
n	150	n	100

[a] From ref 15.

Calculated isothermal compressibilities of hexane from eq 10 ($\kappa_T^{\mathrm{calcd}}$) were compared with those reported by Daridon et al.[20] and Pečar and Doleček[21] (κ_T^{lit}). In Figure 6, residuals between values reported in the literature and those calculated

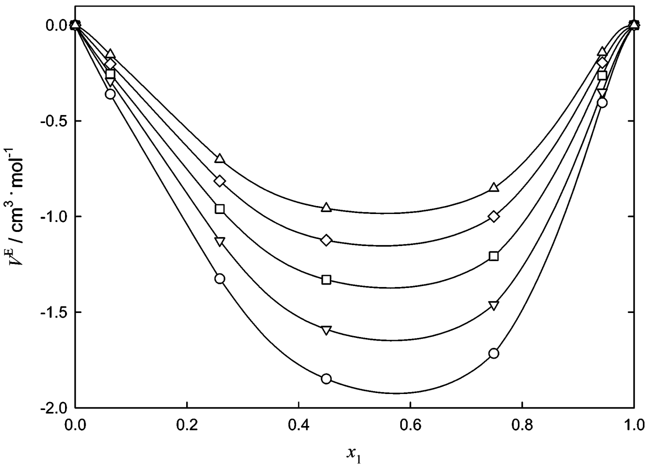

Figure 2. Excess molar volumes V^{E} calculated with the five-parameter equation MTS at ~353 K for the hexane + benzothiophene mixtures: ○, 1 MPa; ▽, 5 MPa; □, 10 MPa; ◇, 15 MPa; and △, 20 MPa. Solid lines denote a trend.

with eq 10 are plotted. Good agreement was observed for this property.

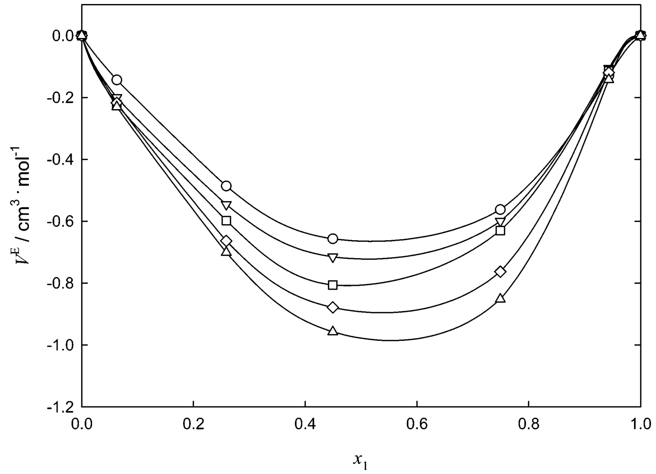

Figure 3. Excess molar volumes V^E calculated with the five-parameter equation MTS at ~20 MPa for the hexane + benzothiophene mixtures: ○, 313 K; ▽, 323 K; □, 333 K; ◇, 343 K; and △, 353 K. Solid lines denote a trend.

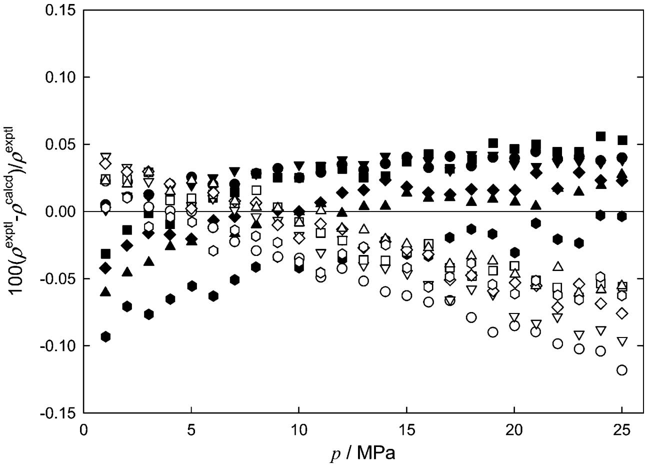

Figure 4. Deviations between experimental densities ρ^{exptl} of hexane with those calculated ρ^{calcd} with the Span and Wagner equation of state[16] (open symbols) and with the Tait equation[17,18] (solid symbols) at: ●, 313.12 K; ▼, 323.05 K; ■, 332.85 K; ◆, 342.73 K; ▲, 352.56 K; and ⬢, 362.40 K.

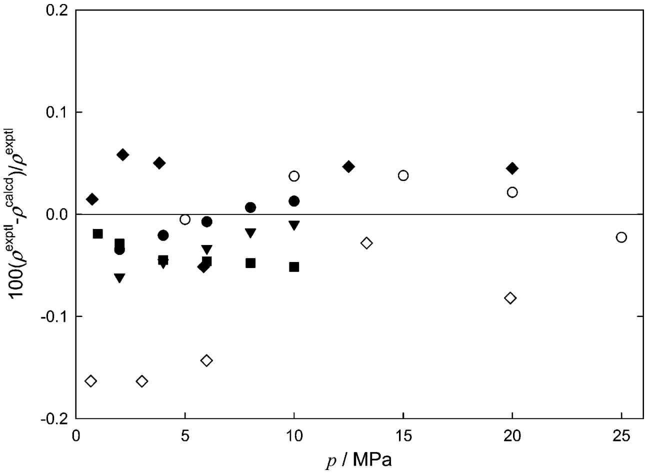

Figure 5. Deviations between experimental densities of hexane reported in the literature ρ^{exptl} with those calculated ρ^{calcd} with eq 2. Sauermann et al.[7] at: ●, 313.15 K; ▼, 333.15 K; ■, 353.15 K. Stewart et al.[8] at: ◆, 310.92 K; ◇, 344.24 K. Troncoso et al.[9] at: ○, 313.15 K.

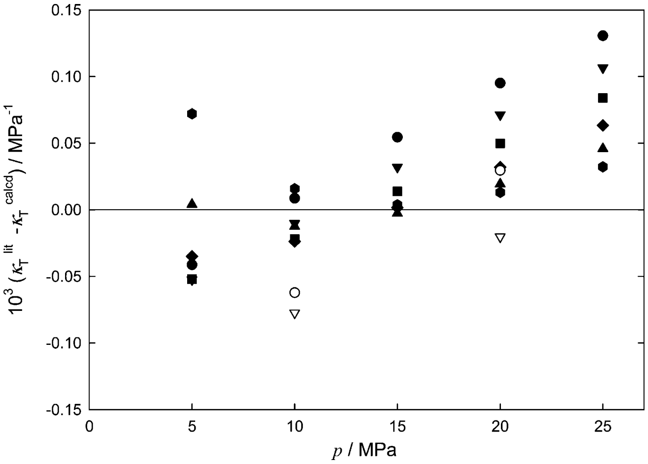

Figure 6. Residuals for the isothermal compressibilities of hexane κ_T^{calcd} calculated with the five-parameter equation and those taken from the literature, κ_T^{lit}. Daridon et al.:[20] ●, 313.15 K; ▼, 323.15 K; ■, 333.15 K; ◆, 343.15 K; ▲, 353.15 K; and ⬢, 363.15 K. Pečar and Doleček:[21] ○, 323.15 K; and ▽, 348.15 K.

Table 8. Residuals between Isobaric Thermal Expansivities α_p^{lit} of Hexane Reported in Ref 21 and Those Values, α_p^{calcd}, Calculated with Equation 2

T/K = 323.15		T/K = 348.15	
p/MPa	$(\alpha_p^{\text{lit}} - \alpha_p^{\text{calcd}})/10^3\cdot\text{K}^{-1}$	p/MPa	$(\alpha_p^{\text{lit}} - \alpha_p^{\text{calcd}})/10^3\cdot\text{K}^{-1}$
10.00	−0.158	10.00	−0.179
20.00	−0.286	20.00	−0.348

There is little data to compare with calculated values for the isobaric thermal expansivities in the correlated range of temperatures and pressures of this work. Table 8 shows residuals between the isobaric thermal expansivities reported by Pečar and Doleček.[21]

Conclusions

Densities of hexane and hexane + benzothiophene mixtures were obtained by means of a vibrating tube densimeter in the temperature range of (313 to 363) K and in the pressure range of (1 to 20) MPa. Densities for hexane + benzothiophene mixtures have not been reported previously. The hexane densities were compared with experimental data from the literature and with densities calculated with the equation of state of Span and Wagner[16] and the Tait equation with parameters taken from Cibulka and Hnedkovský.[18] Good agreement was observed in all cases. The modified Toscani−Szwarc equation[6] yields good representation of densities, isothermal compressibilities, and isobaric thermal expansivities for hexane.

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