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Densities and Excess Volumes of the 1-Chlorobutane + *n*-Hexane System at Temperatures from (283.15 to 333.15) K and Pressures from (0.1 to 35) MPa

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Densities of pure 1-chlorobutane, pure *n*-hexane, and their mixtures have been measured with an accuracy of ± 0.2 kg·m^{-3}, over a temperature range of (283.15 to 333.15) K and a pressure range of (0.1 to 35) MPa using a vibrating tube densimeter. The experimental densities have been correlated by the Tait equation with the temperature-dependent parameters for pure components and by the van Laar-type equation with the temperature- and pressure-dependent parameters for the solution. The excess volumes have been calculated on the basis of experimental data, and the pressure and temperature influence on this property have been discussed.

Introduction

The volumetric properties of liquid mixtures and their constituents are considered among the most important physicochemical data. Although their direct influence on the technological applications is rather limited, they give a deeper insight into the molecular interactions, and hence they are an important tool used to verify thermodynamic models. Despite almost one century of a continuous effort of numerous experimenters, the set of these data covers only a very narrow range of possible systems and values of the parameters. This state concerns all the kinds of thermodynamic data which mainly have been measured at 298 K and under atmospheric pressure.

This paper presents experimental densities and the related properties for the 1-chlorobutane + *n*-hexane system over a broad range of concentrations, temperatures, and pressures. This mixture may be considered as an example of the solution of two components built of linear molecules composed of different kinds of functional groups. It is a typical system for which the group contribution models can be applied or tested.

The densities and excess volumes of the 1-chlorobutane + *n*-hexane system have been reported in the literature at three temperatures, (293.15, 298.15, and 313.15) K. All these measurements were performed under normal pressure.[1–5]

Table 1. Experimental Densities ρ for 1-Chlorobutane and *n*-Hexane as a Function of Temperature T and Pressure p

p/MPa	283.15	293.15	298.15	303.15	313.15	323.15	333.15
			ρ/kg·m^{-3} of 1-Chlorobutane at T/K				
0.1	897.21	886.18	880.63	874.92	863.82	852.43	840.79
2.5	899.51	888.63	883.17	877.59	866.65	855.47	844.06
5.0	901.82	891.13	885.72	880.23	869.49	858.54	847.37
10.0	906.30	895.89	890.65	885.43	874.93	864.35	853.61
15.0	910.57		895.36	890.24	880.07	869.85	859.47
20.0	914.69	904.73	899.79	894.84	884.94	875.03	864.97
25.0	918.63	908.90	904.09	899.24	889.61	879.94	870.17
30.0	922.33	912.88	908.22	903.46	894.04	884.62	875.12
35.0	926.05	916.77	912.17	907.47	898.33	889.10	879.82
			ρ/kg·m^{-3} of *n*-Hexane at T/K				
0.1	668.07	659.18	654.61	649.97	640.82	631.41	621.80
2.5	670.36	661.67	657.21	652.70	643.76	634.61	625.32
5.0	672.69	664.17	659.81	655.36	646.69	637.80	628.77
10.0	677.06	668.87	664.66	660.53	652.13	643.69	635.13
15.0	681.19	673.27	669.24	665.23	657.16	649.12	640.94
20.0	685.08	677.40	673.51	669.63	661.86	654.14	646.27
25.0	688.82	681.33	677.56	673.81	666.28	658.84	651.23
30.0	692.35	685.07	681.40	677.77	670.44	663.23	655.89
35.0	695.65	688.63	685.02	681.45	674.41	667.40	660.30

Experimental Section

Materials. 1-Chlorobutane (Sigma Aldrich, purity stated 99.8 % and water content not greater than 0.01 %) was dried over 0.4 nm molecular sieves for several days, and *n*-hexane (Chemipan, Poland, purity stated 99.9 %) was degassed in an ELMA (Germany) ultrasonic bath at about 320 K for 60 min before measurement. The water used in the calibration was purified and deionized (conductivity below 0.8 μS·cm^{-1}) by a reverse osmosis unit with an ion-exchange system (Cobrabid-Aqua, Poland) and next degassed in the same manner as the pure components. The liquid mixtures were prepared by mass using the WA 36 precision balance manufactured by MeraWag-Poland, with an accuracy of 1·10^{-5} g. The estimated uncertainty of the mole fraction was about 10^{-4}.

Apparatus. The Anton Paar density measuring cell for high pressures and high temperatures (DMA 512P) and the mPDS 2000 evaluation unit were used for the density measurements. The density of a sample was determined by measuring the oscillation period of the U-shaped tube. The pressure was measured with the maximum uncertainty of ± 0.01 MPa, and temperature was kept constant within ± 0.01 K. A detailed description of the apparatus can be found elsewhere.[6]

The densimeter was calibrated with water and an empty evacuated U-tube according to the procedure by Lagourette et al.[7] The densities of water were calculated from the parameters recommended by the International Association for the Properties of Water and Steam.[8]

The combined expanded uncertainty for the measured densities of pure compounds should not exceed ± 0.1 kg·m^{-3} at

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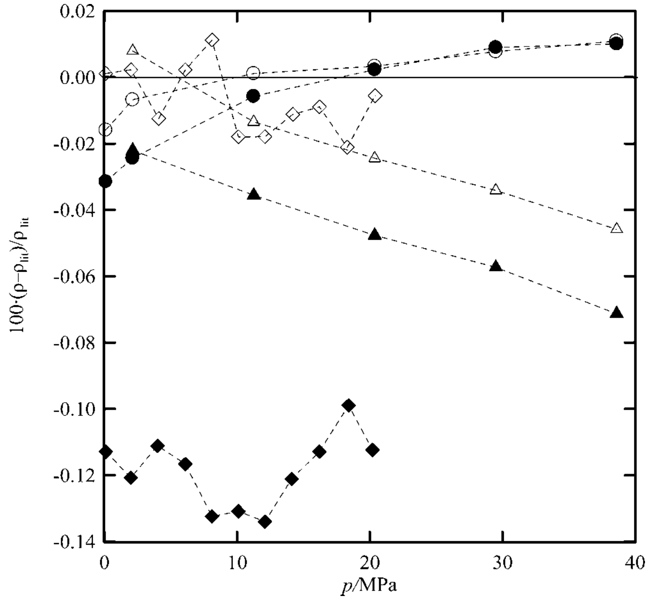

Figure 1. Fractional deviations $100(\rho - \rho_{\text{lit}})/\rho_{\text{lit}}$ between the measured and literature densities of 1-chlorobutane at 298.15 K (hollow symbols) and at 318.15 K (filled symbols) as a function of pressure. The literature data are taken from: (at 298.15 K); Δ, ref 9; ○, ref 10; ◇, ref 11; (at 318.15 K); ▲, ref 9; ●, ref 10; ♦, ref 11. The smoothed measured values were calculated by eqs (1 to 3) with the values of parameters given in Table 2. Dotted interpolation lines visualize the observed trends.

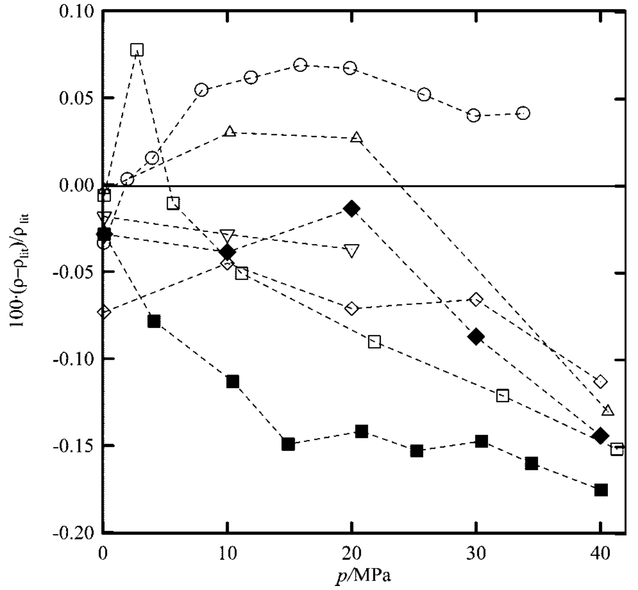

Figure 2. Fractional deviations $100(\rho - \rho_{\text{lit}})/\rho_{\text{lit}}$ between the measured and literature densities of *n*-hexane at 298.15 K (hollow symbols) and 318.15 K (filled symbols) as a function of pressure. The literature data are taken from: (at 298.15 K); Δ, ref 12; □, ref 13; ▽, ref 14; ○, ref 15; ◇, ref 16; (at 318.15 K); ■, ref 13; ◆, ref 16. The smoothed measured values were calculated by eqs (1 to 3) with the values of parameters given in Table 2. Dotted interpolation lines visualize the observed trends.

normal pressure and about ± 0.2 kg·m^{-3} at higher pressures. The latter value is only two times greater than the estimated inaccuracy of the experimental densities of pure water used in the calculations. The actual combined standard uncertainties for pure components are about ± 0.03 kg·m^{-3} as may be concluded from the standard deviations between the raw and correlated data. The combined standard uncertainty for the mixture density must be higher than that of a pure component due to errors in concentration. This is estimated to be ± 0.05 kg·m^{-3}.

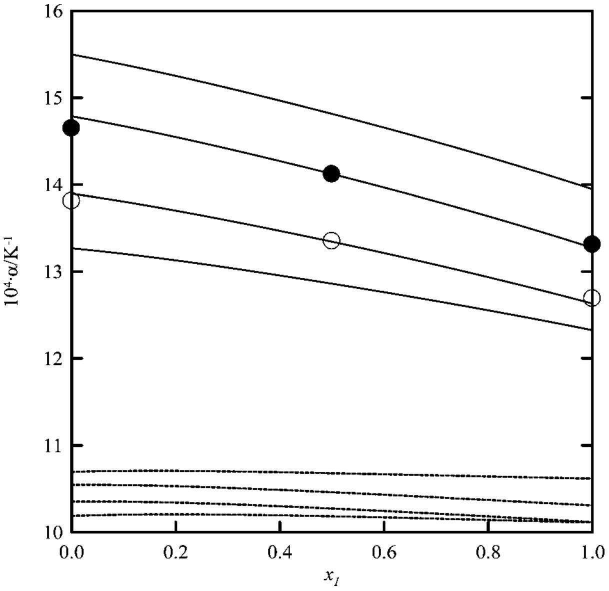

Figure 3. Isobaric expansivities α of the x_1{1-chlorobutane + $(1 - x_1)$*n*-hexane} solutions as a function of concentration x_1 at various temperatures and pressures. The lines are calculated at temperatures *T*/K = (283.15, 298.15, 318.15, and 333.15) through a differentiation of eq 4 with the values of parameters given in Tables 2 and 4: solid, $p = 0.1$ MPa; dashed, $p = 35$ MPa. The higher the temperature, the higher the values of the isobaric expansivity. The symbols represent experimental data of Matilla et al.[19] under 0.1 MPa and at: ○, 298.15 K; ●, 318.15 K.

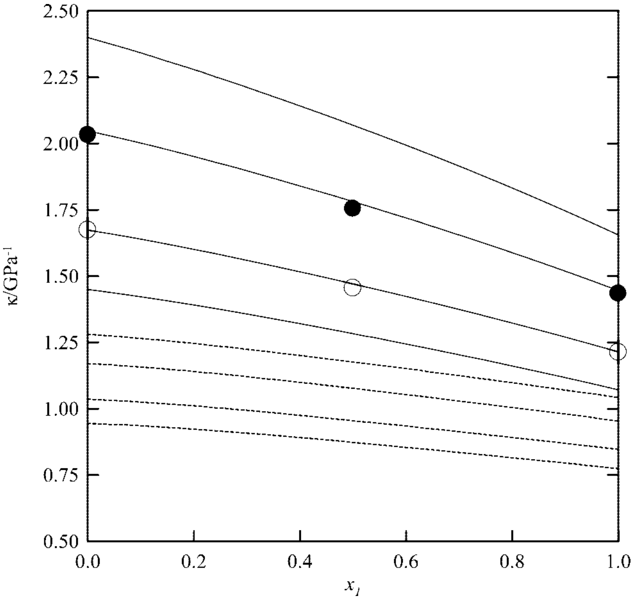

Figure 4. Isothermal compressibilities κ of the x_1{1-chlorobutane + $(1 - x_1)$*n*-hexane} solutions as a function of concentration x_1 at different temperatures and different pressures. The lines are calculated at temperatures *T*/K = (283.15, 298.15, 318.15, and 333.15) through a differentiation of eq 4 with the values of parameters given in Tables 2 and 4: solid, $p = 0.1$ MPa; dashed, $p = 35$ MPa. The higher the temperature, the higher the values of the isothermal compressibility. The symbols represent experimental data of Matilla et al.[19] under 0.1 MPa and at: ○, 298.15 K; ●, 318.15 K.

The calculated combined expanded uncertainty of the excess volume is about ± 0.02 cm^3·mol^{-1}, although the standard deviation of the curve fit suggests that the standard value can be two times lower.

Results

Densities of Pure 1-Chlorobutane and Pure n-Hexane. The densities of pure components were measured at temperatures

Table 2. Coefficients of the Tait Equations (1 to 3) Fitted to the Experimental Densities of 1-Chlorobutane and *n*-Hexane and the Root of Mean Squared Deviations σ of the Fit

	$A\cdot 10^2$	B_i	ρ_{0i}	σ/kg·m^{-3}
1-chlorobutane	8.73074	B_0/MPa = 418.461 B_1/MPa·K^{-1} = −1.71350 B_2/MPa·K^{-2} = 1.84737·10^{-3}	ρ_{00}/kg·m^{-3} = 1403.13 ρ_{01}/kg·m^{-3}·K^{-1} = −3.15555 ρ_{02}/kg·m^{-3}·K^{-2} = 7.26411·10^{-3} ρ_{03}/kg·m^{-3}·K^{-3} = 8.58085·10^{-6}	0.029
n-hexane	8.45619	B_0/MPa = 346.053 B_1/MPa·K^{-1} = −1.48766 B_2/MPa·K^{-2} = 1.66412·10^{-3}	ρ_{00}/kg·m^{-3} = 857.038 ρ_{01}/ kg·m^{-3}·K^{-1} = −0.448186 ρ_{02}/kg m^{-3}·K^{-2} = −7.73814·10^{-4}	0.032

T/K = (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) and under pressures p/MPa = (0.1, 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, and 35.0) at each temperature. They are given in Table 1. The experimental densities were correlated by the Tait equation

$$\rho(T,p) = \frac{\rho_0(T,p_0)}{1 - A\ln\dfrac{B(T)+p}{B(T)+p_0}} \tag{1}$$

with the reference pressure p_0 equal to 0.1 MPa. The ρ_0 and B parameters were assumed to be dependent on temperature in the form of a power expansion, i.e.

$$\rho_0(T,p_0) = \sum_{i=0}^{3} \rho_{0i}(T/\mathrm{K})^i \tag{2}$$

$$B(T) = \sum_{i=0}^{2} B_i(T/\mathrm{K})^i \tag{3}$$

The number of terms in the above expressions was determined statistically. The fitted parameters and the standard deviations are given in Table 2.

Figure 1 shows a comparison between our smoothed densities of 1-chlorobutane and the literature data at (298.15 and 318.15) K and under pressures ranging from (0.1 to 39) MPa.[9–11] As expected, the lowest residuals are at 298.15 K and under low pressures where they do not exceed 0.02 % and are only twice as high at 39 MPa. At the temperature 318.15 K, these discrepancies are considerably higher reaching even 0.12 %, but such a level of residuals is mainly due to the outstanding

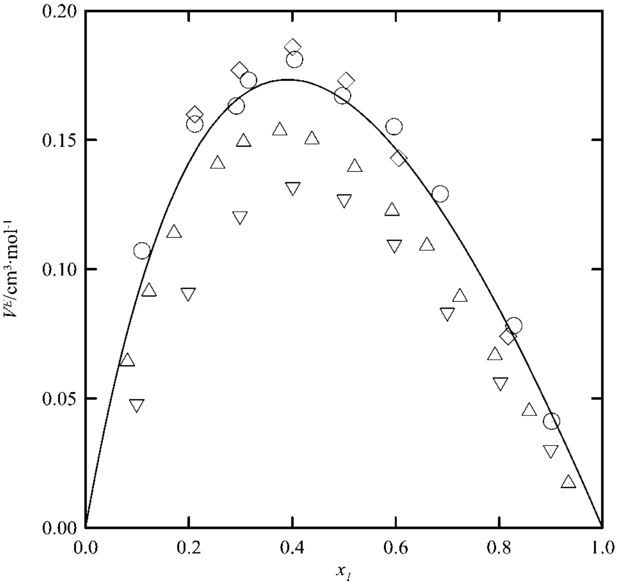

Figure 5. Excess volumes V^E of the x_1{1-chlorobutane + (1 − x_1)*n*-hexane} solutions as a function of concentration x_1 at T = 298.15 K and under p = 0.1 MPa. Symbols denote experimental data taken from: ○, this work; ◇, ref 2; ▽, ref 4; △, ref 5. The solid line is calculated by eqs (4 to 6) with the values of parameters given in Table 4.

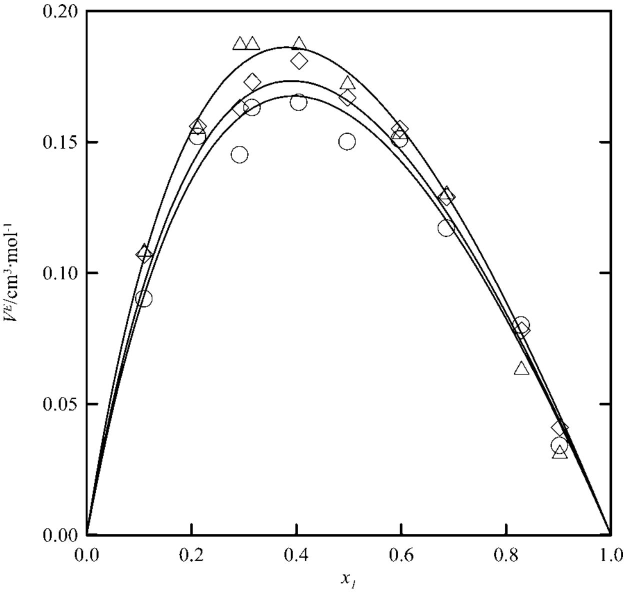

Figure 6. Excess volumes V^E of the x_1{1-chlorobutane + (1 − x_1)*n*-hexane} solutions as a function of concentration x_1 under p = 0.1 MPa and at different temperatures. Symbols denote experimental data taken from this work at temperature: ○, 283.15 K; ◇, 298.15 K; Δ, 333.15 K. The solid lines are calculated by eqs (4 to 6) with the values of parameters given in Table 4.

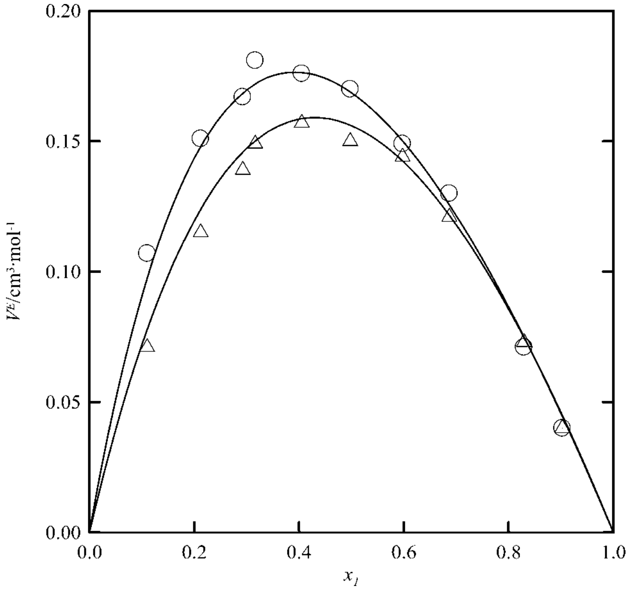

Figure 7. Excess volumes V^E of the x_1{1-chlorobutane + (1 − x_1)*n*-hexane} solutions as a function of concentration x_1 at 323.15 K and under different pressures. Symbols denote experimental data taken from this work under pressure: ○, 0.1 MPa; Δ, 35 MPa. The solid lines are calculated by eqs (4 to 6) with the values of parameters given in Table 4.

Table 3. Experimental Densities ρ for the x_1{1-Chlorobutane + $(1 - x_1)n$-Hexane} Solutions as a Function of Mole Fraction x_1, Temperature T, and Pressure p

	ρ/kg·m^{-3} at p/MPa								
x_1	0.1	2.5	5.0	10.0	15.0	20.0	25.0	30.0	35.0
T = 283.15 K									
0.10985	688.16	690.51	692.85	697.27	701.44	705.42	709.18	712.77	716.20
0.21203	707.78	710.17	712.52	716.94	721.17	725.18	728.95	732.59	736.03
0.29248	724.14	726.49	728.83	733.31	737.55	741.57	745.40	749.06	752.55
0.31601	728.91	731.23	733.62	738.08	742.33	746.36	750.17	753.86	757.33
0.40499	747.80	750.19	752.56	757.05	761.32	765.38	769.24	772.94	776.47
0.49777	768.40	770.77	773.13	777.64	781.91	785.99	789.87	793.59	797.15
0.59750	791.40	793.76	796.11	800.62	804.89	808.98	812.89	816.62	820.23
0.68694	813.19	815.54	817.89	822.39	826.69	830.80	834.70	838.47	842.08
0.82939	849.71	852.04	854.38	858.86	863.18	867.28	871.21	875.01	878.63
0.90250	869.66	871.97	874.31	878.80	883.07	887.19	891.13	894.92	898.57
T = 293.15 K									
0.10985	679.00	681.50	684.03	688.77	693.23	697.41	701.41	705.17	708.81
0.21203	698.47	701.01	703.52	708.30	712.77	717.01	721.03	724.84	728.53
0.29248	714.61	717.13	719.69	724.48	728.99	733.23	737.29	741.13	744.84
0.31601	719.31	721.84	724.38	729.18	733.71	737.99	742.03	745.88	749.61
0.40499	738.08	740.60	743.13	747.97	752.50	756.78	760.90	764.76	768.53
0.49777	758.47	761.00	763.54	768.33	772.88	777.19	781.30	785.20	788.98
0.59750	781.32	783.84	786.39	791.18	795.72	800.04	804.20	808.12	811.92
0.68694	802.85	805.38	807.91	812.71	817.27	821.60	825.76	829.70	833.53
0.82939	839.13	841.63	844.15	848.93	853.49	857.83	861.98	865.95	869.81
0.90250	858.87	861.35	863.85	868.63	873.18	877.51	881.68	885.66	889.53
T = 298.15 K									
0.10985	674.32	676.93	679.56	684.48	689.11	693.45	697.55	701.45	705.16
0.21203	693.72	696.34	698.96	703.92	708.60	712.95	717.10	721.06	724.80
0.29248	709.76	712.38	715.02	719.98	724.66	729.06	733.24	737.22	741.00
0.31601	714.52	717.11	719.75	724.72	729.39	733.80	737.94	741.91	745.72
0.40499	733.09	735.72	738.37	743.38	748.10	752.52	756.74	760.75	764.57
0.49777	753.40	756.03	758.67	763.66	768.37	772.82	777.05	781.09	784.94
0.59750	776.16	778.78	781.41	786.38	791.12	795.57	799.82	803.90	807.76
0.68694	797.59	800.23	802.86	807.84	812.57	817.04	821.30	825.39	829.27
0.82939	833.73	836.30	838.91	843.87	848.59	853.07	857.35	861.46	865.37
0.90250	853.37	855.94	858.53	863.49	868.18	872.66	876.94	881.06	884.99
T = 303.15 K									
0.10985	669.66	672.37	675.06	680.26	685.01	689.49	693.71	697.71	701.46
0.21203	689.16	691.90	694.62	699.79	704.53	708.98	713.22	717.27	721.06
0.29248	704.96	707.69	710.41	715.60	720.39	724.92	729.21	733.29	737.11
0.31601	709.76	712.51	715.21	720.44	725.23	729.73	733.98	738.06	741.91
0.40499	728.25	730.98	733.71	738.89	743.69	748.24	752.58	756.71	760.56
0.49777	748.32	751.02	753.76	759.01	763.87	768.43	772.80	776.94	780.82
0.59750	770.96	773.66	776.40	781.67	786.55	791.14	795.51	799.69	803.62
0.68694	792.32	795.01	797.74	802.98	807.83	812.44	816.83	821.01	824.94
0.82939	828.52	831.20	833.88	839.08	843.86	848.41	852.75	856.96	860.94
0.90250	847.81	850.48	853.16	858.38	863.22	867.82	872.22	876.44	880.41
T = 313.15 K									
0.10985	660.25	663.22	666.15	671.67	676.77	681.54	686.03	690.26	694.28
0.21203	679.39	682.37	685.31	690.86	695.99	700.78	705.32	709.59	713.66
0.29248	695.16	698.14	701.06	706.60	711.76	716.60	721.16	725.44	729.55
0.31601	699.82	702.79	705.74	711.27	716.43	721.27	725.85	730.12	734.28
0.40499	718.21	721.17	724.11	729.65	734.82	739.68	744.28	748.61	752.76
0.49777	738.18	741.14	744.08	749.65	754.83	759.70	764.34	768.68	772.87
0.59750	760.70	763.65	766.58	772.10	777.29	782.18	786.80	791.20	795.40
0.68694	781.81	784.75	787.66	793.20	798.39	803.30	807.96	812.36	816.59
0.82939	817.54	820.43	823.33	828.82	833.99	838.90	843.57	847.97	852.24
0.90250	836.89	839.76	842.65	848.11	853.27	858.17	862.84	867.27	871.55
T = 323.15 K									
0.10985	650.68	653.88	657.08	663.04	668.53	673.62	678.38	682.82	687.05
0.21203	669.65	672.84	676.07	682.03	687.54	692.66	697.47	701.95	706.22
0.29248	685.16	688.38	691.59	697.57	703.11	708.23	713.06	717.58	721.89
0.31601	689.81	693.01	696.23	702.21	707.76	712.92	717.75	722.30	726.62
0.40499	708.00	711.21	714.41	720.41	725.96	731.15	736.01	740.59	744.94
0.49777	727.88	730.97	734.25	740.23	745.81	751.01	755.88	760.48	764.87
0.59750	750.16	753.32	756.52	762.49	768.07	773.25	778.17	782.79	787.22
0.68694	771.11	774.25	777.43	783.36	788.94	794.16	799.07	803.70	808.14
0.82939	806.56	809.67	812.80	818.69	824.21	829.43	834.36	839.01	843.47
0.90250	825.76	828.84	831.94	837.82	843.35	848.55	853.47	858.16	862.63

Table 3. Continued

x_1	ρ/kg·m^{-3} at p/MPa								
	0.1	2.5	5.0	10.0	15.0	20.0	25.0	30.0	35.0
					T = 333.15 K				
0.10985	640.84	644.37	647.85	654.25	660.12	665.54	670.56	675.27	679.71
0.21203	659.59	663.28	666.60	673.04	678.96	684.42	689.51	694.27	698.78
0.29248	674.97	678.48	681.96	688.41	694.34	699.82	704.94	709.73	714.25
0.31601	679.61	683.13	686.60	693.04	698.97	704.46	709.59	714.38	718.92
0.40499	697.62	701.13	704.59	711.02	716.97	722.46	727.62	732.45	737.02
0.49777	717.27	720.76	724.22	730.64	736.59	742.10	747.28	752.13	756.72
0.59750	739.37	742.80	746.27	752.68	758.64	764.16	769.35	774.27	778.90
0.68694	760.13	763.57	766.97	773.35	779.29	784.83	790.03	794.94	799.60
0.82939	795.31	798.68	802.05	808.40	814.33	819.85	825.07	830.00	834.70
0.90250	814.35	817.70	821.05	827.36	833.22	838.75	843.95	848.89	853.59

Table 4. Coefficients of the Equation Fitted to the Experimental Densities of the 1-Chlorobutane + *n*-Hexane System as a Function of Mole Fraction, Temperature, and Pressure, Equations (4 to 6), and the Root of Mean Squared Deviations σ of the Fit

i	a_i/cm^3·mol^{-1}	b_i	σ/kg·m^{-3}
0	1.07757	2.35854	0.052
1	$-9.62495 \cdot 10^{-3}$	$-2.16323 \cdot 10^{-2}$	
2	$3.99783 \cdot 10^{-3}$	$5.27443 \cdot 10^{-3}$	

character of the data of García-Giménez et al.[11] Our data are closest to the second data set of Morávková and Linek[10] with the discrepancies not greater than 0.03 % for the whole examined ranges of temperatures and pressures.

The discrepancies between experimental densities of *n*-hexane[12–16] are greater than for 1-chloroalkane. Our data are situated somewhere between the data reported in the literature, although usually they are slightly lower than the latter ones. This is particularly visible at higher temperatures and under higher pressures. The fractional deviations between our data and those reported in the literature at (298.15 and 323.15) K are shown in Figure 2. The maximum deviations under the highest pressures reach almost 0.20 %, but the average deviations are less than 0.1 % which is consistent with the analysis of the experimental density data of *n*-hexane given by Cibulka and Hnědkovský.[17]

Densities and Mechanical Properties of the 1-Chloroalkane + n-Hexane Mixtures. The densities for the mixtures 1-chloroalkane + *n*-hexane were measured at ten different mole fractions, at temperatures T/K = (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, and 333.15) and under pressures p/MPa = (0.1, 2.5, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, and 35.0). They are given in Table 3.

The mixture densities were correlated by the six-parameter equation in which the excess volume was formally represented by a sum of the van Laar terms[18] in which only one term turned out to be statistically significant

$$\rho(T,p,x_1) = \frac{M_1x_1 + M_2x_2}{M_1x_1/\rho_1^0(T,p) + M_2x_2/\rho_2^0(T,p) + \dfrac{a(T,p)x_1x_2}{b(T,p)x_1 + x_2}} \qquad (4)$$

where M_i, x_i, and ρ_i^0 stand for molecular weight, mole fraction, and density of the ith component, respectively, and $a(T, p)$ and $b(T, p)$ are the parameters linearly dependent on T and p according to the formulas

$$[a(T,p)/\mathrm{cm^3 \cdot mol^{-1}}] = a_0 + a_1[(p/\mathrm{MPa}) - 0.1] + a_2[(T/\mathrm{K}) - 283] \qquad (5)$$

$$b(T,p) = b_0 + b_1[(p/\mathrm{MPa}) - 0.1] + b_2[(T/\mathrm{K}) - 283] \qquad (6)$$

It was confirmed statistically that the higher-order terms in the above expansions could be neglected.

The correlation equation requires six adjustable parameters (a_0, a_1, a_2, b_0, b_1, b_2) which were adjusted to the experimental densities with the overall standard deviation of 0.052 kg·m^{-3}. The values of parameters are given in Table 4.

Equations 1 to 6 enable one to calculate isothermal compressibilities and isobaric expansivities of the mixture. Figures 3 and 4 show typical dependencies of both properties with respect to mole fractions at temperatures T/K = (283.15, 298.15, 318.15, and 333.15) and under pressures (0.1 and 35) MPa. The composition dependencies are monotonous and almost linear with a very weak curvature. The observed linearity is better visible under higher pressures where the difference between properties of pure components is reduced. The calculated mechanical properties agree well with the experimental data of Matilla et al.[19] measured under normal pressure and for equimolar compositions at (298.15 and 313.15) K.

Excess Volumes of the 1-Chloroalkane + n-Hexane Mixtures. Experimental excess volumes were calculated from the measured densities of solutions and pure components and are shown in Table 5.

The excess volumes could be correlated by the Redlich–Kister equation with 2 to 3 parameters per each temperature and pressure, leading to the standard deviations ranging from (0.003 to 0.014) cm^3·mol^{-1}. The overall standard deviation equal to 0.012 cm^3·mol^{-1} was obtained if the excess volumes were calculated on the basis of eq 4 with the values of parameters taken from Table 4.

Figure 5 shows the excess volumes at 298.15 K and 0.1 MPa drawn against the data already reported in the literature. The discrepancies between different sets of experimental data are rather significant, reaching almost 30 % in the vicinity of the maximum value. Our data are very close to the data of Crespo Colin et al.,[2] being higher than the remaining ones.

The values of the experimental excess volumes are positive and rather low if compared to the majority of binary systems, with the maximum values ranging from (0.13 to 0.19) cm^3·mol^{-1}. The composition dependencies are unsymmetrical with the maximum located slightly below 0.4 of the mole fraction of 1-chlorobutane. The excess volumes increase with the increase of temperature and decrease with the increase of pressure. This first observation was noted previously by Domínguez et al.[4] on the basis of the data measured at (298.15 and 313.15) K and under atmospheric pressure.

Figure 6 illustrates how the temperature influences excess volumes under a constant pressure equal to 0.1 MPa, and Figure 7 shows the pressure dependence of the same property at 323.15 K. Both the temperature and pressure influence on the excess volume is rather weak. The values of the derivative $(\partial V^{\mathrm{E}}/\partial T)_P$, which are positive, increase with a decrease of temperature and increase of pressure, while the negative values of the $(\partial V^{\mathrm{E}}/\partial p)_T$

Table 5. Experimental Excess Volumes V^E for the x_1{1-Chlorobutane + $(1 - x_1)n$-Hexane} Solutions as a Function of Mole Fraction x_1, Temperature T, and Pressure p

x_1	V^E/cm^3·mol^{-1} at p/MPa								
	0.1	2.5	5.0	10.0	15.0	20.0	25.0	30.0	35.0
$T = 283.15$ K									
0.10985	0.090	0.082	0.082	0.080	0.077	0.070	0.072	0.067	0.053
0.21203	0.152	0.139	0.139	0.141	0.134	0.127	0.132	0.124	0.116
0.29248	0.145	0.141	0.143	0.140	0.136	0.131	0.131	0.123	0.114
0.31601	0.163	0.165	0.158	0.160	0.154	0.149	0.153	0.141	0.137
0.40499	0.165	0.155	0.154	0.153	0.148	0.143	0.143	0.135	0.127
0.49777	0.150	0.145	0.145	0.145	0.141	0.137	0.139	0.130	0.124
0.59750	0.151	0.148	0.149	0.150	0.149	0.148	0.147	0.139	0.132
0.68694	0.117	0.114	0.115	0.117	0.115	0.113	0.115	0.104	0.103
0.82939	0.080	0.078	0.080	0.082	0.078	0.080	0.081	0.069	0.073
0.90250	0.034	0.035	0.035	0.036	0.037	0.037	0.038	0.027	0.032
$T = 293.15$ K									
0.10985	0.104	0.105	0.103	0.099		0.092	0.086	0.088	0.083
0.21203	0.157	0.153	0.156	0.151		0.142	0.140	0.138	0.131
0.29248	0.160	0.159	0.157	0.154		0.146	0.142	0.141	0.135
0.31601	0.183	0.180	0.180	0.176		0.162	0.160	0.159	0.152
0.40499	0.174	0.173	0.175	0.169		0.161	0.154	0.155	0.147
0.49777	0.160	0.158	0.161	0.162		0.154	0.151	0.150	0.147
0.59750	0.150	0.150	0.151	0.153		0.151	0.145	0.145	0.142
0.68694	0.123	0.122	0.124	0.126		0.121	0.118	0.119	0.116
0.82939	0.075	0.073	0.076	0.078		0.074	0.075	0.075	0.074
0.90250	0.034	0.034	0.036	0.037		0.035	0.036	0.035	0.035
$T = 298.15$ K									
0.10985	0.107	0.108	0.104	0.098	0.093	0.087	0.085	0.083	0.073
0.21203	0.156	0.156	0.156	0.148	0.141	0.140	0.135	0.129	0.121
0.29248	0.163	0.164	0.162	0.157	0.154	0.149	0.144	0.140	0.132
0.31601	0.173	0.177	0.176	0.170	0.171	0.164	0.166	0.165	0.153
0.40499	0.181	0.180	0.179	0.169	0.164	0.160	0.155	0.153	0.146
0.49777	0.167	0.166	0.165	0.162	0.161	0.156	0.154	0.151	0.145
0.59750	0.155	0.155	0.155	0.157	0.154	0.151	0.150	0.146	0.144
0.68694	0.129	0.126	0.124	0.125	0.125	0.121	0.120	0.119	0.117
0.82939	0.078	0.081	0.079	0.081	0.082	0.078	0.078	0.079	0.078
0.90250	0.041	0.041	0.040	0.040	0.044	0.040	0.041	0.041	0.041
$T = 303.15$ K									
0.10985	0.092	0.098	0.095	0.096	0.093	0.086	0.085	0.083	0.081
0.21203	0.106	0.107	0.103	0.113	0.118	0.123	0.123	0.122	0.117
0.29248	0.143	0.147	0.143	0.154	0.153	0.148	0.145	0.143	0.140
0.31601	0.141	0.142	0.142	0.146	0.146	0.148	0.152	0.152	0.145
0.40499	0.150	0.154	0.151	0.164	0.166	0.164	0.159	0.156	0.154
0.49777	0.159	0.167	0.163	0.167	0.162	0.161	0.156	0.155	0.152
0.59750	0.150	0.158	0.153	0.154	0.149	0.146	0.145	0.142	0.138
0.68694	0.120	0.127	0.123	0.128	0.128	0.126	0.124	0.124	0.123
0.82939	0.040	0.045	0.046	0.054	0.062	0.068	0.075	0.076	0.074
0.90250	0.037	0.040	0.038	0.042	0.041	0.041	0.041	0.041	0.042
$T = 313.15$ K									
0.10985	0.107	0.104	0.103	0.096	0.088	0.083	0.079	0.072	0.071
0.21203	0.151	0.148	0.149	0.140	0.134	0.130	0.124	0.119	0.115
0.29248	0.167	0.164	0.168	0.164	0.157	0.150	0.145	0.143	0.138
0.31601	0.181	0.180	0.179	0.177	0.172	0.165	0.159	0.160	0.149
0.40499	0.176	0.178	0.178	0.177	0.174	0.168	0.164	0.161	0.157
0.49777	0.170	0.171	0.171	0.167	0.165	0.162	0.156	0.155	0.150
0.59750	0.149	0.150	0.150	0.154	0.153	0.149	0.149	0.145	0.144
0.68694	0.130	0.129	0.131	0.131	0.131	0.125	0.124	0.122	0.121
0.82939	0.071	0.073	0.073	0.076	0.078	0.074	0.073	0.074	0.073
0.90250	0.040	0.042	0.039	0.042	0.044	0.041	0.041	0.041	0.040
$T = 323.15$ K									
0.10985	0.101	0.102	0.102	0.095	0.090	0.084	0.081	0.080	0.077
0.21203	0.144	0.148	0.144	0.140	0.137	0.133	0.128	0.127	0.123
0.29248	0.178	0.177	0.177	0.173	0.170	0.169	0.165	0.162	0.157
0.31601	0.187	0.189	0.187	0.183	0.178	0.173	0.170	0.164	0.159
0.40499	0.186	0.187	0.189	0.182	0.181	0.175	0.171	0.167	0.163
0.49777	0.165	0.183	0.171	0.169	0.166	0.162	0.160	0.158	0.154
0.59750	0.150	0.154	0.154	0.153	0.151	0.152	0.147	0.146	0.141
0.68694	0.127	0.130	0.131	0.133	0.131	0.129	0.128	0.128	0.125
0.82939	0.066	0.068	0.070	0.072	0.076	0.075	0.072	0.074	0.072
0.90250	0.034	0.035	0.038	0.037	0.037	0.037	0.036	0.035	0.034

Table 5. Continued

x_1	V^E/cm^3·mol^{-1} at p/MPa 0.1	2.5	5.0	10.0	15.0	20.0	25.0	30.0	35.0
					T = 333.15 K				
0.10985	0.108	0.107	0.101	0.099	0.094	0.086	0.083	0.081	0.084
0.21203	0.155	0.122	0.151	0.146	0.138	0.129	0.122	0.118	0.116
0.29248	0.187	0.187	0.186	0.181	0.176	0.168	0.160	0.158	0.158
0.31601	0.187	0.187	0.187	0.185	0.180	0.171	0.164	0.163	0.162
0.40499	0.187	0.187	0.190	0.190	0.185	0.181	0.174	0.172	0.171
0.49777	0.172	0.173	0.175	0.176	0.174	0.172	0.166	0.166	0.167
0.59750	0.153	0.159	0.156	0.159	0.157	0.155	0.152	0.147	0.145
0.68694	0.130	0.130	0.135	0.138	0.140	0.137	0.135	0.135	0.132
0.82939	0.063	0.064	0.067	0.068	0.068	0.068	0.066	0.066	0.064
0.90250	0.031	0.029	0.031	0.032	0.037	0.036	0.036	0.037	0.037

decrease under the same conditions. The extreme values vary in the range (3.7 to 5.4)·10^{-4} cm^3·mol^{-1}·K^{-1} for the former and (−0.65 to −0.95) cm^3·mol^{-1}·GPa^{-1} for the latter derivative.

Conclusions

The volumetric properties of the 1-chloroalkane + *n*-hexane system have been measured for wide ranges of temperature and pressures. The density data were correlated by an equation suitable to represent simultaneously their temperature, pressure, and composition dependence. The related properties, i.e., excess volumes, isobaric expansivities, and isothermal compressibilities, have been derived from the density data or calculated on the basis of the above-mentioned equation. The observed temperature and pressure influence on the volumetric properties is rather weak but evident and able to be detected experimentally.

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