Pressure−Volume−Temperature Properties of Methyl Chloride at High Pressures and Temperatures

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PVT data of methyl chloride were measured up to 400 MPa at eight isotherms ranging from (298.15 to 573.15) K. Experiments were performed with a thin-walled sample holder under equal pressure, both inside and outside. The volume change of the sample was determined with a separation system at 298.15 K by making use of a magnetic float on mercury and a linear variable differential transformer. The specific volume of methyl chloride varies in this region from (0.8366 to 7.8806) $cm^3 \cdot g^{-1}$. The uncertainty of data for specific volumes was estimated to be ± 0.34 % or less. The specific volume data was fitted to the Tait equation of state.

Introduction

The relationship between pressure, volume, and temperature is one of the most fundamental properties of a substance and very useful from both a theoretical and a practical standpoint. Experimental *PVT* property studies can provide valuable information on fluid behavior under various temperatures and pressures. One of these properties is specific volume or density, which is required in a wide range of process design calculations and derivations of thermodynamic and transport properties.

The properties of highly polar fluids at elevated pressures are little known as compared to nonpolar or slightly polar fluids. Methyl chloride is one of the important and widely used compounds in the chemical industry because of its solvent characteristic. It consists of small molecules and has a dipole moment of 6.304×10^{-30} C·m. Such a fluid is also of great interest for the study of intermolecular interaction in dense phases because of the obviously strong interaction. The interparticle distance can be changed continuously from gas-like to liquid-like conditions, and solvent characteristics can be changed drastically by using different pressure variations.

A list of available previous *PVT* measurements of methyl chloride showing the temperature and pressure ranges investigated is given in Table 1. As can be seen from the table, the general lack of *PVT* measurements at pressures above 10 MPa prompted the present study.

Table 1. Previous Measurements of Specific Volume of Methyl Chloride at High Temperature and Pressure

ref	year	temperature (T_{min} to T_{max})/K	pressure (P_{min} to P_{max})/MPa	reported uncertainty, %
1	1939	213 to 393	0.1 to 2	
2	1964	308 to 498	0.1 to 32	0.12
3	1967	473 to 623	0.1 to 35	0.08
4	1978	253 to 313	29 to160	0.13
5	1981	323 to 473	0.1 to 15	0.1 to 0.3

Experimental Section

The experimental setup used in this investigation was similar to the one used by Hilbert et al.[6] The autoclave used is a thick-walled cylindrical vessel made from a Ni−Cr alloy. It was placed in multiple furnace windings. To keep the temperature gradient zone as small as possible, a water cooler was placed just above the electrical furnace. The top end of the autoclave was sealed with a Bridgman's type closure. A sample holder with a volume of 1.0665×10^{-4} m^3 was placed in the autoclave and fixed to the rod of the seal. The bottom opening of the autoclave serves as an access for the pressure transmitting fluid (water) so that the inside and outside pressure of the sample holder was equilibrated. The whole assembly was mounted in a press to eliminate thermal expansion. The sample holder was connected through the bore of the closure rod and high pressure tubing with the mercury separator. A precision tube open at its lower end was dipped into mercury, which acted essentially as a liquid piston for driving the test substance out of the separator into the sample holder. The pressure transmitting fluids (water and oil) separated through bellows are placed in a second autoclave. To avoid volume changes of the experimental setup, other than in the autoclave, the room was maintained at a constant temperature of 298 K.

Pressure was generated by means of an air-driven membrane compressor and measured by a set of precision Bourdon gauges. Pressures were accurate to within 0.1 % of full scale. Temperature was regulated within the fluctuation of ± 0.1 K and measured with three chromel−alumel thermocouples. Measurement of the methyl chloride−mercury interface was achieved by means of a ferromagnet, which was rigidly connected by a wire to a Teflon float. It moves up and down in the bore of nonmagnetic tubing. The position of the magnetic core was located with an accuracy of 10^{-5} m by a linear variable differential transformer.

The volume of whole measurement system was evacuated by means of a vacuum pump and flushed with the test substance from the sample cylinder and evacuated once more. The sample cylinder was weighed with an accuracy of 10^{-7} kg, and the test substance was filled directly in the sample holder. The filling was aided by gently warming the sample cylinder. Then the filling line was isolated from the measurement system. To condensate the test material in the filling line back into the sample cylinder, the cylinder was cooled by liquid nitrogen, and the filling line was heated. The sample cylinder was weighed to determine the amount of test substance introduced in to the system. The loss of the test substance was found to be less than

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10.1021/je060117o CCC: $30.25

5×10^{-6} kg. The temperature and the pressure were set to the value of interest. The heat of compression was allowed to dissipate in a given time. After attaining thermal and mechanical equilibrium, the temperature, the pressure, and the position of the magnetic core were recorded.

Determination of Specific Volumes

The specific volume of methyl chloride as a function of pressure and temperature is calculated from

$$V(P, T) = \frac{V_{\mathrm{SH}}(P, T)}{m_{\mathrm{SH}}(P, T)} \tag{1}$$

where $V_{\mathrm{SH}}(P, T)$ is the volume of the sample holder under the system temperature and pressure. The volume of the holder is determined at 298.15 K under atmospheric pressure. It is corrected due to thermal expansion and external pressure contraction of the sample holder.

$m_{\mathrm{SH}}(P, T)$ is the mass of methyl chloride in the sample holder at system pressure and temperature. It is determined by subtracting the sum of substance in the bore of the autoclave closure and in the dead volume from the total substance introduced into the system. The contents of the volume between the upper end of the closure bore and mercury interface, which is called dead volume, was at 298 K under the system pressure. The mass of the substance in the dead volume was experimentally determined for each measurement pressure. Thus, the top end of the closure bore was sealed to isolate the dead volume. A weighed amount of methyl chloride was introduced into the dead volume, and the mercury interface was recorded at each preselected pressure. Then the amount of substance filled was changed, and the procedure was repeated. A relationship between substance filled and displacement of the interface at each preselected pressure was found by least-squares fitting. This method eliminates various corrections due to compression.

The volume of the closure bore was $3.27 \times 10^{-7} \mathrm{m}^3$. The substance within the bore was under the system pressure and at some intermediate temperature. It was experimentally determined by sealing the closure bore at the lower end. All measurements were repeated at preselected pressures and at preselected autoclave temperatures to simulate the same temperature gradient. The substance within the bore was found by subtracting the amount of the substance within the dead volume, from the total substance.

Relative error increases as pressure is reduced and as temperature increases. It is 0.16 % at highest pressure and lowest temperature point and 0.34 % at the lowest pressure and highest temperature point.

Methyl chloride was obtained from Matheson Company and specified as 99.5 % pure by the manufacturer. It was solidified by liquid nitrogen before its use, while noncondensable gases were pumped off.

Results and Discussion

The experimental specific volumes of methyl chloride were measured along eight isotherms in the range of temperatures (298 to 573) K up to 400 MPa. The results listed in Table 2 are used to calculate the compressibility factor ($Z = PV/RT$), which is plotted in Figure 1 as a function of pressure. The previous *PVT* measurements were conducted below 30 MPa and performed with smaller errors limits than present studies as it can be seen in Table 1. The previous and present results are shown in Figure 2 over low pressure and high temperature ranges. A direct comparison is only possible with one measurement point of Mansoorian et al.[5] at 10 MPa and 473 K. At this point their results lay 0.12 % lower. A direct comparison with the smoothed results of Hsu and McKetta[2] and Suh and Storvick[3] is not possible because of the different units of pressure used. To make a comparison with the results of these authors, the specific volumes were calculated from their measurement of compressibility using 50487.7 kg·mol^{-1} molar mass of methyl chloride.

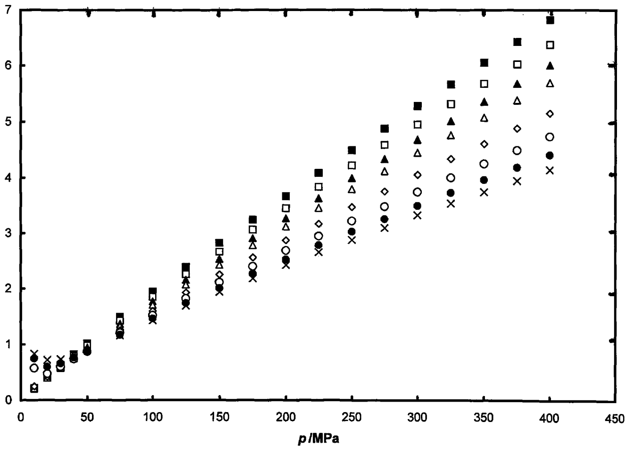

Figure 1. Variation of the compressibility factors, *Z*, with pressure, *P*, for methyl chloride: ■, $T = 298$ K; □, $T = 323$ K; ▲, $T = 348$ K; △, $T = 373$ K; ◇, $T = 423$ K; ○, $T = 473$ K; ●, $T = 523$ K; ×, $T = 573$ K.

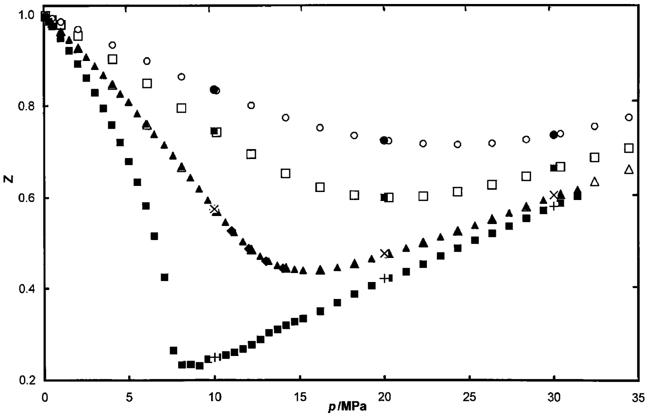

Figure 2. Compressibility factors, *Z*, for methyl chloride over low pressure and high-temperature ranges: △, ref 3, $T = 473$ K; □, ref 3, $T = 523$ K; ○, ref 3, $T = 573$ K; ▲, ref 2, $T = 423$ K; ■, ref 2, $T = 473$ K; ◇, ref 5, $T = 473$ K; this work; +, $T = 423$ K; ×, $T = 473$ K; ■, $T = 523$ K; ●, $T = 573$ K.

Table 2. Experimental Specific Volumes of Methyl Chloride, V/cm^3·g^{-1} at T = (298 to 573) K and at P = (10 to 400) MPa

	298	323	348	373	423	473	523	573
10	1.0662	1.1310	1.2009	1.3012	1.7302	4.4677	6.4422	7.8806
20	1.0472	1.1001	1.1594	1.2330	1.4664	1.8576	2.5857	3.4167
30	1.0296	1.0786	1.1309	1.1874	1.3495	1.5604	1.9001	2.3168
40	1.0123	1.0587	1.1029	1.1547	1.2792	1.4397	1.6516	1.9276
50	0.9994	1.0431	1.0832	1.1276	1.2341	1.3607	1.5041	1.6972
75	0.9752	1.0098	1.0430	1.0828	1.1596	1.2502	1.3439	1.4570
100	0.9545	0.9852	1.0162	1.0477	1.1139	1.1830	1.2611	1.3466
125	0.9395	0.9622	0.9892	1.0189	1.0753	1.1353	1.1988	1.2768
150	0.9237	0.9449	0.9696	0.9963	1.0484	1.0996	1.1534	1.2215
175	0.9102	0.9316	0.9533	0.9771	1.0203	1.0685	1.1168	1.1776
200	0.9001	0.9178	0.9370	0.9590	1.0003	1.0426	1.0879	1.1454
225	0.8905	0.9076	0.9251	0.9441	0.9818	1.0212	1.0656	1.1145
250	0.8810	0.8978	0.9147	0.9328	0.9678	1.0035	1.0434	1.0863
275	0.8704	0.8870	0.9030	0.9200	0.9519	0.9865	1.0203	1.0633
300	0.8631	0.8777	0.8942	0.9104	0.9409	0.9729	1.0044	1.0469
325	0.8544	0.8694	0.8839	0.8995	0.9295	0.9587	0.9890	1.0280
350	0.8484	0.8622	0.8766	0.8906	0.9167	0.9470	0.9755	1.0120
375	0.8408	0.8542	0.8670	0.8810	0.9064	0.9357	0.9626	0.9929
400	0.8366	0.8474	0.8600	0.8736	0.8963	0.9239	0.9483	0.9763

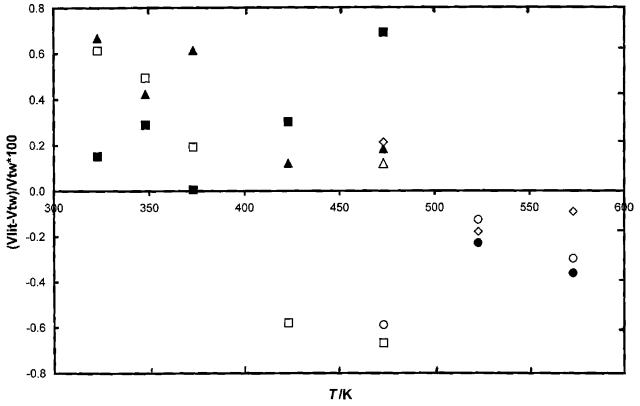

Figure 3. Comparison of the specific volume of methyl chloride between the literature, V_{lit}, and this work, V_{tw}: ■, ref 2, $P = 10$ MPa; □, ref 2, $P = 20$ MPa; ▲, ref 2, $P = 30$ MPa; △, ref 5, $P = 10$ MPa; ○, ref 3, $P = 10$ MPa; ●, ref 3, $P = 20$ MPa; ◇, ref 3, $P = 30$ MPa.

Table 3. Coefficient of the Tait Equation for Methyl Chloride

P_0/MPa	V_0/cm^3·g^{-1}	T/K	A	B/MPa	SD[a]
10	1.0472	298.15	0.0949	35.0	0.00132
10	1.1310	323.15	0.0973	22.2	0.00090
10	1.2009	348.15	0.0995	13.9	0.00118
10	1.3012	373.15	0.0977	4.0	0.00098
20	1.4664	423.15	0.0992	−12.3	0.00168
30	1.1309	473.15	0.1027	10.1	0.00114
40	1.6516	523.15	0.1116	−32.0	0.00188
50	1.6972	573.15	0.1227	−38.6	0.00177

[a] SD, standard deviation, in V/cm^3·g^{-1}.

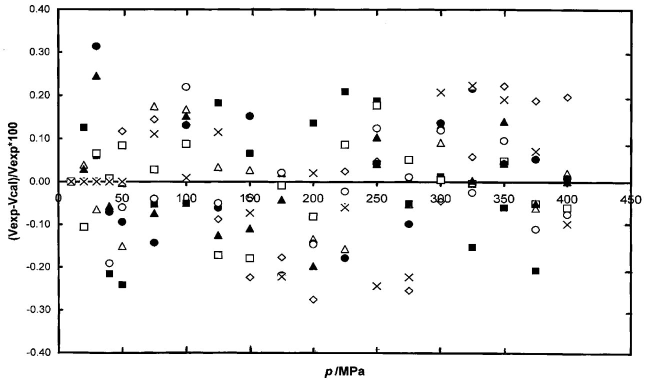

Figure 4. Relative deviations between experimental specific volumes, V_{exp}, and calculated values by the Tait equation, V_{calc}: ■, $T = 298$ K; □, $T = 323$ K; ▲, $T = 348$ K; △, $T = 373$ K; ○, $T = 423$ K; ●, $T = 473$ K; ◇, $T = 523$ K; ×, $T = 573$ K.

Then, the corresponding specific volumes were calculated by the method of interpolation in the temperature range of (323 to 573) K and the pressure range of (10 to 30) MPa. Relative deviations of specific volumes from the present study are depicted in Figure 3 as a function of temperature along three isobars over the range of (10 to 30) MPa. As can be seen from Figure 3, agreement is close and can be considered with in the experimental errors.

The so-called Tait equation[7] is one of the best empirical equations of state for liquids. In its integrated form this equation is usually written for an isotherm:

$$V = V_0\left[1 - A\ln\frac{B + P}{B + P_0}\right] \qquad (2)$$

Here A and B are temperature-dependent parameters. V_0 is the specific volume at a reference pressure P_0. The parameters of this equation were evaluated from the experimental PVT data for each of the eight isotherms by the method of generalized nonlinear least squares and are given in Table 3 together with the standard deviation in specific volumes. The variances of specific volumes between experimental measurement points and calculated from the Tait equation are shown in Figure 4. Using the Tait equation in conjunction with the related thermodynamic equation, it is possible to drive many thermodynamic properties of interest.

Conclusion

The specific volume or density of methyl chloride data were reported in the literature above 10 MPa by Hsu and McKetta[2] in the temperature range of (406 to 498) K up to 31 MPa, by Suh and Storvick[3] in the temperature range of (473 to 623) K up to 34 MPa, by Kumagai and Iwasaki[4] in the temperature range of (253 to 313) K up to 160 MPa, and by Mansoorian et al.[5] in the temperature range of (448 to 473) K up to 15 MPa. This work fills the gap thoroughly in the temperature range of (298 to 573) K and extends the pressure range up to 400 MPa. A comparison of the specific volume values of this work with the previously reported values in the literature revealed an agreement with in the experimental uncertainty of 0.34 %. The so-called Tait equation provides a reasonable description of methyl chloride at high temperature and pressure.

Acknowledgment

The author is greatly indebted to the late Prof. Dr. E. U. Franck for his guidance, help, and comments made during the course of this work, which was done at the Institute for Physical Chemistry, Karlsruhe University, Karlsruhe, Germany.

Note Added after ASAP Publication

There were some errors in the version published ASAP on June 30, 2006. The author byline and corresponding author footnotes were changed, an acknowledgment was added, and units in the Abstract, Introduction, and Tables 2 and 3 were changed. The corrected version was published ASAP on August 28, 2006.

Literature Cited

(1) Tanner, H. G.; Benning, A. F.; Mathewson, W. F. Thermodynamic properties of methyl chloride. *Ind. Eng. Chem.* **1939**, *31*, 878−883.
(2) Hsu, C. C.; McKetta, J. J. Pressure−volume−temperature properties of methyl chloride. *J. Chem. Eng. Data* **1964**, *9*, 45−51.
(3) Suh, K. W.; Storvick, T. S. Gas compressibility factors at high temperature and high pressure by the Burnett method: methyl chloride. *AIChE J.* **1967**, *13*, 231−236.
(4) Kumagai, A.; Iwasaki, H. Pressure volume temperature relationships of several polar liquids. *J. Chem. Eng. Data* **1978**, *23*, 193−195.
(5) Mansoorian, H.; Hall, K. R.; Holste, J. C.; Eubank, P. T. The density of gaseous ethane and of fluid methyl chloride and the vapor pressure of methyl chloride. *J. Chem. Thermodyn.* **1981**, *13*, 1001−1024.
(6) Hilbert, R.; Tödheide, K.; Franck, E. U. *PVT* Data for water in the ranges 20 to 600 °C and 100 to 4000 bar. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 636−643.
(7) Hayward, A. T. J. Compressibility equations for liquids: a comparative study. *Br. J. Appl. Phys.* **1967**, *18*, 965−977.

Received for review March 13, 2006. Accepted May 30, 2006.

JE060117O