

PRESSURE-VOLUME-TEMPERATURE RELATIONSHIPS OF
LIQUID DICHLOROMETHANE AND TRICHLOROMETHANE

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The specific volumes of liquid dichloromethane and trichloromethane were measured at constant temperature by the variable volume method using a glass piezometer in the temperature range from 273 to 348 K and in the pressure range up to 100 MPa. The specific volume vs. pressure isotherms are expressed by the Tait equation within an accuracy of 0.07%.

The PVT relationships of fluids provide source of the most fundamental thermodynamic data. The Tait equation is considerably used for describing PVT data, but its use has been limited to compounds for which the Tait parameters are available. The PVT data for polar liquids are useful in correlating the Tait parameters for a wide variety of liquids containing nonpolar and polar substances. Relatively few measurements of polar liquids have been reported in the literature. In our previous studies, the PVT data have been obtained for polar liquids of NH_3 ,¹⁾ SO_2 ,²⁾ CCl_2F_2 , CHClF_2 , CH_3Cl , CH_3I , CH_3Br , $\text{C}_2\text{H}_5\text{Br}$, $\text{CH}_3\text{COOCH}_3$,³⁾ and $\text{CH}_3\text{COOC}_2\text{H}_5$,⁴⁾ but these data were insufficient for investigating the polar correction for the Tait parameters. The purpose of this paper was to obtain the specific volumes of CH_2Cl_2 and CHCl_3 in the temperature range from 273 to 348 K and at pressures up to 100 MPa. The compressibility data for the chlorine substituted methanes were obtained only at 298 K by Newitt and Weale.⁵⁾

The apparatus and the experimental procedure are the same as those reported previously.³⁾ The estimated error in the specific volume due to the uncertainty of mass, volume, temperature, and pressure measurements does not exceed 0.04%. CH_2Cl_2 and CHCl_3 of reagent grade were obtained from Nakarai Chemicals Ltd., and used without further purification. The gas chromatography analysis showed that the CH_2Cl_2 was not contaminated with foreign matters, but the CHCl_3 with 0.45 wt% $\text{C}_2\text{H}_5\text{OH}$.

The measured specific volumes are shown in Table 1. The values of the saturated liquid specific volume for CHCl_3 in the literature⁶⁾ are lower by 0.35% than the ones obtained in this study. The corresponding values for CH_2Cl_2 are not available in the literature. The compression values at 298 K determined by Newitt and Weale⁵⁾ are 4.7 % (maximum dev.) less than the ones obtained for both substances in this study.

The Tait equation can be written in terms of the specific volume, V_p , at pressure, p , as:

$$V_p = V_0 (1 - C \ln((p+B)/(p_0+B))), \quad (1)$$

where V_0 is the specific volume at the saturated vapor pressure, p_0 , and C, B the Tait parameters. The two Tait parameters were determined from the experimental pressure-volume data for each isotherms by the least squares method, as listed in Table 2. The maximum deviations of the experimental PVT data from the Tait equation are 0.07% for CH_2Cl_2 and 0.04% for CHCl_3 , respectively.

The effects of polarity and temperature on the Tait parameter, B, will be discussed elsewhere.⁷⁾

Table 1. Specific volumes of dichloromethane and trichloromethane

$V_p(\text{CH}_2\text{Cl}_2)/10^{-3}\text{m}^3\text{kg}^{-1}$				$V_p(\text{CHCl}_3)/10^{-3}\text{m}^3\text{kg}^{-1}$				
T/K	P/ 10^5 Pa			T/K	P/ 10^5 Pa			
	298.15	323.15	348.15		273.15	298.15	323.15	348.15
(p_0)	(0.6) ^a	(1.4) ^a	(2.9) ^a	(p_0)	(0.1) ^a	(0.3) ^a	(0.7) ^a	(1.6) ^a
101	0.7593	0.7874	0.8190	108	0.6574	0.6782	0.7013	0.7266
253	0.7517	0.7780	0.8073	254	0.6515	0.6709	0.6925	0.7149
405	0.7424	0.7657	0.7909	401	0.6446	0.6622	0.6815	0.7019
557	0.7332	0.7546	0.7772	547	0.6381	0.6545	0.6723	0.6907
709	0.7256	0.7453	0.7660	694	0.6323	0.6474	0.6639	0.6809
861	0.7183	0.7370	0.7562	840	0.6270	0.6413	0.6569	0.6725
1013	0.7118	0.7291	0.7475	987	0.6220	0.6356	0.6506	0.6652
	0.7059	0.7221	0.7392		0.6177	0.6304	0.6445	0.6582

^aSaturated vapor pressure, $p_0/10^5$ Pa

Table 2. Tait equation parameters for dichloromethane and trichloromethane

CH_2Cl_2			CHCl_3		
T/K	B/ 10^5 Pa	C	T/K	B/ 10^5 Pa	C
298.15	1001	} 0.1010	273.15	1108	} 0.0952
323.15	793		298.15	899	
348.15	616		323.15	733	
			348.15	583	

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