

Benedict-Webb-Rubin Equation of State for an alternative fuel, Dimethyl ether, and Estimation of Thermophysical Properties

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INTRODUCTION

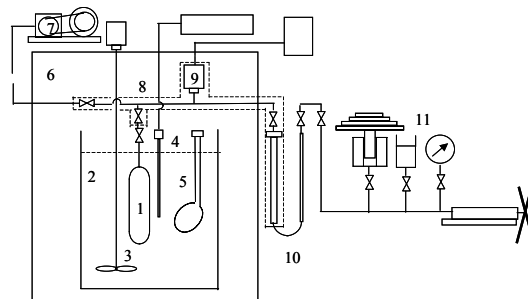
The industrial production of dimethyl ether (DME) is now about 10,000 ton/year in Japan, and DME has been mainly used as an aerosol propellant¹. Recently, DME can be directly synthesized from water gas, carbon monoxide and hydrogen, by use of a new type catalyst dispersed in fluids. So, a large amount of DME will be supplied in future. Considering the molecular structure, the physical properties of DME are similar to those of light hydrocarbons in liquefied petroleum gas (LPG), propane or butane, and the combustion properties also similar to those of gas oil. Then, DME is expected to be an alternative energy for industrial, domestic and diesel fuels. However, comparing with propane and butane, there are few available data about physical properties of DME. The members of research group, mainly organized by High Pressure Gas Safety Institute and Liquefied Petroleum Gas Center of Japan, have intensively investigated thermophysical properties to establish safety instructions for DME. This study is an activity of this project. Therefore, P-V-T relationship and vapor pressure were measured for DME. The eight constants, in Benedict-Webb-Rubin (BWR) equation of state, were optimized by applying Joffe's corresponding state theory. The BWR equation well predicted experimental compressibility factor and vapor pressure of DME. Using the BWR eq., latent heat of vaporization, isochoric heat capacity, isobaric heat capacity and speed of sound were also calculated.

EXPERIMENTAL

In this study, two experimental apparatus were employed. One was for P-V-T measurement, and other for vapor pressure. Figure 1 shows a schematic diagram of apparatus for P-V-T measurement. The apparatus was based on a constant volume method. The equipment and the procedure of measurement have been already described elsewhere^{2,3}. The cell was made of stainless steel. The inner volume and

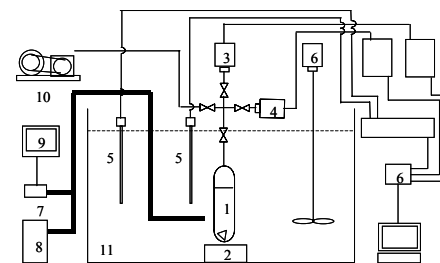
the vacant mass was about 63 cm³ and 0.67 kg, respectively. The precise inner volume was calibrated up to 0.0004 cm³ by weighing the mass of the cell filled with pure water at 298.15 K. The mass was measured with a direct reading balance (EXACT AV 1581, Japan) by a minimum capacity of 0.1 mg and a maximum of 1 kg. The experimental range of temperature was from 350.00 to 450.00 K. and the precise temperature was measured by a thermister thermometer (Technoseven D461, Yokohama, Japan) within a precision of 0.01 K. The pressure was monitored by a pressure sensor (Erich Brosa EBM 1408-0325, Germany) with a precision of 10 kPa. The precise pressure was determined by a dead weight tester (Nagano Keiki PD22, Tokyo) with a resolution of 2 kPa. In the pressure measurement, a mercury U-tube was used to isolate the experimental system, the dead weight tester and its silicone oil.

Figures 2 and 3 show a schematic diagram of vapor pressure measurement. The apparatus were also based on a constant volume method. The apparatus, shown in Fig. 2, was used in the temperature range from 238.31 to 313.16 K. The cell was made of Pyrex glass, specially designed in our previous work⁴. The inner volume was about 37 cm³ and the maximum working pressure was up to 7.5 MPa. The medium in a constant temperature bath employed was pure water or aqueous solution of ethylene glycol. The experimental temperature was measured by a thermister thermometer. The pressure was measured by an absolute pressure sensor (Kyowa PHS-2KA, Tokyo) with a maximum of 200 kPa, and a pressure gauge (Kyowa PG-10KU, Tokyo) with a maximum of 1MPa. These sensors



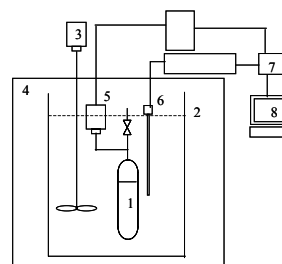
1: High Pressure Cell 2: Oil Bath 3: Agitator 4: Thermistor Thermometer 5: Heater 6: Air Chamber 7: Vacuum Pump 8: Ribbon Heater 9: Pressure Sensor 10: High Pressure Mercury U-tube 11: Dead Weight Tester:

Figure 1 A schematic diagram of apparatus for P-V-T measurement



1: Glass Cell 2: Magnetic Stirrer 3: Pressure Sensor 4: Absolute Pressure Sensor 5: Thermistor Thermometer 6: Agitator 7: Light Scope 8: Light Source 9: CRT 10: Vacuum Pump 11: Water-Ethylene glycol Bath 12: Data Logger 13: Personal Computer

Figure 2 A schematic diagram of apparatus for vapor pressure measurement at 238.31-313.16 K



1: High Pressure Cell 2: Oil Bath 3: Agitator 4: Air Chamber 5: Absolute Pressure Sensor 6: Thermistor Thermometer 7: Data Logger 8: Personal Computer

Figure 3 A schematic diagram of apparatus for for vapor pressure measurement at 317.15-397.65 K

have a minimum resolution within 0.01 kPa. Otherwise, the apparatus, shown in Fig. 3, was used in the temperature range from 317.15 to 397.65 K. The cell was made of stainless steel, and the inner volume was about 40 cm³. The medium in a constant temperature bath employed was silicone oil, which is the same as that in P-V-T measurement. The cell connected with pressure sensor was soaked in the silicone oil bath, and the equilibrium temperature and pressure were measured by a thermister thermometer and two absolute pressure sensors. The absolute pressure sensors employed were Kyowa PHS-50KA, Tokyo with a maximum of 5 MPa, and Kyowa PHS-200KA, Tokyo, with a maximum pressure of 20 MPa.

RESULT AND DISCUSSION

Figure 4 shows the experimental results of P-V-T relationship for DME. The reliability of experimental data was ensured by measuring P-V-T relationship for propane and butane at the same temperatures. As shown in the figure, the pressure dependence of the compressibility factor was increased in the vicinity of the critical point.

Figure 5 shows the experimental result of vapor pressure for DME. According to the literature, the data of vapor pressure have been reported by Holldorff et al⁵. in the temperature range from 253.85 to 320.51 K. As shown in the figure, the experimental data agreed well with those of literature.

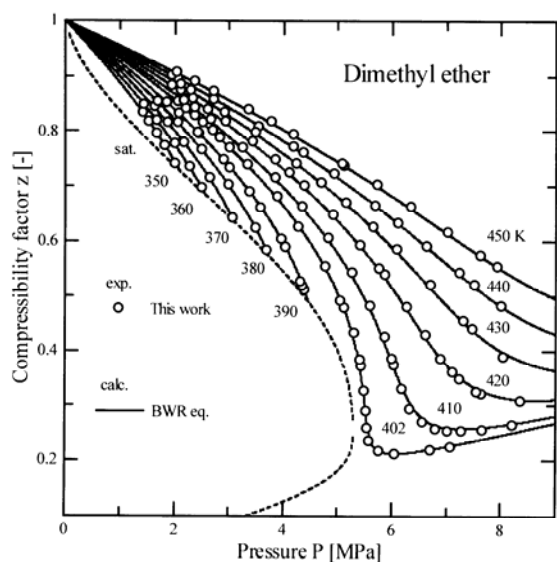


Figure 4 Compressibility factor for DME

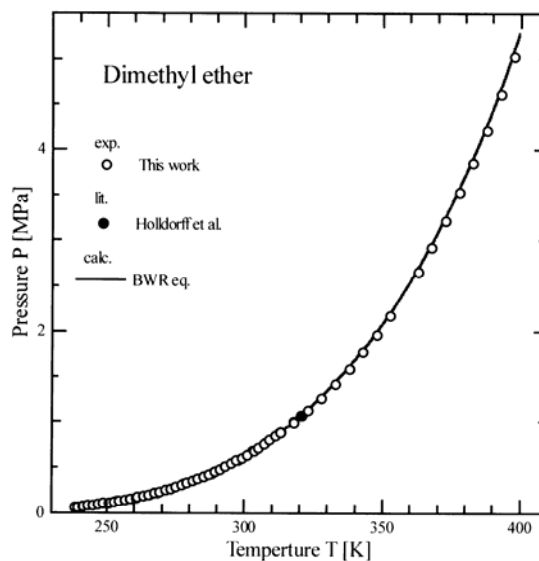


Figure 5 Vapor Pressure for DME

To calculate the thermophysical properties, equation of state was constructed for DME. The equation employed was Benedict-Webb-Rubin (BWR) eq.⁶ The equation is given below:

$$P = RT\rho + (B_0RT - A_0 - \frac{C_0}{T^2})\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6 + \frac{c\rho^3}{T^2}(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \quad (1)$$

Though the eight constants, A_0 , B_0 , C_0 , a , b , c , α , γ , for propane and butane can be obtained from the literature⁷, those for DME have not been determined. Applying Joffe's corresponding state theory⁸, BWR eq. can be converted to the following non-dimensional form:

$$P_r = \frac{T_r}{v_r} + (B_{0r}T_r - A_{0r} - \frac{C_{0r}}{T_r^2})\frac{1}{v_r^2} + (b_rT_r - a_r)\frac{1}{v_r^3} + \frac{a_r\alpha_r}{v_r^6} + \frac{c_r}{T_r^2v_r^3}(1 + \frac{\gamma_r}{v_r^2})\exp(-\frac{\gamma_r}{v_r^2}) \quad (2)$$

where P_r , T_r and v_r are reduced properties using critical temperature and pressure.

$$P_r = \frac{P}{P_c} \quad (3)$$

$$T_r = \frac{T}{T_c} \quad (4)$$

$$v_r = \frac{P_c}{\rho RT_c} \quad (5)$$

Compared with eq. (1), the non-dimensional constants in eq. (2) are given by:

$$A_{0r} = A_0 \frac{P_c}{R^2 T_c^2} \quad (6)$$

$$B_{0r} = B_0 \frac{P_c}{T_c} \quad (7)$$

$$C_{0r} = C_0 \frac{P_c}{R^2 T_c^4} \quad (8)$$

$$a_r = a \frac{P_c^2}{R^3 T_c^3} \quad (9)$$

$$b_r = b \frac{P_c^2}{R^2 T_c^2} \quad (10)$$

$$c_r = c \frac{P_c^2}{R^3 T_c^5} \quad (11)$$

$$\alpha_r = \alpha \frac{P_c^3}{R^3 T_c^3} \quad (11)$$

$$\gamma_r = \gamma \frac{P_c^3}{R^2 T_c^2} \quad (12)$$

If the corresponding state theory is perfect, the same value can be obtained for non-dimensional constants from critical properties of any substance. However, the values from those of propane are slightly different from those of butane. So, in this study, a linear relation, similar to Lee-Kesler eq.⁸, was assumed for non-dimensional constants:

$$Q_r = \frac{Q_{r,R1} - Q_{r,R2}}{\omega_{R1} - \omega_{R2}}(\omega - \omega_{R2}) + Q_{r,R2} \quad (Q_r : A_{0r}, B_{0r}, C_{0r}, a_r, b_r, c_r, \alpha_r, \gamma_r) \quad (13)$$

where ω_{R1} and ω_{R2} is an acentric factor for propane and butane. Figure 6 shows the calculation result, as Joffe-LK method, at 402.00 K. The calculation result shows a good reproducibility. In our previous work concerning BWR eq., the better correlation results can be obtained by optimization for three constants, c , α , γ , using the experimental data in the vicinity of the critical point. The calculation result, as Joffe-LK-T method, was also illustrated in Fig. 6. The calculation of Joffe-LK-T method shows better correlation than those of Joffe-LK method. In Figs. 4, the calculation of the compressibility factor at other temperature was also illustrated. As shown in the figure, BWR equation shows a good reproducibility in the whole range

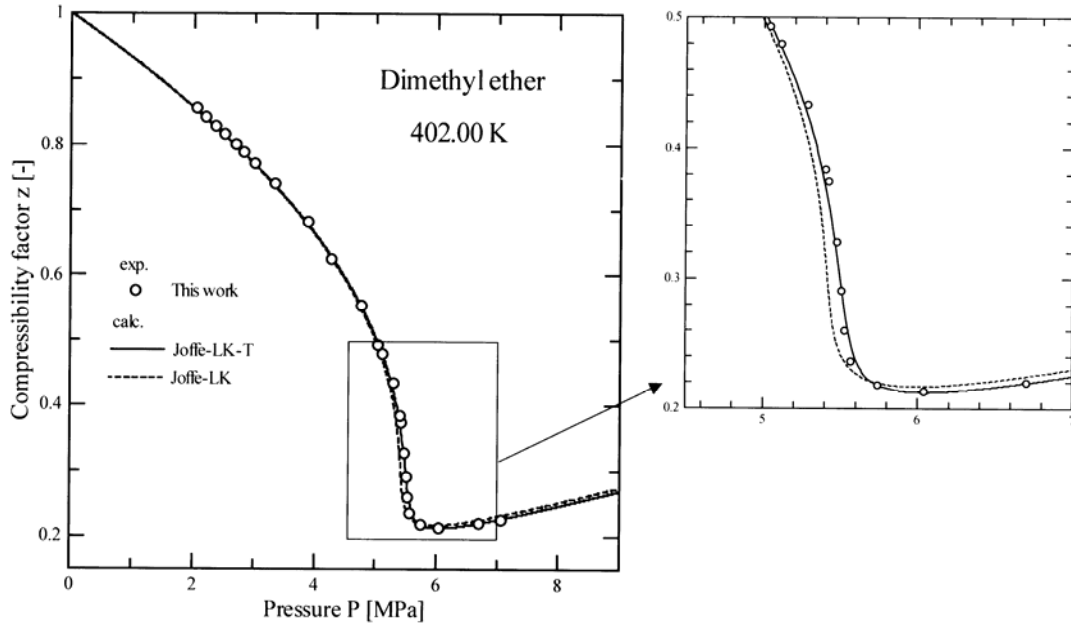


Figure 6 Determination of BWR constants for DME

of temperature. The deviation between experimental data and calculation was within 1.6 %. Fig. 5 shows the prediction of vapor pressure. As shown in the figure, BWR eq. well predicted not only for compressibility factor but for vapor pressure. Then, the other physical properties were calculated. For example, latent heat of vaporization, isochoric heat capacity, isobaric heat capacity and speed of sound can be calculated by the following equations:

$$\Delta h = T \Delta v \frac{dP}{dT} \quad (14)$$

$$C_v = C_p^{id}(T) + T \int_{\infty}^v \left(\frac{\partial^2 P}{\partial T^2} \right) dv - R \quad (15)$$

$$C_p = C_v - \frac{T(\partial P / \partial T)_v^2}{(\partial P / \partial v)_p} \quad (16)$$

$$u = \left[-v^2 \left(\frac{\partial P}{\partial v} \right)_T \times \frac{C_p}{C_v} \right]^{0.5} \quad (17)$$

where C_p^{id} is isobaric heat capacity at ideal gas state. The value can be evaluated by the following equation:

$$C_p^{id}(T) = C_{p,a} + C_{p,b}T + C_{p,c}T^2 + C_{p,d}T^3 \quad (18)$$

where the values of constants, $C_{p,a}$, $C_{p,b}$, $C_{p,c}$, $C_{p,d}$, can be available in the literature⁸. Figure 7 show the calculation results for latent heat of vaporization, isochoric heat capacity, isobaric heat capacity and speed of sound.

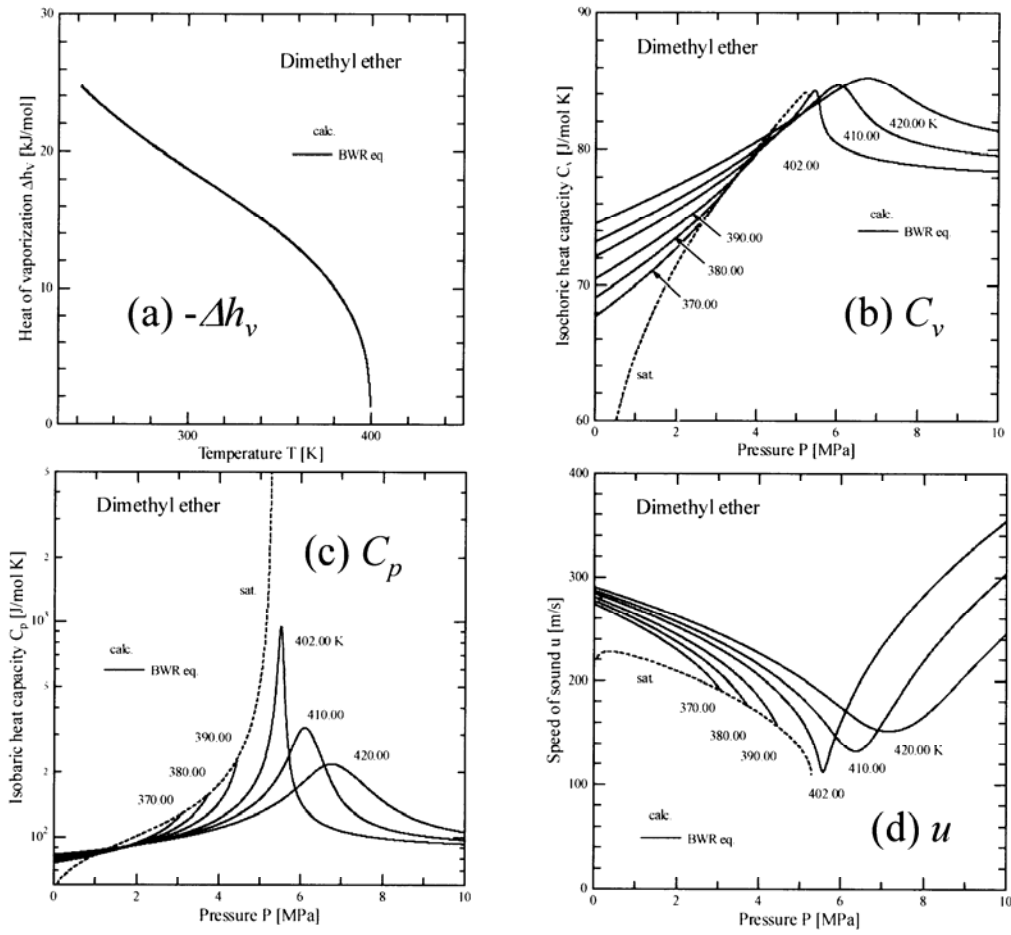


Figure 7 Calculation for (a) latent heat of vaporization, (b) isochoric heat capacity, (c) isobaric heat capacity and (d) speed of sound for DME

CONCLUSION

Reliable data of P-V-T relationship and vapor pressure can be obtained for DME by use of apparatus based on a constant volume method. Using corresponding state theory and experimental data, the eight constants of BWR eq. was determined. BWR eq. provides us various physical properties with high accuracy.

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