

Vapor-Liquid Equilibrium of a Ternary System containing Dimethyl ether (DME) and Light Hydrocarbons

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INTRODUCTION

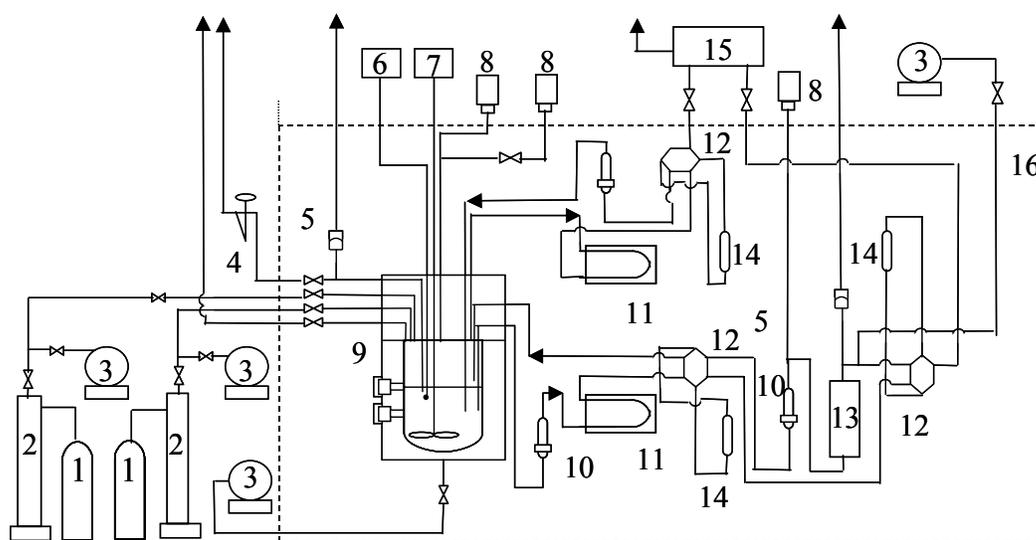
Recently, dimethyl ether (DME) has been paid much attention as a clean fuel. DME has many advantages as a substitute for liquefied petroleum gas (LPG). Sulfur oxides (SO_x), and particulate matters (PM) are not produced at the combustion. Infrastructures and equipments for LPG can be used with slight improvements, because physical properties of DME are similar to those of light hydrocarbons, propane and butane. Now, the industrial production of DME is about 10,000 ton/year in Japan, and the DME has been mainly used as an aerosol propellant. In this last decade, DME can be directly synthesized from water gas, carbon monoxide and hydrogen, by use of a new type catalyst dispersed in fluids, and a pilot plant has already produced DME with a rate of 100 ton/day¹. So, a huge amount of DME will be supplied in the future of Japan. Though the experimental data of vapor-liquid equilibrium (VLE) are essential for the practical usage of fuel mixture, there are few data containing DME and light hydrocarbons. In this study, a recirculate type apparatus was designed to measure VLE, and the experimental VLE data were obtained for the three binary, propane + DME, DME + butane, propane + butane, and a ternary, propane + DME + butane, systems at 313.15 K. The binary data were correlated with Benedict-Webb-Rubin (BWR) equation of state and a conventional mixing rule. Using the optimized binary interaction parameters, VLE was estimated for the ternary system.

EXPERIMENTAL

Figure 1 shows a schematic diagram of a recirculate type apparatus. The apparatus was specifically designed for this study, and based on a recirculate method². The equilibrium cell was made of stainless steel, and its inner volume was about 200 cm³. The maximum working pressure of the cell was estimated up to 10 MPa. Two pressure resistance windows were equipped with the cell, and phase

behavior can be observed by a fiber scope and a CCD camera. The cell was held in a water bath with volume about 450 L. Two magnetic driven recirculating pumps were also equipped in the cell. One was for vapor phase, the other for liquid phase. In the recirculating line, two oscillation U-tube densimeters (Anton Paar 512P, Gratz, Austria) were also equipped. The densimeters were calibrated with nitrogen, carbon dioxide, propane and butane at 313.15 K. The precision of the densimeter was within 0.01 kg/m^3 . The experimental temperature was measured by a thermister thermometer (Technoseven D461, Yokohama, Japan) with a precision of 0.01 K. The pressure was measured by two absolute pressure sensors. One was Kyowa PHS-A-5KP, Tokyo with a capacity of 500 kPa and a resolution of 0.01 kPa. Other was Kyowa PHS-A-20KP, Tokyo with a capacity of 2MPa and a resolution of 0.0001 MPa. The procedure of the measurements was described below:

First, the liquefied sample was fed into the evacuated cell by two syringe pumps (ISCO 260D, Lincoln, U. S.). Using the automatic pressure regulator (STEC UR-7340MO-B, Tokyo), the mixture, with different composition, can be successively loaded without changing temperature and pressure. After attaining a constant temperature and pressure, re recirculation was stopped to measure the density, and successively small portion of vapor and liquid phase was individually picked up by using six-way valve. For the determination of the composition, the sample of vapor



1: Sample Gas Cylinder **2:** Syringe Pump **3:** Vacuum Pump **4:** Automatic Pressure Regulator **5:** Safety Valve **6:** Thermistor Thermometer **7:** Agitator **8:** Pressure Sensor **9:** Equilibrium Cell **10:** Circulation Pump **11:** Oscillation U-tube Densimeter **12:** Six-way Valve **13:** Surge Tank **14:** Sampling Bomb **15:** FID Gas Chromatograph **16:** Water Bath

Figure 1 Schematic Diagram of a Recirculate type Apparatus

phase was directly sent to a gas chromatograph (GL Science GC-353B, Tokyo) equipped with a capillary column (Variant Molsieve 5A Plot, i. d. 0.53 mm, length 50 m). Otherwise, the sample of liquid phase was expanded in a surge tank, and completely vaporized. The vaporized sample was sent to the gas chromatograph. The precision of composition analysis was estimated to be within 0.001 mole fraction.

RESULT AND DISCUSSION

To ensure the reliability of the experimental data, VLE was measured for propane + DME. Figure 2 shows VLE for propane + DME at 313.15 K. In the figure, the data of Horstmann et al.³ were also illustrated. As shown in the figure, the azeotropic point can be seen in the vicinity of pure propane. Though the azeotropic point was not clearly observed, the experimental data agreed well with those of literature.

Figures 3 and 4 show VLE for DME + butane and propane + butane at 313.15 K, respectively. In the figure 3, the data of Fernandez et al.⁴ was illustrated. In the two systems, there was no azeotropic point. The data for DME + butane showed a similar tendency with the data of literature. Otherwise, VLE for propane + butane can be regarded as an ideal mixture.

Figure 5 shows VLE for propane + DME + butane at 0.8830 MPa and 313.15 K. The experimental pressure was almost the same as that of pure DME. As shown in the figure, the composition of vapor phase became close to that of liquid phase around pure DME.

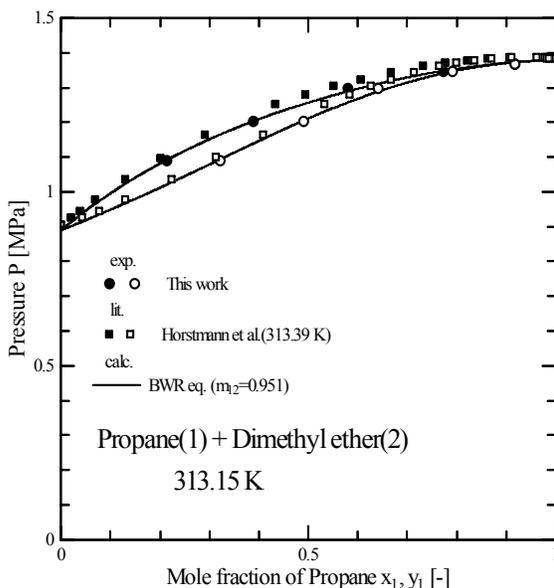


Figure 2 VLE for Propane(1) + DME(2) at 313.15 K

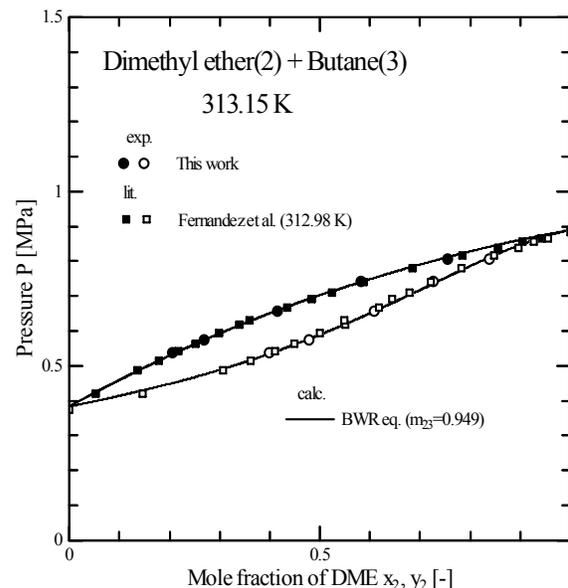


Figure 3 VLE for DME(2) + Butane(3) at 313.15 K

Figure 6 shows the summary for the experimental result of liquid density measurement. The corner of triangular prism indicates pure propane, DME and butane, respectively. The height corresponds to the density. As shown in the figure, the liquid density tends to increase with increasing DME concentration.

The experimental data were correlated with equation of state. The equation employed was Benedict-Webb-Rubin (BWR) eq.⁵

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

where A_0 , B_0 , C_0 , a , b , c , α and γ are so called BWR constants. The values for propane and butane can be obtained from the literature⁶, and those for DME have been already reported in our previous work.

The mixing rule employed was Stotler-Benedict eq.⁷

$$A_0 = \sum_i \sum_j x_i x_j m_{ij} (A_{0i} A_{0j})^{1/2} \quad (2) \quad B_0 = \sum_i \sum_j x_i x_j \frac{B_{0i} + B_{0j}}{2} \quad (3)$$

$$C_0 = \sum_i \sum_j x_i x_j (C_{0i} C_{0j})^{1/2} \quad (4) \quad a = \left(\sum_i x_i a_i^{1/3} \right)^3 \quad (5) \quad b = \left(\sum_i x_i b_i^{1/3} \right)^3 \quad (6)$$

$$c = \left(\sum_i x_i c_i^{1/3} \right)^3 \quad (7) \quad \alpha = \left(\sum_i x_i \alpha_i^{1/3} \right)^3 \quad (8) \quad \gamma = \left(\sum_i x_i \gamma_i^{1/3} \right)^3 \quad (9)$$

where m_{ij} is a binary interaction parameter. In this study, the binary parameters were optimized by using the experimental data. In Figs. 2-4, the optimized results were also illustrated. Using the binary parameter, the calculation showed good reproducibility for the three binary systems. Table 1 listed the optimized binary interaction parameters. The value for propane + DME was similar to that for DME + butane, and the value for propane + butane was almost unity. Using the optimized binary interaction parameters, VLE and liquid density were estimated for propane + DME + butane. Figures 5 and 6 show the calculation results of VLE and liquid density for propane + DME + butane at 0.8830 MPa and 313.15 K. As shown in the figures,

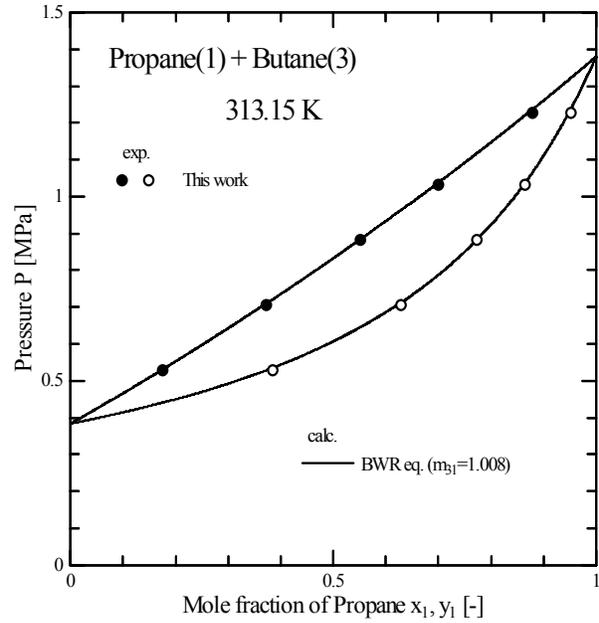


Figure 4 VLE for Propane(1) + Butane(3) at 313.15 K

calculations well predicted VLE and liquid density with a high accuracy. Figure 8 shows the calculation of the ternary VLE in the whole range of composition. Vapor-liquid-liquid equilibrium (VLLE) was not observed in the calculation, and VLE was maintained in the whole range of composition. Azeotropic point was calculated

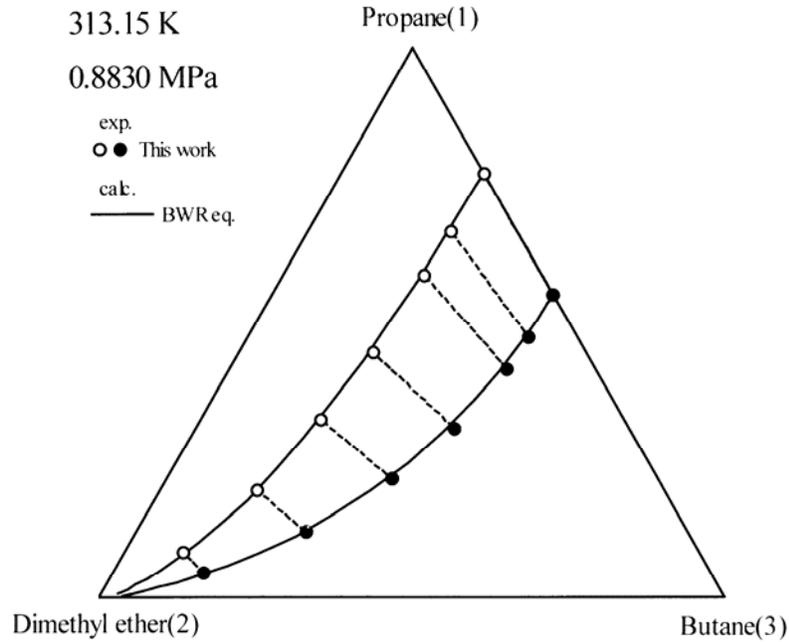


Figure 5 VLE for Propane(1) + DME(2) + Butane(3) at 0.8830 MPa and 313.15 K

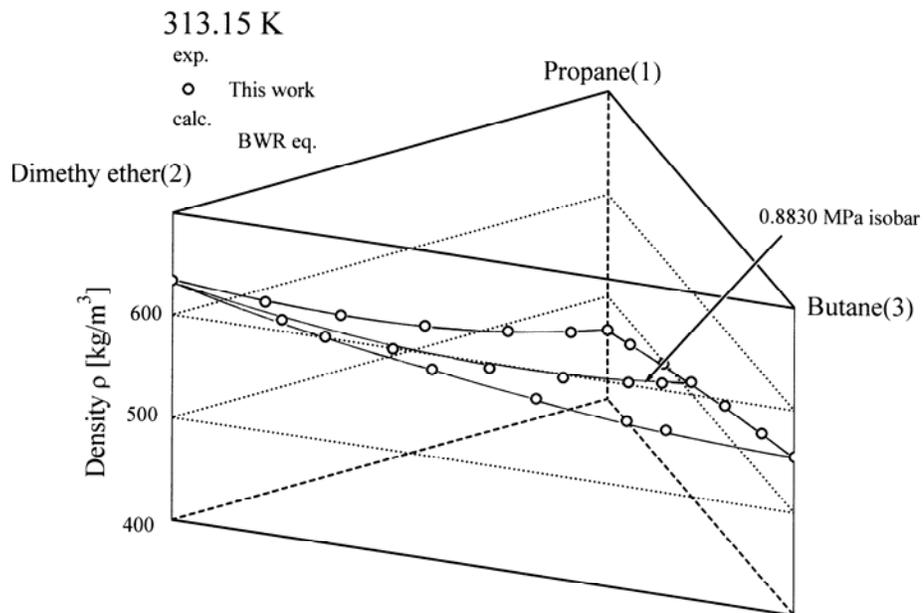


Figure 6 Liquid Density for Propane(1) + DME(2) + Butane(3) at 0.8830 MPa and 313.15 K

just in the binary, propane + DME.

Table 1 Optimized Binary Interaction Parameters

	Propane(1) + DME(2)	DME(2) + Butane(3)	Propane(1) + Butane(3)
m_{ij} [-]	0.951	0.949	1.008

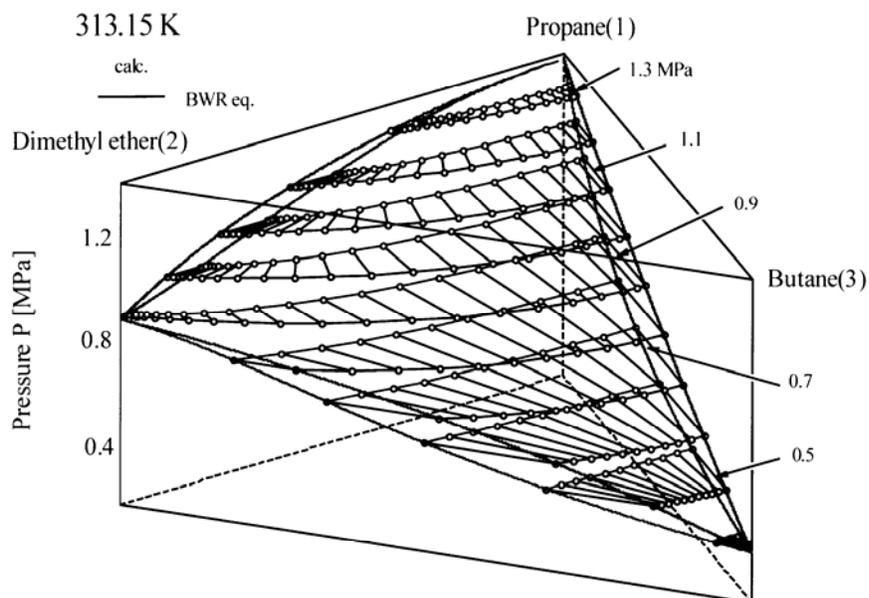


Figure 7 Calculated VLE for Propane(1) + DME(2) + Butane(3) at 313.15 K

CONCLUSION

Reliable data of VLE and liquid density can be obtained for binary and ternary systems containing propane, DME and butane by use of apparatus specially designed in this study. Using optimized binary interaction parameters in the mixing rule of BWR eq., the VLE can be well predicted for multi component system containing DME and LPG.

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REFERENCES

- 1) http://www.aist.go.jp/aist_e/aist_today/2003_10/hot_line/hot_line_13.html
- 2) Hiaki, T., H. Miyagi, T. Tsuji, M. Hongo, J. Supercritical Fluids, 13, 23(1998)
- 3) Horstmann, S., G. Birke, K. Fischer, J. Chem. Eng. Data, 49, 38(2004)
- 4) Fernandez, M. E. P., J. C. G. Calado, J. A. Zollweg, W. B. Streett, 74, 289(1992)
- 5) Benedict, M., G. B. Webb, L. C. Rubin, J. Chem. Phys., 8, 334(1940)
- 6) Cooper, H. W., J. C. Goldfrank, Hydrocarbon Processing, 46, 141(1967)
- 7) Stotler, H. H., M. Benedict, Chem. Eng. Progr. Symp. Ser. No. 6, 49, 25(1953)