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# Binary mixtures of carbon dioxide and dimethyl ether as alternative refrigerants and their vapor-liquid equilibrium data prediction

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## Abstract

Vapor-liquid equilibrium (VLE) data were predicted for the binary mixture of carbon dioxide ($CO_2$) and dimethyl ether (DME) at ten temperatures ranging from 273.15 to 386.56 K and pressure upto 7.9 MPa to observe this mixture's potential of COP enhancement and capacity modulation as a working fluid in a refrigeration system. Since the mixtures are zeotropic in nature and the components of the mixtures have good thermophysical properties, zero ozone depleting potential (ODP) and low global warming potential (GWP), they are considered as promising alternative refrigerants. The Benedict-Web-Rubin (BWR) and the modified Benedict-Web-Rubin (MBWR) equations of state (EoS) have been used for the prediction of VLE data. For the BWR and MBWR equations of state, respective constant binary interaction parameters have been determined by using the available experimental VLE data of $CO_2$/DME mixtures. The predicted VLE data have been compared with the experimental data and the data obtained from REFPROP version 8.0. Among the comparison results, BWR EoS shows good agreement with the experimental data.

*Keywords:* Vapor-liquid equilibrium, Alternative refrigerant, Carbon dioxide, Dimethyl ether.

## 1. Introduction

Zeotropic mixtures of suitable fluids are becoming the important candidates as the alternatives of the existing HCFCs and HFCs refrigerants which are not benign to environment. The major reasons can be explained briefly by the following points (Arora, 1967; Arora, 1972; Jakobs and Kruse, 1979; Didon and Bivens, 1990; Rajapaksha, 2007): (1) limited number of pure fluids available that can be used as alternative refrigerants, (2) it is possible to improve the coefficient of performance (COP) by utilizing the gliding temperature of zeotropic mixtures during phase change process in counterflow heat exchangers, (3) by selecting the combination among the suitable fluids and by tuning their mass fraction in the mixture it is possible to keep the systems in suitable pressure level, (4) in case of zeotropic mixtures it is possible to achieve continuous capacity control of the system by changing the mass fraction and (5) zeotropic mixtures can provide alternatives to the existing refrigerants for the minimization of the global warming problem and ozone layer depletion.

In this paper, the zeotropic mixtures of carbon dioxide ($CO_2$) and dimethyl ether (DME) have been considered as promising alternative refrigerants. Table 1 summarizes some of the key thermophysical properties of $CO_2$, DME, R22, R407C, R410A, and $NH_3$. Both the $CO_2$ and DME have zero ozone depleting potential (ODP) and low global warming potential (GWP) (Calm and Hourahan, 2007). Pure DME is nontoxic and has high latent heat of vaporization, high liquid thermal conductivity, low liquid density, low viscosity, and high specific heat. On the other hand, $CO_2$ is nonflammable and nontoxic and has comparable low liquid density. The high latent heat of vaporization leads to a small mass flow rate of a working fluid for a given cooling requirement, which can result in the decrease of pressure drops in the heat exchanger. The higher thermal conductivity, lower viscosity, lower surface tension, and higher specific heat have a positive effect on the improvement of heat transfer behavior. Moreover, low liquid density require small amount of refrigerant charge to the refrigeration systems for the same refrigeration load. These excellent thermophysical properties of DME and $CO_2$ make their mixtures favorable to consider as promising alternative refrigerants. However, pure $CO_2$ and DME exhibit some limitations regarding high operating pressure and flammability, respectively, but in case of their mixture, DME would minimize the problem of high operating pressure of $CO_2$ while $CO_2$ would reduce the flammability of DME.

**Table 1** Thermophysical properties of $CO_2$, DME, R22, R407C, R410A, and $NH_3$

| Refrigerant | $CO_2$ | DME | R22 | R407C | R410A | $NH_3$ |
|---|---|---|---|---|---|---|
| $^a$Molar mass (kg kmol$^{-1}$) | 44.01 | 46.068 | 86.468 | 86.204 | 72.585 | 17.03 |
| $^a$Critical Temperature(°C) | 30.978 | 127.15 | 96.145 | 86.029 | 71.35 | 132.25 |
| $^a$Liquid density at 0°C (kg m$^{-3}$) | 927.43 | 699.99 | 1281.5 | 1236.2 | 1170.0 | 638.57 |
| $^a$Latent heat of vaporization at 0°C (kJ kg$^{-1}$) | 230.89 | 430.89 | 205.05 | 217.33 | 226.29 | 1262.25 |
| $^a$$C_v$ of liquid at 0°C (kJ kg$^{-1}$ K$^{-1}$) | 0.94493 | 1.5115 | 0.67111 | 0.87818 | 0.88589 | 2.8003 |
| $^a$Liquid thermal conductivity at 0°C (W m $^{-1}$ K$^{-1}$) | 0.11043 | 0.16131 | 0.09474 | 0.09625 | 0.10309 | 0.55920 |
| $^a$Liquid viscosity at 25°C ($\times 10^{-6}$ kg m$^{-1}$s$^{-1}$) | 57.048 | 126.73 | 164.39 | 154.19 | 117.97 | 131.68 |
| $^a$Vapor viscosity at 25°C ($\times 10^{-6}$ kg m$^{-1}$ s$^{-1}$) | 20.157 | 9.1566 | 12.511 | 12.598 | 13.663 | 9.8346 |
| $^a$Surface tension at 0°C (N m$^{-1}$) | 0.00454 | 0.01438 | 0.01169 | 0.01066 | 0.00906 | 0.03291 |
| $^b$ODP | 0 | 0 | 0.050 | 0 | 0 | 0 |
| $^b$GWP(100 Yr) | 1 | 1 | 1810 | 1800 | 2100 | < 1 |
| $^b$LFL (Lower flammability level) (%) | None | 3.4 | None | None | None | 15 |
| $^b$OEL (Occupational exposure limit) (ppm) | 5000 | 1000 | 1000 | 1000 | 1000 | 25 |

$^a$ From REFPROP 8.0 (Lemmon *et al*., 2007)
$^b$ From HPAC engineering (Calm and Hourahan, 2007)

Koyama *et al*. (2006) experimentally investigated the performance of heat pump systems with a binary refrigerant mixture $CO_2$/DME (90/10 mass%) and a pure refrigerant $CO_2$. They found that the $CO_2$/DME system operates with almost the same maximum heating COP of the $CO_2$ system but at considerably lower discharge pressure at the maximum heating COP condition. Onaka *et al*. (2007) did performance analysis of a heat pump using $CO_2$/DME mixture refrigerant and pure $CO_2$ refrigerant. Their results show that increasing the mass fraction of DME in the mixture increases the maximum COP and decreases the pressure at the maximum COP condition. In both the work of Koyama and Onaka the vapor liquid equilibrium property prediction of $CO_2$/DME mixture were done by MBWR equation of state where the adjusted binary interaction parameter was not sufficient to give accurate prediction at the high temperature region.

Accurate prediction of vapor-liquid equilibrium (VLE) data of $CO_2$/DME mixture are essential to evaluate the performance of the refrigeration and heat pump cycles and to determine the optimum composition for the best performance of the system running with this binary mixture. REFPROP version 8.0 (Lemmon *et al*., 2007) has included DME as a new substance in their fluid list but the appropriate mixing parameter for the $CO_2$/DME mixture has not been specified. Their calculating mixing parameters which are not sufficiently adjusted cause error in the prediction of vapor-liquid equilibrium properties, especially in near the critical point. Tsang and Streett (1981) compared their experimental results of VLE of $CO_2$/DME mixture with the predictions of three equations of state: the Redlich-Kwong equation, the Peng-Robinson equation, and the Dalters equation. To use these equations they had obtained the interaction parameters by adjusting them with their experimental data at the middle range of temperature 35.30°C. Among these three equations, the Peng-Robinson equation predicts phase composition in good agreement with experiment but few deviations in the lower pressure region. In the present work Benedict-Web-Rubin equation of state (Benedict *et al*., 1940) and modified Benedict-Web-Rubin equation of state (Nishiumi and Saito, 1975) have been used to calculate the VLE data. The constants of Benedict-Web-Rubin equation of state (BWR EoS) for DME and $CO_2$ have been taken from Saito (1976) as well as Tamura and Tsuji (2006), respectively. The only available experimental VLE data of $CO_2$/DME mixture of Tsang and Streett (1981) is used for necessary comparison and to obtain the binary interaction parameters for the BWR and MBWR equation of state. Afroz *et al*. (2008) experimentally measured the heat transfer coefficient and pressure drop during in-tube condensation of $CO_2$/DME mixtures, where it was found that the increase of mass fraction of $CO_2$ in the mixture decreases the heat transfer coefficient and pressure drop. In Afroz *et al*. (2008), for the prediction of vapor-liquid equilibrium data of $CO_2$/DME mixtures BWR equation of state was used. The author thinks that the results of the prediction of vapor-liquid equilibrium data of $CO_2$/DME mixtures should be published for other researchers who are thinking about $CO_2$/DME mixture as alternative refrigerant.

## 2. Equations of state

The BWR EoS has alrady been used with success over wide range of temperature and pressure. In this work we have used the following BWR equation with the necessary constants for $CO_2$ (Saito, 1976) and DME (Tamura & Tsuji, 2006) as shown in the Table 2.

$$\begin{aligned} P = {} & \mathrm{R}T\rho + (\mathrm{B_o R}T - \mathrm{A_o} - \mathrm{C_o}/T^2)\rho^2 + (\mathrm{bR}T - \mathrm{a})\rho^3 + \alpha \mathrm{a}\rho^6 + (\mathrm{c}\rho^3/T^2) \\ & (1+\gamma\rho^2)\exp(-\gamma\rho^2) \end{aligned} \tag{1}$$

Here, $P$ is the pressure, $T$ is the temperature, $\rho$ is the density and R is the universal gas constant.

**Table 2** BWR constants for pure $CO_2$ and pure DME [ Units: atm, l, mol, K]

| Constants | $CO_2$ (Saito, 1976) | DME (Tamura & Tsuji, 2006) |
|---|---|---|
| $A_o$ | 2.7342 | 6.481724431285 |
| $B_o$ | 0.04987 | 0.0849171503 |
| $C_o \times 10^{-6}$ | 0.1384071 | 0.5640624061 |
| a | 0.13655 | 0.8141362842339 |
| b | 0.004119 | 0.0182611298 |
| $c \times 10^{-6}$ | 0.01488994 | 0.1244916445 |
| $\gamma$ | 0.005387 | 0.0160753772 |
| $\alpha$ | 0.0000845 | 0.000349173541 |

For the $CO_2$/DME mixture the constants of the BWR equation has been obtained by the following mixing rule-

$$\begin{aligned} & \mathrm{A_o} = \sum_i \sum_j x_i x_j m_{ij} (\mathrm{A_{o_i}} \mathrm{A_{o_j}})^{1/2} && \mathrm{B_o} = \sum_i \sum_j x_i x_j (\mathrm{B_{o_i}} + \mathrm{B_{o_j}})/2 \\ & \mathrm{C_o} = \sum_i \sum_j x_i x_j (\mathrm{C_{o_i}} \mathrm{C_{o_j}})^{1/2} && \mathrm{a} = (\sum_i x_i \mathrm{a}_i^{1/3})^3 \\ & \mathrm{b} = (\sum_i x_i \mathrm{b}_i^{1/3})^3 && \mathrm{c} = (\sum_i x_i \mathrm{c}_i^{1/3})^3 \\ & \alpha = (\sum_i x_i \alpha_i^{1/3})^3 && \gamma = (\sum_i x_i \gamma_i^{1/3})^3 \end{aligned} \tag{2}$$

In the above equations, $x$ represents mole fraction, $m_{ij}$ is the binary interaction parameter and $i, j$ are the components of binary relations. Several modifications of BWR equation of state were done by many authors by increasing the number of constants for improving the overall accuracy. MBWR equation of state proposed by Nishiumi and Saito, 1975 is one of the many modifications of BWR equation of state. In this work, we have also used the following modified Benedict-Web-Rubin (MBWR) equation of state proposed by Nishiumi and Saito, 1975 for the prediction of VLE data of $CO_2$/DME mixture and for necessary comparisons-

$$\begin{aligned} P = {} & \mathrm{R}T\rho + (\mathrm{B_o R}T - \mathrm{A_o} - \mathrm{C}_o/T^2 + \mathrm{D_o}/T^3 - \mathrm{E}_o/T^4)\rho^2 + (\mathrm{bR}T - \mathrm{a} - \mathrm{d}/T \\ & - \mathrm{e}/T^4 - \mathrm{f}/T^{23})\rho^3 + \alpha(\mathrm{a} + \mathrm{d}/T + \mathrm{e}/T^4 + \mathrm{f}/T^{23})\rho^6 + \\ & (\mathrm{c}/T^2 + \mathrm{g}/T^8 + \mathrm{h}/T^{17})\rho^3(1+\gamma\rho^2)\exp(-\gamma\rho^2) \end{aligned} \tag{3}$$

where the constants for pure substance are –

$$
\begin{aligned}
&\mathrm{A_o} = (1.28438 - 0.920731\,\omega)\mathrm{R}T_\mathrm{c} / \rho_\mathrm{c} \\
&\mathrm{B_o} = (0.443690 - 0.115449\,\omega) / \rho_\mathrm{c} \\
&\mathrm{C_o} = (0.356306 - 1.70871\,\omega)\mathrm{R}T_\mathrm{c}^3 / \rho_\mathrm{c} \\
&\mathrm{D_o} = (0.0307452 - 0.179433\,\omega)\mathrm{R}T_\mathrm{c}^4 / \rho_\mathrm{c} \\
&\mathrm{E_o} = [0.006450 - 0.022143\,\omega\exp(-3.8\omega)]\mathrm{R}T_\mathrm{c}^5 / \rho_\mathrm{c} \\
&\mathrm{a} = (0.484011 + 0.754130\,\omega)\mathrm{R}T_\mathrm{c} / \rho_\mathrm{c}^2 \\
&\mathrm{b} = (0.528629 + 0.349261\,\omega) / \rho_\mathrm{c}^2 \\
&\mathrm{c} = (0.504087 + 1.32245\,\omega)\mathrm{R}T_c^3 / \rho_c^2 \\
&\mathrm{d} = (0.0732828 + 0.463492\,\omega)\mathrm{R}T_\mathrm{c}^2 / \rho_\mathrm{c}^2 \\
&\mathrm{e} = [4.65593 \times 10^{-3} - 3.07393 \times 10^{-2}\,\omega + 5.58125 \times 10^{-2}\,\omega^2 \\
&\qquad - 3.40721 \times 10^{-3}\exp(-7.72753\,\omega - 45.3152\,\omega^2)]\mathrm{R}T_\mathrm{c}^5 / \rho_\mathrm{c}^2 \\
&\mathrm{f} = [0.679 \times 10^{-13} + 8.08 \times 10^{-13}\,\omega - 16.0 \times 10^{-13}\,\omega^2 - 0.363078 \times 10^{-13} \\
&\qquad \exp(30.9009\,\omega - 283.680\,\omega^2)]\mathrm{R}T_\mathrm{c}^{24} / \rho_\mathrm{c}^2 \\
&\mathrm{g} = [2.20 \times 10^{-5} - 1.065 \times 10^{-4}\,\omega - 1.09 \times 10^{-5}\exp(-26.024\,\omega)]\mathrm{R}T_\mathrm{c}^9 / \rho_\mathrm{c}^2 \\
&\mathrm{h} = [-2.40 \times 10^{-11} + 11.8 \times 10^{-11}\,\omega - 2.05 \times 10^{-11}\exp(-21.52\,\omega)\mathrm{R}T_\mathrm{c}^{16} / \rho_\mathrm{c}^2 \\
&\alpha = (0.0705233 - 0.044448\,\omega) / \rho_\mathrm{c}^3 \\
&\gamma = (0.544979 - 0.270896\,\omega) / \rho_\mathrm{c}^2
\end{aligned}
\tag{4}
$$

Here, $\omega$ is the accentic factor and the subscript $c$ represents critical point.

For mixture the above constants can be obtained by using the following mixing rule-

$$
\begin{aligned}
&\mathrm{A_o} = \sum_i\sum_j x_i x_j \mathrm{A}_{\mathrm{o}_{ij}} && \mathrm{B}_o = \sum_i\sum_j x_i x_j \mathrm{B}_{\mathrm{o}_{ij}} \\
&\mathrm{C_o} = \sum_i\sum_j x_i x_j \mathrm{C}_{\mathrm{o}_{ij}} && \mathrm{D_o} = \sum_i\sum_j x_i x_j \mathrm{D}_{\mathrm{o}_{ij}} \\
&\mathrm{E_o} = \sum_i\sum_j x_i x_j \mathrm{E}_{\mathrm{o}_{ij}} && \mathrm{a} = (\sum_i x_i \mathrm{a}_i^{1/3})^3 \\
&\mathrm{b} = (\sum_i x_i \mathrm{b}_i^{1/3})^3 && \mathrm{c} = (\sum_i x_i \mathrm{c}_i^{1/3})^3 \\
&\mathrm{d} = (\sum_i x_i \mathrm{d}_i^{1/3})^3 && \mathrm{e} = (\sum_i x_i \mathrm{e}_i^{1/3})^3 \\
&\mathrm{f} = (\sum_i x_i \mathrm{f}_i^{1/3})^3 && \mathrm{g} = \sum_i x_i \mathrm{g}_i \\
&\mathrm{h} = \sum_i x_i \mathrm{h}_i && \alpha = (\sum_i x_i \alpha_i^{1/3})^3 \\
&\gamma = (\sum_i x_i \gamma_i^{1/2})^2 &&
\end{aligned}
\tag{5}
$$

For calculating the constants with suffix *ij* the following three mixing rules have been used

$$
\begin{aligned}
&\rho_{\mathrm{c}_{ij}} = [\tfrac{1}{2}(\rho_{\mathrm{c}_i}^{-1/3} + \rho_{\mathrm{c}_j}^{-1/3})]^{-3} \\
&T_{\mathrm{c}_{ij}} = m_{ij}\sqrt{T_{\mathrm{c}_i} T_{\mathrm{c}_j}} \\
&\omega_{ij} = \tfrac{1}{2}(\omega_i + \omega_j)
\end{aligned}
\tag{6}
$$

## 3. Calculation Method

To relate quantitatively the variables that describe the state of equilibrium of two-phase (liquid-vapor) of a binary mixture, the following conditions of thermodynamic equilibrium are necessary to satisfy

$$\begin{aligned} T_{\mathrm{v}} &= T_{\mathrm{l}} \\ P_{\mathrm{v}} &= P_{\mathrm{l}} \\ f_{\mathrm{v}_1} &= f_{\mathrm{l}_1} \\ f_{\mathrm{v}_2} &= f_{\mathrm{l}_2} \end{aligned} \tag{7}$$

Where, *f* is the fugacity, the numbers 1,2 represents the two components ($CO_2$ and DME, respectively) in the binary mixture and the subscripts v and l represent vapor and liquid, respectively.
The fugacities can be related with the mixture composition by the eq. (8) and eq. (9) for BWR and MBWR equation of states, respectively.

$$\begin{aligned} \mathrm{R}T\ln\frac{f_i}{x_i} &= \mathrm{R}T\ln(\mathrm{R}T\rho)+2\rho\sum_j x_j\left[\left(\frac{\mathrm{B}_{\mathrm{o}_i}+\mathrm{B}_{\mathrm{o}_j}}{2}\right)\mathrm{R}T-m_{ij}\left(\mathrm{A}_{\mathrm{o}_i}\mathrm{A}_{\mathrm{o}_j}\right)^{1/2}-\frac{\left(\mathrm{C}_{\mathrm{o}_i}\mathrm{C}_{\mathrm{o}_j}\right)^{1/2}}{T^2}\right] \\ &+\frac{3}{2}\rho^2\left[\mathrm{R}T\left(\mathrm{b}^2\mathrm{b}_i\right)^{1/3}-\left(\mathrm{a}^2\mathrm{a}_i\right)^{1/3}\right]+\frac{3}{5}\rho^5\left[\mathrm{a}\left(\alpha^2\alpha_i\right)^{1/3}+\alpha\left(\mathrm{a}^2\mathrm{a}_i\right)^{1/3}\right] \\ &+\frac{3\rho^2\left(\mathrm{c}^2\mathrm{c}_i\right)^{1/3}}{T^2}\left[\frac{1}{\gamma\rho^2}-\left(\frac{1}{\gamma\rho^2}+\frac{1}{2}\right)\exp\left(-\gamma\rho^2\right)\right] \\ &-\frac{2\mathrm{c}}{T^2}\frac{\gamma_i^{1/2}}{\gamma^{3/2}}\left[1-\left(1+\gamma\rho^2+\frac{1}{2}\gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \end{aligned} \tag{8}$$

$$\begin{aligned} \mathrm{R}T\ln\frac{f_i}{x_i} &= \mathrm{R}T\ln(\mathrm{R}T\rho)+2\rho\sum_j x_j\left[\mathrm{B}_{\mathrm{o}_{ij}}\mathrm{R}T-\mathrm{A}_{\mathrm{o}_{ij}}-\frac{\mathrm{C}_{\mathrm{o}_{ij}}}{T^2}+\frac{\mathrm{D}_{\mathrm{o}_{ij}}}{T^3}-\frac{\mathrm{E}_{\mathrm{o}_{ij}}}{T^4}\right] \\ &+\frac{3}{2}\rho^2\left[\mathrm{R}T\left(\mathrm{b}^2\mathrm{b}_i\right)^{1/3}-\left(\mathrm{a}^2\mathrm{a}_i\right)^{1/3}-\frac{\left(\mathrm{d}^2\mathrm{d}_i\right)^{1/3}}{T}-\frac{\left(\mathrm{e}^2\mathrm{e}_i\right)^{1/3}}{T^4}-\frac{\left(\mathrm{f}^2\mathrm{f}_i\right)^{1/3}}{T^{23}}\right] \\ &+\frac{3}{5}\rho^5\left[\alpha\left\{\left(\mathrm{a}^2\mathrm{a}_i\right)^{1/3}+\frac{\left(\mathrm{d}^2 d_i\right)^{1/3}}{T}+\frac{\left(\mathrm{e}^2\mathrm{e}_i\right)^{1/3}}{T^4}+\frac{\left(\mathrm{f}^2\mathrm{f}_i\right)^{1/3}}{T^{23}}\right\}+\left(\mathrm{a}^2\mathrm{a}_i\right)^{1/3}\left\{\mathrm{a}+\frac{\mathrm{d}}{T}+\frac{\mathrm{e}}{T^4}+\frac{\mathrm{f}}{T^{23}}\right\}\right] \\ &+\rho^2\left[\frac{3\left(\mathrm{c}^2\mathrm{c}_i\right)^{1/3}}{T^2}+\frac{\mathrm{g}_i+2\mathrm{g}}{T^8}+\frac{\mathrm{h}_i+2\mathrm{h}}{T^{17}}\right]\times\left[\frac{1}{\gamma\rho^2}-\left(\frac{1}{\gamma\rho^2}+\frac{1}{2}\right)\exp\left(-\gamma\rho^2\right)\right] \\ &-2\left(\frac{\mathrm{c}}{T^2}+\frac{\mathrm{g}}{T^8}+\frac{\mathrm{h}}{T^{17}}\right)\frac{\gamma_i^{1/2}}{\gamma^{3/2}}\times\left[1-\left(1+\gamma\rho^2+\frac{1}{2}\gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right] \end{aligned} \tag{9}$$

For the two-component, two-phase system, the number of independent intensive properties is two. In such a system the intensive properties of interest usually are $x_{i_1}$, $x_{i_v}$, *T*, and *P*. Two of these, any two, must be specified before the remaining two can be found. For example, if the inputs are *T* and *P* then the vapor phase and liquid phase mole fractions of two-components in the binary mixture have to be obtained. The calculation method for solving this problem has been shown in the flow chart of Figure 1, where *x* represents mole fraction of component 1(more volatile, $CO_2$) and 2 (less volatile, DME) in the binary mixture. Alternatively, if the inputs are the liquid phase mole fraction of the two components and the temperature then the pressure and vapor phase mole fractions are asked to be found, or might be other combinations of known and unknown variables.

Before going to calculate the phase equlibrium properties of $CO_2$/DME binary mixture, the binary interaction parameter $m_{ij}$ is needed to find for the use in BWR and MBWR equation of state. Figure 2 and Figure 3 show optimum values of the binary interaction parameter $m_{ij}$ for BWR and MBWR equation of state at different temperatures and pressures, which have been determined using the experimental results of *P*, *T*, $x_{i_1}$ and $x_{i_v}$ (Tsang & Streett, 1981). The experimental *P* and *T* data have been used as the input and $m_{ij}$ is determined by minimizing the deviation between the experimental liquid mole fraction of $CO_2$ and the calculated one by the developed program as shown in the Figure 1. Many subroutines have been developed together with the main program to calculate density and fugacity, which are not shown in the flow chart. For example, to calculate the density of the liquid and vapor phase, pressure, temperature, phase (Liquid/Vapor) and all the constants of BWR and MBWR equation of states are given as input in the subroutine of density and using the BWR and MBWR equation of states the densities have been calculated. In the Figure 2 and Figure 3, the average value of optimum $m_{ij}$ for BWR and MBWR equations of state are around

1.015 and 0.98, respectively. In the present calculation, therefore, $m_{ij}$ for BWR equation of state has been taken as 1.015 for the whole analysis range, while for MBWR it is 0.98.

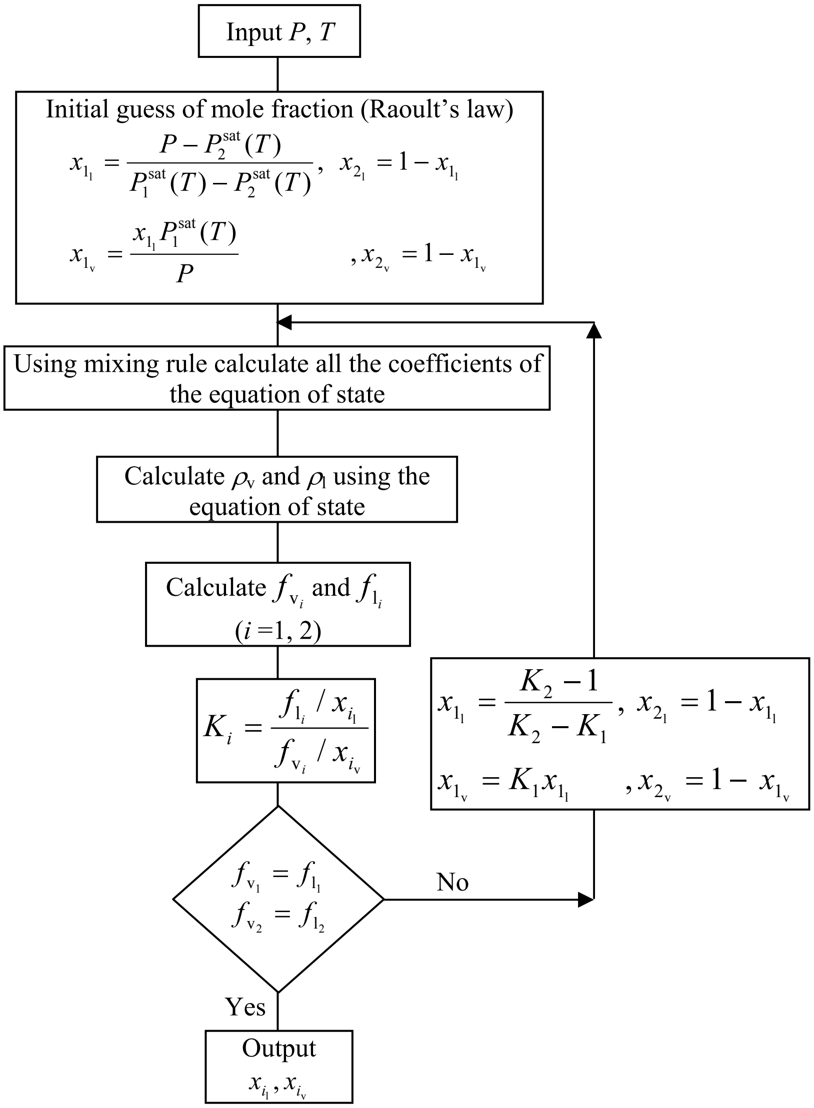

**Figure 1** Flow chart for finding the liquid and vapor mole fractions of two components of the binary mixture at liquid-vapor phase equilibrium

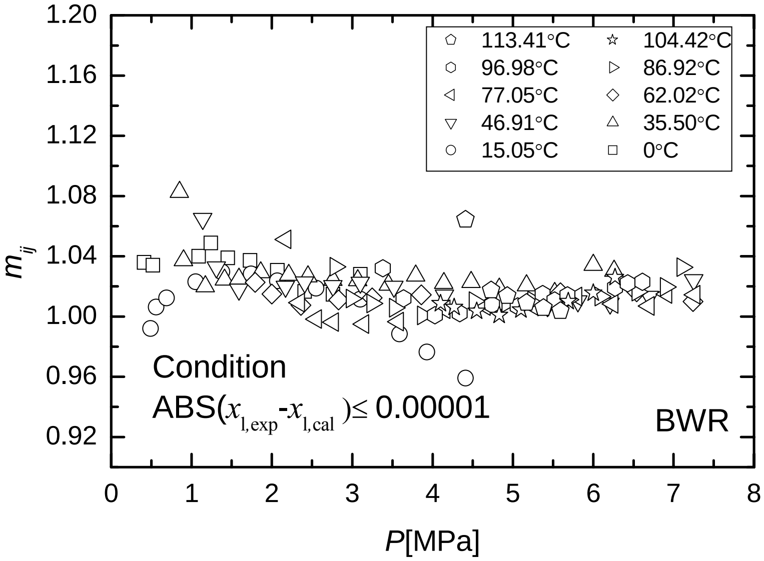

**Figure 2** Optimum $m_{ij}$ at different temperatures and pressures for BWR equation of state

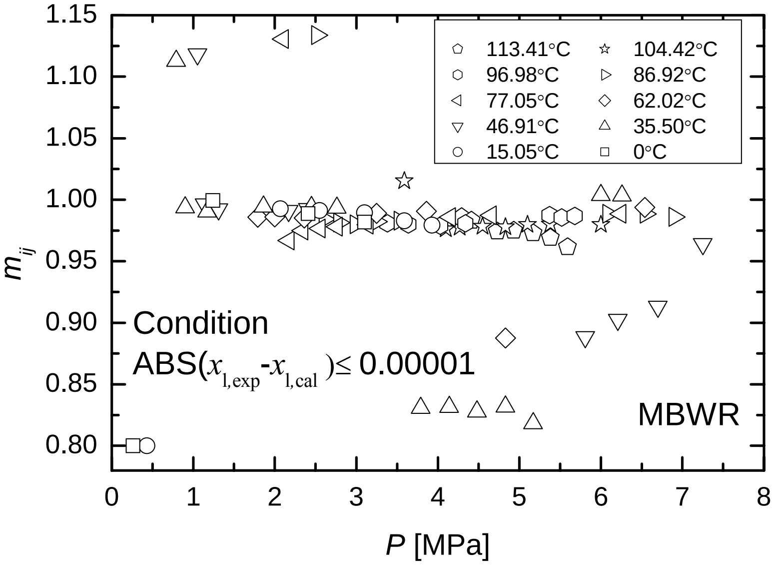

**Figure 3** Optimum $m_{ij}$ at different temperatures and pressures for MBWR equation of state

## 4. Results and discussion

Figure 4 shows all the calculation results of vapor-liquid equilibrium data for the binary mixture of $CO_2$/DME at ten temperatures ranging from 273.15 to 386.56 K and pressure upto 7.9 MPa using BWR equation of state and the experimental results of Tsang & Streett, 1981. The solid circle and the open square symbols represent the experimental data of vapor phase and liquid phase pressures respectively at different mole fraction of $CO_2$ in the mixture at different temperatures. The predicted data shows good agreement with the experimental results. From this figure, it is also observed that the $CO_2$/DME binary mixture shows zeotropic behavior and the saturation pressure difference between the $CO_2$ and DME at a fixed temperature is significantly large. The refrigerant pressure is strongly related to its density at a certain application temperature, which determines the magnitude of the volumetric refrigeration capacity. If a refrigeration system is charged with mixtures whose components have different volumetric refrigerating effect, the system capacity can be modulated by varying the composition of the refrigerant mixture.

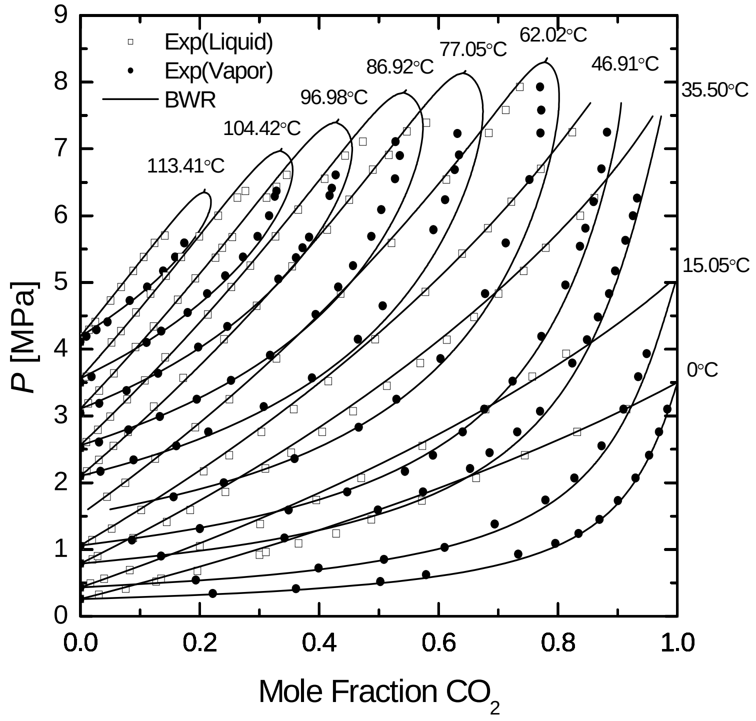

**Figure 4** Vapor-liquid equilibrium results of $CO_2$/DME binary mixture calculated by the BWR equation of state and that of the experiment of Tsang and Streett (1981).

Figure 5 shows the comparison among the vapor-liquid equilibrium results of BWR, MBWR, REFPROP 8.0, and the experiment (Tsang and Streett, 1981). REFPROP can predict the experimental VLE data of $CO_2$/DME mixture well with their estimated binary interaction parameter upto temperature about 45°C; after that temperature, it cannot predict VLE data for all mixture compositions of $CO_2$/DME system at high pressure. This is because of their estimated binary interaction parameter, which was not obtained from the experimental VLE data of $CO_2$/DME system. The MBWR also cannot predict the experimental data for high temperature. This may be due to the choice of a constant binary interaction parameter and accentric factor for the whole analysis range of temperature and pressure which are not suitable for the high temperature like 113.41 °C. Further analysis is necessary to check the applicability of MBWR equation of state (Nishiumi and Saito, 1975 ) for the $CO_2$/DME mixture by adjusting the binary interaction parameter $m_{ij}$ and the mixture accentric factor for high temperature. In the present analysis, BWR equation of state shows better agreement among the others throughout the whole analysis range.

Figure 6 shows the relative deviations between the experimental bubble point pressure data and the calculated results by the BWR equation of state. In Figure 7, comparison of dew point composition of the experimental data and those obtained by the BWR equation of state has been shown. Experimental $T$ and $x_1$ value have been used as the input, and bubble point pressure $P$ and dew point composition $x_v$ have been calculated to obtain the deviation between the experimental and calculated results.

Due to the use of a constant binary interaction parameter for the whole analysis range, some of the predictions of the experimental bubble point pressure and vapor composition show greater deviation. In the Figure 2 and Figure 3, it is found that for a certain pressure and temperature combination there is an optimum binary interaction parameter for both the BWR and MBWR equation of states; so to get the best prediction of VLE the interaction parameter should also be changed with the pressure and temperature. Further analysis is required to get correlation for the interaction parameter in terms of pressure, temperature, and compositions.

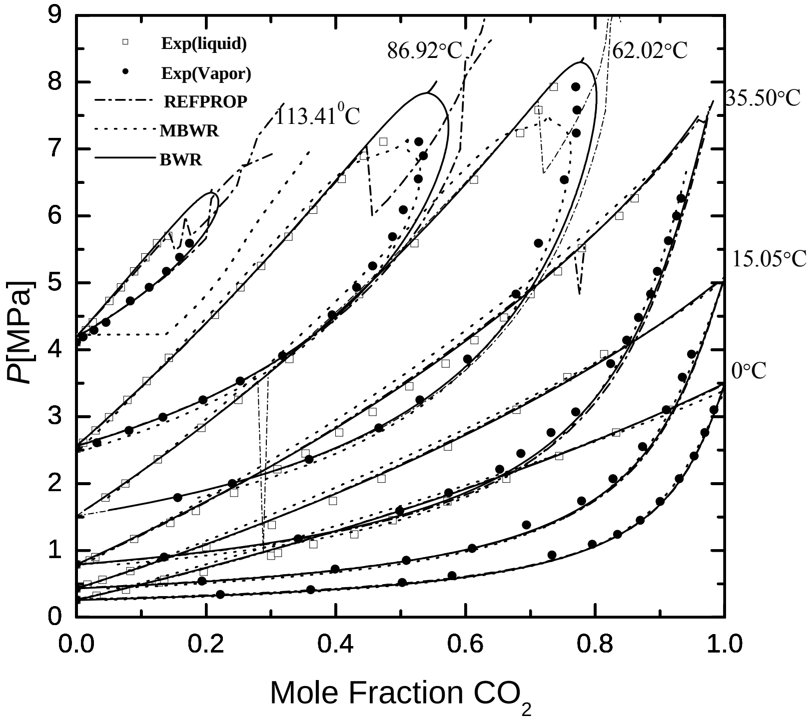

**Figure 5** Comparisons among the calculated (BWR, MBWR and REFPROP 8.0) and experimental (Tsang & Streett, 1981) vapor-liquid equilibrium results.

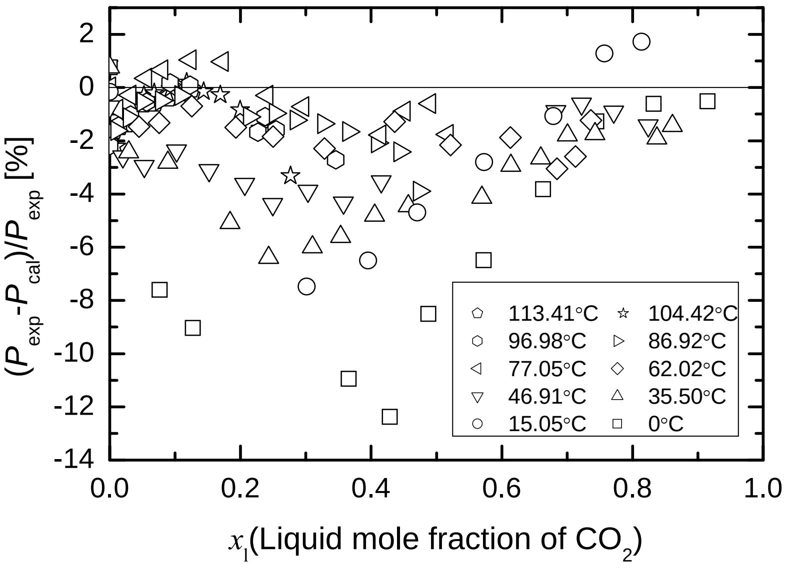

**Figure 6** Deviations of calculated bubble point pressure by BWR equation of state from the experimental results

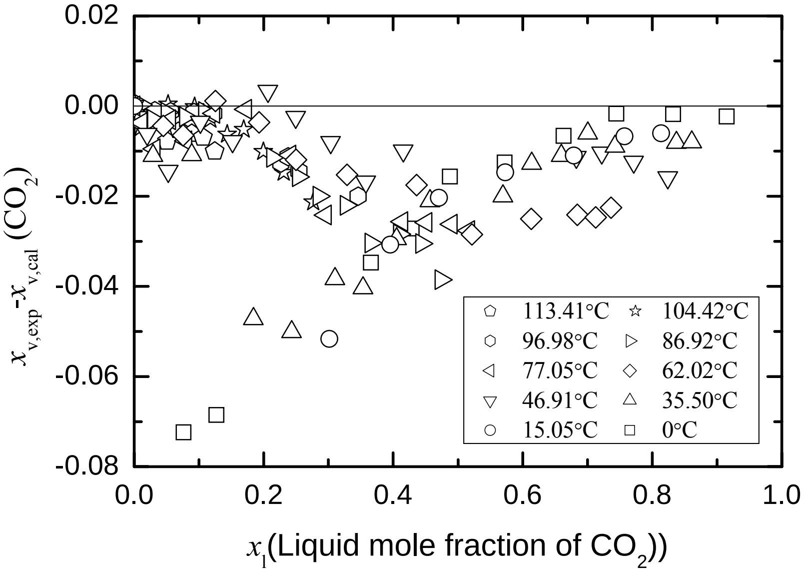

**Figure 7** Deviations of calculated vapor mole fraction by BWR equation of state from the experimental results

Figure 8 shows the variation of dew point temperature and bubble point temperature at different saturation pressures for different mixture compositions of $CO_2$/DME zeotropic mixture. The dew and bubble point temperature have been calculated by the BWR equation of state where the inputs are the pressure and liquid/vapor mole fractions and the outputs are the bubble point/dew point temperature. For a specific mixture composition, the difference between the dew point temperature and bubble point temperature at any specified saturation pressure is called the temperature glide. From the Figure 8 it can be seen that at a specific mixture composition the space between the dew line and bubble line becomes higher at low pressure than the high pressure. Therefore, the temperature glide of the $CO_2$/DME mixture with a specific mixing composition increases as the pressure decreases. This can be explained clearly by the Figure 9, which is a temperature glide versus mixing composition graph at different pressure.

The maximum glide at constant pressure is found within 0.5 to 0.6 mole fraction of $CO_2$. For 1000 kPa pressure, the maximum temperature glide is found 38.75°C at 0.54 mole fraction of $CO_2$. Figure 9 indicates that $CO_2$/DME zeotropic mixture is a blend having high gliding temperature. If this temperature glide reduces the mean temperature difference between the refrigerant and the secondary fluid, the use of zeotropic mixtures of $CO_2$ and DME can result in a COP enhancement of a refrigeration system.

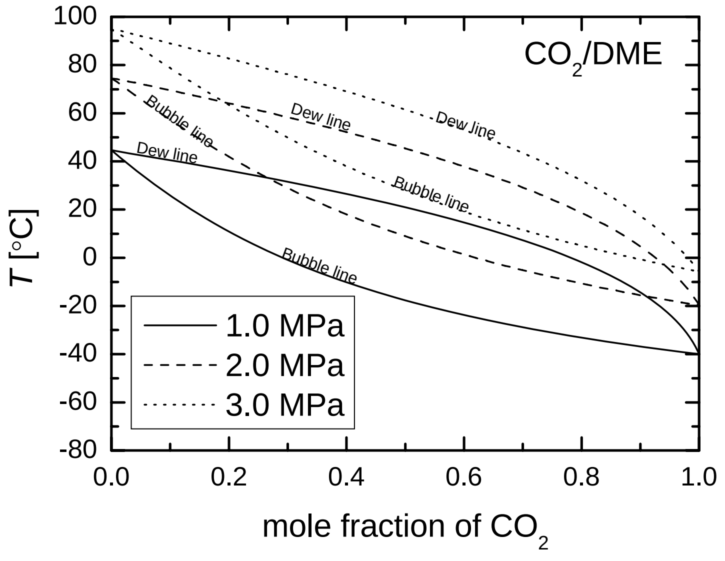

**Figure 8** Temperature-mole fraction diagram of $CO_2$/DME mixture obtained by the BWR equation of state

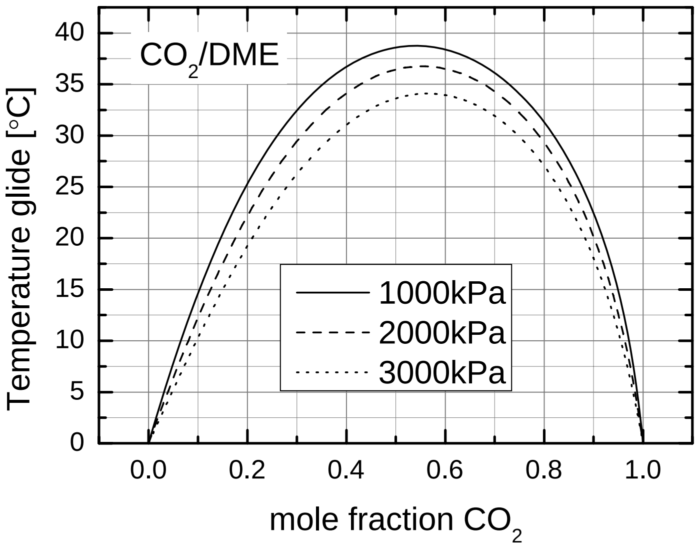

**Figure 9** Temperature glide at different mixture composition of $CO_2$/DME zeotropic mixture

## 5. Conclusions

Isothermal vapor-liquid equilibrium data have been predicted for the binary mixture of $CO_2$ and DME at ten temperatures ranging from 273.15 to 386.56 K and pressure upto 7.9 MPa. BWR and MBWR equations of state and REFPROP version 8.0 (Lemmon *et al.*, 2007) have been used for the prediction of VLE data. Optimum binary interaction parameters for the BWR and MBWR equations of states have been found as 1.015 and 0.98, respectively. The predicted data of VLE by the BWR, MBWR equations of state have been compared with the experimental data of Tsang & Streett, 1981. In the present prediction, BWR equation of state shows better agreement with the experimental data than the MBWR equation of state and REFPROP version 8.0. Further analysis is necessary to check the applicability of MBWR equation of state (Nishiumi and Saito, 1975 ) for the $CO_2$/DME mixture at high temperature by adjusting the binary interaction parameter $m_{ij}$ and the mixture accentric factor. Moreover, MBWR equation of states proposed by other authors available in the literature may be used to check the applicability for the $CO_2$/DME mixture in the whole analysis range of the temperature and pressure. The REFPROP fails to calculate the VLE data near critical zone as their calculating binary interaction parameter is not sufficiently adjusted by the experimental data of $CO_2$/DME mixture. The VLE characteristics of $CO_2$/DME zeotropic mixture shows that the saturation pressure difference between $CO_2$ and DME at a fixed temperature is significantly large which can help to modulate the refrigeration system capacity by varying the composition of the mixture. The $CO_2$/DME mixture shows high temperature glide, which can be used to reduce the mean temperature difference between the refrigerant and the secondary fluid of a refrigeration system. This characteristics of $CO_2$/DME zeotropic mixture has potential of the COP enhancement for the refrigeration system.

**Nomenclature**

| | |
|---|---|
| ABS | absolute value |
| Cal | calculated value |
| Exp | experimental value |
| $f$ | fugacity |
| $m$ | interaction parameter |
| $P$ | pressure, (Pa) |
| R | universal gas constant, (l atm $mol^{-1}$ $K^{-1}$) |
| $T$ | temperature, (K) |
| $x$ | liquid mole fraction |
| $y$ | vapor mole fraction |
| $\rho$ | density, (kg $m^{-3}$) |
| $\omega$ | accentric factor |

**Subscripts**

| | |
|---|---|
| c | critical |
| *i* | component 1, 2 |
| *j* | component 1, 2 |
| l | liquid |
| v | vapor |
| 1 | $CO_2$ |
| 2 | DME |

**Superscripts**

| | |
|---|---|
| sat | saturation |

## References

Afroz H.M.M., Miyara A., Tsubaki K., 2008. Heat transfer coefficients and pressure drops during in-tube condensation of $CO_2$/DME mixture refrigerant. *International Journal of refrigeration*, Vol. 31, No.8, pp. 1458-1466.

Arora C.P., 1967. Power saving in refrigerating machines using mixed refrigerants. *Proceedings*, 12th International Congress of Refrigeration, IIR, pp. 397-409.

Arora C.P., 1971. Low temperatures in refrigerating machines with R12 and R13 mixtures. *Proceedings*, 13th International Congress of Refrigeration, IIR, pp. 621-327.

Benedict M., Webb G. B., Rubin L. C., 1940. An Empirical equation for thermodynamic properties of light hydrocarbons and their mixtures: I. Methane, Ethane, Propane, and n-Butane. *Journal of Chemical Physics,* Vol.8, No.4, pp. 334–345.

Calm J.M., Hourahan G.C., 2007. Refrigerant data update. *HPAC Engineering,* Vol.79, No.1, pp.50-64.

Didion D.A., Bivens D.B., 1990. Role of refrigerant mixtures as alternatives to CFCs. *International Journal of Refrigeration,* Vol.13, pp. 163-175.

Jakobs R., Kruse H., 1979. The use of non-azeotropic refrigerant mixtures in heat pumps for energy savings. *International Journal of Refrigeration,* Vol.2, pp. 29-33.

Koyama S, Takato N, Kuwahara K, Jin D, Xue J, Miyara A., 2006. Experimental study on the performance of a refrigerant mixture $CO_2$/DME system. In: Proc. JSRAE Annual Conf., JASRAE, p133-136 [In Japanese].

Lemmon E.W., Huber M.L., McLinden M.O., 2007. Reference fluid thermodynamic and transport properties. NIST standard reference database 23, Ver.8.0.

Nishiumi H., Saito S., 1975. An improved generalized BWR equation of state applicable to low reduced temperatures. *Journal of Chemical Engineering, Japan*, Vol.8, No.5, pp. 356-360.

Onaka Y, Miyara A, Tsubaki K, Koyama S., 2007. Performance analysis on heat pump cycle of $CO_2$/DME mixture refrigerant. In: Proc. JSRAE Annual Conf., JASRAE, p333-336 [In Japanese].

Rajapaksha L., 2007. Influence of special attributes of zeotropic refrigerant mixtures on design and operation of vapor compression refrigeration and heat pump systems. *Energy conversion and management,* Vol.48, pp. 539-545.

Saito S., 1976. Basic of equilibrium property calculation. Baifukan, Tokyo, Japan, (in Japanese language).

Tamura S., Tsuji T., 2006. DME data book. KHK, Tokyo, (in Japanese language).

Tsang C. Y., Streett W. B., 1981. Vapor-liquid equilibrium in the system Carbon Dioxide/ Dimethyl Ether. *Journal of Chemical Engineering Data,* Vol.26 , pp. 155-159.

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