High-pressure Vapor-Liquid Equilibrium Studies for DME-CO₂-CH₃OH and DME-CO₂-C₂H₅OH Systems[*]

ZHENG Danxing(郑丹星)[**], **WU Xianghong**(武向红), **CAO Wen**(曹文) and **WANG Ning**(王宁)
School of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Abstract In this study, the Gibbs-Duhem equation was applied to make the thermodynamic consistency test and thermodynamic model estimation for systems of CO_2-DME (dimethyl ether), DME-CH_3OH, CO_2-CH_3OH and DME-C_2H_5OH systems on the basis of the vapor-liquid equilibrium (VLE) experimental data in published reports. And the NRTL binary interaction parameters of the systems mentioned above were regressed by the VLE data and were subjected to a thermodynamic consistency test because the study showed that PR-NRTL model combination was appropriate for the four systems mentioned above. The regressed binary interaction parameters were used to estimate the VLE for DME-CO_2-CH_3OH at temperatures of 313.15K and 333.15K, and the estimated result was coincident with the experimental data. On the basis of the predicted VLE data for systems of DME-CO_2-CH_3OH and DME-CO_2-C_2H_5OH, the VLE behaviors of the two systems were studied by the phase diagrams of these two ternary systems, with the forms of both the two dimensional and three dimensional phase diagrams, respectively.
Keywords phase equilibria, model reduction, dimethyl ether, phase diagram

1 INTRODUCTION

Dimethyl ether is considered to be a clean fuel of the 21st century. The technique of directly producing DME from coal contributes much to the efficient use of energy and limiting the emission of CO_2 and promotes the implementation of the clean-coal tactic[1]. With the development of the interrelated techniques, the study of high pressure vapor liquid equilibrium (VLE) from multi-species systems with DME and CO_2 has become the focus of studies in the recent years[2—6].

The material description of the above-mentioned VLE data for CO_2-DME, DME-CH_3OH, C_2H_5OH-DME, CO_2-CH_3OH, and CO_2-C_2H_5OH systems including the reported time and the regions of pressure and temperature of experimental conditions are listed in Table 1. The table also shows the data for the ternary system of DME-CO_2-CH_3OH[2—13].

In early studies, researchers began to investigate the VLE models for these systems. The Redilich-Kister equation, Peng-Robinson equation, NRTL equation, UNIFAC equation, UNIQUAC equation, and Margules equation are mentioned frequently in their researches. In these articles, the models and parameters were always appropriate for only one system. A model that could be applied to any system would be more useful[14—16].

To focus on proposing a reasonable model and demonstrate its applicability to several systems, this study made a thermodynamic consistency test for the experimental data of four binary systems composed of CO_2-DME, DME-CH_3OH, C_2H_5OH-DME, and CO_2-CH_3OH, on the basis of the binary system data involving species such as CO_2, DME, CH_3OH, and C_2H_5OH. The rechecking test was applied to these three systems, and then, the model was used in the study of the two ternary systems composed of DME-CO_2-CH_3OH and DME-CO_2-C_2H_5OH, on the basis of the predicted VLE data and plotted phase diagrams with the forms of planar and three-dimensional forms, respectively.

2 THERMODYNAMIC CONSISTENCY TEST OF EXPERIMENTAL DATA

Gibbs-Duhem equation imposes a constraint on activity coefficients that may not be satisfied by experimental values containing a systematic error[17—19].

$$\sum_i x_i \mathrm{d} \ln \gamma_i = 0 \quad (i=1,\ 2) \tag{1}$$

At VLE state, the fugacities of all species for vapor phase and liquid phase have

$$y_i p \hat{\phi}_i^g \left(T, p, \underline{y}\right) = x_i \gamma_i \left(T, \underline{x}\right) f_i^\theta \quad (i=1, 2) \tag{2}$$

Then the system pressure is

$$p = \sum_{i=1}^{2} y_i p = \sum_{i=1}^{2} x_i \gamma_i f_i^\theta / \hat{\phi}_i^g \tag{3}$$

The excess Gibbs energy of a binary system can be written as:

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{4}$$

Differentiation of Eq.(4) with respect to x_1 and x_2, respectively, then substituting them in Eq.(1) gives:

$$\ln \gamma_1 = \frac{G^E}{RT} + x_2 \frac{\mathrm{d}}{\mathrm{d}x_1}\left(\frac{G^E}{RT}\right) \tag{5}$$

Table 1   VLE data for the systems that composed of CO$_2$, DME, CH$_3$OH, and C$_2$H$_5$OH

System	Temperature, K	Pressure, MPa	Ref.
CO$_2$-DME	273.15, 288.2, 308.65, 320.06, 335.17, 350.2, 360.07, 370.13, 377.57, 386.56	3.10, 4.41, 6.26, 7.25, 7.93, 7.39, 7.11, 6.11, 6.37, 5.70	[2]
	282.20, 308.65, 320.12	4.12, 6.33, 6.79	[3]
DME-CH$_3$OH	273.15, 293.15, 313.15, 333.15, 353.15, 373.15, 393.15, 413.15, 433.15, 453.15	0.255, 0.521, 0.900, 1.461, 2.243, 3.256, 4.663, 5.481, 6.081, 6.674	[4]
	253.52, 352.68	0.035, 1.042	[5]
	353.15	2.24	[6]
DME-C$_2$H$_5$OH	332.95, 353.25, 373.15	1.253, 1.772, 3.160	[7]
	293.15	0.5125	[8]
CO$_2$-CH$_3$OH	250, 273.15, 290, 310, 330	1.586, 3.447, 5.164, 7.743, 10.645	[9]
	313.2	8.21	[10]
	313.4	7.713	[11]
CO$_2$-C$_2$H$_5$OH	313.2	8.15	[10]
	304.2, 308.2	7.22, 7.67	[12]
	333.5, 453.2	2.0, 14.0	[13]
DME-CO$_2$-CH$_3$OH	313.15, 333.15	4.88, 6.14	[6]

$$\ln \gamma_2 = \frac{G^{\mathrm{E}}}{RT} + x_1 \frac{\mathrm{d}}{\mathrm{d}x_2}\left(\frac{G^{\mathrm{E}}}{RT}\right) \quad (6)$$

Substitution into Eq.(3) reduces it to:

$$p = x_1 \frac{f_1^{\theta}}{\hat{\phi}_1^{\mathrm{g}}} \exp\left[\frac{G^{\mathrm{E}}}{RT} + x_2 \frac{\mathrm{d}}{\mathrm{d}x_1}\left(\frac{G^{\mathrm{E}}}{RT}\right)\right] +$$
$$x_2 \frac{f_2^{\theta}}{\hat{\phi}_2^{\mathrm{g}}} \exp\left[\frac{G^{\mathrm{E}}}{RT} + x_1 \frac{\mathrm{d}}{\mathrm{d}x_2}\left(\frac{G^{\mathrm{E}}}{RT}\right)\right] \quad (7)$$

Combined with Eqs.(2), (5), (6), and (7), we have

$$y_{i,\mathrm{cal}} = x_i \gamma_i f_i^{\theta} / p \hat{\phi}_i^{\mathrm{g}} \quad (8)$$

If the average absolute deviations between the experimental values and the calculation values are less than 0.01, it could be considered that the data has passed through the thermodynamics consistency test[14]. The model parameters used in the thermodynamic consistency test come from "Vapor-Liquid Equilibrium Data Collection" by Gemehling et al.[20].

This study applies the above approach to calculate the values of $y_{i,\mathrm{cal}}$ for four systems composed of CO$_2$-DME, DME-CH$_3$OH, C$_2$H$_5$OH-DME, and CO$_2$-CH$_3$OH, shown in Table 1. Constructed between $\Delta y = y_{\mathrm{cal}} - y_{\mathrm{exp}}$ and x_i, if the experimental data is distributed more widely on the abscissa, the concentration extensions of the data are extensive. The consistency of the data is comparatively better, if the experimental data is concentrated mostly on $\Delta y = 0$ on the vertical coordinate.

The consistency of only a few data tested one by one in Table 1 is better. For instance, the test results shown in Figs.1—4 are for the system composed of

CO$_2$-DME at 308.65K by Jonasson et al.[3], the system composed of DME-CH$_3$OH at 353.15K by Teodorescu et al.[6], the system composed of C$_2$H$_5$OH-DME at 293.15K by Dahlhoff et al.[8], and the system composed of CO$_2$-CH$_3$OH at 273.15K by Hong et al.[9]. The concentrations of data for these four systems are distributed widely; furthermore, the average absolute deviation of the mole fraction of the vapor phase between the experimental and the calculated value is less than 0.01. It is obvious that most of the experimental data points focus on $\Delta y = 0$ on the abscissa in the figures. The average absolute deviations of the mole fraction of the vapor phase for the experimental value and the calculated value are 0.00845 for CO$_2$-DME, 0.00992 for DME-CH$_3$OH, 0.00025 for DME-C$_2$H$_5$OH, and 0.00042 for CO$_2$-CH$_3$OH. Therefore, the results prove the validity of the experimental data for these four systems, which were all subjected to the thermodynamics consistency test.
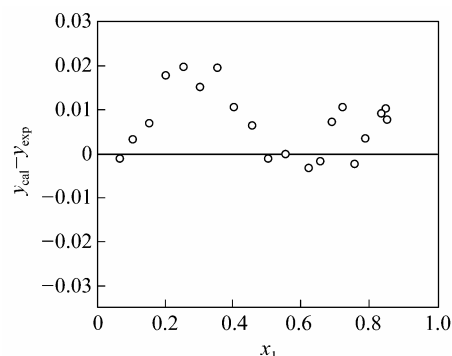

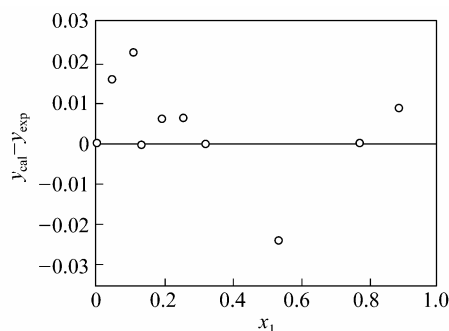**Figure 1   Test result for CO$_2$ (1)-DME (2) at 308.65K[3]**

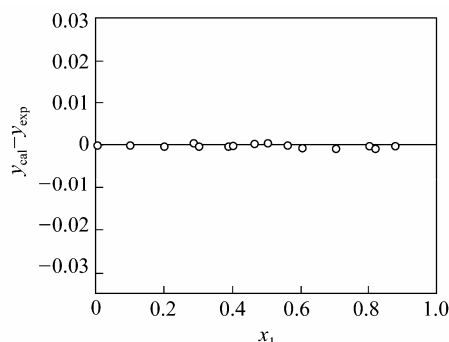**Figure 2   Test result for DME(1)-CH$_3$OH(2) at 353.15K[6]**

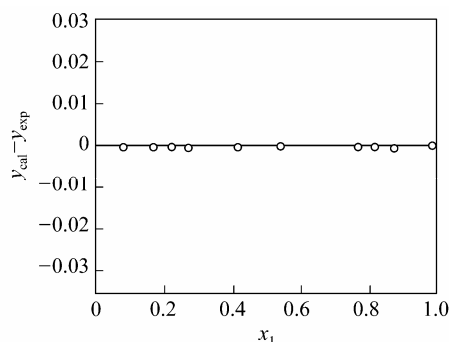**Figure 3   Test result for C$_2$H$_5$OH(1)-DME(2) at 293.15K[8]**

Figure 4   Test result for CO$_2$(1)-CH$_3$OH(2) at 273.15K[9]

3   STUDY FOR BINARY SYSTEMS COMPOSED OF CO$_2$-DME, DME-CH$_3$OH, DME-C$_2$H$_5$OH, AND CO$_2$-CH$_3$OH

The binary parameters of NRTL model $(g_{ij}-g_{jj})/R$, $(g_{ji}-g_{ii})/R$ and α_{ij} were obtained by regressing the experimental data as shown in Table 2 for five binary systems composed of CO$_2$-DME, DME-CH$_3$OH, CO$_2$-CH$_3$OH, and DME-C$_2$H$_5$OH, and CO$_2$-C$_2$H$_5$OH .

To cite instances in illustration of the validity of adopting the PR-NRTL model combination in this study, the detailed estimations for the four binary systems of CO$_2$-DME, DME-CH$_3$OH, CO$_2$-CH$_3$OH and DME-C$_2$H$_5$OH are listed in Table 3. The deviations of the liquid phase for the four systems are very small. The average absolute deviations of the mole fraction of the vapor phase between the experimental values and the predicted values are 0.00036 for CO$_2$-DME, 0.00043 for DME-CH$_3$OH, 0.00019 for C$_2$H$_5$OH-DME and 0.00030 for CO$_2$-CH$_3$OH.

4   PHASE DIAGRAMS OF TERNARY SYSTEMS COMPOSED OF CO$_2$, DME, CH$_3$OH, AND C$_2$H$_5$OH

In the calculation of ternary systems' VLE data, the temperature, pressure, and the ratio of x_2/x_3 are fixed, where, x_2 is the mole fraction of CH$_3$OH or C$_2$H$_5$OH in the system and x_3 is the mole fraction of DME. By changing x_1, which is the mole ratio of CO$_2$, a series of data can be calculated for illustrating a part of the VLE line in the phase diagram. For a set of given temperatures and pressures, several parts of lines can be plotted by altering the ratio of x_2/x_3. The whole VLE line can be obtained by connecting these lines.

With the data calculated by the PR-NRTL model combination, diagrams of different temperatures and pressures could be plotted. First, a set of

Table 2   Interaction parameters of the NRTL model

Component i	Component j	$(g_{ij}-g_{jj})/R$	$(g_{ji}-g_{ii})/R$	α_{ij}
CO$_2$	DME	426.2114	−282.5555	0.3000
DME	CH$_3$OH	−546.9672	505.0935	0.3000
CO$_2$	CH$_3$OH	771.0888	−1.3137	0.3000
DME	C$_2$H$_5$OH	311.5694	−3.5719	0.3000
CO$_2$	C$_2$H$_5$OH	525.9896	−76.5646	0.3000

Table 3   Results estimated by the PR-NRTL model combination

System	Deviation of pressure Δp, MPa		Deviation of vapor phase Δy_1	
	Maximum	Average	Maximum	Average
CO$_2$ + DME	0.05478	0.01194	0.02157	0.00845
DME + CH$_3$OH	0.01593	0.00441	0.02373	0.00922
C$_2$H$_5$OH+DME	0.00069	0.00030	0.00064	0.00025
CO$_2$+ CH$_3$OH	0.02206	0.00916	0.00063	0.00042

temperature and pressure were selected. Then, by changing the proportion of the three species' composition, a series of VLE data could be calculated. Finally, with these data, it was possible to plot VLE points in a ternary system phase diagram. The vapor region line was obtained by connecting the vapor points. The liquid region line was also plotted in the same way. Therefore, the lines in the phase diagram are concise and follow regular forms.

Figure 5 shows the phase diagram of the DME-CO₂-CH₃OH system at 2.57MPa and 313.15K. There are two real lines on the left and right, respectively, which are the liquid phase line and the vapor phase line. The blank band at the left corner is the liquid phase and the blank band at the right corner is the vapor phase. Between them is the coexisting band of the vapor phase and liquid phase. The dashed lines connecting the given VLE points in the liquid phase line and vapor phase line denote the phase separating behaviors of the system. In Fig.5, either pure DME or pure CO₂ are vapor at 0.62MPa and 313.15K, respectively; therefore, the region that is close to pure DME or CO₂ is a vapor phase as well. The liquid phase of CH₃OH is similar.
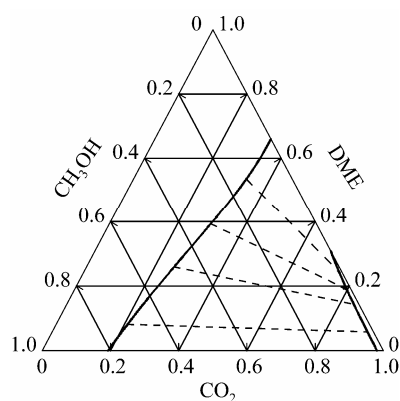

Figure 5   Phase diagram for DME-CO₂-CH₃OH at 2.57MPa and 313.15K

Taking a subsequent step, the above figures were put at pressures of 0.62MPa, 1.36MPa, 2.57MPa, and 3.81MPa at the same temperatures, respectively, together to form a three dimensional diagram as shown in Fig.6. It is made up of four planar diagrams parallel to each other corresponding to figures as in Fig.5, and arranged by pressure, which is marked on the left axis of the figure. The effect of changing the pressure for the liquid phase line and the vapor phase line is illustrated clearly. By integrating these four figures, a general understanding of the ternary system's VLE state at 313.15K can be obtained.

In Fig.6, the plotted results can be visually compared with the experimental data of Teodorescu *et al.*[6]. Point A₁ is the liquid composition of the experimental data at 0.62MPa and 313.15K, and points B₁, C₁, and D₁ are the liquid compositions of 1.36MPa,

2.57MPa and 3.81MPa, respectively. As shown in Fig.6, A₁, B₁ and C₁ almost tally with the protected values in the liquid phase lines. However, D₁ does not accord well, which shows that the PR-NRTL model combination could predict liquid phase composition better at lower and medium pressure for the DME-CO₂-CH₃OH system. Furthermore, point A₂ is the vapor composition of the experimental data at 0.62MPa and 313.15K and points B₂, C₂, and D₂ are liquid composition points of 1.36MPa, 2.57MPa, and 3.81MPa, respectively. Point A₂ does not agree with the vapor phase line well; however, points B₂, C₂, and D₂ all lie almost in the vapor phase lines. This shows that the PR-NRTL model combination could predict vapor behavior better at medium and high pressure for the DME-CO₂-CH₃OH system.
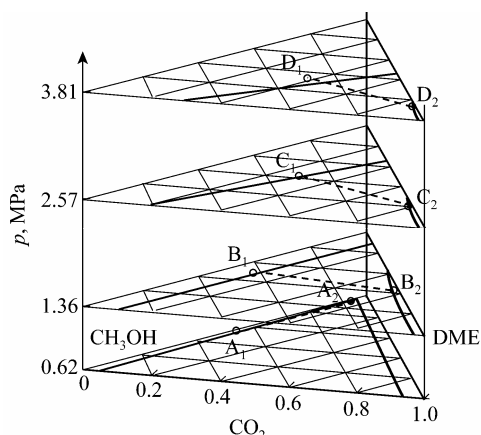

Figure 6   Three-dimensional phase diagram of DME-CO₂-CH₃OH at 313.15K

Correspondingly, the phase diagram for the DME-CO₂-C₂H₅OH system at a pressure of 2.5MPa and at a temperature of 313.15K is illustrated in Fig.7. Fig.8 shows the three dimensional diagram of the DME-CO₂-C₂H₅OH system at 313.15K.
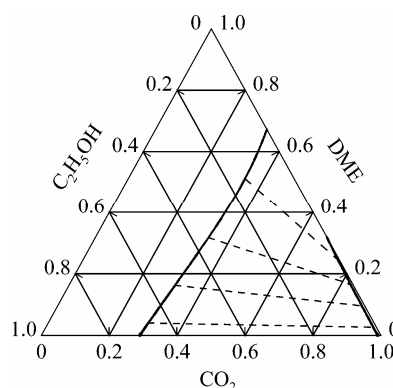

Figure 7   Phase diagram for DME-CO₂-C₂H₅OH at 2.5MPa and 313.15K

Comparing these two series of diagrams, their trends are quite similar when the pressure is increased. However, the liquid and vapor phase lines of the DME-CO₂-CH₃OH system are different from that of
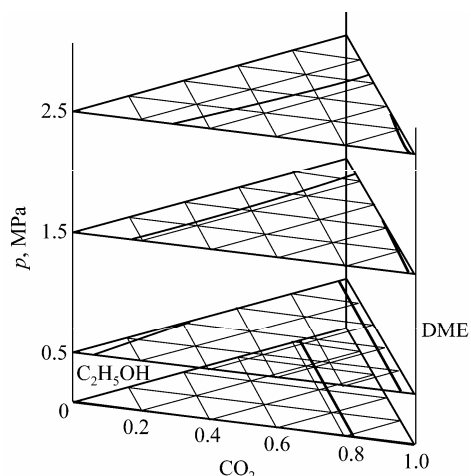
Figure 8   Three dimensional phase diagram of DME-CO$_2$-C$_2$H$_5$OH at 313.15K

the DME-CO$_2$-C$_2$H$_5$OH system at the same pressure, because the solubility of CO$_2$ in CH$_3$OH is better than in C$_2$H$_5$OH, while the concentration of DME is almost the same in CH$_3$OH and C$_2$H$_5$OH.

From Fig.6 and 8, it is obvious that the VLE behaviors impacted by the pressure change for the two systems are quite similar because the equilibrium characteristics of CH$_3$OH or C$_2$H$_5$OH to CO$_2$ are the same as those of DME. The lower the pressure, the more evident is the influence of DME existence. When the pressure is higher than 1MPa, DME will become liquid. Thus, the vapor regions will be shrink with the increase of pressure and the liquid region will be gradually expanded. The vapor and liquid phase lines will cross at the DME axis when the pressure reaches about 0.9MPa, as the vapor pressure of DME is at 0.887MPa and 313.15K.

5   CONCLUSION

(1) On the basis of the Gibbs-Duhem equation and selecting the PR-NRTL model combination, thermodynamic consistency tests were conducted for the experimental vapor liquid data of CO$_2$-DME, DME-CH$_3$OH, DME-C$_2$H$_5$OH, and CO$_2$-CH$_3$OH on the basis of the published reports reported from 1980 to 2001. Some of them passed the test, involving the data by Jonasson *et al*. for the CO$_2$-DME system at 308.15K, Teodorescu *et al*. for the DME-CH$_3$OH system at 353.15K, Dahlhoff *et al*. for the DME-C$_2$H$_5$OH system at 293.15K, and Hong *et al*. for the CO$_2$-CH$_3$OH system at 290K.

(2) The study of the binary systems composed of CO$_2$-DME, DME-CH$_3$OH, CO$_2$-CH$_3$OH, and DME-C$_2$H$_5$OH proved that the PR-NRTL model combination is appropriate for these four binary systems.

(3) This work regressed on the parameters of the NRTL model form CO$_2$-DME, DME-CH$_3$OH, C$_2$H$_5$OH-DME, CO$_2$-CH$_3$OH, and CO$_2$-C$_2$H$_5$OH binary systems on the basis of the data passed through ther-

modynamics consistency test, then predicted the VLE data of DME-CO$_2$-CH$_3$OH, and DME-CO$_2$-C$_2$H$_5$OH two ternary systems at 313.15K and at several pressures.

(4) With the data predicted by the PR-NRTL model, two series of planar ternary system phase diagrams were plotted, and then the three dimensional diagrams were plotted as well.

(5) From analyzing the VLE behaviors of these diagrams, such as the changes of vapor and liquid phase lines, the fundamental characteristics and interactive relationships of species in the systems were evident. And in the three dimensional diagram of the DME-CO$_2$-CH$_3$OH system, the experimental data of Teodorescu *et al*.[6] almost tallied quite closely with the data predicted by the PR-NRTL model.

NOMENCLATURE

$(g_{ij}-g_{jj})/R$, $(g_{ji}-g_{ii})/R$, α_{ij}	binary parameters of NRTL model
f	fugacity
p	pressure, kPa
T	temperature, K
x	liquid mole fraction
y	vapor mole fraction
γ	activity coefficient
ϕ	fugacity coefficient

Subscripts

cal	calculated data
exp	experimental data
g	gas or vapor phase
i, j, k	i, j, or kth component
θ	standard state
$\wedge$	property of a component in a mixture

REFERENCES

1 Adachi, Y., Komoto, M., Watanabe, I., Ohno, Y., Fujimoto, K., "Effective utilization of remote coal through dimethyl ether synthesis", *Fuel*, **79**(3), 229—234(2000).

2 Tsang, C.Y., Streett, W.B., "Vapor-liquid equilibrium in the system carbon dioxide/dimethyl ether", *J. Chem. Eng. Data*, **26**(2), 155—159(1981).

3 Jonasson, A., Persson, O., Fredenslund, A., "High-pressure solubility of carbon dioxide and carbon monoxide in dimethyl ether ", *J. Chem. Eng. Data*, **40**(1), 296—300(1995).

4 Chang, E., Calado, J., Streett, W.B., "Vapor-liquid equilibrium in the system dimethyl ether/methanol from 0 to180℃ and at pressures to 6.7 MPa", *J. Chem. Eng. Data*, **27**(3), 293—298(1982).

5 Holldorff, H., Knapp, H., "Vapor-liquid-liquid equilibria of the binary mixtures methyl chloride-methanol and dimethyl ether-methyl chloride and of the ternary mixture dimethyl ether-methyl chloride-methanol", *Fluid Phase Equilibria*, **43**(3), 29—44(1988).

6 Teodorescu, M., Rasmussen, P., "High-pressure vapor-liquid equilibria in the systems nitrogen+dimethyl ether, methanol+dimethyl ether, carbon dioxide+dimethyl ether+methanol, and nitrogen+dimethyl ether+methanol", *J. Chem. Eng. Data*, **46**(3), 640—646(2001).

7 Elbaccouch, M., Elliott, J., "High-pressure vapor-liquid equilibrium for dimethyl ether+ethanol and dimethyl ether+ethanol+water", *J. Chem. Eng. Data*, **45**(6), 1081—1087(2000).

8 Dahlhoff, G., Fennig, P A., Hammer, H., Oorschot, M.V., "Vapor-liquid equilibria in quaternary mixtures of di-

methyl ether+n-butane+ethanol+water", *J. Chem. Eng., Data*, **45**(5), 887—892(2000).

9 Hong, J. H., Kobayashi, R., "Vapor-liquid equilibrium studies for the carbon dioxide-methanol system", *Fluid Phase Equilibria*, **41**(3), 269—276(1988).

10 Yoon, J. H., Lee, H.S., Lee, H., "High-pressure vapor-liquid equilibria for carbon dioxide+methanol, carbon dioxide+ethanol, and carbon dioxide+methanol+ethanol", *J. Chem. Eng. Data*, **38**(1), 53—55(1993).

11 Suzuki, K., Sue, H., Itou, M., Smith, R.L., Inomata, H., Saito, S., "Isothermal vapor-liquid equilibrium data for binary systems at high pressures: carbon dioxide-methanol, carbon dioxide-ethanol, carbon dioxide-1-propanol, methane-ethanol, methane-1-propanol, ethane-ethanol, and ethane-1-propanol systems", *J. Chem. Eng. Data*, **35**(2), 63—66(1990).

12 Takishima, S., Saiki, K., Arai, K., Saito, S., "Phase equilibria for CO₂-C₂H₅OH-H₂O system", *J. Chem. Eng. Japan*, **19**(2), 48—56(1986).

13 Zhu, H.G., Tian, Y.L., Chen, L., "High-pressure phase equiliria for binary ethanol system containing supercritical CO₂", *Chin. J. Chem. Eng.*, **9**(3), 322—325(2001).

14 Valtza, A., Chapoya, A., Coqueleta, C., Paricaudb, P., Richona, D., "Vapour–liquid equilibria in the carbon dioxide–water system,measurement and modelling from 278.2 to 318.2K", *Fluid Phase Equilibria*, **226**, 333—344(2004).

15 Cassel, E., Matt, M., Rogalski,M., Solimande, R., "Phase equilibria modeling for bonary systems that contain CO₂", *Fluid Phase Equilibria*, **134**, 63—74(1997).

16 Keshtar, A., Jalali, F., Moshfeghian, M., "Evaluation of vapor-liquid equilibrium of CO₂ binary system using UNIQUAC-based huron-vidal mixing rules", *Fluid Phase Equilibria*, **140**, 107—128(1997).

17 Jackson, P.L., Wilsak, R.A., "Thermodynamic consistency tests based on the Gibbs-Duhem equation applied to isothermal, binary vapor-liquid equilibrium data: date evaluation and model testing", *Fluid Phase Equilibria*, **103**(2), 155—197(1995).

18 Fredenslund, P., Gmehling, J., Rasmussen, P., Vapor-Liquid Equilibria Using UNFIFAC, Elsevier Scientific Publishing Co., Amsterdam, (1977).

19 Valderrama, J., Alvarez, V., "A versatile thermodynamic consistency test for incomplete phase equilibrium data of high-pressure gas-liquid mixtures", *Fluid Phase Equilibria*, **226**, 149—159(2004).

20 Gemehling, J., Onken, U., Rarey-Nies, J.R., Vapor-liquid Equilibrium Data Collection, Chemistry Data Series, Frnkfurt/Main: DECHEMA, 1981—1988.