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Measurement of Vapor–Liquid Equilibrium for the DME + Diisopropyl Ether Binary System and Correlation for the DME + CO_2 + Diisopropyl Ether Ternary System

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Abstract Vapor–liquid equilibrium (VLE) data have been measured with a static-type VLE apparatus for the dimethyl ether (DME)–diisopropyl ether (DIPE) binary system at five temperatures within the range from 293.04 K to 352.70 K. An isothermal correlation for the experimental data has been carried out based on the Peng-Robinson equation of state. The regressed binary interaction parameters were used to estimate VLE for the DME–CO_2–DIPE ternary system at 298.15 K. From the study, it is demonstrated that DIPE is an excellent absorbent for separation in the DME synthesis process from syngas.

Keywords CO_2 Capture · Diisopropyl ether · DME absorption separating · Vapor–liquid equilibria

List of Symbols

a, b	Parameters, Peng-Robinson equation of state
p	Pressure
p_c	Critical pressure
R	Universal gas constant
T	Temperature (K)
T_c	Critical temperature (K)
T_r	Reduced temperature
V	Molar volume

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Greek

α Function, Peng-Robinson equation of state
ω Acentric factor

1 Introduction

Dimethyl ether (DME) is considered to be a clean fuel of the twenty-first century, and the emission of CO_2 has been identified as the major contributor to global warming and climate change. The technique of DME synthesis from syngas contributes much to the efficient use of energy by limiting the emission of CO_2 and promotes implementation of clean-coal strategies [1]. Diisopropyl ether (DIPE), an excellent solvent, is expected to absorb DME. Therefore, the vapor–liquid equilibrium (VLE) data for CO_2–DME–DIPE are very important for DME absorption for separation in the DME synthesis process from syngas.

The VLE data for the CO_2–DME [2,3] binary system have been obtained by Tsang and Streett [2] and by Jonasson et al. [3]. The VLE data for the CO_2–DIPE system have been obtained by Zhang et al. [4] only at temperatures of 299.15 K, 308.65 K, and 318.15 K. Accordingly, after exploring some VLE experimental methods of other researchers [5–7], this study developed a VLE apparatus for studying the DME–DIPE binary system. Then, the experimental data have been analyzed based on the Peng-Robinson (PR) equation of state (EoS). The regressed binary interaction parameters were used to study the VLE behavior for the DME–CO_2–DIPE ternary system.

2 Experimental Study of the DME + DIPE Binary System

2.1 Chemicals and Apparatus

Dimethyl ether with a purity greater than 99.99 mass % is purchased from Shandong Jiutai Company. Diisopropyl ether is purchased from Tianjin Jinke Fine Chemical Company; the purity was greater than 99 mass %. These chemicals are used without further purification.

The VLE apparatus of this study is shown in Fig. 1. There are mainly three sections that include the high-pressure equilibrium cell, the input of sample, and the on-line gas chromatographic (GC) system for determining the compositions of the equilibrium phases.

The equilibrium cell was made of stainless steel with an internal volume of 160 mL and a maximum operation pressure of 6 MPa. The water bath was mixed by a stirrer, cooled by a refrigerator, and heated by an electric heater to ensure an even temperature. A temperature controller (Model LC-6, JULABO, Germany) was used to control the temperature of the water bath. The temperature stability is ±0.03 K. The temperature of the equilibrium cell was measured with a Pt-100 resistance temperature probe, and connected to the temperature controller (Model LC-6, JULABO, Germany). The combined uncertainty in temperature is 50 mK. The pressure was measured by a pressure transducer (Model PTX7511, GE Co.) with a full scale of 0 to 6 MPa, and the uncertainty in pressure is 0.0035 MPa.

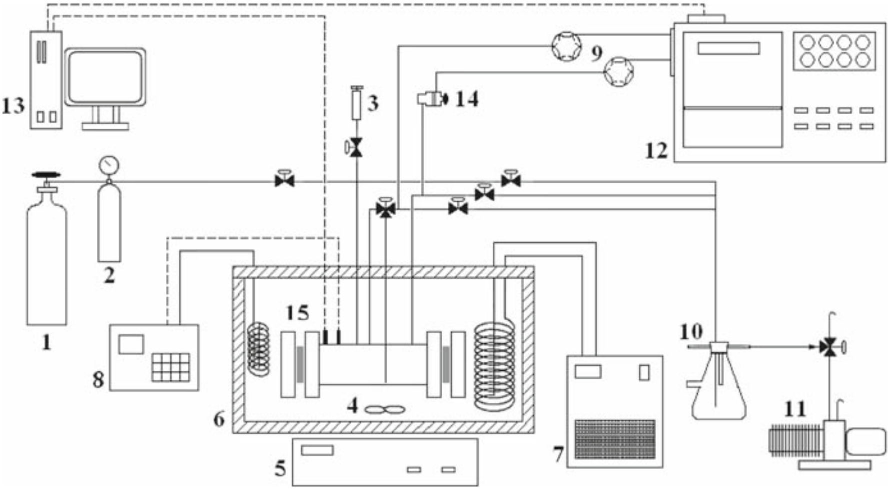

Fig. 1 Schematic diagram of the experiment apparatus: 1. Gas cylinder, 2. Gas storage tank, 3. Liquid injector, 4. Stirrer, 5. Magnetic mixer, 6. Constant-temperature water bath, 7. Refrigerator, 8. Temperature controller, 9. Six-way valve, 10. Cushion tank, 11. Vacuum pump, 12. Gas chromatograph, 13. Computer, 14. Relief valve, 15. Equilibrium cell

On-line analyses for the equilibrium compositions were carried out using a gas chromatograph produced by Shimaden Co. (Model GC-9A) with an estimated uncertainty of 0.001 in mole fraction. A vapor six-way valve (Shimaden Co.) is used to control the injection volume (1 mL). A liquid six-way valve is a Valco Model C1 with a 2 μL sample loop.

2.2 Results and Discussion

In this study, p–T–x–y data for the DME–DIPE binary system were measured at 293.04 K, 312.93 K, 332.90 K, and 352.70 K and pressures ranging from 0.26 MPa to 1.13 MPa. The measured VLE compositions at various temperatures and pressures for this binary mixture are shown in Table 1. The subscript exp denotes the experimental value to describe the mole fractions of the liquid and vapor phases, i.e., x and y, respectively.

All the experimental results were correlated with the PR EoS [8,9], since the PR EoS has been widely used and is regarded as a reliable method at high pressures [10–12]. This can be expressed as follows:

$$p = \frac{RT}{V-b} - \frac{a\alpha}{V^2+2bV-b^2} \tag{1}$$

with

$$a = 0.45725R^2T_c^2/p_c \tag{2}$$

$$b = 0.0778RT_c/p_c \tag{3}$$

Table 1 VLE data for the DME (1)–DIPE (2) binary system

P (MPa)	$x_{\text{exp}}(1)$	$x_{\text{cal}}(1)$	$\Delta x(\%)$	$y_{\text{exp}}(1)$	$y_{\text{cal}}(1)$	$\Delta y(\%)$
$T = 293.04$ K						
0.560	0.4101	0.4140	0.39	0.9705	0.9684	−0.21
0.467	0.3557	0.3567	0.10	0.9636	0.9624	−0.12
0.400	0.3098	0.3100	0.02	0.9561	0.9552	−0.09
0.335	0.2659	0.2640	−0.19	0.9468	0.9461	−0.07
0.263	0.2237	0.2190	−0.47	0.9366	0.938	0.14
$T = 312.93$ K						
0.768	0.4332	0.4371	0.39	0.9511	0.9508	−0.03
0.656	0.3773	0.3795	0.22	0.9392	0.9403	0.11
0.525	0.3038	0.3053	0.15	0.9199	0.9212	0.13
0.447	0.2627	0.2627	0	0.9087	0.9076	−0.11
0.335	0.2131	0.2084	−0.47	0.8834	0.8895	0.61
$T = 332.90$ K						
0.935	0.3925	0.4021	0.96	0.9033	0.9092	0.59
0.823	0.3421	0.3511	0.90	0.8898	0.8911	0.13
0.666	0.2893	0.2926	0.33	0.8678	0.8699	0.21
0.459	0.2094	0.2075	−0.19	0.8203	0.8247	0.44
0.374	0.1777	0.1736	−0.41	0.8010	0.8026	0.16
$T = 352.70$ K						
1.130	0.3668	0.3781	1.13	0.8544	0.8558	0.14
1.001	0.3295	0.3373	0.78	0.8385	0.8374	−0.11
0.840	0.2836	0.2868	0.32	0.8092	0.8112	0.2
0.670	0.2360	0.2344	−0.16	0.7775	0.7797	0.22
0.498	0.1853	0.1800	−0.53	0.7366	0.7391	0.25

$$\alpha = \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\left(1 - T_{\text{r}}^{0.5}\right)\right]^2 \tag{4}$$

The mixing rule is

$$a\alpha = \sum_i \sum_j y_i y_j \, (a\alpha)_{ij} \tag{5}$$

$$b = \sum_i y_i b_i \tag{6}$$

$$(a\alpha)_{ij} = \left(1 - k_{ij}\right)\sqrt{(a\alpha)_i \, (a\alpha)_j} \tag{7}$$

$$k_{ij} = k_{ji} \tag{8}$$

$$k_{ii} = 0 \tag{9}$$

where k_{ij} indicates the binary interaction parameters for obtaining better agreement in mixture EOS calculations, which can be regressed by fitting the EOS to VLE data.

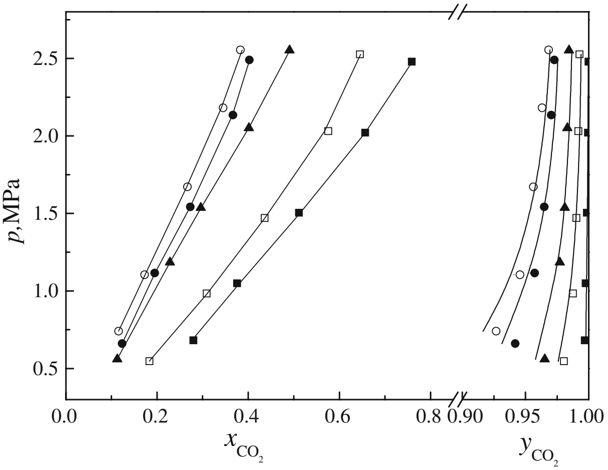

Fig. 2 VLE data of CO_2(1)–DIPE (2) system at five temperatures: (■) 265.15 K; (□) 273.15 K; (▲) 293.15 K; (●) 313.15 K; (○) 333.15 K.; –PR EOS

Table 2 Interaction parameters of the PR EoS for three binary systems composed of CO_2–DIPE, DME–DIPE, and CO_2–DME

Component *i*	CO_2	DME	CO_2
Component *j*	DIPE	DIPE	DME
k_{ij}	0.075	−0.013	−0.02

The critical properties and acentric factors used in the PR EoS were selected from the literature [13]. The measured data in this study agree well with the calculated data. The data are reported in Table 1. The subscript cal denotes the calculated values for the mole fractions of the liquid and vapor phases. The maximum relative deviation of the liquid phase is 1.13 %, and the average relative deviation is 0.41 %. The maximum relative deviation of the vapor phase is 0.61 %, and the average relative deviation is 0.20 %. The interaction parameter k_{ij} that was obtained is −0.013.

3 VLE Data of the CO_2 + Diisopropyl Ether Binary System

p–*T*–*x*–*y* data for the CO_2–DIPE binary system were measured previously in our laboratory at five temperatures, 265.15 K, 273.15 K, 293.15 K, 313.15 K, and 333.15 K, and at five pressures, 0.5 MPa, 1.0 MPa, 1.5 MPa, 2.0 MPa, and 2.5 MPa [14].

The experimental and calculated data at different temperatures are illustrated in Fig. 2. The interaction parameter k_{ij} of the PR EoS was obtained by regressing these experimental data. The interaction parameter k_{ij} is 0.075 at 298.15 K.

The interaction parameters k_{ij} of the PR EoS are shown in Table 2 for three binary systems composed of CO_2–DIPE, DME–DIPE, and CO_2–DME, in which the interaction parameter k_{ij} of CO_2–DME was obtained from Tsang and Streett [2].

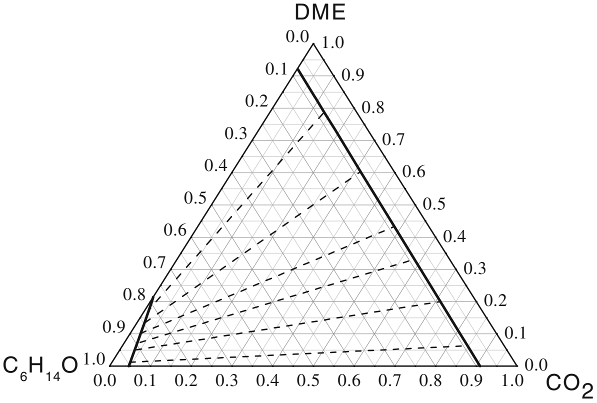

Fig. 3 Phase diagram for DME–CO_2–DIPE at 0.3 MPa and 298.15 K

4 Investigation of the DME + CO_2 + Diisopropyl Ether Ternary System

The regressed binary interaction parameters were used to estimate VLE for DME–CO_2–DIPE at 298.15 K. In the calculation of ternary systems, the temperature, pressure, and the ratio of x_2 versus x_3 are fixed, where x_2 is the mole fraction of DME in the system, and x_3 is the mole fraction of CO_2. By changing x_1, which is the mole ratio of DIPE, 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 versus x_3. The whole VLE line can be obtained by connecting these lines.

Figure 3 shows the phase diagram of the DME–CO_2–DIPE ternary system at 0.3 MPa and 298.15 K. 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–liquid phases. 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.

The phase diagram of the DME–CO_2–DIPE system at other pressures can be determined with this method [15]. Figures 4 and 5 show phase diagrams of the DME–CO_2–DIPE system at 0.4 MPa and 0.5 MPa.

It can be seen from Figs. 3, 4, and 5 that the liquid-phase lines have a trend to move right with increasing pressure. The ranges of the liquid-phase are gradually extended. At this temperature, the liquid mole fraction of DME increases significantly with increasing pressure; it changes from 0.2146 to 0.3571. However, the change of the CO_2 in the liquid phase is not prominent when the pressure increases, as it only changes from 0.0472 to 0.0812. In Fig. 5, the liquid mole fraction of DME can reach a value of 0.36 at 0.5 MPa. It agrees with the correlated data calculated from the experimental data of this study.

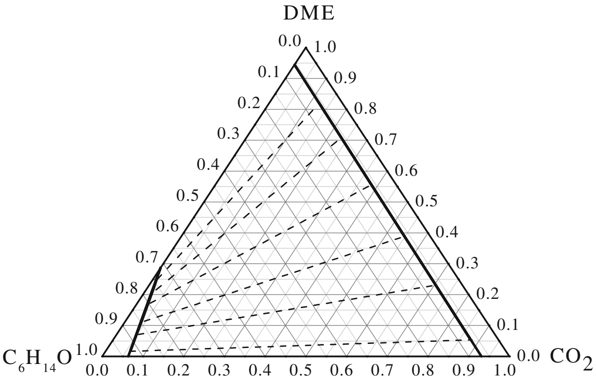

Fig. 4 Phase diagram for DME–CO_2–DIPE at 0.4 MPa and 298.15 K

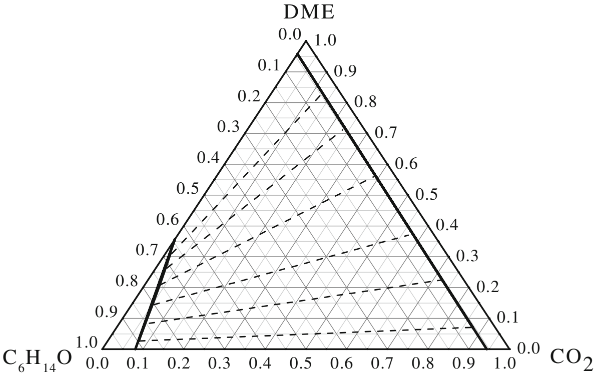

Fig. 5 Phase diagram for DME–CO_2–DIPE at 0.5 MPa and 298.15 K

5 Conclusions

A VLE study for the DME–CO_2–DIPE ternary system is presented in this article. The VLE data of the DME–DIPE binary system were measured at 293.04 K, 312.93 K, 332.90 K, and 352.70 K and correlated with the PR EoS. The calculated data agree well with the measured data. Then, the regressed interaction parameters of the three binary systems composed of CO_2–DIPE, DME–DIPE, and CO_2–DME were used to estimate VLE for the DME–CO_2–DIPE ternary system at 298.15 K. The VLE behavioral study of the ternary system demonstrated that DIPE is an excellent absorbent for DME for separation in the DME synthesis process from syngas.

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