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Vapor−Liquid Equilibrium Data of the Binary Systems in Oxidative Carbonylation of Dimethyl Ether Synthesizing Dimethyl Carbonate

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Vapor−liquid equilibrium data for the carbon monoxide + dimethyl carbonate, oxygen + dimethyl carbonate, and dimethyl ether + dimethyl carbonate systems were measured at 293 K, 313 K, 353 K, and 373 K and at elevated pressures up to 12.00 MPa. The measurements were carried out in a cylindrical autoclave with a moveable piston and an observation window. The experimental data were correlated using the Peng−Robinson−Stryjek−Vera equation of state (EOS) with the two-parameter van der Waals II mixing rule.

Introduction

Dimethyl carbonate (DMC), referred to a cornerstone of organic synthesis and a green chemical, is one of the most important chemicals in the chemical industry because of its negligible ecotoxicity, low bioaccumulation, persistence, and high reactive activity.[1] It is being comsidered as an alternative fuel additive to replace methyl-*tert*-butyl ether (MTBE).[2] The synthesis chemistry of DMC has been reported,[3,4] and of interest is the nonphosgene oxidative carbonylation of dimethyl ether to DMC in commercial processes.

$$CO + 0.5O_2 + CH_3OCH_3 \rightarrow CH_3OCOOCH_3 \qquad (1)$$

The thermodynamic calculation shows that the free energy of the above reaction is $-189\ \text{kJ}\cdot\text{mol}^{-1}$ at 373 K and standard conditions; therefore, it is a thermodynamically feasible reaction.[5] In comparison with the oxidative carbonylation of methanol,[4] there is no water in the reaction, which makes the separations much easier and economic. The phase behavior, especially vapor−liquid equilibrium, is important in the design, development, and operation involving the separation of product in DMC production.

Vapor−liquid equilibrium data for carbon monoxide (CO) + dimethyl carbonate (DMC), oxygen (O_2) + dimethyl carbonate (DMC), and dimethyl ether (DME) + dimethyl carbonate (DMC) have not been previously measured. This paper presents vapor−liquid equilibrium data for the three binary systems at (293 to 373) K and at pressures up to 12.00 MPa. Correlations of the experimental data were performed using the Peng−Robinson−Stryjek−Vera equation of state (EOS) with the two-parameter van der Waals II mixing rule.

Experimental Section

Materials and Their Purities. Instrumental grade CO, O_2, and DME with mass fraction of 99.99 % were obtained from Jinjing Gas Company. The three gases were dried with anhydrous $CaCl_2$ powder. DMC supplied by Kewei Pure Chemical Company was used without further purification; however[13], it was degassed for 2 h at low temperature (273 K). The mass fraction of DMC was ascertained to be more than 99 % by gas chromatographic analysis.

Table 1. Critical Constants and Acentric Factors[9]

substance	T_c/K	p_c/MPa	ω
dimethyl carbonate	548.00	4.50	0.385
carbon monoxide	132.85	3.49	0.053
oxygen	154.58	5.04	0.022
dimethyl ether	399.90	5.44	0.012

Table 2. $p-x(y)$ Data of the DME (1) + DMC (2) System at Four Temperatures

p/MPa	x_1	y_1	p/MPa	x_1	y_1
	$T = 293$ K			$T = 313$ K	
0.01	0	0	0.02	0	0
0.10	0.0899	0.8700	0.20	0.0857	0.8157
0.20	0.2186	0.9240	0.30	0.1930	0.8760
0.30	0.3640	0.9480	0.40	0.2830	0.9050
0.35	0.4739	0.9590	0.50	0.3540	0.9220
0.40	0.5825	0.9680	0.60	0.4584	0.9460
0.45	0.7196	0.9830	0.70	0.5520	0.9724
0.52	1.0000	1.0000	0.79	0.7092	0.9812
			0.90	1.0000	1.0000
	$T = 353$ K			$T = 373$ K	
0.07	0	0	0.14	0.0000	0
0.40	0.0810	0.5940	0.50	0.0330	0.3452
0.60	0.1330	0.7071	1.00	0.1620	0.6828
0.80	0.2290	0.8069	1.50	0.3218	0.8136
1.01	0.2940	0.8333	2.05	0.4563	0.8767
1.20	0.3970	0.8834	2.50	0.6239	0.9336
1.60	0.5850	0.9248	3.00	0.8203	0.9724
2.00	0.7743	0.9641	3.26	1.0000	1.0000
2.24	1.0000	1.0000			

Experimental Apparatus and Procedures. The experiments were carried out in a high-pressure autoclave with a movable piston which has been described previously.[6,7] The tubelike autoclave is made of austentitic manganese steel and has a length of 300 mm and outer and inner diameters of 120 mm and 20 mm, respectively. After samples were introduced into the autoclave, the pressure was changed while maintaining a constant temperature, which was achieved by adjusting the movable piston. The temperature was measured with a

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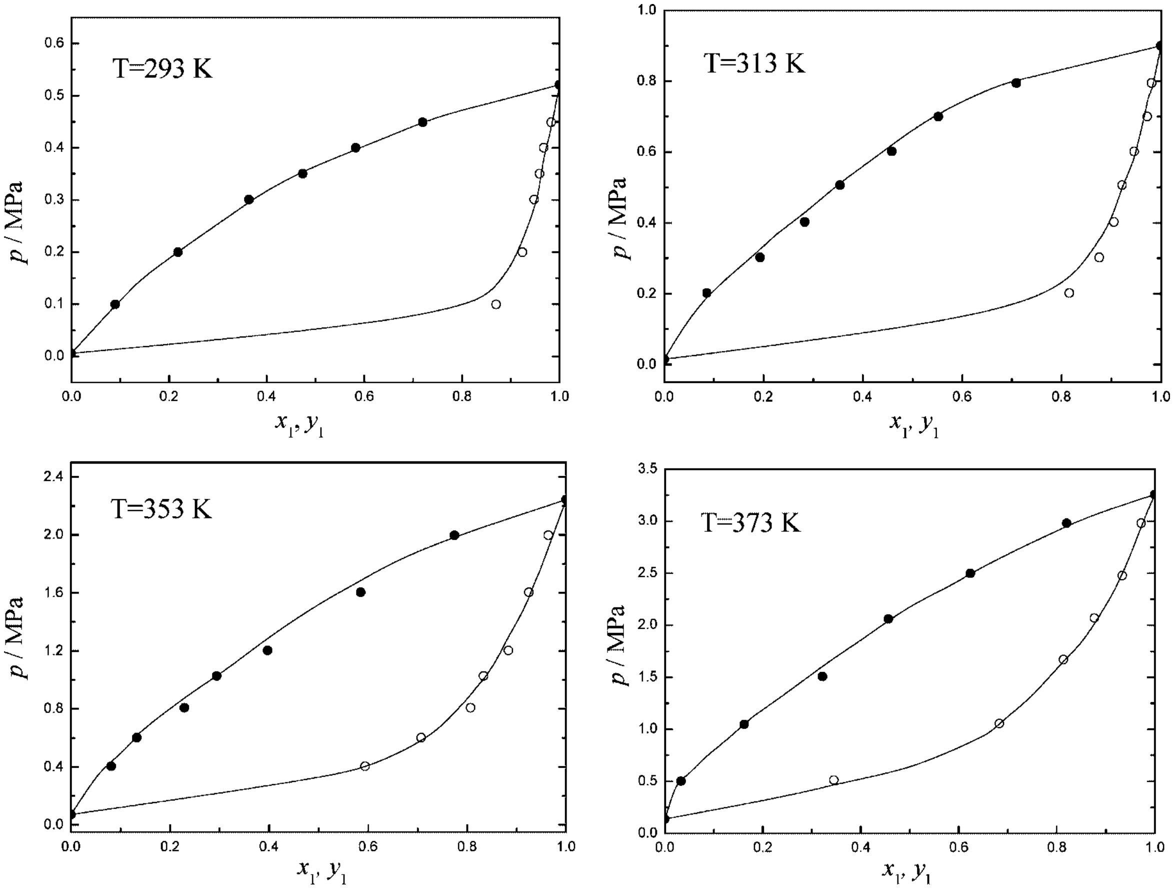

Figure 1. p, x_1, y_1 diagrams of the DME (1) + DMC (2) binary system at four temperatures: ●, ○, experiment; —, fitted using the Peng−Robinson−Stryjek−Vera equation of state (EOS) with the two-parameter van der Waals II mixing rule. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

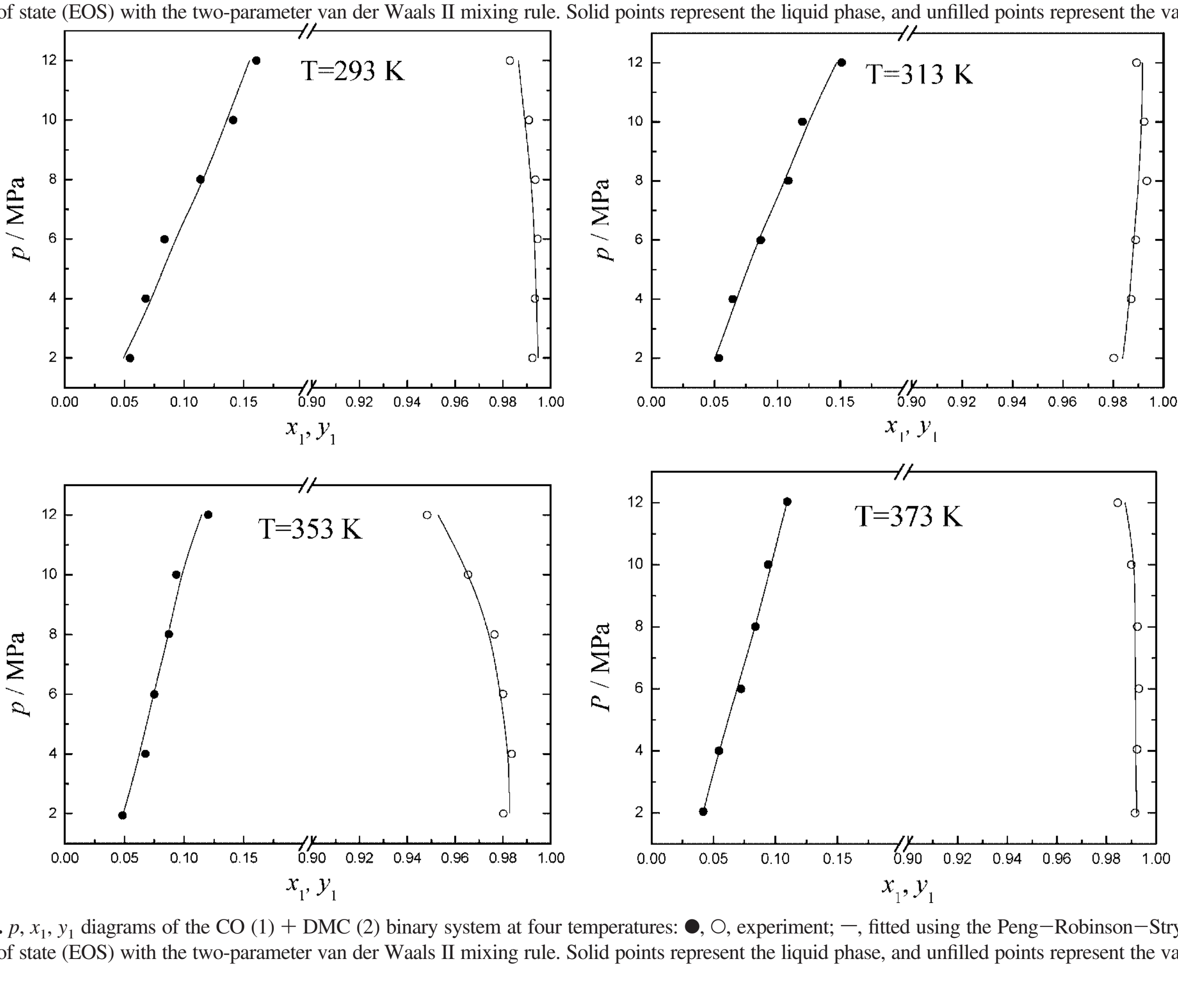

Figure 2. p, x_1, y_1 diagrams of the CO (1) + DMC (2) binary system at four temperatures: ●, ○, experiment; —, fitted using the Peng−Robinson−Stryjek−Vera equation of state (EOS) with the two-parameter van der Waals II mixing rule. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

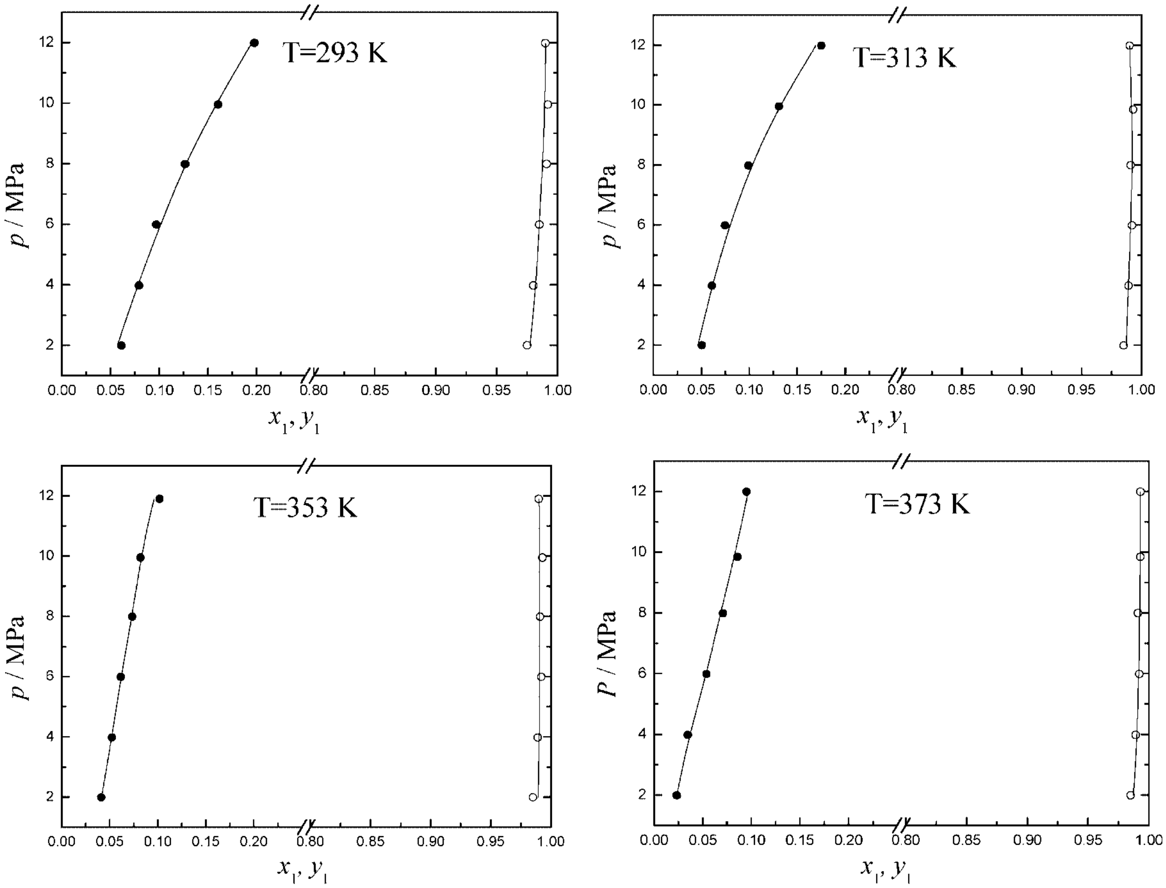

Figure 3. p, x_1, y_1 diagrams of O_2 (1) + DMC (2) binary system at four temperatures: ●, ○, experiment; —, fitted using the Peng−Robinson−Stryjek−Vera equation of state (EOS) with the two-parameter van der Waals II mixing rule. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

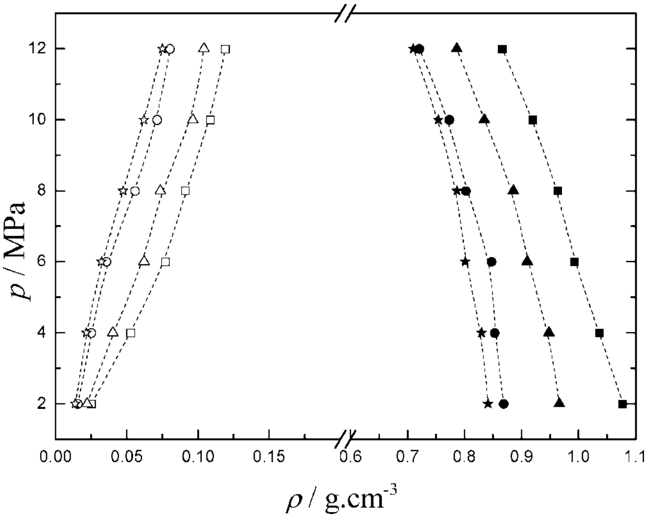

Figure 4. p, ρ diagrams of the CO (1) + DMC (2) binary system at four temperatures: ■, □, 293 K; ▲, Δ, 313 K; ●, ○, 353 K; ★, ☆, 373 K; ..., the changing trend of data. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

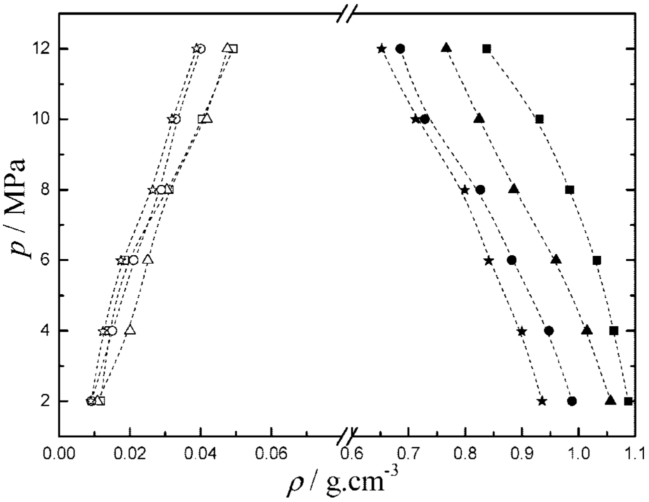

Figure 5. p, ρ diagrams of O_2 (1) + DMC (2) binary system at four temperatures: ■, □, 293 K; ▲, Δ, 313 K; ●, ○, 353 K; ★, ☆, 373 K; - - -, the changing trend of data. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

calibrated thermocouple inside the cell. The temperature can be controlled within ± 0.1 K and the pressure within ± 0.01 MPa.

Before each measurement, the view cell was first evacuated with a vacuum pump. DMC was then charged into the cell. The gas was pressurized into the cell through a steel vessel. After that, the view cell with stirring was heated to the given temperature. Phase equilibrium was achieved when the constant pressure was maintained for 2 h at the given temperature. Samples of the liquid and gas phases were removed using the upper and lower valves, respectively, and then they were placed into a previously evacuated and weighed small steel vessel through a needle valve. During this process, the pressure inside the autoclave was kept constant by pushing the piston toward the chamber with the screw-driven pump. The total mass of the samples was measured by using a balance with an uncertainty of ± 0.0001

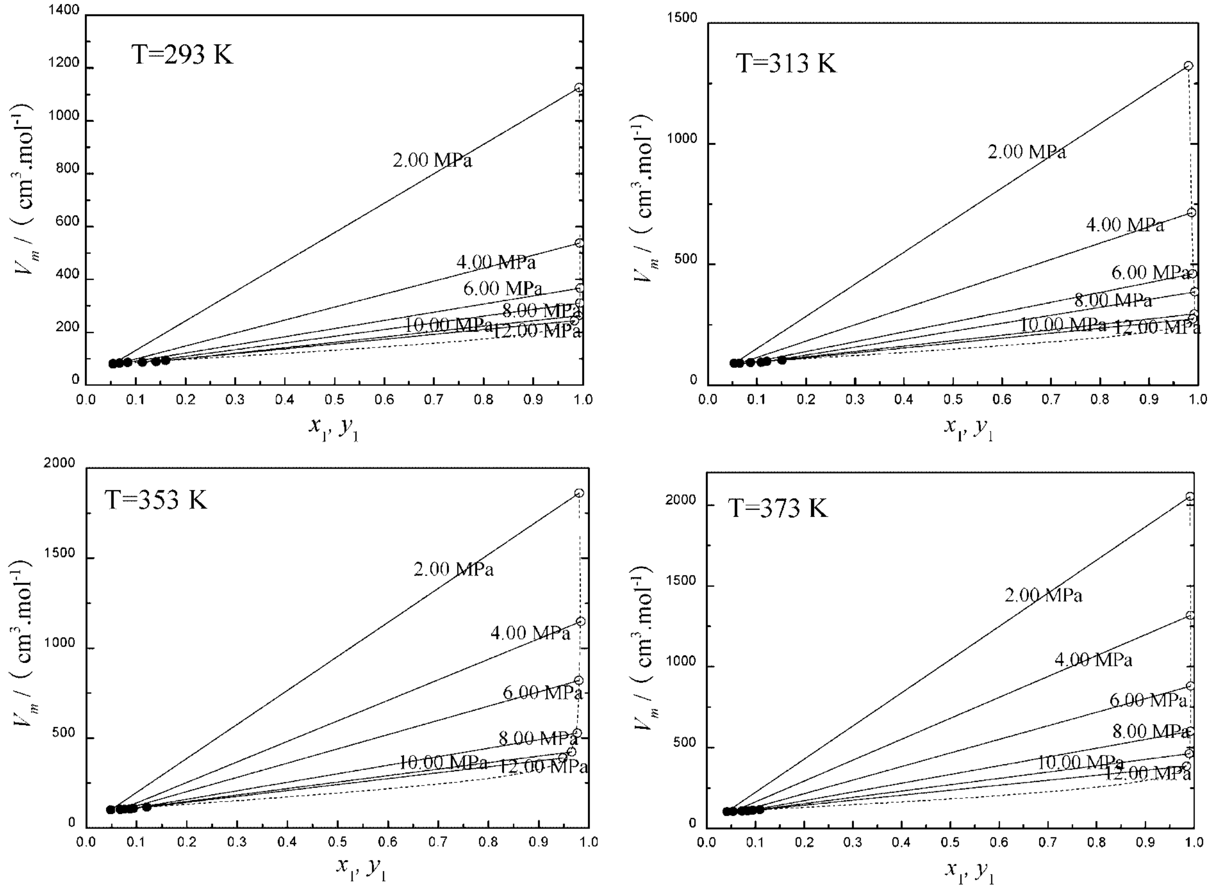

Figure 6. V_m, x_1, y_1 diagrams of the CO (1) + DMC (2) binary system at four temperatures. - - -, the changing trend of data; —, the isobars. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

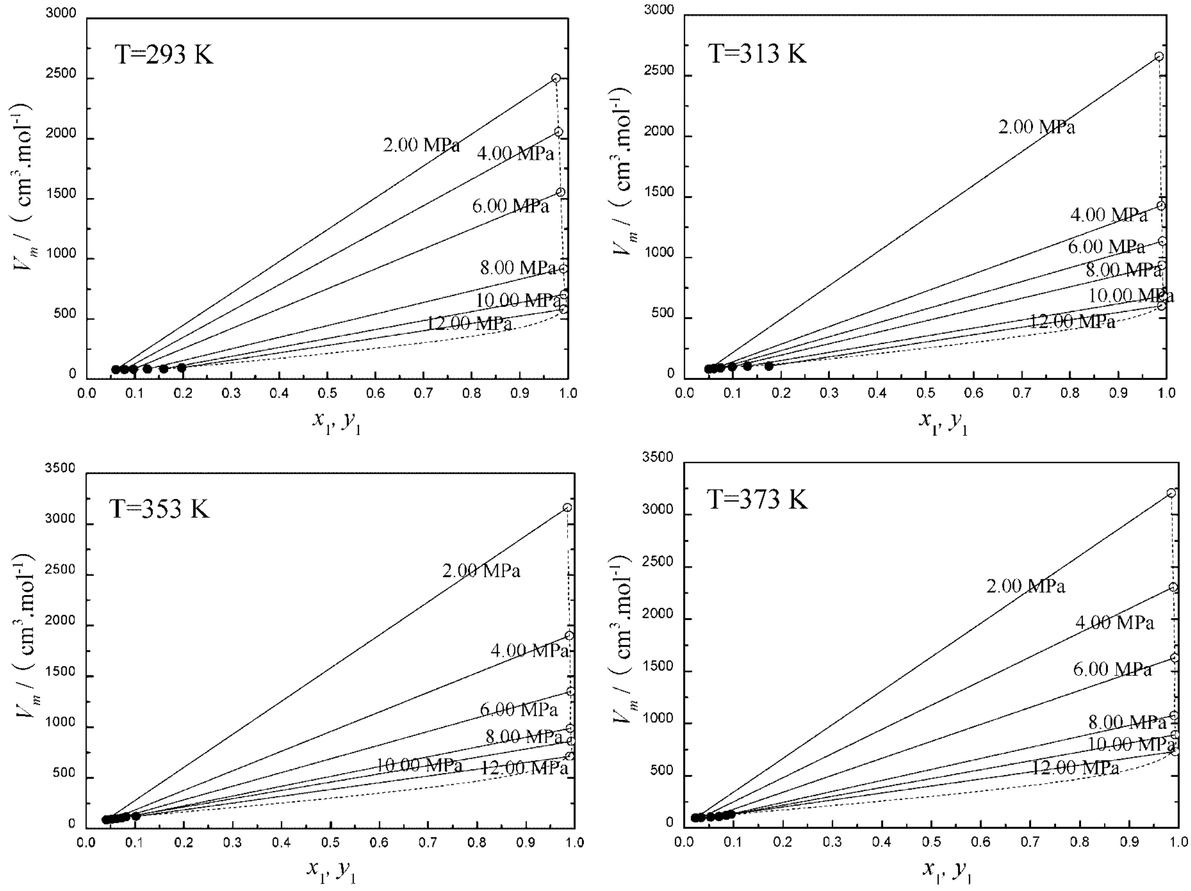

Figure 7. V_m, x_1, y_1 diagrams of the O_2 (1) + DMC (2) binary system at four temperatures. - - -, the changing trend of data; —, the isobars. Solid points represent the liquid phase, and unfilled points represent the vapor phase.

Table 3. Vapor−Liquid Phase Equilibria Data of the CO (1) + DMC (2) and O_2 (1) + DMC (2) Systems at Various Temperatures and Pressures

		CO (1) + DMC (2)		
p/MPa	x_1	ρ_l/g·cm^{-3}	y_1	ρ_V/g·cm^{-3}
		T = 293 K		
2.00	0.0547	1.0780	0.9924	0.0253
4.00	0.0679	1.0365	0.9935	0.0528
6.00	0.0838	0.9925	0.9945	0.0773
8.00	0.1138	0.9635	0.9936	0.0914
10.00	0.1413	0.9197	0.9909	0.1087
12.00	0.1606	0.8659	0.9830	0.1193
		T = 313 K		
2.00	0.0534	0.9664	0.9803	0.0221
4.00	0.0646	0.9480	0.9871	0.0403
6.00	0.0868	0.9102	0.9892	0.0622
8.00	0.1087	0.8857	0.9934	0.0735
10.00	0.1199	0.8348	0.9923	0.0965
12.00	0.1511	0.7866	0.9893	0.1043
		T = 353 K		
2.00	0.0485	0.8687	0.9803	0.0157
4.00	0.0677	0.8530	0.9837	0.0253
6.00	0.0752	0.8474	0.9801	0.0357
8.00	0.0873	0.8024	0.9765	0.0560
10.00	0.0936	0.7733	0.9655	0.0715
12.00	0.1204	0.7207	0.9483	0.0804
		T = 373 K		
2.00	0.0418	0.8412	0.9916	0.0139
4.00	0.0545	0.8298	0.9924	0.0216
6.00	0.0723	0.8013	0.9930	0.0323
8.00	0.0840	0.7867	0.9925	0.0474
10.00	0.0943	0.7543	0.9900	0.0620
12.00	0.1095	0.7101	0.9846	0.0751
		O_2 (1) + DMC (2)		
p/MPa	x_1	ρ_l/g·cm^{-3}	y_1	ρ_V/g·cm^{-3}
		T = 293 K		
2.00	0.0612	1.0876	0.9750	0.0118
4.00	0.0791	1.0624	0.9800	0.0142
6.00	0.0970	1.0320	0.9850	0.0186
8.00	0.1266	0.9847	0.9910	0.0311
10.00	0.1605	0.9313	0.9920	0.0405
12.00	0.1977	0.8380	0.9900	0.0492
		T = 313 K		
2.00	0.0506	1.0566	0.9850	0.0109
4.00	0.0610	1.0148	0.9890	0.0201
6.00	0.0748	0.9602	0.9920	0.0251
8.00	0.0990	0.8857	0.9910	0.0305
10.00	0.1307	0.8248	0.9930	0.0418
12.00	0.1750	0.7666	0.9900	0.0476
		T = 353 K		
2.00	0.0412	0.9885	0.9850	0.0092
4.00	0.0523	0.9478	0.9890	0.0151
6.00	0.0614	0.8822	0.9920	0.0211
8.00	0.0733	0.8267	0.9910	0.0289
10.00	0.0820	0.7288	0.9930	0.0331
12.00	0.1018	0.6853	0.9900	0.0401
		T = 373 K		
2.00	0.0233	0.9355	0.9853	0.0090
4.00	0.0347	0.9002	0.9891	0.0124
6.00	0.0539	0.8413	0.9922	0.0175
8.00	0.0710	0.7989	0.9915	0.0265
10.00	0.0858	0.7125	0.9936	0.0319
12.00	0.0953	0.6525	0.9933	0.0389

g. The volume of the sample was determined by measuring the distance between the positions of the piston before and after taking the sample, Δl, and the known inner diameter of the autoclave. The positions of the piston were measured with the help of a Hall probe connected to the piston. The uncertainty of Δl was ± 0.1 mm. The densities of the samples were determined using the ratio of the masses to the volume of the sample. The cooled vessel was connected to a previously evacuated glass bulb of known volume, and then the gas in the sample was allowed to flow into the glass bulb. The bulb was at room temperature, and its temperature was measured with a thermometer. The pressure of gas inside the glass bulb was measured with an absolute-pressure meter with uncertainty of ± 10 Pa. Because the pressure of the gas inside the bulb is very low (typically 20 kPa), the number of moles of the gas was easily calculated using the ideal gas equation of state. The mass of gas was also calculated using a mass different method.[11] The mass of the DMC is the difference between the total mass of the sample taken and the mass of the gas. Finally, the mole fraction of the two phases could be obtained for the given p and T. The uncertainty in density, ρ, was ± 0.0001 g·cm^{-3}. The molar fractions of the three systems were determined with an uncertainty of < 0.001.

Correlations

In this work, the experimental data were correlated using the Peng−Robinson−Stryjek−Vera equation of state with the two-parameter van der Waals II mixing rules which have been used in our earlier paper.[7]

The Peng−Robinson−Stryjek−Vera equation of state[8] has the following form

$$p = \frac{RT}{V_m - b} - \frac{a(T)}{V_m(V_m + b) + b(V_m - b)} \tag{2}$$

with

$$a(T) = a_c\alpha(T) = \frac{0.45724R^2T_c^2\alpha(T)}{p_c} \tag{3}$$

$$b = \frac{0.07780RT_c}{p_c} \tag{4}$$

$$\alpha(T) = [1 + k(1 - T_r^{0.5})]^2 \tag{5}$$

$$T_r = \frac{T}{T_c} \tag{6}$$

$$k = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \tag{7}$$

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{8}$$

where T_c and p_c are the critical temperature and critical pressure of the pure components, respectively, and ω is the acentric factor. The critical data T_c and p_c and acentric factors are listed in Table 1.

The two-parameter van der Waals II mixing rule[10] was used as follows

$$a_M = \sum_i \sum_j x_i x_i (a_i a_j)^{\frac{1}{2}}(1 - k_{ij}) \tag{9}$$

$$b_M = \sum_i \sum_j x_i x_j \frac{(b_i + b_j)}{2}(1 - n_{ij}) \tag{10}$$

where k_{ij} and n_{ij} are the binary interaction parameters.

The fitting was performed at each temperature by minimizing the following objective function

$$F = 5\sum_{i=1}^{N}\left(\frac{p - p_{calcd}}{p}\right)^2 + \sum_{i=1}^{N}\sum_{j=1}^{M}\left(\frac{y_j - y_{j,calcd}}{y_j}\right)^2 \tag{11}$$

where the subscript calcd represent calculated values.

Table 4. Fitted Results for Three Binary Systems CO (1) + DMC (2), O_2 (1) + DMC (2), and DME (1) + DMC (2)

T/K	k_{12}	n_{12}	$^a p_{\mathrm{ARE}}$/%	$^b y_{\mathrm{ARE}}$/%
DME (1) + DMC (2)				
293	0.08	−0.34	0.82	1.33
313	−0.19	−0.5	1.97	1.45
353	−0.06	−0.32	3.96	1.91
373	0.058	0.20	0.58	2.50
CO (1) + DMC (2)				
293	−0.15	−0.34	0.26	0.03
313	−0.05	−0.45	0.26	0.01
353	−0.51	0.39	0.19	0.06
373	0.09	0.33	0.59	0.04
O_2 (1) + DMC (2)				
293	0.14	0.40	0.44	0.02
313	−0.25	−0.18	0.54	0.04
353	0.02	0.05	0.41	0.06
373	−0.10	0.01	0.19	0.07

[a] Average relative errors of p: $p_{\mathrm{ARE}} = (\sum_{i=1}^{n} p_{\mathrm{exptl},i} - p_{\mathrm{calcd},i}/p_{\mathrm{exptl},i})/n$. [b] Average relative errors of pressure of y: $y_{\mathrm{ARE}} = (\sum_{i=1}^{n} y_{\mathrm{exptl},i} - y_{\mathrm{calcd},i}/y_{\mathrm{exptl},i})/n$.

Results and Discussion

The measured equilibrium pressures p and the corresponding liquid + vapor mole fraction (x_1 and y_1) at four temperatures for the system DME + DMC were given in Table 2. The result is presented graphically in Figure 1. Since the vapor pressure of DME and its solubility in DMC were much greater than CO and O_2, the above method of analyzing compositions was not suitable for this binary system. The equilibrium compositions of two phases were analyzed by gas chromatography (GC-3800 from Varian Company). The uncertainty of the mole fraction was estimated as ± 0.002.

The systems CO + DMC and O_2 + DMC were measured at four temperatures (293 K, 313 K, 353 K, and 373 K) over the pressure range from (2.00 to 12.00) MPa. The measured gas + liquid phase mole fraction (x_1 and y_1) and densities (ρ_l and ρ_g) at various temperatures and pressures for two binary mixtures are shown in Table 3. The p, $x(y)$ diagrams of the systems CO + DMC and O_2 + DMC are shown in Figures 2 and 3, respectively. The lines represent the isotherms fitted with the Peng−Robinson−Stryjek−Vera equation of state using the van der Waals II mixing rule which shows the best agreement with the experimental data compared with other equations of state.[11] The measured results show that both the solubility of CO, O_2, or DME in DMC and the content of DMC in the vapor phase increase with elevated pressure.

The fitted k_{12} and n_{12} parameters and the average deviations between the correlations using the Peng−Robinson−Stryjek−Vera equation and the experiment for the three systems at different temperatures are summarized in Table 4. From Table 4, the values of k_{12} and n_{12} are all very small. The nonzero n_{12} value shows that the systems are asymmetric, and the small k_{12} value indicates that the interaction forces between the small esters and gas are very weak. Parameters k_{12} and n_{12} do not have a definite trend with temperature, and the correlations show good agreement with the experiments.

Figure 4 and 5 give the isothermal p, ρ curves for systems of CO + DMC and O_2 + DMC. The densities of the vapor phases increase with pressure, but the densities of the liquid phases decrease with pressure. The molar volumes of the mixture at different T and p can be obtained from the densities and mole fractions. Those results are shown in Figures 6 and 7. The thin lines connecting the conjugate points in the two phases are isobars.

Conclusions

VLE data for CO, O_2, and DME with DMC are measured at 293 K, 313 K, 353 K, and 373 K and pressures up to 12.00 MPa. The VLE data are correlated using the cubic type Peng−Robinson−Stryjek−Vera equation of state with the van der Waals II mixing rule. The optimally fitted binary parameters are reported, and correlation results are satisfactorily observed. Furthermore, the mixing densities and mole volumes of vapor and liquid phases at different T and p are also presented.

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