Available online at www.sciencedirect.com
ScienceDirect
Fluid Phase Equilibria 248 (2006) 89–95
FLUID PHASE EQUILIBRIA
www.elsevier.com/locate/fluid

Vapor–liquid equilibria for the ternary mixture of carbon dioxide + 1-propanol + propyl acetate at elevated pressures

Chen-Hsi Cheng, Muoi Tang, Yan-Ping Chen *

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, ROC

Received 8 April 2006; received in revised form 22 July 2006; accepted 24 July 2006
Available online 27 July 2006

Abstract

Vapor–liquid equilibrium (VLE) data for the ternary mixture of carbon dioxide, 1-propanol and propyl acetate were measured in this study at 308.2, 313.2, and 318.2 K, and at pressures ranging from 4 to 10 MPa. A static type phase equilibrium apparatus with visual sapphire windows was used in the experimental measurements. New VLE data for CO_2 in the mixed solvent were presented. These ternary VLE data at elevated pressures were also correlated using either the modified Soave–Redlich–Kwong or Peng–Robinson equation of state (EOS), and by employing either the van der Waals one-fluid or Huron–Vidal mixing model. Satisfactory correlation results from both EOS models are reported with temperature-independent binary interaction parameters. It is observed that at 318.2 K and 10 MPa, 1-propanol may probably be separated from propyl acetate into the vapor phase at the entire concentration range in the presence of high pressure CO_2.

Keywords: Experimental data; VLE; Ternary system

1. Introduction

Application of supercritical carbon dioxide in extraction, reaction and separation is recognized as a green technology in order to replace the use of organic solvents. Supercritical CO_2 was used for the enzymatic reaction together with the product recovery due to the extraction effect [1]. The esterification of acetic acid with ethanol to form ethyl acetate was recently investigated using supercritical CO_2 [2,3]. In our previous study [4], a list of recent vapor–liquid equilibrium (VLE) data sources for ternary systems involving high pressure CO_2, alcohol and ester compounds was presented. It is indicated that ternary VLE data for such systems are still inadequate, and more experimental data are required for engineering applications. We have measured the VLE data for CO_2 and esters using either the semi-flow or static apparatus at pressures up to 13 MPa [5,6], and for the ternary systems of CO_2 with ethanol and ethyl acetate up to 7 MPa [4]. The purposes for measuring the VLE data at high pressures involving CO_2 and ester compounds are: (1) using supercritical CO_2, the esterification of organic acid with alcohol can be a green process with less amount of acid catalyst [3]. (2) The esterification reaction products can be separated due to the supercritical extraction effect without the formation of the azeotropic compound. From the experimental data in our previous study of CO_2 + ethanol + ethyl acetate, it was observed that ethanol can be separated from ethyl acetate into the vapor phase at 313.2 K and 7 MPa. In this study, we extended our measurements to CO_2 + 1-propanol + propyl acetate. It was attempted to investigate the appropriate condition for separating 1-propanol and propyl acetate in the presence of high pressure CO_2. The VLE data were measured at three temperatures of 308.2, 313.2, and 318.2 K, with the pressures range from 4 to 10 MPa. The experimental data were also correlated using the equation of state (EOS) method where the modified Soave–Redlich–Kwong (MSRK) EOS [7] and the widely used Peng–Robinson (PR) EOS [8] were employed. The van der Waals one-fluid (VDW1) mixing model and the Huron–Vidal mixing model [9] were applied in the correlation. The optimally fitted binary interaction parameters are presented and the accuracies of correlation results from these models are compared.

* Corresponding author. Fax: +886 2 2362 3040.
E-mail address: ypchen@ntu.edu.tw (Y.-P. Chen).

0378-3812/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2006.07.016

2. Experimental

2.1. Chemicals

High pressure liquefied carbon dioxide with purity more than 99.9 mass% was purchased from San-Fu Chemical Co. (Taiwan). 1-Propanol and propyl acetate were purchased from Merck Co. and Sigma–Aldrich Co., respectively. Both chemicals had purity greater than 99.5 mass% from the gas chromatograph (GC) test where no water content was detected. These chemicals were used without further purification. The properties of pure 1-propanol and propyl acetate were measured in this study and the results are shown in Table 1. The refractive indices were measured at 298.2 ± 0.1 K using an Abbe refractometer, Atago 3T, with an accuracy of ± 0.0001. The densities of pure compounds were measured at 298.2 ± 0.1 K using the Anton Paar DMA 58 density meter with an accuracy of ± 0.1 kg/m^3. From the comparison with literature values shown in Table 1, the purities of pure chemicals are acceptable for VLE measurements.

2.2. Apparatus

The phase equilibrium apparatus has been described in our previous study [4]. It was a static-type apparatus where the coexisting phases were recirculated, sampled, and analyzed. The equilibrium cell has an internal volume of 320 mL equipped with three pairs of visual sapphire windows (Sitec, Switzerland) for visual observation of the phase behavior. The pressure in the equilibrium cell was measured by a Druck gauge (PDCR-4031, up to 700 bar) with a digital indicator (DPI-281). The temperature of the equilibrium cell was measured by a K-type thermocouple with a resolution of 0.01 K. The accuracies for the temperature and pressure measurements in our experimental ranges are ± 0.1 K and ± 0.01 MPa, respectively. The liquid phase in the cell was recirculated using a magnetic pump (Micropump, series 180-HP) to reach phase equilibrium. The vapor sampling valve (Valco, 6UW) and the liquid sampling valve (Rheodyne, 7010) were used in this study. The GC (Shimadzu, 14B) column was packed with Porapak P, and was equipped with a thermal conductivity detector (TCD) for on-line analyses. Helium was used as the carrier gas with a flow rate of 45 mL/min. The temperature for the TCD was kept at 483.2 K and the temperature for the GC column was programmed from 383.2 to 463.2 K. The equilibrium cell and sampling valves were all immersed in a water bath where the temperature was controlled at the desired value ± 0.1 K. Heating tapes were used in the sampling line to avoid any condensation.

2.3. Calibration procedures

The volumes of the sampling loops had been calibrated using distilled water controlled at 298.2 K, as shown in our previous study [4]. The volumes were determined as 21.83 and 4.52 μL for the vapor and liquid sampling loops, respectively.The calibration of GC was made by plotting the peak areas against the number of moles of the pure gas or liquid sample, as shown in previous literature [10,11]. A digital balance (Mettler Toledo AX105, with accuracy of 2 ± 10^{-5} g) was used to evaluate the weight and number of moles for the liquid samples. The GC peak areas for 1-propanol and propyl acetate were plotted against their number of moles, and the curves were satisfactorily correlated by third order polynomial equations. Calibrations for the gas samples were performed when carbon dioxide was pressurized to a desired value at a given temperature. The molar volumes for carbon dioxide at various T and P were obtained using the database of NIST [12]. The calibration curves for CO_2 at various T and P were also well fitted with third order polynomial equations.

2.4. Experimental procedures

The experimental apparatus was firstly evacuated using a vacuum pump. The liquid mixture of 1-propanol and propyl acetate at a specific composition (1-propanol mole fractions of 0.7143, 0.6667, 0.6, 0.5 and 0.2857) was degassed for 20 min before charging into the equilibrium cell that was immersed in a water bath. Carbon dioxide was then fed into the cell through a high pressure pump until the system reached a desired pressure. To enhance rapid phase equilibrium, the liquid phase mixture was recirculated using a magnetic pump at a flow rate of 320 mL/min. The equilibrium vapor and liquid phases were visually observed through the windows of the cell after 0.5 h of recirculation. The system was then settled for 3.5 h to reach the final equilibrium state. The final pressure was then recorded and the equilibrium compositions of the two phases were analyzed using GC. The equilibrium compositions were the averaged values of at least five repeated measurements. The sampling loops were then evacuated to remove any residual sample. The reproducibility for the measured vapor and liquid mole fractions were estimated to be ± 0.0001 and ± 0.0002, respectively.

3. VLE calculation models

The experimentally measured VLE data were further correlated using the equation of state (EOS) models. The equal fugacity criterion was employed and the VLE were solved by

Table 1
Comparison of the measured refractive indices and densities for pure compounds with literature data

Compound	n^D ($T = 298.2$ K)		ρ (kg m^{-3}, $T = 298.2$ K)		GC purity (mass%)
	Experimental	Literature	Experimental	Literature	
1-Propanol	1.3839	1.3837 [19]	799.7	799.8 [19]	99.5
Propyl acetate	1.3828	1.3828 [19]	882.5	882.6 [19]	99.5

flash calculations. The binary interaction parameters in the mixing rules were optimally fitted using the binary VLE data in literature, and it was intended to justify if these binary parameters can be directly employed in correlating the ternary VLE data. Two commonly used engineering EOS were employed in this study. The MSRK EOS has the following form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1}$$

$$a = 0.42748\frac{R^2T_c^2}{P_c}\alpha(T) \tag{2}$$

$$b = 0.08664\frac{RT_c}{P_c} \tag{3}$$

$$\alpha(T) = 1 + (1 - T_r)(m + n/T_r) \tag{4}$$

where the parameters m and n are available for many pure fluids [7]. The PR EOS has the following form:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{5}$$

$$a = 0.45724\frac{R^2T_c^2}{P_c}\alpha(T) \tag{6}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{7}$$

$$\alpha(T) = \left[1+(0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{8}$$

The EOS parameters were determined from the critical constants and acentric factors of pure fluids that are listed in Table 2.

Table 2
Pure component properties used in this study

Component	T_c [20] (K)	P_c [20] (bar)	ω [20]	m [7]	n [7]
Carbon dioxide	304.19	73.82	0.228	0.5809	0.2727
1-Propanol	536.78	51.75	0.629	0.6917	0.6958
Propyl acetate	549.40	33.30	0.389	0.7672	0.3457

For mixture calculations, the following mixing models were employed. For the van der Waals one-fluid (VDW1) mixing model, the EOS parameters were determined by

$$a_m = \sum\sum x_i x_j (a_i a_j)^{0.5}(1 - k_{ij}) \tag{9}$$

$$b_m = \sum x_i b_i \tag{10}$$

where k_{ij} is the binary interaction parameter and was determined by fitting to the experimental VLE data. Another mixing model presented by Huron and Vidal [9] was also employed in this study. In this mixing model, the excess Gibbs energy calculated from an EOS was set equal to that from an activity coefficient model at an infinite pressure limit. Applying the NRTL activity coefficient model [13], the EOS parameters were evaluated from the following equations:

$$a_m = b_m\sum_{i=1}^{n} x_i \times \left[\frac{a_i}{b_i} - \frac{1}{\ln 2}\left(\frac{\sum_{j=1}^{n} x_j C_{ji} b_j \exp(-\alpha_{ji}C_{ji}/(RT))}{\sum_{j=1}^{n} x_j b_j \exp(-\alpha_{ji}C_{ji}/(RT))}\right)\right] \tag{11}$$

$$b_m = \sum_{i=1}^{n} x_i b_i \tag{12}$$

where the non-randomness factor α was taken as 0.3 in our correlation. The binary parameters C_{ij} and C_{ji} in the NRTL model were determined also by fitting to the experimental VLE data.

The VLE data shown in literature [10,14–16] have been correlated in this study for three binary systems of CO_2 + 1-propanol, CO_2 + propyl acetate and propyl acetate + 1-propanol. The optimally fitted temperature-independent binary interaction parameters in either the VDW1 or Huron–Vidal mixing model were evaluated through flash calculations by minimizing the following objective function:

$$\text{obj} = \sum_{i=1}^{n}[|y_i^{cal} - y_i^{exp}| + |x_i^{cal} - x_i^{exp}|] \tag{13}$$

The correlation results are shown in Tables 3 and 4 for the VDW1 or Huron–Vidal mixing model, respectively. Generally,

Table 3
Correlation results for the VLE data of binary systems using the PR and the MSRK EOS with the VDW1 mixing model

EOS	T (K)	P (MPa)	k_{12}	AADx_1 (%)	AADy_1 (%)	Total data points	Reference
CO_2 (1) + 1-propanol (2)							
PR	313.4–333.4	0.52–10.82	0.096	3.09	0.28	29	[10,14]
MSRK	313.4–333.4	0.52–10.82	0.090	3.71	0.31	29	[10,14]
CO_2 (1) + propyl acetate (2)							
PR	303.2–323.2	2.07–9.17	−0.160	1.60	0.14	57	[15]
MSRK	303.2–323.2	2.07–9.17	−0.172	1.99	0.16	57	[15]
Propyl acetate (1) + 1-propanol (2)							
PR	373.0–367.7	0.10	0.023	0.02	3.26	38	[16]
MSRK	373.0–367.7	0.10	0.026	0.03	3.50	38	[16]

AAD$x_1 = (100/N)\sum|(x_1^{cal} - x_1^{exp})/x_1^{exp}|$; AAD$y_1 = (100/N)\sum|(y_1^{cal} - y_1^{exp})/y_1^{exp}|$, where N is the number of data points.

Table 4
Correlation results for the VLE data of binary systems using the PR and the MSRK EOS with the Huron–Vidal mixing model

EOS	T (K)	P (MPa)	α	C_{12} (J/mol)	C_{21} (J/mol)	AADx_1 (%)	AADy_1 (%)	Total data points	Reference
CO_2 (1) + 1-propanol (2)									
PR	313.4–333.4	0.52–10.82	0.3	283.40	132.07	0.93	0.24	29	[10,14]
MSRK	313.4–333.4	0.52–10.82	0.3	256.10	64.57	0.97	0.23	29	[10,14]
CO_2 (1) + propyl acetate (2)									
PR	303.2–323.2	2.07–9.17	0.3	471.98	−625.88	1.00	0.12	57	[15]
MSRK	303.2–323.2	2.07–9.17	0.3	738.78	−893.79	1.30	0.13	57	[15]
Propyl acetate (1) + 1-propanol (2)									
PR	373.0–367.7	0.10	0.3	432.17	−78.28	0.02	2.75	38	[16]
MSRK	373.0–367.7	0.10	0.3	412.92	−103.64	0.01	2.74	38	[16]

AAD$x_1 = (100/N)\sum|(x_1^{cal} - x_1^{exp})/x_1^{exp}|$; AAD$y_1 = (100/N)\sum|(y_1^{cal} - y_1^{exp})/y_1^{exp}|$, where N is the number of data points.

the MSRK and PR EOS yielded comparable accuracy in correlating the binary VLE data. The Huron–Vidal mixing model with the NRTL activity coefficient model has two adjustable parameters, and presents relatively superior results for VLE correlation near the critical region of binary mixtures. These optimally fitted binary interaction parameters were directly applied in predicting the ternary VLE results and comparing with the experimental measured data.

4. Results and discussion

The measured VLE data in this study for the ternary system CO_2 (1) + 1-propanol (2) + propyl acetate (3) at 308.2, 313.2, and 318.2 K are presented in Tables 5–7, respectively. Five compositions for 1-propanol in the feed of 1-propanol + propyl acetate were included for each isotherm in our experiments. For each feed composition, VLE data were measured at the given temperature and at four or five pressures ranging from 4 to 10 MPa. The mole fraction of CO_2 in the vapor phase was more than 0.99. The mole fractions of 1-propanol and propyl acetate in the vapor phase increased with temperature and decreased with pressure.

Table 8 presents the predicted results by directly applying the binary interaction parameters from correlating the binary VLE data. It is shown that the prediction was not satisfactory where a relatively large deviation in liquid phase composition was obtained. One possible reason is that the literature VLE data for the binary mixture of propyl acetate + 1-propanol were at atmospheric pressure that was far from the pressure range in this study. If the binary interaction parameters for propyl acetate + 1-propanol were taken as the only adjustable parameter in fitting the ternary VLE data, improved correlation results were obtained as shown in Table 8. The correlation results became more acceptable by fitting the temperature-independent binary interaction parameters directly to the ternary VLE data. This is the same conclusion as we have discussed in our previous study [4].

Graphical presentations of the ternary VLE data are shown in Figs. 1 and 2 at 308.2 K and two isobars of 4 and 7 MPa,

Table 5
VLE data for the ternary system of CO_2 (1) + 1-propanol (2) + propyl acetate (3) at T = 308.2 K

P (MPa)	x_1	x_2	x_3	y_1	y_2	y_3
4.12	0.2949	0.5323	0.1728	0.9896	0.0073	0.0031
5.07	0.3412	0.5177	0.1411	0.9928	0.0051	0.0021
6.11	0.3826	0.4800	0.1374	0.9955	0.0032	0.0013
7.10	0.5600	0.3600	0.0800	0.9971	0.0021	0.0008
4.16	0.2921	0.5004	0.2075	0.9898	0.0070	0.0032
5.03	0.3312	0.4686	0.2002	0.9927	0.0051	0.0022
6.06	0.3909	0.4261	0.1830	0.9957	0.0028	0.0015
7.01	0.5826	0.3221	0.0953	0.9970	0.0020	0.0010
3.99	0.3075	0.4138	0.2787	0.9897	0.0066	0.0037
5.02	0.3405	0.3877	0.2718	0.9921	0.0050	0.0029
6.09	0.3954	0.3825	0.2221	0.9960	0.0023	0.0017
6.99	0.6246	0.2693	0.1061	0.9969	0.0020	0.0011
3.98	0.4000	0.3100	0.2900	0.9897	0.0065	0.0038
5.00	0.4183	0.3000	0.2817	0.9921	0.0049	0.0030
6.05	0.4642	0.2931	0.2427	0.9959	0.0021	0.0020
7.10	0.6823	0.2054	0.1123	0.9968	0.0019	0.0013
3.99	0.5291	0.1724	0.2985	0.9898	0.0063	0.0039
5.03	0.5503	0.1667	0.2830	0.9921	0.0048	0.0031
6.01	0.5900	0.1500	0.2600	0.9959	0.0020	0.0021
7.14	0.7829	0.1000	0.1171	0.9961	0.0018	0.0021

Table 6
VLE data for the ternary system of CO_2 (1) + 1-propanol (2) + propyl acetate (3) at T = 313.2 K

P (MPa)	x_1	x_2	x_3	y_1	y_2	y_3
4.03	0.2402	0.6469	0.1129	0.9892	0.0076	0.0032
5.09	0.2942	0.6047	0.1011	0.9923	0.0055	0.0022
6.00	0.3679	0.5606	0.0715	0.9943	0.0041	0.0016
7.07	0.5278	0.4019	0.0703	0.9970	0.0022	0.0008
4.07	0.2548	0.5998	0.1454	0.9891	0.0075	0.0034
5.07	0.3127	0.5487	0.1386	0.9922	0.0055	0.0023
6.02	0.3609	0.5131	0.1260	0.9940	0.0040	0.0020
7.09	0.5690	0.3105	0.1205	0.9969	0.0021	0.0010
4.07	0.2809	0.5000	0.2191	0.9887	0.0075	0.0038
5.05	0.3396	0.4786	0.1818	0.9917	0.0054	0.0029
6.01	0.3739	0.4500	0.1761	0.9940	0.0039	0.0021
7.13	0.6316	0.2094	0.1590	0.9967	0.0021	0.0012
4.06	0.4000	0.3000	0.3000	0.9887	0.0074	0.0039
4.98	0.4800	0.2350	0.2850	0.9915	0.0054	0.0031
5.95	0.5150	0.2200	0.2650	0.9935	0.0037	0.0028
7.00	0.7201	0.1179	0.1620	0.9966	0.0020	0.0014
4.06	0.5937	0.1000	0.3063	0.9887	0.0073	0.0040
5.01	0.6372	0.0746	0.2882	0.9915	0.0053	0.0032
6.02	0.6732	0.0580	0.2688	0.9934	0.0036	0.0030
6.99	0.7856	0.0500	0.1644	0.9959	0.0019	0.0022

Table 7
VLE data for the ternary system of CO_2 (1) + 1-propanol (2) + propyl acetate (3) at $T = 318.2$ K

P (MPa)	x_1	x_2	x_3	y_1	y_2	y_3
4.01	0.2000	0.7000	0.1000	0.9880	0.0085	0.0035
5.07	0.2500	0.6609	0.0891	0.9920	0.0057	0.0023
6.02	0.3592	0.5800	0.0608	0.9941	0.0042	0.0017
7.07	0.4714	0.4874	0.0412	0.9969	0.0023	0.0008
10.0	0.8584	0.1212	0.0204	0.9978	0.0019	0.0003
4.11	0.2291	0.5855	0.1854	0.9879	0.0085	0.0036
5.08	0.2978	0.5368	0.1654	0.9920	0.0056	0.0024
6.05	0.3600	0.5000	0.1400	0.9939	0.0041	0.0020
7.02	0.5100	0.3823	0.1077	0.9968	0.0022	0.0010
4.11	0.3000	0.4000	0.3000	0.9879	0.0083	0.0038
5.02	0.3548	0.3800	0.2652	0.9915	0.0055	0.0030
5.96	0.4300	0.3500	0.2200	0.9939	0.0040	0.0021
7.03	0.6088	0.2612	0.1300	0.9966	0.0021	0.0013
9.93	0.8605	0.0904	0.0491	0.9978	0.0016	0.0006
4.02	0.4042	0.2900	0.3058	0.9880	0.0081	0.0039
5.03	0.4742	0.2507	0.2751	0.9913	0.0055	0.0032
6.07	0.5200	0.2300	0.2500	0.9934	0.0038	0.0028
7.01	0.6641	0.1759	0.1600	0.9965	0.0021	0.0014
4.05	0.5900	0.1216	0.2884	0.9880	0.0079	0.0041
5.00	0.6459	0.1000	0.2541	0.9912	0.0054	0.0034
5.99	0.7000	0.0800	0.2200	0.9933	0.0038	0.0029
6.96	0.7706	0.0700	0.1594	0.9957	0.0020	0.0023
9.95	0.8964	0.0151	0.0885	0.9976	0.0008	0.0016

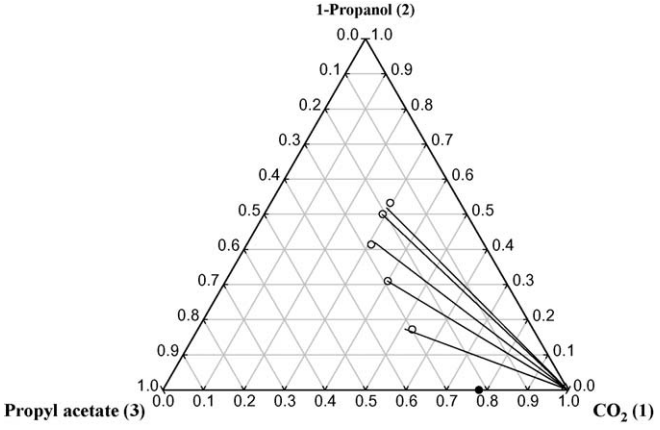

Fig. 1. Vapor–liquid equilibria for carbon dioxide (1) + 1-propanol (2) + propyl acetate (3) at $T = 308.2$ K and $P = 4$ MPa ((◯) and (△) mole fractions of the liquid and vapor phases measured in this study; (●) mole fraction of the liquid phase from literature [15]; (—) calculated results using the PR EOS with the VDW1 mixing model).

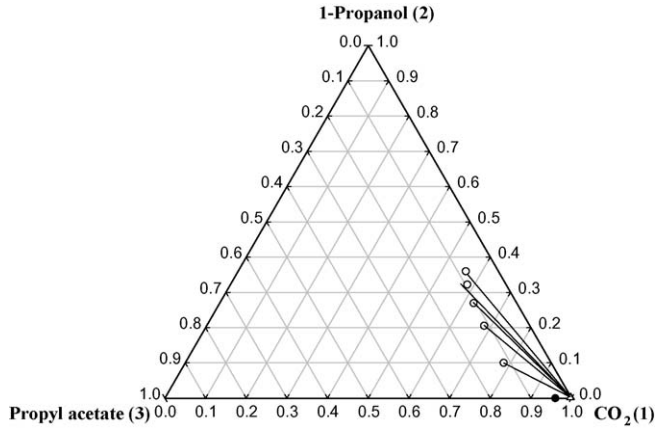

Fig. 2. Vapor–liquid equilibria for carbon dioxide (1) + 1-propanol (2) + propyl acetate (3) at $T = 308.2$ K and $P = 7$ MPa. ((◯) and (△) mole fractions of the liquid and vapor phases measured in this study; (●) mole fraction of the liquid phase from literature [15]; (—) calculated results using the PR EOS with the VDW1 mixing model).

respectively. Fig. 3 shows the VLE data at 7 MPa at the other temperature of 318.2 K. These three figures indicate that the liquid compositions for 1-propanol and propyl acetate increased with temperature but decreased with pressure. The solid tie lines in these figures represent the calculated results using the PR EOS and the VDW1 mixing model with the binary interaction parameters fitted to the ternary VLE data. Satisfactory agreement between the experimental and correlated results is demonstrated.In our previous study [4], separation of the alcohol and acetate compounds in the presence of high pressure CO_2 for the esterification process was investigated. Similar effect was analyzed in this work for the mixture of 1-propanol (2) and propyl acetate (3). As discussed in previous literature [17], component 2 can be separated into the vapor phase when the separation factor α_{23} ($\alpha_{23} = (y_2/x_2)/(y_3/x_3)$) is greater than unity. In our experimental range, the α_{23} values were found greater than unity at 318.2 K and 10 MPa over the entire concentration range. It was also shown in literature [18], a solvent-free $y^* - x^*$ plot was used to illustrate the separation effect. The solvent-free mole fractions (z_i^*) were defined as

$$z_i^* = \frac{n_i}{\sum_{j \neq CO_2} n_j} \tag{14}$$

Table 8
Correlation results for the ternary VLE data of CO_2 (1) + 1-propanol (2) + propyl acetate (3)

EOS	Mixing model	Predicted results		Adjustment of BIP for (2) + (3)[a]		BIP fitted to ternary VLE data[b]	
		AADx_1 (%)	AADy_1 (%)	AADx_1 (%)	AADy_1 (%)	AADx_1 (%)	AADy_1 (%)
PR	VDW1	11.51	0.18	5.31	0.25	1.82	0.26
	Huron–Vidal	8.08	0.18	4.81	0.24	1.61	0.19
MSRK	VDW1	11.70	0.17	5.85	0.25	2.39	0.27
	Huron–Vidal	10.49	0.19	5.34	0.25	2.34	0.15

BIP: binary interaction parameters.
[a] PR EOS: $k_{23} = -0.184$; $C_{23} = 214.82$, $C_{32} = -489.88$; MSRK EOS: $k_{23} = -0.174$; $C_{23} = 562.29$, $C_{32} = -773.29$; C_{ij}[=]J/mol.
[b] PR EOS: $k_{12} = 0.191$, $k_{13} = -0.005$, $k_{23} = 0.008$; $C_{12} = 1130.44$, $C_{21} = 70.92$, $C_{13} = -348.15$, $C_{31} = -109.48$, $C_{23} = 233.47$, $C_{32} = 144.83$; MSRK EOS: $k_{12} = 0.197$, $k_{13} = 0.010$, $k_{23} = 0.023$; $C_{12} = 1544.91$, $C_{21} = 74.38$, $C_{13} = 1063.03$, $C_{31} = -779.84$, $C_{23} = 2480.64$, $C_{32} = -12.74$.

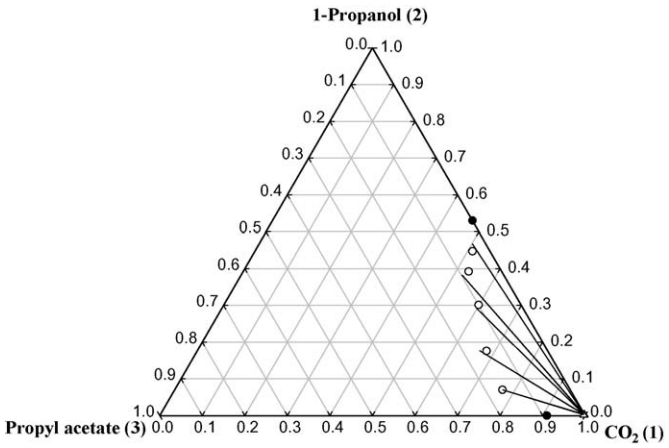

Fig. 3. Vapor–liquid equilibria for carbon dioxide (1) + 1-propanol (2) + propyl acetate (3) at $T = 318.2$ K and $P = 7$ MPa. ((◯) and (△) mole fractions of the liquid and vapor phases measured in this study; (●) mole fraction of the liquid phase from literature [14,15]; (—) calculated results using the PR EOS with the VDW1 mixing model).

The plot of the CO_2-free basis ($y_2^* - x_2^*$) curves is shown in Fig. 4 at 318.2 K and at two pressures of 7 and 10 MPa. At atmospheric pressure, the binary mixture of 1-propanol and propyl acetate has an azeotrope with 1-propanol mole fraction of 0.62 [16]. At 318.2 K and 10 MPa, the relative volatility of 1-propanol to propyl acetate was greater than unity over the entire compositions range and no azeotrope was found. This experimental result demonstrated that with the supercritical extraction effect at a proper pressure, the formation of azeotropic mixture could probably be eliminated. The selectivity changed where more 1-propanol was separated into the vapor phase.

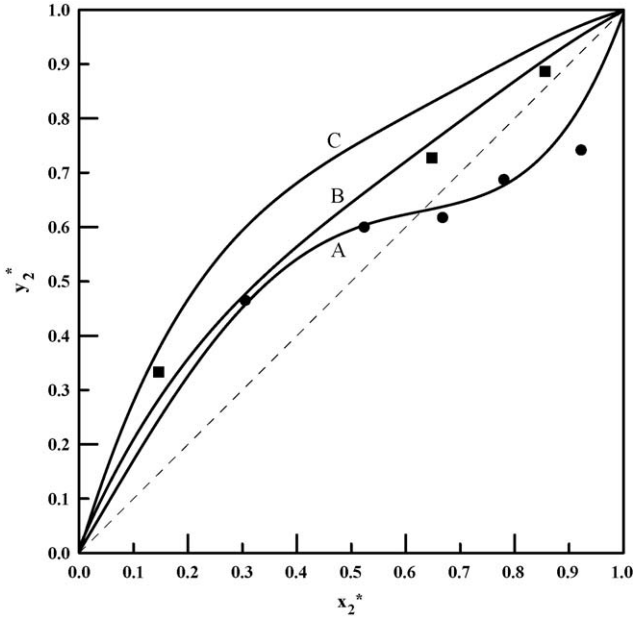

Fig. 4. Plot of the CO_2-free $y_2^* - x_2^*$ curves at 318.2 K for the ternary mixture CO_2 (1) + 1-propanol (2) + propyl acetate (3). Experimental data: (●) $P = 7$ MPa; (■) $P = 10$ MPa. Calculated results using the PR EOS with the VDW1 mixing model; (—) A, 7 MPa; B, 10 MPa; C, 12 MPa.

Using the optimally fitted binary interaction parameters, the calculated ($y_2^* - x_2^*$) curve at 12 MPa from the Peng–Robinson EOS is also presented in Fig. 4. The possibility of eliminating the azeotrope is demonstrated again at this pressure.

5. Conclusions

Experimental VLE data for the ternary mixture of carbon dioxide with 1-propanol and propyl acetate are reported at 308.2, 313.2, and 318.2 K and pressures from 4 to 10 MPa. The modified Soave–Redlich–Kwong or Peng–Robinson EOS with either the van der Waals one-fluid or Huron–Vidal mixing model were used in correlating the ternary experimental VLE data. With the temperature-independent binary parameters fitted to the ternary VLE data, the Huron–Vidal mixing rule with NRTL activity coefficient model yielded superior results. The experimental data were analyzed on the CO_2-free basis. It is shown that at 318.2 K and 10 MPa, 1-propanol could be separated from propyl acetate over the entire concentration range in the presence of high pressure CO_2.

List of symbols

a, b	parameters in the equation of state
C	binary interaction parameter in the NRTL model
f	fugacity
k	binary interaction parameters in the mixing model
n	number of mole
P	pressure
R	gas constant
T	temperature
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase

Greek letter

α	non-randomness factor in the NRTL model

Subscripts

c	critical properties
i, j	component i or j
m	mixture
r	reduced properties
1, 2	component 1 or 2

Superscripts

cal	calculated value
exp	experimental data
*	CO_2-free basis

Acknowledgement

The authors are grateful to the National Science Council, ROC for supporting this research.

References

[1] A.A. Chrisochoou, K. Schaber, K. Stephen, J. Chem. Eng. Data 42 (1997) 558–561.

[2] L.A. Blanchard, J.F. Brennecke, Green Chem. 3 (2001) 17–19.
[3] Z. Hou, B. Han, X. Zhang, H. Zhang, Z. Liu, J. Phys. Chem. B 105 (2001) 4510–4513.
[4] C.H. Cheng, Y.P. Chen, Fluid Phase Equilib. 242 (2006) 169–175.
[5] W.H. Hwu, C.H. Cheng, M. Tang, Y.P. Chen, Fluid Phase Equilib. 215 (2004) 237–244.
[6] C.H. Cheng, Y.P. Chen, Fluid Phase Equilib. 234 (2005) 77–83.
[7] J.A. Sandarusi, A.J. Kidnay, V.F. Yesavage, Ind. Eng. Chem. Process Des. Dev. 25 (1986) 957–963.
[8] D.Y. Peng, D.B. Robinson, Ind. Eng. Chem. Fundam. 15 (1976) 59–64.
[9] M.J. Huron, J. Vidal, Fluid Phase Equilib. 3 (1979) 255–271.
[10] K. Suzuki, H. Sue, M. Itou, R.L. Smith, H. Inomata, K. Arai, S. Saito, J. Chem. Eng. Data 35 (1990) 63–66.
[11] J.H. Yoon, H. Lee, B.H. Chung, Fluid Phase Equilib. 102 (1994) 287–292.
[12] http://webbook.nist.gov/chemistry.
[13] H. Renon, J.M. Prausnitz, AIChE J. 14 (1968) 135–144.
[14] V. Vandana, A.S. Teja, J. Chem. Eng. Data 40 (1995) 459–461.
[15] Z. Wanger, Fluid Phase Equilib. 110 (1995) 175–182.
[16] J. Ortega, J. Ocon, J.A. Pena, C. De Alfonso, M.I. Paz-Andrade, J. Fernandez, Can. J. Chem. Eng. 65 (1987) 982–990.
[17] J.S. Lim, Y.Y. Lee, H.S. Chun, J. Supercrit. Fluids 7 (1994) 219–230.
[18] P. Traub, K. Stephan, Chem. Eng. Sci. 45 (1990) 751–758.
[19] TRC Thermodynamic Tables, Non-Hydrocarbons, Thermodynamics Research Center, The Texas A&M University System, College Station, TX, 1993.
[20] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gas and Liquids, 5th ed., McGraw Hill Inc., New York, 2001.