



Vapor–liquid equilibria of carbon dioxide with ethyl benzoate, diethyl succinate and isoamyl acetate binary mixtures at elevated pressures

Li-Chia Feng, Kong-Wei Cheng, Muoi Tang¹, Yan-Ping Chen*

Department of Chemical Engineering, National Taiwan University, Taipei, 106, Taiwan, ROC

Received 12 January 2001; received in revised form 14 May 2001; accepted 21 May 2001

Abstract

Vapor–liquid equilibrium (VLE) data of CO₂ with ethyl benzoate, diethyl succinate, and isoamyl acetate binary mixtures were measured by a semi-flow type apparatus at 308.15, 318.15, and 328.15 K over the pressure range from 1.0 to 13 MPa. New VLE results for CO₂ with esters are presented and the Henry's constants are determined. These VLE data were also correlated using the Soave–Redlich–Kwong and the Peng–Robinson equations of state with various types of the van der Waals, composition-dependent and Huron–Vidal mixing rules. It is shown that both equations of state with the van der Waals mixing rules and two adjustable parameters give satisfactory correlation results. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vapor–liquid equilibria; Binary mixture; Data

1. Introduction

Phase equilibrium data at high pressures for supercritical fluid systems are becoming more important owing to the increasing applications of the dense gases. Carbon dioxide is often used for supercritical fluid extraction because it is nontoxic and it has relatively low critical temperature and pressure. Vapor–liquid equilibrium (VLE) data at high pressures for carbon dioxide with esters are not adequate [1,2]. Recently, some experimental

measurements for carbon dioxide with esters are shown in the literature [3,4] which are useful for thermodynamic modeling and process design. In this work, a semi-flow apparatus was used to measure the high pressure VLE for three binary systems of CO₂ (1) + ethyl benzoate (2), CO₂ (1) + diethyl succinate (2), and CO₂ (1) + isoamyl acetate (2). Ethyl benzoate (C₉H₁₀O₂) is used as a solvent and in the production of styrene. Diethyl succinate (C₈H₁₄O₄) is used as a chemical intermediate and plasticizer. Isoamyl acetate (C₇H₁₄O₂) is used as in flavoring, perfumery and solvents. The experiments were carried out at temperatures of 308.15, 318.15, and 328.15 K. The pressure ranged from 1.0 to 13 MPa. Using the VLE data

* Corresponding author. Fax: +886-2-2362-3040.

E-mail address: ypchen@ccms.ntu.edu.tw (Y.-P. Chen).

¹ Present address: Department of Chemical Engineering, Chinese Culture University, Taipei, Taiwan, ROC.

at each isotherm, the Henry's law constants were evaluated. The experimental results were also correlated by employing the Soave–Redlich–Kwong [5] and the Peng–Robinson [6] equations of state with various mixing rules. Optimal binary parameters are reported and satisfactory correlation results are presented.

2. Experimental section

2.1. Chemicals

Liquefied carbon dioxide was available with purity greater than 99.8 mol% from San-Fu Chemical Co. (Taiwan). Ethyl benzoate, diethyl succinate, and isoamyl acetate were purchased from Merck Co. The purity of these chemicals was better than 99 mol%. No further purification of these chemicals was made. The pure compound properties were measured in this study, and the comparison with literature data is shown in Table 1. The refractive indices of the pure compounds were measured at 293.15 K by an Abbe refractometer, Atago 3T, with an accuracy of ± 0.0001 . The densities of pure chemicals were measured at 293.15 K using the Anton Paar DMA 60/602 density meter with an accuracy of $\pm 1.0 \times 10^{-5} \text{ g cm}^{-3}$.

2.2. Apparatus

A semi-flow phase equilibrium apparatus, as shown in Fig. 1, was used in this study. Similar experimental apparatus and procedures have been given in the previous literature [7,8]. The apparatus consisted of three sections for the input of the

supercritical fluid, the phase contact at the equilibrium cells and the analyses of the compositions of the equilibrium phases.

Pure CO₂ from a cylinder was liquefied through a cooler at $-6.5 \text{ }^\circ\text{C}$. It was then compressed by a metering pump (ConstaMetric 3200 P/F, LCD Analytical Inc.), and was heated through a pre-heating coil immersed in a water bath before introducing into the pre-saturation and equilibrium cells. Each head of the pump was equipped with a cooling jacket, in which aqueous alcohol at $-6.5 \text{ }^\circ\text{C}$ was used, to improve the fluid compression. A desired pressure was set in the experiment and was maintained at its value by a back pressure regulator (Tescom) during the vapor–liquid equilibrium measurements.

One pre-saturation cell and an equilibrium cell, each with a volume of 300 cm³, were used in this study. The cells (Whitey) were made by stainless steel and were immersed in a water bath. The experimental temperature and pressure were measured using a calibrated quartz thermometer (INS), and a calibrated pressure gauge (Heise). The accuracy for temperature measurement is $\pm 0.1 \text{ K}$, and that for pressure measurement is $\pm 0.02 \text{ MPa}$. The metering valves (Autoclave) and needle valves (Whitey) were also maintained at the experimental temperature to ensure an equilibrium condition.

The solvent (ester) component from either a liquid or vapor sample was collected in a flask cooled by an ice bath. A wet tester meter was used to measure the volume of the solute (CO₂) in the vapor phase. The volume of the liquid phase was determined by measuring the volume displaced in a column filled with water. The accuracy for these measurements is better than $\pm 0.25\%$.

Table 1

Comparison of the measured refractive indices and densities of pure fluids with literature data

Component	n^D (293.15 K)		ρ (293.15 K) (gcm ⁻³)		T_b (K) [21]	Purity (mol%)
	Experiment	Literature [21]	Experiment	Literature [21]		
Ethyl benzoate	1.5052	1.5035	1.0462	1.0469	486.55	>99.0
Diethyl succinate	1.4203	1.4200	1.0402	1.0403	489.65	>99.0
Isoamyl acetate	1.4008	1.3981	0.8732	0.8712	415.25	>99.0

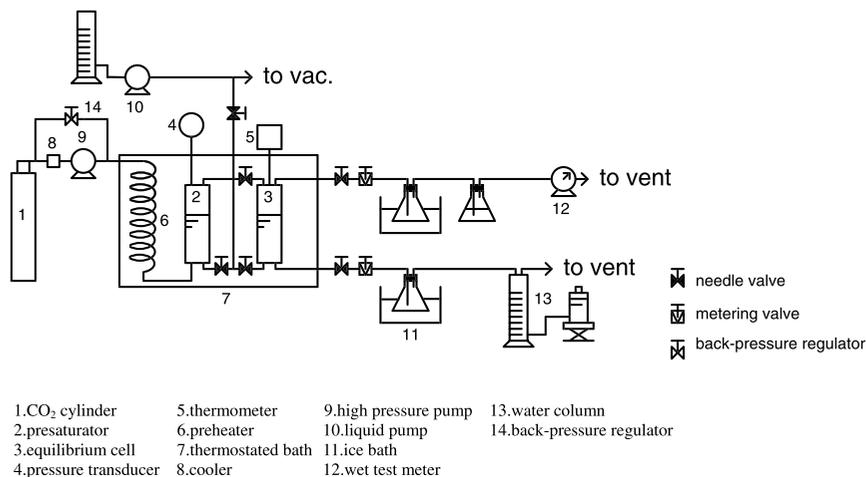


Fig. 1. Schematic diagram of the experimental apparatus.

3. Experimental procedures

Pure liquid solvent of ester compound was initially fed into the pre-saturation and equilibrium cells. Air in these cells was displaced by the flowing CO₂. The two cells were maintained at a constant temperature in a water bath, and CO₂ was charged into the cells at a desired pressure. Vapor–liquid equilibrium was reached after 2 h, and either the vapor or liquid sample was then expanded to atmospheric pressure through the metering valves. The samples were analyzed by the gravimetric method in this study. The volume of solute from the vapor or liquid phase was measured by using a wet test meter or a water column, respectively. The number of moles of the minor ester component that might vaporize into the gas phase was corrected by using the ideal gas equation of state $n = P^{vp}V/RT$, where P^{vp} was the vapor pressure of the ester compound and V was the volume of CO₂ recorded by the wet tester meter. The reported compositions are the average values of at least three repeated measurements. The flow rate of CO₂ was 25 l/h. The flow rates had also been varied from 10 to 40 l/h, and no change had been observed for the measured compositions. With these procedures, it was ensured that the compositions in the liquid or gas phase had reached the equilibrium values. The reproducibility of the measured composition is better

than $\pm 2\%$ for the minor component in the liquid phase. The reproducibility for the minor component in the vapor phase is $\pm 1.0 \times 10^{-4}$ mole fraction.

4. Results and discussion

The validity of the experimental system was first determined by measuring the vapor–liquid equilibrium for the binary mixture of carbon dioxide (1) and 1-octanol (2) at 328.15 K. The experimental results are reported in Table 2, and are also shown graphically in Fig. 2. The measured results using the present apparatus are in satisfactory agreement with those in the previous literature [9]. The measured equilibrium compositions and the corresponding equilibrium ratios (K_1 values) for three binary mixtures of CO₂ with ethyl benzoate, diethyl succinate and isoamyl acetate are presented in Tables 3–5, respectively. Graphical presentations of the experimental results are shown in Figs. 3–5. It was reported in literature [10,11] that the thermodynamic consistency for the VLE data at high pressures can be examined by the K values. According to this method, the K_1 values were plotted against pressure for each binary mixture. The slope for each plot should be close to -1 in order to satisfy the thermodynamic consistency. We have tested our

Table 2

Comparison of the VLE measurement results for the binary mixture of CO₂ (1) + 1-octanol (2) at 328.15 K

P(MPa)	Literature data [9]		P(MPa)	This work	
	x_1	y_1		x_1	y_1
4.00	0.2406	0.9996	3.00	0.1694	0.9993
6.00	0.3533	0.9997	5.45	0.3077	0.9993
8.00	0.4785	0.9993	7.38	0.4273	0.9994
10.00	0.5856	0.9977	9.89	0.5727	0.9983
12.00	0.6674	0.9876	12.14	0.6653	0.9851
15.00	0.7772	0.9435	13.38	0.7103	0.9734

experimental data by plotting the K_1 values against pressure for each binary mixture, as shown in Figs. 6–8, respectively. The slope for each plot is close to -1 and it is found that our results satisfied the empirical thermodynamic consistency requirement. The solubility of carbon dioxide in three ester compounds at 328.15 K is shown in Fig. 9. Ethyl benzoate has the structure with an aromatic group. It is relatively more difficult for CO₂ to dissolve into ethyl benzoate than the other two esters without ring structure, hence the solubility of CO₂ in ethyl benzoate is the lowest at a fixed pressure. The solubility of CO₂ in isoamyl acetate is the highest owing to its lowest boiling point. The solubility of the ester compounds in the vapor phase were not significant at low pressures. The solubility increased dramatically at equilibrium pressures higher than the critical point of carbon dioxide.

The Krichevsky–Ilinskaya (KI) equation [12] is generally applicable for the correlation of gas solubility data over a wide concentration range. The Henry's constant can then be evaluated from the regression of the solubility data:

$$\ln \frac{f_1}{x_1} = \ln H_{12}^* + \frac{A(x_2^2 - 1)}{RT} + \frac{V_1^\infty(P - P_2^{\text{sat}})}{RT} \quad (1)$$

where H_{12}^* is the Henry's constant at the vapor pressure of the solvent (P_2^{sat}), A is the Margules constant and V_1^∞ is the partial molar volume of the gas at infinite dilution. In this study, V_1^∞ was estimated from the generalized equation proposed by Brelvi and O'Connell [13] with the modified Rackett model [14] for calculating the liquid den-

sity. Carbon dioxide was a dominating component in the gas phase and its fugacity in the gas mixture (f_1) was calculated by employing the Lewis fugacity rule:

$$f_1 = f_1^0 y_1 \quad (2)$$

where f_1^0 is the fugacity of pure carbon dioxide calculated by the equation reported by Huang et al. [15]. The value of H_{12}^* and the Margules constant A in the KI equation were determined by the least squares algorithm, and the results are shown in Table 6. It is observed that the average absolute deviation of data regression is small, and the solubility data were satisfactorily correlated by

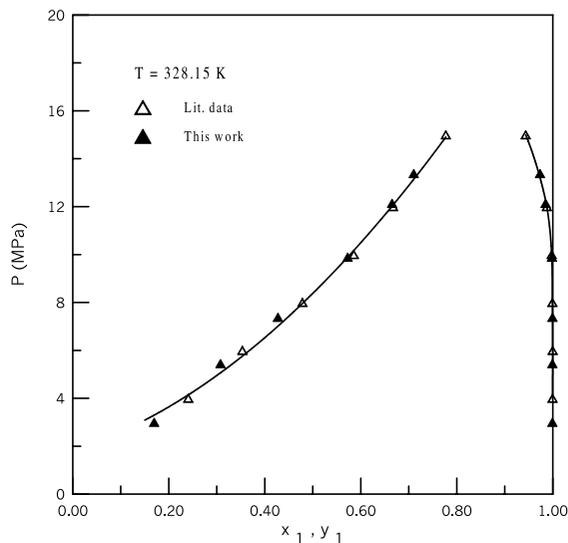


Fig. 2. Comparison of the P_{xy} data for the binary mixture of carbon dioxide (1) + 1-octanol (2) at 328.15 K.

Table 3

Experimental VLE results for the binary mixture of CO₂(1) + ethyl benzoate (2)

Pressure (MPa)	Composition		Equilibrium constant K_1
	x_1	y_1	
$T = 308.15$ K			
1.34	0.1476	0.9996	6.772
2.52	0.2685	0.9996	3.723
3.91	0.3959	0.9996	2.525
4.48	0.4548	0.9995	2.198
5.07	0.5008	0.9995	1.996
5.62	0.5559	0.9986	1.798
6.38	0.6247	0.9983	1.598
7.69	0.7566	0.9980	1.319
$T = 318.15$ K			
2.00	0.1900	0.9998	5.262
3.07	0.2856	0.9997	3.500
3.76	0.3397	0.9997	2.943
4.45	0.3877	0.9997	2.579
5.15	0.4470	0.9996	2.236
5.93	0.5050	0.9994	1.979
6.67	0.5553	0.9994	1.800
7.69	0.6250	0.9994	1.599
10.01	0.7607	0.9897	1.301
$T = 328.15$ K			
1.65	0.1375	0.9996	7.270
3.17	0.2526	0.9996	3.957
4.33	0.3305	0.9995	3.024
4.95	0.3730	0.9995	2.680
5.89	0.4364	0.9993	2.290
6.65	0.4871	0.9993	2.052
7.10	0.5133	0.9992	1.947
8.84	0.6157	0.9987	1.622
10.31	0.6789	0.9948	1.465
11.05	0.7185	0.9919	1.381
12.24	0.7591	0.9839	1.296

the KI equation. The Henry's constants increased with temperature for a given solvent owing to that the solubility of carbon dioxide decreased with increasing temperature.

The measured vapor–liquid equilibrium data were also correlated using the equation of state method. The Peng–Robinson (PR) equation [6]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (3)$$

$$a = 0.45724(R^2T_c^2/P_c)\{1 + \alpha[1 - (T/T_c)^{0.5}]\}^2 \quad (4)$$

$$\alpha = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

$$b = 0.07780RT_c/P_c \quad (6)$$

and the Soave–Redlich–Kwong (SRK) equation [5]:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (7)$$

$$a = 0.42747(R^2T_c^2/P_c)\{1 + \beta[1 - (T/T_c)^{0.5}]\}^2 \quad (8)$$

Table 4

Experimental VLE results for the binary mixture of CO₂(1) + diethyl succinate (2)

Pressure (MPa)	Composition		Equilibrium constant K_1
	x_1	y_1	
$T = 308.15$ K			
1.53	0.2341	0.9998	4.271
2.02	0.3006	0.9998	3.326
2.45	0.3587	0.9997	2.787
3.02	0.4315	0.9997	2.317
3.38	0.4612	0.9997	2.168
3.96	0.5317	0.9997	1.880
4.91	0.6379	0.9997	1.567
5.86	0.7246	0.9996	1.380
6.96	0.8420	0.9993	1.187
$T = 318.15$ K			
1.53	0.2038	0.9998	4.906
2.02	0.2645	0.9997	3.780
2.48	0.3138	0.9996	3.185
3.07	0.3801	0.9996	2.630
3.45	0.4136	0.9996	2.417
4.05	0.4742	0.9996	2.108
4.89	0.5416	0.9996	1.846
5.86	0.6346	0.9995	1.575
7.00	0.7298	0.9993	1.369
7.94	0.7661	0.9992	1.304
$T = 328.15$ K			
1.48	0.1688	0.9996	5.922
2.01	0.2270	0.9994	4.403
2.45	0.2705	0.9994	3.695
3.03	0.3289	0.9992	3.038
4.07	0.4157	0.9992	2.404
4.91	0.4914	0.9992	2.033
5.93	0.5694	0.9991	1.755
7.03	0.6482	0.9990	1.541
8.03	0.6905	0.9983	1.446
9.07	0.7545	0.9982	1.323
10.10	0.7972	0.9980	1.252

Table 5

Experimental VLE results for the binary mixture of CO₂ (1) + isoamyl acetate (2)

Pressure (MPa)	Composition		Equilibrium constant
	x_1	y_1	
T = 308.15 K			
1.03	0.1591	0.9993	6.281
2.08	0.3121	0.9993	3.202
3.03	0.4253	0.9989	2.349
4.00	0.5396	0.9989	1.851
4.96	0.6693	0.9989	1.492
6.00	0.7737	0.9984	1.290
6.93	0.8717	0.9963	1.143
T = 318.15 K			
1.00	0.1283	0.9998	7.793
2.02	0.2513	0.9993	3.977
3.00	0.3605	0.9993	2.772
3.96	0.4663	0.9993	2.143
5.00	0.5719	0.9989	1.747
6.00	0.6637	0.9985	1.504
7.00	0.7765	0.9984	1.286
8.03	0.8776	0.9983	1.138
T = 328.15 K			
1.03	0.1191	0.9998	8.395
2.01	0.2244	0.9991	4.452
2.98	0.3184	0.9988	3.137
3.76	0.3916	0.9988	2.551
4.93	0.5034	0.9986	1.984
6.00	0.5978	0.9982	1.670
7.00	0.6639	0.9981	1.503
8.03	0.7579	0.9969	1.315
9.07	0.8562	0.9961	1.163

$$\beta = 0.480 + 1.574\omega - 0.176\omega^2 \quad (9)$$

$$b = 0.08664RT_c/P_c \quad (10)$$

were used to correlate the experimental results. The equation of state parameters a and b for each pure fluid are evaluated from its critical properties and acentric factor [5,6]. Table 7 lists the critical properties and the acentric factors for the pure compounds used in this study.

Various mixing models were applied in this study to evaluate the equation of state parameters for mixtures. For the van der Waals one-fluid (VDW1) mixing rules with one binary parameter, we have

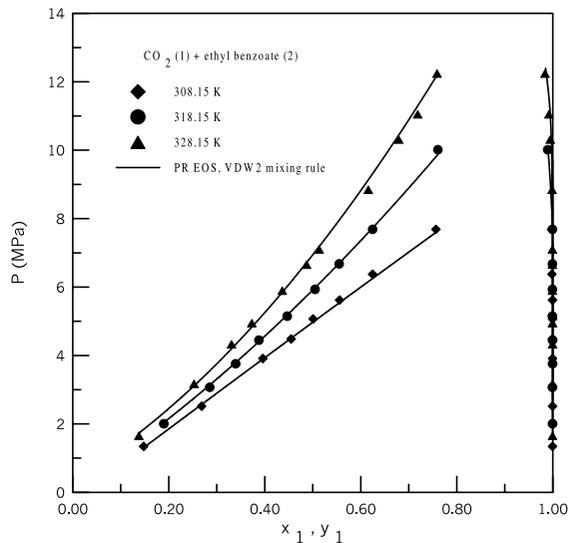


Fig. 3. VLE results of the binary mixture of CO₂ (1) + ethyl benzoate (2).

$$a_m = \sum \sum x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad (11)$$

$$b_m = \sum x_i b_i \quad (12)$$

The volume parameter of a mixture can also be evaluated using an additional binary parameter (VDW2 mixing rule):

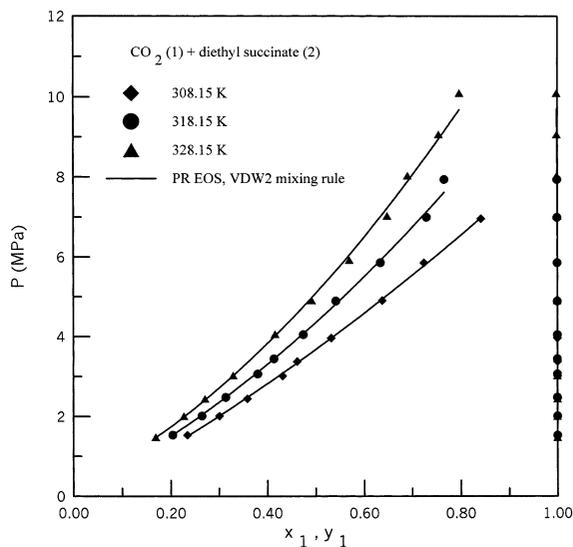


Fig. 4. VLE results of the binary mixture of CO₂ (1) + diethyl succinate (2).

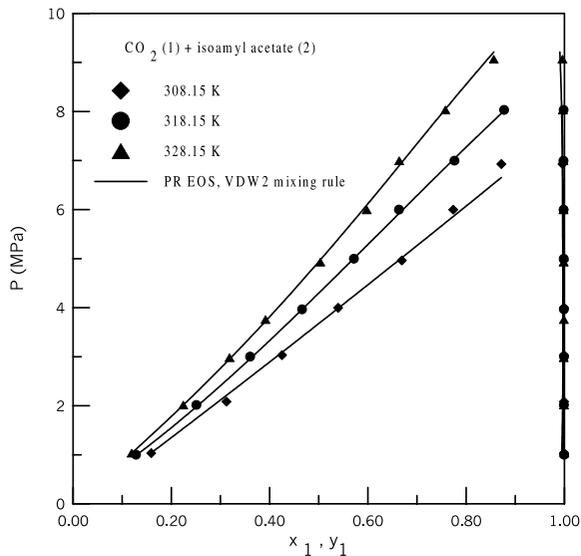


Fig. 5. VLE results of the binary mixture of CO₂ (1) + isoamyl acetate (2).

$$b_m = \sum \sum x_i x_j \frac{(b_i + b_j)}{2} (1 - m_{ij}) \quad (13)$$

The binary parameters were taken as temperature-independent in this study, and their optimal values were determined from data regression.

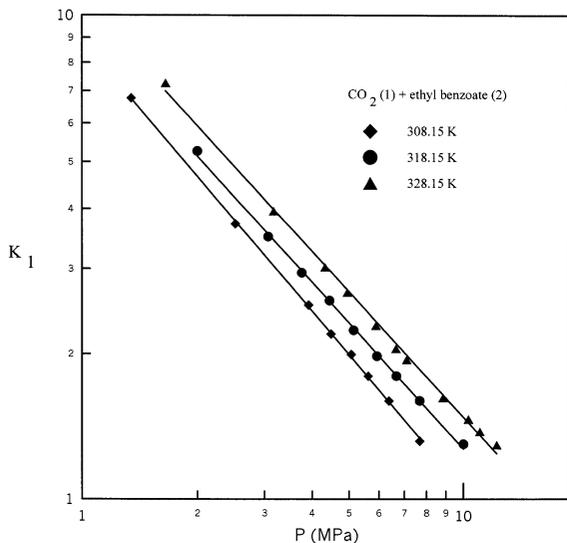


Fig. 6. Equilibrium ratios for the binary mixture of CO₂ (1) + ethyl benzoate (2).

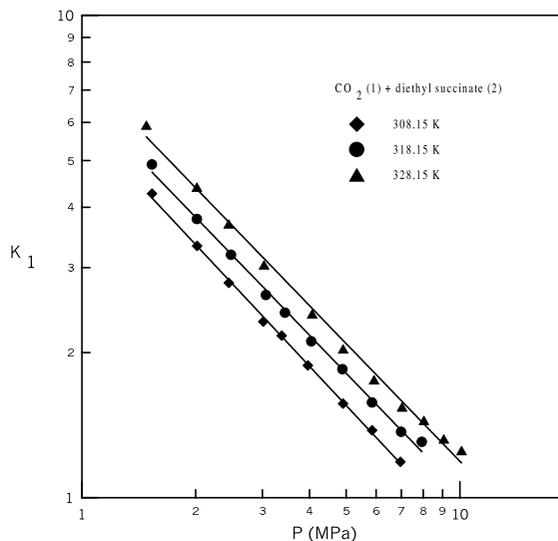


Fig. 7. Equilibrium ratios for binary mixture of CO₂ (1) + diethyl succinate (2).

Panagiotopoulos and Reid [16] assumed that the binary parameters are composition-dependent (Panagiotopoulos–Reid mixing rule), the mixture volume parameter for an equation of state was determined by Eq. (14), and the mixture energy parameter was written as

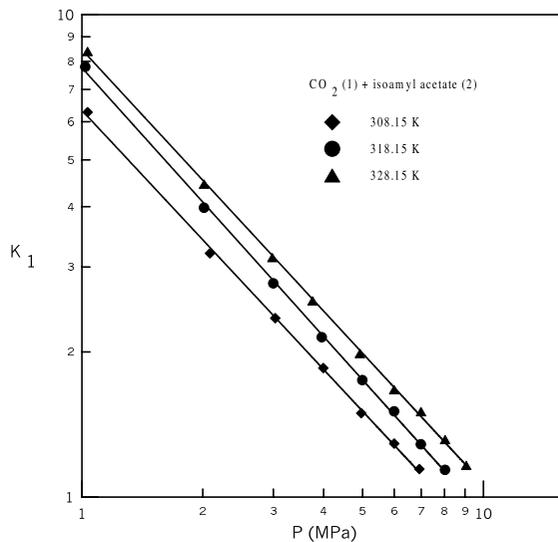


Fig. 8. Equilibrium ratios for the binary mixture of CO₂ (1) + isoamyl acetate (2).

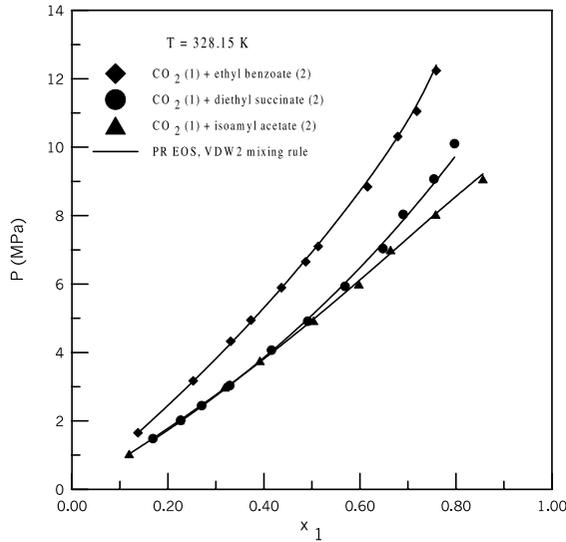


Fig. 9. Solubilities of CO_2 in various ester compounds at 328.15 K.

$$a_m = \sum \sum x_i x_j (a_i a_j)^{0.5} [1 - k_{ij} + (k_{ij} - k_{ji}) x_i] \quad (14)$$

This mixing model can be used in correlating the binary VLE experimental data, although it suffers from the Michelsen–Kistenmacher syndrome [17] in extension to multicomponent systems.

In addition to the traditional van der Waals type mixing models, a group contribution mixing model has been proposed by Huron and Vidal [18]. In this mixing model, the excess free energy calculated from an equation of state at an infinite

Table 7

Pure component properties used in this work [21]

Component	T_c (K)	P_c (MPa)	ω
Carbon dioxide	304.1	7.38	0.2280
Ethyl benzoate	698.0	3.18	0.4787
Diethyl succinate	660.0	2.53	0.7374
Isoamyl acetate	599.0	2.84	0.4140

pressure reference state was set equal to that from an activity coefficient model. The NRTL [19] and UNIQUAC [20] activity coefficient models were employed in this study with the cubic type equations of state. The optimal binary parameters in the NRTL and the UNIQUAC models were regressed from the experimental VLE data. The following objective function was used in the data regression of this study:

$$\text{obj} = \sum \left| \frac{P^{\text{exp}} - P^{\text{cal}}}{P^{\text{exp}}} \right|_i + \sum |y_2^{\text{exp}} - y_2^{\text{cal}}|_i \quad (15)$$

The optimally fitted binary parameters for various equations of state with the van der Waals type mixing rules are presented in Table 8. It is observed that either the Peng–Robinson or Soave–Redlich–Kwong equation with van der Waals mixing rules yielded satisfactory results. The optimal NRTL and UNIQUAC parameters regressed from the Huron–Vidal method are shown in Table 9. It is shown that the results with the

Table 6

Parameters of the KI equation for three binary systems

Systems	T (K)	$H_{1,2}^*$ (bar)	A (J/mol)	\bar{V}_1^∞ (cm ³ /mol)	AAD (%)
$\text{CO}_2(1) + \text{ethyl benzoate (2)}$	308.15	99.79	1241.86	47.05	3.14
	318.15	116.05	1345.41	47.96	2.94
	328.15	134.70	1494.24	48.99	3.58
$\text{CO}_2(1) + \text{diethyl succinate (2)}$	308.15	66.86	608.38	49.20	2.15
	318.15	74.33	471.55	50.43	1.81
	328.15	87.70	622.57	51.85	1.51
$\text{CO}_2(1) + \text{isoamyl acetate (2)}$	308.15	68.29	787.06	53.74	2.78
	318.15	83.65	1022.22	55.89	3.75
	328.15	92.83	1003.22	58.32	3.36

$$\text{AAD}(\%) = \left(\frac{100}{n} \right) \sum_{k=1}^n \left\{ \left| \frac{\left(\frac{f_1}{x_1} \right)^{\text{cal}} - \left(\frac{f_1}{x_1} \right)^{\text{exp}}}{\left(\frac{f_1}{x_1} \right)^{\text{exp}}} \right| \right\}_k$$

Table 8

Correlated results of experimental VLE data of three binary mixtures using various EOS mixing rules

Mixing rule	Peng–Robinson EOS					Soave–Redlich–Kwong EOS					
	k_{12}	k_{21}	m_{12}	AADP(%)	AADy(%)	k_{12}	k_{21}	m_{12}	AADP(%) ^a	AADy(%) ^b	
CO ₂ (1) + ethyl benzoate (2)											
VDW1		0.071			1.00	0.05	0.071			0.86	0.08
VDW2		0.070		−0.001	0.94	0.06	0.071		0.0	0.86	0.08
Panagiotopoulos–Reid		0.072	0.070		0.94	0.06	0.072	0.071		0.86	0.08
CO ₂ (1) + diethyl succinate (2)											
VDW1		0.021			1.56	0.05	0.020			1.52	0.05
VDW2		0.027		0.005	1.26	0.05	0.024		0.004	1.24	0.05
Panagiotopoulos–Reid	0.014		0.025		1.27	0.05	0.014	0.025		1.27	0.05
CO ₂ (1) + isoamyl acetate (2)											
VDW1		0.049			1.33	0.18	0.052			1.31	0.15
VDW2		0.050		0.002	1.31	0.18	0.053		0.002	1.28	0.15
Panagiotopoulos–Reid	0.046		0.049		1.30	0.18	0.050	0.053		1.28	0.15

$$^a \text{AADP}(\%) = \frac{100}{n} \sum_{i=1}^n \frac{|P^{\text{exp}} - P^{\text{cal}}|_i}{P^{\text{exp}}}$$

$$^b \text{AADy}_1(\%) = \frac{100}{n} \sum_{i=1}^n \frac{|y_{1,i}^{\text{exp}} - y_{1,i}^{\text{cal}}|_i}{y_{1,i}^{\text{exp}}}$$

NRTL model show a relatively larger deviation than those from the van der Waals mixing rules. The Huron–Vidal type mixing rule with the UNIQUAC model shows comparable good results with the traditional van der Waals mixing rules. Graphical presentations of the calculated results from the Peng–Robinson equation of state with dual interaction parameters are also shown in Figs. 3–5.

5. Conclusion

The vapor–liquid equilibrium data of three binary systems of carbon dioxide with ethyl benzoate, diethyl succinate, and isoamyl acetate are reported at 308.15, 318.15, and 328.15 K and pressures up to 13 MPa. The KI equation was used to correlate the experimental data and the Henry’s constants are determined. The Peng–Robinson and Soave–Redlich–Kwong equations of state with various mixing models were also used to correlate the experimental data. It shows that both the Peng–Robinson and Soave–Redlich–Kwong equations of state with the van der Waals mixing rules and two optimally fitted parameters gave satisfactory regression results.

Acknowledgements

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

Appendix A. Nomenclature

a, b	parameters in the equation of state.
A	Margules parameter in the KI equation
K	equilibrium ratio, $K = y/x$
k	binary interaction parameter in the mixing rule
f_1^0	fugacity of carbon dioxide
f	fugacity
H_{12}^*	Henry constant at P_2^{sat}
m	binary interaction parameter in the mixing rule
P	pressure
P^{vp}	vapor pressure of ester compound
R	gas constant
T	temperature

Table 9

Correlated results of the experimental VLE data of three binary mixtures by the Huron–Vidal mixing rules with the NRTL and the UNIQUAC activity coefficient models

EOS	$A_{12}(\text{J mol}^{-1})$	$A_{21}(\text{J mol}^{-1})$	α	AADP(%) ^a	AADy(%) ^b
<i>NRTL model</i>					
CO ₂ (1) + ethyl benzoate (2)					
PR	10 078.77	−3913.26	0.2	2.91	0.09
SRK	9833.12	−3972.61	0.2	2.71	0.08
CO ₂ (1) + diethyl succinate (2)					
PR	8429.05	−4330.32	0.2	2.43	0.05
SRK	7729.54	−4258.45	0.2	2.15	0.05
CO ₂ (1) + isoamyl acetate (2)					
PR	9324.84	−3906.96	0.2	2.62	0.18
SRK	8900.40	−3890.15	0.2	2.41	0.15
<i>UNIQUAC model</i>					
CO ₂ (1)+ ethyl benzoate (2)					
PR	987.40	1373.23		1.21	0.08
SRK	1044.14	1215.00		1.12	0.07
CO ₂ (1) + diethyl succinate (2)					
PR	431.84	1628.18		1.66	0.05
SRK	282.62	1662.07		1.64	0.05
CO ₂ (1) + isoamyl acetate (2)					
PR	789.01	1496.63		1.43	0.17
SRK	684.68	1511.26		1.42	0.15

$$^a \text{AADP}(\%) = \frac{100}{n} \sum_{i=1}^n \frac{|P^{\text{exp}} - P^{\text{cal}}|_i}{P^{\text{exp}}}$$

$$^b \text{AAD}y_1(\%) = \frac{100}{n} \sum_{i=1}^n \frac{|y_1^{\text{exp}} - y_1^{\text{cal}}|_i}{y_{1,i}^{\text{exp}}}$$

T_b	boiling point temperature
V_1^∞	partial molar volume of a gas at infinite dilution
V	volume of CO ₂
v	molar volume
x	mole fraction of liquid phase
y	mole fraction of vapor phase

Subscripts

C	critical properties
i, j	component i or j
m	mixture
1,2	component 1 or 2

Superscript

cal	calculated value
exp	experimental data
sat	saturated condition

References

- [1] I. Wichterle, J. Linek, Z. Wagner, H.V. Kehiaian, Vapor–liquid equilibrium bibliographic database, ELDATA SARRL, Montreuil, 1993.
- [2] Z. Wagner, Vapour–liquid equilibrium at high pressure in the system containing carbon dioxide and propyl acetate, *Fluid Phase Equilib.* 110 (1995) 175–182.
- [3] V. Riha, G. Brunner, Phase equilibrium of fish oil ethyl esters with supercritical carbon dioxide, *J. Supercritical Fluids* 15 (1999) 33–50.
- [4] R.M.M. Stevens, X.M. Shen, T.W. de Loos, J. de Swaan Arons, A new apparatus to measure the vapor–liquid equilibria of low volatility compounds with near critical carbon dioxide, experimental and modeling results for carbon dioxide + n-butanol, + 2-butanol, + 2-butyl acetate and + vinyl acetate systems, *J. Supercritical Fluids* 11 (1997) 1–14.
- [5] G. Soave, Equilibrium constants from a modified Redlich–Kwong equation of state, *Chem. Eng. Sci.* 27 (1972) 1197–1203.

- [6] D.Y. Peng, D.B. Robinson, A new two constant equation of state, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64.
- [7] R.J. Lee, K.C. Chao, Extraction of 1-methylnaphthalene and m-cresol with supercritical carbon dioxide and ethane, *Fluid Phase Equilib.* 43 (1988) 329–340.
- [8] K.W. Cheng, S.J. Kuo, M. Tang, Y.P. Chen, Vapor–liquid equilibria at elevated pressure of binary mixture of carbon dioxide with methyl salicylate, eugenol, and diethyl phthalate, *J. Supercritical Fluids* 18 (2000) 87–99.
- [9] W.L. Weng, M.J. Lee, Phase equilibrium measurement for the binary mixtures of 1-octanol plus CO₂, C₂H₆ and C₂H₄, *Fluid Phase Equilib.* 73 (1992) 117–125.
- [10] D.E. Matschke, G. Thodos, Vapor–liquid equilibria for the ethane–propane system, *J. Chem. Eng. Data* 7 (1962) 232–234.
- [11] T. Sato, T. Sugeta, N. Nakazawa, K. Otake, M. Satom, K. Ishihara, M. Kato, High pressure of vapor–liquid and vapor–liquid–liquid equilibria for system containing supercritical carbon dioxide, water and furfural, *Fluid Phase Equilib.* 108 (1995) 293–303.
- [12] I.R. Krichevsky, A.A. Ilinskaya, Partial molar volumes of gas dissolved in liquids (the thermodynamics of dilute solution of nonelectrolytes), *Acta Physicochim USSR* 20 (1945) 327–348.
- [13] S.W. Brelvi, J.P. O’Connell, Corresponding state correlation for liquid compressibility and partial molar volume of gases at infinite dilution in liquids, *AIChE J.* 18 (1972) 1239–1243.
- [14] C.F. Spencer, R.P. Danner, Improved equation for prediction of saturated liquid density, *J. Chem. Eng. Data* 17 (1972) 236–241.
- [15] F.H. Huang, M.H. Li, L.L. Lee, K.E. Starling, F.T.H. Chung, An accurate equation of state for carbon dioxide, *J. Chem. Eng. Jpn.* 18 (1985) 490–496.
- [16] A.Z. Panagiotopoulos, R.C. Reid, New mixing rule for cubic equation of state for highly polar asymmetric systems, *ACS Symposium Series* 300 (1986) 571–582.
- [17] M.L. Michelsen, H. Kistenmacher, Composition dependent interaction coefficients, *Fluid Phase Equilib.* 58 (1990) 229–230.
- [18] M.J. Huron, J. Vidal, New mixing rules in simple equation of state for representing vapor–liquid equilibria of strongly non-ideal mixtures, *Fluid Phase Equilib.* 3 (1979) 255–271.
- [19] H. Renon, J.M. Prausnitz, Local compositions in thermodynamic excess functions for liquid mixture, *AIChE J.* 14 (1968) 135–144.
- [20] D.S. Abrams, J.M. Prausnitz, Statistical thermodynamic of liquid mixture: A new expression for the excess Gibbs energy of partly or completely miscible system, *AIChE J.* 21 (1975) 116–128.
- [21] T.E. Daubert, R.P. Danner, *Physical and thermodynamic properties of pure chemicals: Data compilation*, Hemisphere, New York, 1989.