Isothermal Vapor−Liquid Equilibria for Binary Mixtures of Carbon Dioxide with Hexyl Acetate, Cyclohexyl Acetate, or Phenyl Acetate at Elevated Pressures

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Isothermal vapor−liquid equilibrium phase compositions were measured for three binary systems of carbon dioxide with different C6-acetates—hexyl acetate, cyclohexyl acetate, and phenyl acetate—at temperatures from 333.15 K to 413.15 K and pressures up to 20 MPa. The solubility isotherm of the acetates in the vapor phase exhibits a minimum value at subcritical pressures of carbon dioxide. Henry's constants were calculated by fitting the Krichevsky−Ilinskaya equation to the isothermal equilibrium data. The constants increase with increasing temperature for these three binary systems. The new phase equilibrium data were correlated with the Soave−Redlich−Kwong, the Peng−Robinson, and the Patel−Teja equations of state. The Peng−Robinson equation with two-parameter (k_{a12} and k_{b12}) van der Waals mixing rules is marginally better than other methods for the investigated systems.

Introduction

Low-volatility esters have been increasingly used as "cleaner" solvents in the processing of polymer materials. However, it is difficult to remove these spent solvents from highly viscous materials by conventional separation methods. Among several other alternative techniques, supercritical fluid extraction can be a feasible means to serve the purpose. Supercritical fluids have long been recognized as efficient media for the removal of waste solvents, due to their solvating properties and unique characteristics of fast penetration with high selectivity of extraction. The vapor−liquid equilibrium (VLE) data of esters + supercritical fluids are needed for feasibility studies and development of this separation process. In the present study, isothermal VLE data were measured for three binary systems containing carbon dioxide with a C6-acetate—hexyl acetate, cylcohexyl acetate, or phenyl acetate—at temperatures from 333.15 K to 413.15 K and pressures up to 20 MPa. No VLE data are available in the literature for these three binary systems at the comparable conditions of this work.

Equations of state (such as the Soave−Redlich−Kwong,[1] the Peng−Robinson,[2] and the Patel−Teja[3]) with some variations of mixing rules have widely been applied to calculate VLE properties for mixtures containing supercritical fluids.[4−8] The conventional van der Waals one-fluid mixing rules (vdW) and the Huron−Vidal type mixing rules (EOS/g^E) have most commonly been used. However, none of the mixing rules appears to be distinctly superior to the others for all supercritical fluid systems.[8] The vdW mixing rules were used in conjunction with the Soave−Redlich−Kwong (SRK), Peng−Robinson (PR), and Patel-Teja (PT) equations of state to correlate the new VLE data obtained from this work.

Experimental Section

Apparatus and Procedures. A semiflow-type apparatus was used in this work for measurements of phase equilibrium properties. A description of the equipment and its operation has been presented in detail elsewhere.[9,10] The heart of the apparatus is a presaturator and an equilibrium cell that were placed in a thermostatic bath. The bath temperature was controlled to within ±0.03 K. The equilibrium temperature was measured by a microthermometer (model 1506, ±0.02 K, Hart Scientific) with a platinum RTD probe. A pressure transducer (model PDCR-330, 0−35 MPa, ±0.1%, Druck Ltd.) connected to a digital readout (model DPI 261, Druck Ltd.) monitored the equilibrium pressure. The saturated vapor stream was diverted to a sampling flask, which was immersed in an ice bath, after its pressure and temperature were reduced. The heavier component (acetates) was trapped in the flask and later weighed to determine its mass by an analytical electronic balance with a precision of ±0.1 mg. The corresponding quantity of gas (carbon dioxide) liberated from the sample was measured with a wet test meter. Liquid sample was taken from the bottom of the equilibrium cell, while the pressure of the cell was maintained constantly by a continuous vapor stream from the presaturator passing over the top of the equilibrium cell. A similar method was used for composition analysis of liquid samples, but a graduated cylinder, instead of the wet test meter, was employed to collect the liberated carbon dioxide. Fluctuation of pressure in the equilibrium cell was regulated to within ±0.01 MPa during the period of sample collection. At least four replicated samples of each phase were taken at an experimental condition, and the equilibrium composition was determined by averaging the replications. The uncertainty of the reported mole fractions for the minor component is within ±2% under normal experimental conditions, but could be as high as ±10% for those values below 10^{-4}.

Materials. Carbon dioxide (99.8+%) was purchased from Liu-Hsiang Co. The purities of hexyl acetate (Aldrich), cyclohexyl acetate (TCI), and phenyl acetate (Lancaster)

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Table 1. Critical Constants, Acentric Factor, and Vapor Pressure of Pure Substances

compound	T_c (K)	P_c (MPa)	V_c (cm^3 mol^{-1})	ω	A^a	B^a	C^a	ρ^L (at 298.15 K)
carbon dioxide	304.1[b]	7.38[b]		0.239[b]				
hexyl acetate	616.55[c]	2.548[c]	509.5[c]	0.549[d]	6.4606	1688.63	−64.384	0.876
cyclohexyl acetate	653.75[c]	3.170[c]	442.5[c]	0.413[d]	7.4289	2418.5	0	0.970
phenyl acetate	686.17[c]	3.673[c]	401.5[c]	0.438[d]	7.6938	2660.5	0	1.073

[a] $\log(P^{sat}) = A - [B/(T + C)]$, where P^{sat} is vapor pressure in kPa and T is temperature in K. The Antoine constants for hexyl acetate were taken from Arce et al.[11] The Antoine constants for cyclohexyl acetate and phenyl acetate were determined by fitting vapor pressure data to the Antoine equation, in which the data of cyclohexyl acetate were measured in this study and those of phenyl acetate were taken from Perry and Green.[12] [b] Taken from Reid et al.[13] [c] Determined from the Joback group contribution model (Reid et al.).[13] [d] Determined from the Lee−Kesler model (Reid et al.).[13]

Table 2. Phase Compositions for Carbon Dioxide (1) + Hexyl Acetate (2)

P (MPa)	x_1	y_2	P (MPa)	x_1	y_2
		T = 333.15 K			
1.0	0.119	0.00229	6.0	0.569	0.00197
2.0	0.229	0.00172	7.0	0.642	0.00242
3.0	0.321	0.00149	8.0	0.699	0.00293
4.0	0.418	0.00160			
		T = 373.15 K			
2.0	0.156	0.00802	8.0	0.512	0.00786
4.0	0.287	0.00634	10.0	0.605	0.0107
5.0	0.352	0.00577	12.0	0.682	0.0160
6.0	0.404	0.00631			
		T = 413.15 K			
2.0	0.114	0.0320	9.0	0.454	0.0235
4.0	0.227	0.0212	12.0	0.567	0.0291
5.0	0.275	0.0211	15.0	0.674	0.0410
6.0	0.325	0.0212			

Table 3. Phase Compositions for Carbon Dioxide (1) + Cyclohexyl Acetate (2)

P (MPa)	x_1	y_2	P (MPa)	x_1	y_2
		T = 333.15 K			
2.0	0.193	0.00192	7.5	0.621	0.00323
4.0	0.370	0.00181	9.0	0.733	0.00502
6.0	0.519	0.00244			
		T = 373.15 K			
2.0	0.131	0.00835	10.0	0.549	0.00998
4.0	0.254	0.00640	12.0	0.623	0.0151
6.0	0.359	0.00678	14.0	0.710	0.0236
8.0	0.456	0.00815			
		T = 413.15 K			
2.0	0.0959	0.0327	9.0	0.396	0.0221
4.0	0.194	0.0228	12.0	0.501	0.0268
6.0	0.275	0.0200	15.0	0.599	0.0297

are at least 99%. All of the chemicals were used without further purification. The physical properties of these pure compounds are listed in Table 1.

Experimental Results

Tables 2−4 report the equilibrium phase compositions for carbon dioxide (1) + hexyl acetate (2), + cyclohexyl acetate (2), and + phenyl acetate (2), respectively, at temperatures from 333.15 K to 413.15 K and pressures up to 20 MPa. Figures 1 and 2 compare the mole fractions of the acetates in the vapor phase (y_2) at 333.15 K and at 413.15 K, respectively. These two graphs exhibit a minimum solubility on each isotherm at subcritical pressures of carbon dioxide. The magnitude of the saturated vapor compositions of the acetates follows the sequence of phenyl acetate < hexyl acetate < cyclohexyl acetate at 333.15 K over the entire pressure range, as shown in Figure 1. However, Figure 2 shows that y_2 values of hexyl acetate are greater than those of cylcohexyl acetate at 413.15 K at pressures >6 MPa.

The mole fraction of carbon dioxide in the liquid phase (x_1) follows the sequence of phenyl acetate < cyclohexyl acetate < hexyl acetate, over the entire experimental conditions. Figure 3 shows a graphical comparison of x_1 at the equilibrium temperature of 413.15 K.

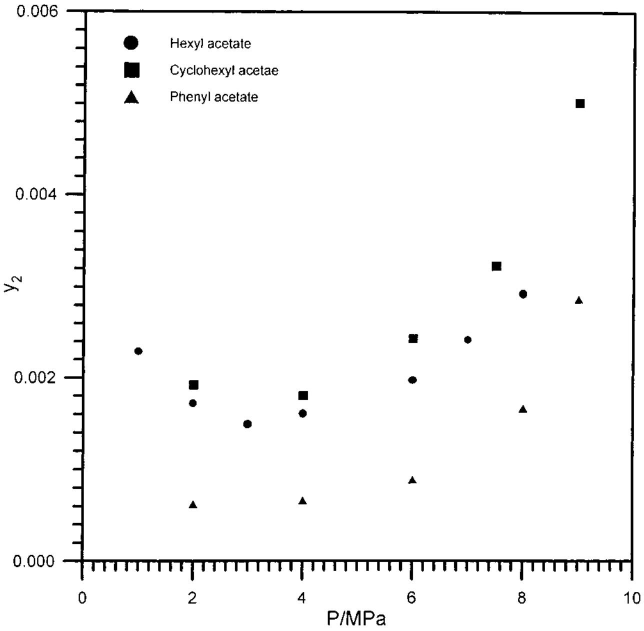

Figure 1. Comparison of the saturated vapor composition of different acetates (y_2) at 333.15 K.

Table 4. Phase Compositions for Carbon Dioxide (1) + Phenyl Acetate (2)

P (MPa)	x_1	y_2	P (MPa)	x_1	y_2
		T = 333.15 K			
2.0	0.144	0.00063	8.0	0.532	0.00167
4.0	0.279	0.00067	9.0	0.599	0.00288
6.0	0.407	0.00089			
		T = 373.15 K			
2.0	0.100	0.00386	10.0	0.438	0.00549
4.0	0.194	0.00306	12.0	0.512	0.00843
6.0	0.280	0.00334	14.0	0.584	0.0130
8.0	0.362	0.00401	16.0	0.657	0.0221
		T = 413.15 K			
2.0	0.0734	0.0152	12.0	0.412	0.0146
4.0	0.153	0.0107	15.0	0.497	0.0200
6.0	0.220	0.0103	18.0	0.578	0.0286
9.0	0.319	0.0109	20.0	0.635	0.0331

Figure 4 illustrates the variation of equilibrium ratios (K values) with temperature and pressure for carbon dioxide + cyclohexyl acetate. K_2 isotherms are crossed over in the pressure range of 9−13 MPa. Similar behavior may also exist in the other two systems, but it is not clearly shown by the experimental results.

Henry's Constants

Tables 2−4 reveal that the solubility of carbon dioxide in the liquid phase (x_1) increases with a decrease of

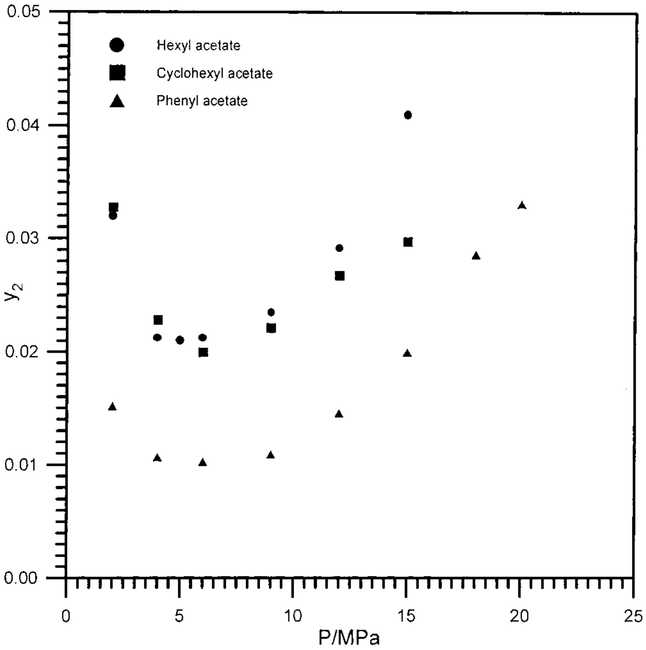

Figure 2. Comparison of the saturated vapor composition of different acetates (y_2) at 413.15 K.

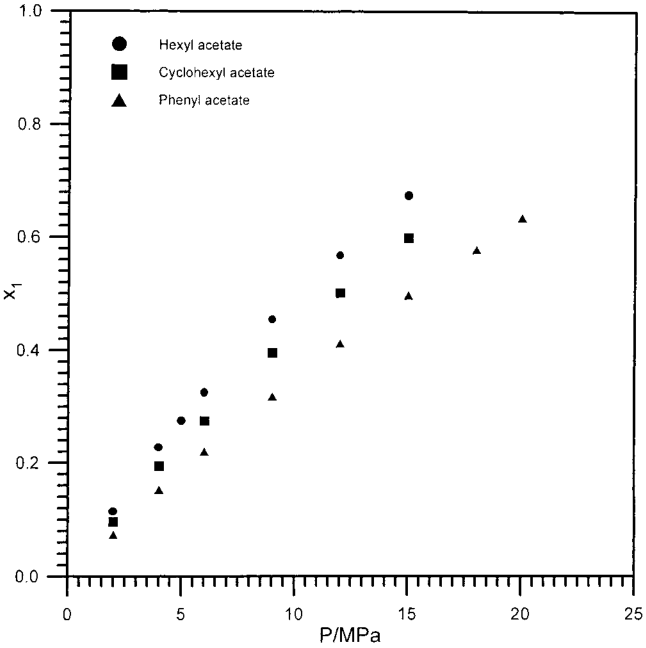

Figure 3. Comparison of the saturated liquid composition of carbon dioxide (x_1) in different acetates at 413.15 K.

temperature and with an increase of pressure. The Krichevsky−Ilinskaya (KI) equation[14] was adopted to describe the pressure effect on the solubility of carbon dioxide. The KI equation is given by

$$\ln(f_1/x_1) = \ln H_{1,2}^* + [A(x_2^2 - 1)/RT] + \bar{V}_1^\infty(P - P_2^{\mathrm{sat}})/RT \tag{1}$$

where $H_{1,2}^*$ is Henry's constant at the vapor pressure of the acetates (P_2^{sat}), A is the Margules constant, and $\bar{V}_1^\infty$ is the partial molar volume of carbon dioxide at infinite dilution. Henry's constant of carbon dioxide dissolved in the heavy liquid can be calculated from the VLE data according to eq 1. In this study, $\bar{V}_1^\infty$ was estimated with the generalized equation of Brelvi and O'Connell[15] in which

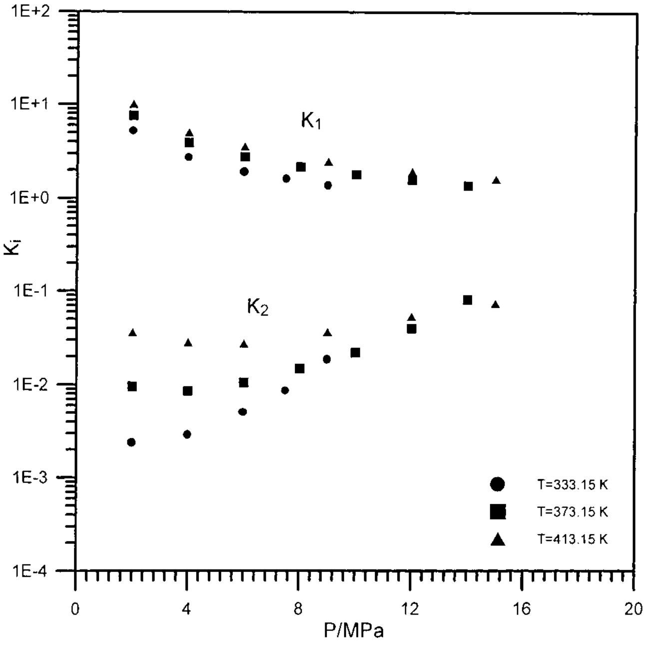

Figure 4. K values of carbon dioxide (1) + cyclohexyl acetate (2).

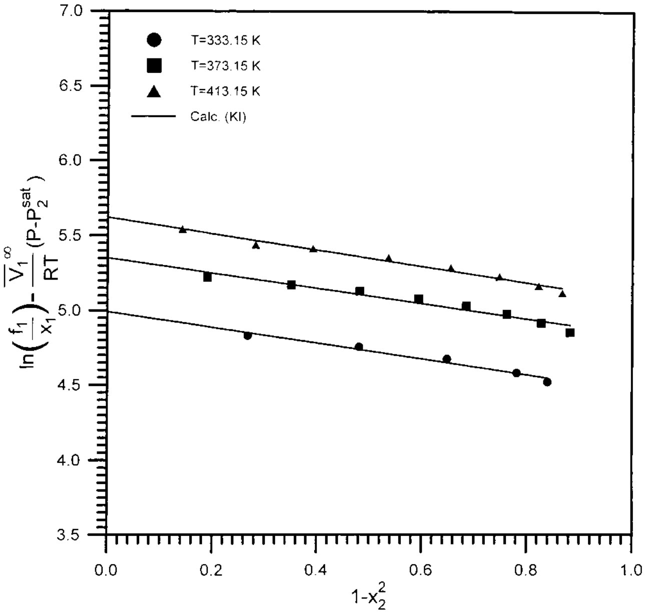

Figure 5. Correlation with the KI equation for carbon dioxide (1) + phenyl acetate (2).

liquid density was calculated with the modified Rackett model (Spencer and Danner).[16] The fugacity of carbon dioxide in the vapor phase (f_1) was computed on the basis of the Lewis fugacity rule

$$f_1 = f_1^\circ y_1 \tag{2}$$

where f_1° is the fugacity of the pure carbon dioxide that was calculated from the equation of Huang et al.[17] The Lewis rule was valid for calculating the fugacity of carbon dioxide in the vapor phase, because all of the mole fractions of carbon dioxide in the vapor phase are >0.9 over the entire experimental conditions.[18] The values of $H_{1,2}^*$ and the Margules constant were then determined from regression of the KI equation to the VLE data. Figure 5 shows that the KI equation closely represents the pressure effect on the solubility of carbon dioxide in phenyl acetate. The correlated results are summarized in Table 5. Figure 6

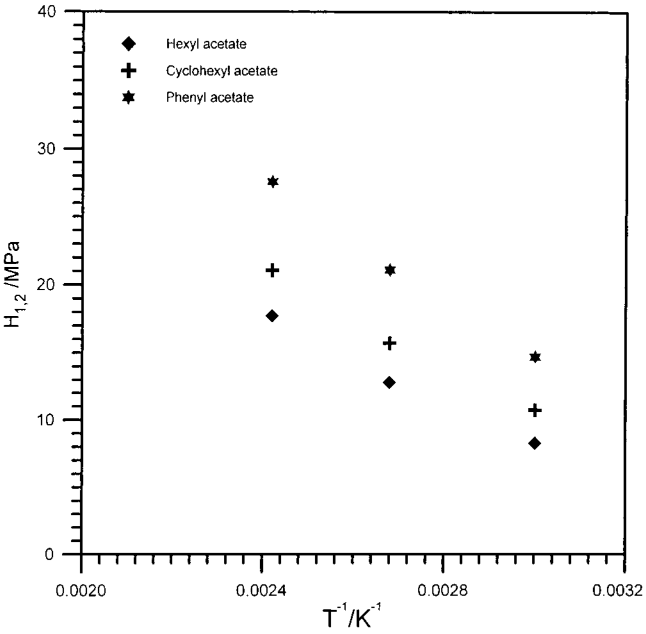

Figure 6. Temperature effect on Henry's constants.

Table 5. Correlated Results of the Krichevsky−Ilinskaya (KI) Equation

	T	$H_{1,2}$*	A	V_1^{∞}	AAD[a]
component (2)	K	MPa	J·mol^{-1}	cm^3·mol^{-1}	%
hexyl acetate	333.15	8.29	347	52.1	1.2
	373.15	12.80	646	61.4	1.5
	413.15	17.73	1293	81.7	1.3
cyclohexyl acetate	333.15	10.74	1030	52.3	2.0
	373.15	15.71	1168	61.0	1.8
	413.15	21.06	1562	78.6	1.4
phenyl acetate	333.15	14.70	1447	43.9	1.9
	373.15	21.08	1567	48.5	2.4
	413.15	27.58	1853	56.1	1.6

[a]
$$\text{AAD}\ (\%) = \frac{100}{n}\sum_{k=1}^{n}\frac{|(f_1/x_1)_k^{\text{calcd}} - (f_1/x_1)_k^{\text{exptl}}|}{(f_1/x_1)_k^{\text{exptl}}}$$

illustrates the temperature effect on Henry's constant, indicating that the Henry's constant of each binary system increases with increasing temperature. At a given temperature, the magnitude of Henry's constant of carbon dioxide dissolving in the acetates follows the sequence of phenyl acetate > cyclohexyl acetate > hexyl acetate.

Data Correlations with Equations of State

The SRK,[1] PR,[2] and PT[3] equations of state with the vdW one-fluid mixing rules were used in this study to correlate the new VLE data. In the calculations, the mixture constants θ_m of the equation of state (i.e., a_m, b_m, and c_m) were defined as

$$\theta_m = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j \theta_{ij} \tag{3}$$

The combining rules of a_{ij} and b_{ij} were given, respectively, as

$$a_{ij} = (1 - k_{aij})(a_i a_j)^{0.5} \tag{4}$$

and

$$b_{ij} = (1 - k_{bij})(b_i + b_j)/2 \tag{5}$$

where k_{aij} and k_{bij} are binary interaction parameters. The value of c_{ij} for the PT equation of state was calculated by

$$c_{ij} = (c_i + c_j)/2 \tag{6}$$

The optimal values of the binary interaction parameters were obtained from bubble-point pressure calculations by using a modified Levenberg−Marquardt algorithm to minimize the following objective function π

$$\pi = \frac{100}{2n}\sum_{k=1}^{n}\left(\frac{|P_k^{\text{calcd}} - P_k^{\text{exptl}}|}{P_k^{\text{exptl}}} + \left|y_{2,k}^{\text{calcd}} - y_{2,k}^{\text{exptl}}\right|\right) \tag{7}$$

where n is the number of data points.

The interaction parameter k_{bij} is often set as zero in most practical applications, particularly for symmetric mixtures. For the purpose of comparison, the calculated results with the one-parameter (k_{aij}) vdW mixing rules (with $k_{bij} = 0$, denoted vdW-1) and the two-parameter (k_{aij} and k_{bij}) vdW mixing rules (denoted vdW-2) are given in Table 6, where the entries of $\Delta P/P$ and Δy_2 were defined, respectively, by

$$\Delta P/P\ (\%) = \frac{100}{n}\sum_{k=1}^{n}\frac{|P_k^{\text{calcd}} - P_k^{\text{exptl}}|}{P_k^{\text{exptl}}} \tag{8}$$

and

$$\Delta y_2 = \frac{100}{n}\sum_{k=1}^{n}|y_{2,k}^{\text{calcd}} - y_{2,k}^{\text{exptl}}| \tag{9}$$

The PR equation of state appears to be marginally better than the two other equations of state for these investigated systems. Figures 7 and 8 compare the calculated bubble pressures and saturated vapor compositions with the experimental values for carbon dioxide + phenyl acetate. Figure 7 shows that the one-parameter vdW mixing rule (vdW-1) overestimates the bubble pressures at elevated pressures. Using the second binary interaction parameter k_{b12} (vdW-2) improves the accuracy of the calculation of bubble pressures, especially in the high-pressure range.

Conclusions

Isothermal VLE data have been measured for binary mixtures of carbon dioxide with hexyl acetate, cyclohexyl acetate, and phenyl acetate at temperatures from 333.15 K to 413.15 K and pressures up to 20 MPa. Each y_2 isotherm exhibits a minimum solubility at subcritical pressures of carbon dioxide. Whereas the saturated vapor compositions of hexyl acetate and cyclohexyl acetate are obviously greater than those of phenyl acetate, the solubilities of carbon dioxide in the acetates follow the sequence of hexyl acetate > cyclohexyl acetate > phenyl acetate under the same experimental conditions. K_2 isotherms are crossed over in the pressure range from 9 MPa to 13 MPa for carbon dioxide + cyclohexyl acetate.

The KI equation represents well the pressure effect on the gas solubilities. Henry's constants determined from the VLE data with the KI equation were found to increase with an increase of temperature. At a given temperature, the magnitude of Henry's constants of carbon dioxide dissolving in the acetates is in the order of phenyl acetate > cyclohexyl acetate > hexyl acetate.

Table 6. Results of Bubble-Pressure Calculations from the Equations of State (EOS)

	carbon dioxide + hexyl acetate				carbon dioxide + cyclohexyl acetate				carbon dioxide + phenyl acetate				grand	grand
EOS	k_{a12}	k_{b12}	AAD $\Delta P/P$ (%)	AAD Δy_2 (10^{-2})	k_{a12}	k_{b12}	AAD $\Delta P/P$ (%)	AAD Δy_2 (10^{-2})	k_{a12}	k_{b12}	AAD $\Delta P/P$ (%)	AAD Δy_2 (10^{-2})	AAD $\Delta P/P$ (%)	AAD Δy_2 (10^{-2})
SRK	0.0386	0	1.95	0.21	0.0428	0	1.09	0.38	0.0609	0	3.09	0.24	2.09	0.27
	0.0463	0.0095	1.44	0.23	0.0421	−0.0006	1.06	0.38	0.0472	−0.0132	1.29	0.23	1.27	0.28
PR	0.0330	0	1.63	0.08	0.0405	0	0.93	0.23	0.0602	0	3.49	0.13	2.07	0.14
	0.0420	0.0094	1.02	0.10	0.0365	−0.0036	0.87	0.26	0.0440	−0.0161	1.67	0.13	1.20	0.16
PT	0.0021	0	1.93	0.07	0.0257	0	0.96	0.28	0.0433	0	3.49	0.14	2.19	0.16
	0.0154	0.0132	1.06	0.08	0.0227	−0.0029	0.89	0.28	0.0304	−0.0160	2.20	0.13	1.41	0.16

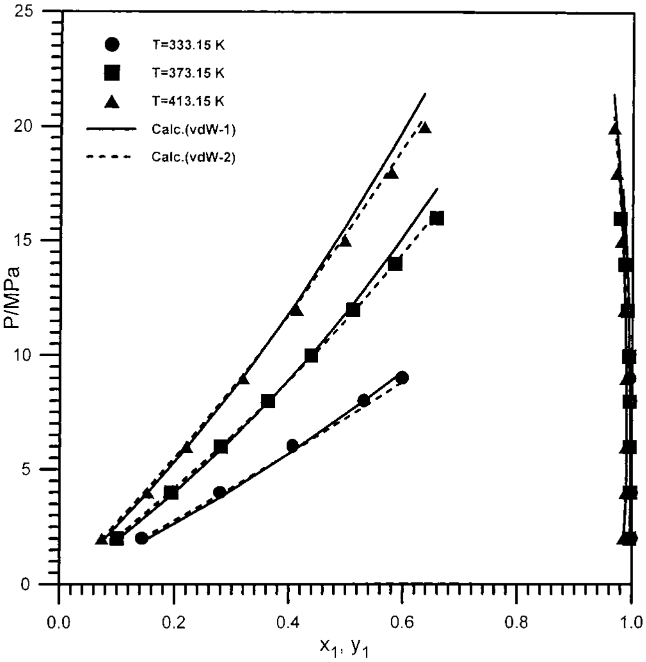

Figure 7. Comparison of the calculated results from the PR equation of state with the experimental values for carbon dioxide (1) + phenyl acetate (2).

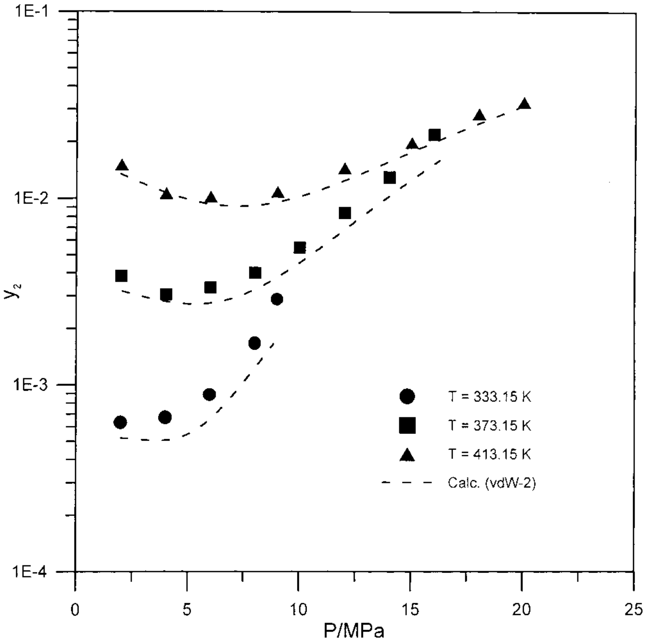

Figure 8. Comparison of the calculated saturated vapor compositions of phenyl acetate y_2 from the PR equation of state with the experimental values for carbon dioxide (1) + phenyl acetate (2).

The new VLE data were correlated with the Soave−Redlich−Kwong, Peng−Robinson, and Patel−Teja equations of state by using the vdW one-fluid mixing rules. The use of an additional binary interaction parameter k_{b12} in the combining rule for covolume constant improves the accuracy of bubble-pressure calculations with any of the tested equations of state. It is also indicated that the results from the Peng−Robinson equation are marginally better than those from the other two equations of state.

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