Solubility of Carbon Dioxide in Acetone and Propionic Acid at Temperatures between 298 K and 333 K

T. Adrian and G. Maurer*

Lehrstuhl für Technische Thermodynamik, Universität Kaiserslautern, D-67653 Kaiserslautern, Germany

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The solubility of carbon dioxide in organic solvents acetone and propionic acid has been measured with an analytical method. The composition and the density of the liquid phase in the binary vapor−liquid equilibrium have been investigated at (313 and 333) K (for the system carbon dioxide + acetone) and at (298, 313, and 333) K (for the system carbon dioxide + propionic acid) at pressures up the binary critical pressure. The experimental results for the phase equilibrium have been correlated with the Peng−Robinson EOS applying several mixing rules.

Introduction

In supercritical fluid chromatogrophy as well as in supercritical fluid extraction carbon dioxide is often used as the supercritical solvent. Organic solvents are often added as entrainers to increase the solubility of low-volatile organic compounds. Therefore, the binary phase behavior of systems carbon dioxide + organic solvent is required for the design of such separation processes.

High-pressure vapor−liquid equilibrium data of the system carbon dioxide + acetone have been reported in the literature at temperatures between (291 and 323) K: Katayama et al. (1975) reported results for 298 K and 313 K, Xu et al. (1991) for 313 K and 323 K, and Day et al. (1996) for temperatures between (291 and 313) K. Traub and Stephan (1990) gave some results for (308, 313, and 323) K. Kato et al. (1991) investigated the vapor−liquid equilibrium at 298 K. Giacobbe (1992) determined carbon dioxide solubilities in acetone at 293 K and 303 K at pressures up to 1 MPa. Gurdial et al. (1993) determined binary critical pressures at temperatures from (304 to 323) K. Thus the results of the present work extend the temperature range of experimental VLE data to 333 K.

The only literature source for experimental results on the high-pressure vapor−liquid equilibrium of the system carbon dioxide + propionic acid is at 313 K (Willson, 1988).

Experimental Section

Materials. Carbon dioxide (purity better than 0.9995 mole fraction) was obtained from TV Kohlensäure, Ludwigshafen, Germany. Acetone (Ace) (p.a. grade, purity better than 0.995 mass fraction) and propionic acid (HPr) (purity better than 0.99 mass fraction) were purchased from Merck, Darmstadt, Germany.

Apparatus. The apparatus and the experimental procedures used here have been described in detail by Wendland et al. (1993, 1994). Therefore only a short description is given here. A thermostated equilibrium view cell with two sapphire windows is charged with the pure components. After equilibration, temperature is measured with calibrated platinum resistance thermometers and the pressure is measured with calibrated gauges. The apparatus has been developed to enable analysis of coexisting liquid phases of three-phase equilibria of the type L_1L_2V. Therefore, the cell is equipped with two external loops, in which samples from two coexisting liquid phases can be recirculated independently by two HPLC pumps. However, in this work both sample loops were mostly used to recirculate the (single) liquid phase of the vapor−liquid equilibrium. Only in a few experiments (close to the critical point) the (dense) vapor phase was also recirculated. Samples of the liquid phase are withdrawn from these loops through sample valves for a gas-chromatographic analysis. Furthermore, for measuring the density of the liquid phase, the loops are connected to a vibrating tube densimeter. Pressure and temperature of critical points were determined by visual observation of the critical opalescence.

The uncertainty of the experimental results for the temperature is less than ±0.05 K, and for the pressure it is ±5 kPa for vapor−liquid equilibria and ±10 kPa for the determination of critical points. The relative error in the determination of the carbon dioxide mole fraction and the liquid phase density is less than 1.5% and 0.2%, respectively.

Results and Comparision to Literature Data

In the present work the binary vapor−liquid equilibrium of the system carbon dioxide + acetone at (313 and 333) K and of the system carbon dioxide + propionic acid at (298, 313, and 333) K was investigated at pressures ranging from about 1 MPa up to the binary critical pessure. For the system carbon dioxide + acetone the gas phase was only analyzed at 333 K at a single pressure near the critical point. For the system carbon dioxide + propionic acid the composition of the gas phase was determined at (313 and 333) K for one pressure near the critical point. Furthermore, the binary critical pressure of the vapor−liquid phase envelope was determined. The experimental results for the mole fraction x_{CO_2} of the liquid phase L and the gas phase V as well as for the density ρ of the phases and the critical pressure of the phase envelope (L = V) are summarized in Tables 1 and 2.

As no literature data are available for the vapor−liquid equilibrium of the system carbon dioxide + acetone at 333 K, only the new experimental data for 313 K can directly be compared to published data sets. That comparison is shown in Figure 1. The new experimental results agree well with the results of Katayama et al. (1975) and those of Xu et al. (1991). For preset temperature and pressure, deviations in the liquid phase composition are typically about 0.3 mol %. However, the agreement with the results of Day et al. (1996) is less satisfying.

The density of the liquid phase is shown in Figure 2 as a function of pressure. The circular symbols mark the

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* Author to whom correspondence should be adressed.

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Table 1. Carbon Dioxide + Acetone at 313 K and 333 K: Vapor–Liquid Equilibria, Liquid Phase Densities, and Binary Critical Points

T/K	p/MPa	phase	x_{CO_2}	ρ/g dm^{-3}
313.15	1.001	L	0.1482	785
	2.000	L	0.2921	802
	3.004	L	0.4275	817
	3.008	L	0.4239	817
	4.018	L	0.5504	826
	5.037	L	0.6700	829
	5.039	L	0.6692	829
	6.002	L	0.7787	813
	6.993	L	0.8796	764
	7.532	L	0.9272	701
	8.003	L	0.9659	585
	8.048	L = V		
333.15	0.987	L	0.1021	755
	2.011	L	0.2175	765
	3.008	L	0.3206	773
	3.985	L	0.4129	781
	5.016	L	0.5076	784
	6.009	L	0.5963	782
	7.023	L	0.6820	771
	8.002	L	0.7616	744
	9.012	L	0.8456	681
	9.499	L	0.8898	605
		V	0.9403	432
	9.603	L = V		

Table 2. Carbon Dioxide + Propionic Acid at Temperatures between (298 and 333) K: Vapor–Liquid Equilibria, Liquid Phase Densities, and Binary Critical Points

T/K	p/MPa	phase	x_{CO_2}	ρ/g dm^{-3}
298.15	1.009	L	0.1292	990
	1.993	L	0.2505	990
	2.995	L	0.3853	987
	3.996	L	0.5291	979
	4.995	L	0.7103	951
	5.506	L	0.8224	912
	5.997	L	0.9406	830
313.15	2.019	L	0.1973	971
	4.024	L	0.3956	963
	4.943	L	0.4938	956
	6.023	L	0.6202	935
	7.014	L	0.7638	891
	7.501	L	0.8355	842
	8.003	L	0.9255	744
	8.303	L	0.9778	617
		V	0.9926	
	8.347	L = V		
333.15	2.010	L	0.1486	947
	4.014	L	0.2919	941
	6.013	L	0.4376	927
	8.029	L	0.5992	895
	8.986	L	0.6861	862
	10.01	L	0.7963	798
	10.50	L	0.8660	700
		V	0.9752	
	10.74	L = V		

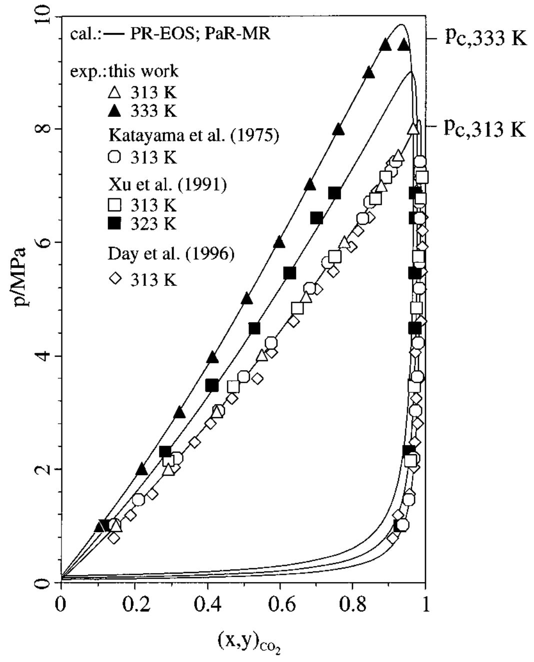

Figure 1. Vapor–liquid equilibrium in the system carbon dioxide + acetone at (313 and 333) K: comparison of experimental data with results from the Peng–Robinson EOS (Panagiotopolous–Reid mixing rule).

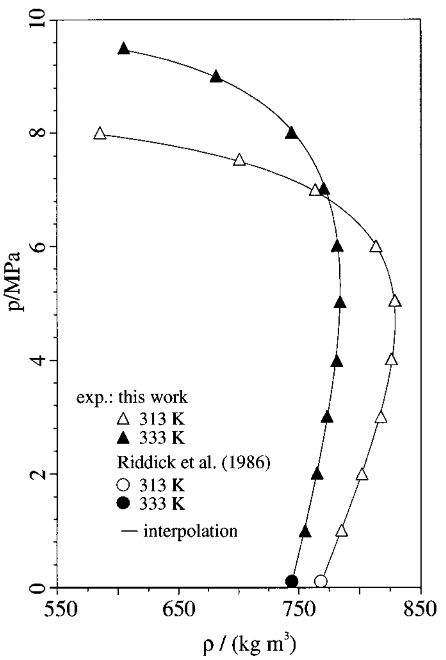

Figure 2. Carbon dioxide + acetone at (313 and 333) K: density of the liquid in vapor–liquid equilibrium.

density of the pure liquid acetone at atmospheric pressure as reported by Riddick et al. (1986). Increasing the pressure, i.e., adding carbon dioxide, results in two concurrent effects: a compression of the solvent and an expansion of the liquid due to the increasing concentration of the solute. At low pressures, the first effect predominates over the second, while the reverse behavior is observed at high pressures. A comparison of the new data for the critical points with literature data of Gurdial et al. is given in Figure 3. The critical pressures determined in the present work are systematically (by about 3%) lower than those of Gurdial et al.

A comparison between the new results and literature data (Willson, 1988) for the vapor–liquid equilibrium of the system carbon dioxide + propionic acid reveals a maximum deviation in the liquid phase carbon dioxide mole fraction (for preset temperature and pressure) of about 3 mol % at a pressure of about 6 MPa and a carbon dioxide mole fraction of about 0.6 (cf. Figure 4). The density of the liquid phase as a function of pressure is shown in Figure 5. At (313 and 333) K the influence of the solubility of carbon dioxide in the liquid phase (i.e., the liquid phase expansion) predominates over the influence of pressure on the density of the solvent already at very low pressures. Only at 298 K and low pressures the increase of the density of the solvent with rising pressure predominates over the liquid phase expansion.

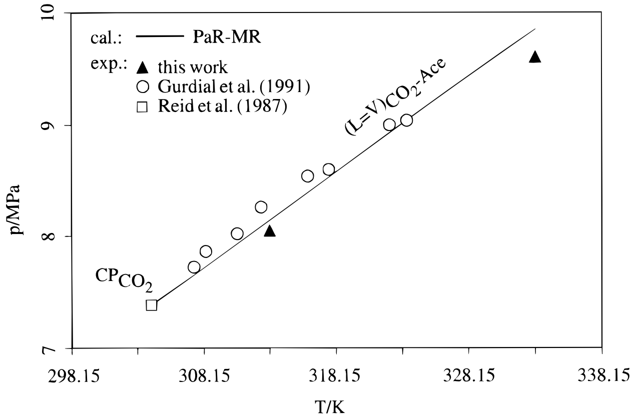

Figure 3. Critical points in the system carbon dioxide + acetone: comparison of experimental data with results from the Peng–Robinson EOS (Panagiotopolous–Reid mixing rule).

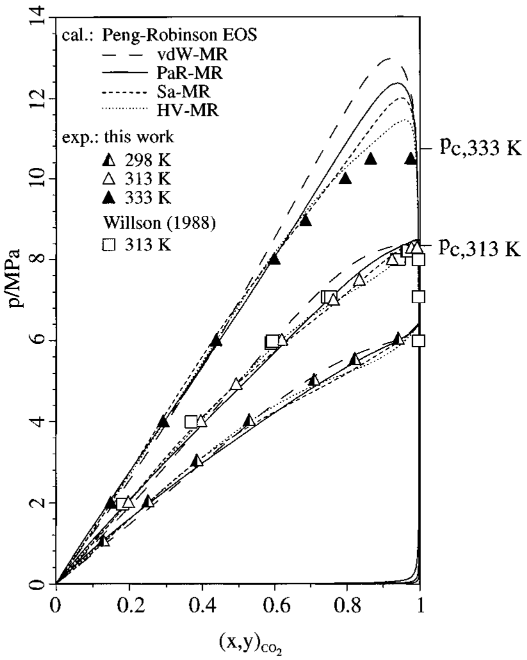

Figure 4. Vapor–liquid equilibrium in the system carbon dioxide + propionic acid at temperatures between (298 and 333) K: comparison of experimental data with results from the Peng–Robinson EOS (four different mixing rules).

Correlation

The Peng–Robinson equation of state (Peng and Robinson, 1976) was used to correlate the experimental results:

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

p is the pressure, T is the temperature, R is the universal gas constant, and v is the molar volume. Through parameters b and a free volume effects and intermolecular attractive interactions are taken into account. For a pure component the volume parameter b and the attractive interaction parameter a are described as usual by:

$$b = 0.07780\,\frac{RT_c}{p_c} \tag{2}$$

$$a(T) = \alpha(T)\;a(T_c) \tag{3}$$

$a(T_c)$ is the pure component attractive interaction parameter at the critical temperature.

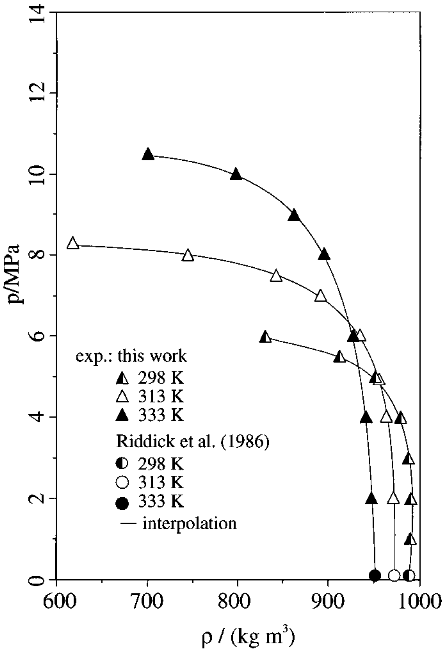

Figure 5. Carbon dioxide + propionic acid: density of the liquid in vapor–liquid equilibrium at temperatures between (298 and 333) K.

$$a(T_c) = 0.45724\,\frac{R^2T_c^2}{p_c} \tag{4}$$

The correlation of Melhem et al. (1989) was selected to describe the influence of temperature on parameter α:

$$\ln \alpha(T) = m(1 - T/T_c) + n(1 - \sqrt{T/T_c})^2 \tag{5}$$

Melhem et al. determined parameters m and n for more than 100 pure substances (including acetone) from vapor pressure data. However, no parameters are available for propionic acid. They were determined from vapor pressure data of propionic acid reported by Jasperson et al. (1989) and Ambrose et al. (1981) applying a procedure similar to that of Melhem et al. Critical properties of propionic acid were taken from Simmrock et al. (1986) ($T_c = 612.1$ K and $p_c = 5.370$ MPa). The resulting values are $m = 1.1342$ and $n = 0.0049$.

Several well-known mixing rules were applied to extend the Peng–Robinson equation of state to mixtures. A linear mixing rule without any binary parameters was used for volume parameter b:

$$b = \sum_{i=1}^{N_c} x_i b_i \tag{6}$$

The attractive interaction parameter of the mixture a was described by two different procedures. For some calculations the usual quadratic mixing rule:

$$a = \sum_{i=1}^{N_C}\sum_{j=1}^{N_C}(1 - K_{ij})x_i x_j\sqrt{a_i a_j} \quad \text{with} \quad K_{ii} = 0 \tag{7}$$

was used, where $K_{ij} = K_{ji}$ is a binary, temperature dependent interaction parameter. Three different proposals for the binary parameter K_{ij} were used. In the so-called "van der Waals" mixing rule, K_{ij} does not depend on concentration, but might depend on temperature:

$$K_{ij}(T) = K_{ji}(T) \tag{8}$$

Table 3. Binary Interaction Parameters of the Peng−Robinson EOS for the Correlation of Vapor−Liquid Equilibria in the Systems Carbon Dioxide + Acetone and Carbon Dioxide + Propionic Acid and Comparison with Experimental Data

	CO_2 (1)−ACE (2)				CO_2(1)−HPr (2)			
mixing rule	k_{12}	k_{21}	l_{12}	Δp^a (%)	k_{12}	k_{21}	l_{12}	Δp (%)
vdW-MR	0.0114			0.83	0.0070			5.61
PaR-MR	0.0066	0.0144		0.60	0.0340	−0.0049		3.15
Sa-MR	0.0166	0.0102	−0.0058	0.57	0.0047	−0.0170	0.0408	1.87
mixing rule	k_{12}		α_{12}	Δp (%)	k_{12}		α_{12}	Δp (%)
HV2-MR	0.0223		0.0215	0.50	−0.0311		−0.0272	2.47
HV2m-MR	0.0143		0.5358	0.83	−0.0192		−0.4567	2.77
mixing rule	C_{12} (kJ mol $^{-1}$)	C_{21} (kJ mol $^{-1}$)	α_{12}	Δp (%)	C_{12} (kJ mol $^{-1}$)	C_{21} (kJ mol $^{-1}$)	α_{12}	Δp (%)
HV-MR	66.7049	0.1476	0.2552	0.53	−6.6912	1.4041	−0.4146	1.45

[a] $\Delta p = 1/N \sum_{i=1}^{N} |(p_{\rm exp} - p_{\rm calc})/p_{\rm exp}|_i$.

Panagiotopoulos and Reid (1986) assumed an influence of concentration on K_{ij}. Their mixing rule requires two binary parameters k_{ij} and $k_{ji} \neq k_{ij}$:

$$K_{ij} = k_{ij} - (k_{ij} - k_{ji})x_i \tag{9}$$

Sandoval et al. (1989) modified that mixing rule by introducing a third binary interaction parameter $l_{ij} = l_{ji}$:

$$K_{ij} = \frac{k_{ij} + k_{ji}}{2} - \frac{k_{ij} - k_{ji}}{2} x_i - \frac{k_{ji} - k_{ij}}{2} x_j + l_{ij}[x_i(1 - x_i) + x_j(1 - x_j)] \tag{10}$$

Besides the quadratic mixing rule also three modifications of the "Huron−Vidal" mixing rule were used for parameter a. Huron and Vidal (1979) suggested to introduce expressions for the excess Gibbs energy of liquid mixtures into the mixing rule for the attractive interaction parameter of an equation of state. The rules applied in the present work are based on the NRTL equation of Renon and Prausnitz (1968) for the excess Gibbs energy:

$$a = b\sum_{i=1}^{N_C} x_i \left(\frac{a_i}{b_i} - \frac{1}{\Lambda} \frac{\sum_{j=1}^{N_C} x_j C_{ji} b_j \exp\left(-\alpha_{ji}\frac{C_{ji}}{RT}\right)}{\sum_{k=1}^{N_C} x_k b_k \exp\left(-\alpha_{ki}\frac{C_{ki}}{RT}\right)} \right) \quad \text{with} \quad C_{ii} = 0 \tag{11}$$

b and b_i are the volume parameters of the mixture (cf. eq 6) and the pure component i, respectively.

Λ is a numerical constant:

$$\Lambda = \frac{1}{2\sqrt{2}} \ln\left(\frac{2 + \sqrt{2}}{2 - \sqrt{2}}\right) \tag{12}$$

C_{ij} is a binary interaction parameter of the NRTL equation, and α_{ij} is a binary volume correction parameter also resulting from the NRTL equation. The three modifications applied here differ in the assumptions for C_{ij} and α_{ji}.

In a three-parameter version—called HV-MR—the binary parameters are C_{ij}, C_{ji} ($\neq C_{ij}$) and $\alpha_{ij} = \alpha_{ji}$. Two simple two-parameter versions were also used. In both versions parameter α is used as before, but parameter C_{ij} is modified. C_{ij} is expressed as the difference of two terms: $C_{ij} = g_{ij} - g_{ii}$. g_{ii} is a pure component property, $g_{ii} = \Lambda a_i/b_i$, while g_{ij} is a binary mixture parameter.

In the mixing rule abbreviated by HV2-MR (cf. Huron and Vidal (1979)) interaction parameter g_{ij} is

$$g_{ij} = -\frac{\sqrt{b_i b_j}}{(b_i + b_j)/2}\sqrt{g_{ii}\, g_{jj}}(1 - k_{ij}) \tag{13}$$

while in the mixing rule abbreviated by HV2m-MR (cf. Wendland (1994)) it is:

$$g_{ij} = -\sqrt{\frac{b_j}{b_i}}\sqrt{g_{ii}\, g_{jj}}(1 - k_{ij}) \tag{14}$$

Thus in the HV2 and HV2m mixing rules, g_{ij} is expressed by a binary interaction parameter $k_{ij} = k_{ji}$.

Discussion

For the determination of the interaction parameters of the six mixing rules presented above, temperature and liquid phase composition was preset and the relative deviation in pressure was minimized, but no density data were used. As the temperature range of the new experimental data covers only 30 K (carbon dioxide + acetone) and 35 K (carbon dioxide + propionic acid) respectively, no influence of temperature on the binary parameters was taken into account. Binary parameters as well as a comparison between correlated and experimentally determined data are given in Table 3.

For the system carbon dioxide + acetone the parameters were fitted exclusively using the new data at 313.15 K and 333.15 K. However, the correlations are also suited to represent the results of Xu et al. at 323.15 K. Figure 1 shows a typical comparison between correlated and experimental results applying the Panagiotopoulos−Reid mixing rule. It is especially note worthy that the experimental results for the vapor−liquid critical pressure at 313 K and 333 K are also well given by the equation of state; e.g., at T/K = 313.15; $p_{\rm c,exp}/p_{\rm c,calc} = 0.988$ and at T/K = 333.15; $p_{\rm c,exp}/p_{\rm c,calc} = 0.975$ (cf. Figure 3). For the system carbon dioxide + acetone, all tested mixing rules—even the one-parameter van der Waals mixing rule—give nearly the same representation of the phase behavior.

As it was to be expected the correlations are less satisfying for the system carbon dioxide + propionic acid. All mixing rules give an nearly equal representation of the experimental data at 298 K and 313 K—i.e., at temperatures below or only slightly above the critical temperature of carbon dioxide. At 333 K all mixing rules reveal the often observed deficiency of overestimating the two-phase region near the critical point. The differences decrease with increasing number of binary parameters. The mixing rule of Sandoval et al. (Sa-MR) and the three-parameter Huron−Vidal mixing rule (HV-MR) give the best agreement with the new experimental results. However, also with these mixing rules the critical pressure is too high by

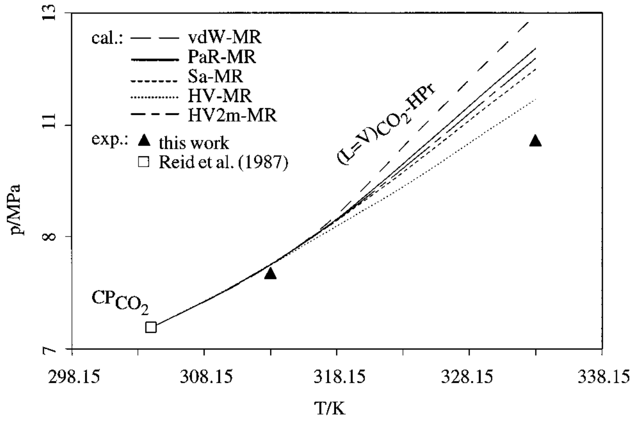

Figure 6. Critical points in the system carbon dioxide + propionic acid: comparison of experimental data with results from the Peng−Robinson EOS (five different mixing rules).

about 11.7% (Sa-MR) and 6.7% (HV-MR) (cf. Figure 4 and 6). One of the reasons for the poor correlation of the near critical region might be due to neglecting the association of propionic acid. It can be expected that neglecting the association of propionic acid also results in a less accurate prediction of the propionic acid concentration of the vapor phase.

The densities of the pure liquids acetone and propionic acid calculated with the Peng−Robinson EOS are about 10% lower than the experimental value. Therefore, it is not suprising that also for the binary systems with carbon dioxide predicted liquid phase densities show similar deviations from the experimental data. Nevertheless, the model predicts qualitatively the two concurrent phenomena caused by increasing the pressure, i.e., a compression of the liquid as well as the liquid phase expansion due to the increasing concentration of the solute.

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