High-Pressure Vapor−Liquid Equilibria of the Ternary System Carbon Dioxide + Vinyl Acetate + 2-Butanol. Experimental and Modeling Results

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Bubble-point and dew-point pressures and vapor−liquid critical points of the ternary system (x_1)carbon dioxide + (x_2)vinyl acetate + (x_3)2-butanol were measured in the temperature range 278−510 K up to 14 MPa in a high-pressure capillary glass tube apparatus, using the synthetic method. The system has been investigated for varying carbon dioxide compositions at fixed ratios of vinyl acetate and 2-butanol (x_2/x_3 = 1/3 and 3/1) and at fixed 2-butanol composition (x_3 = 0.15). Modeling of the vapor−liquid equilibria of the ternary system has been performed using two equation of state (EOS) methods: (1) the Stryjek−Vera modification of the Peng−Robinson EOS with the Wong−Sandler mixing rules (PRSV/WS) implementing the NRTL-G^E model; (2) the LCVM model, which is the translated modified PR EOS with the linear combination of Vidal and Michelsen mixing rules implementing the UNIFAC-G^E model.

Introduction

Enzyme-catalyzed reactions in near-critical carbon dioxide can offer certain advantages over the performance of enzyme-catalyzed reactions in water or organic solvents. From an engineering point of view, near-critical carbon dioxide can have advantages in the downstream processing, e.g., rectification and fractionation to obtain pure products. Besides, it does not leave harmful residues in the products, which can be advantageous in food and pharmaceutical industry (Kamat et al., 1995). The study of enzymatic reactions in near-critical solvents is only possible when the phase behavior of the reactants with the solvent is known (McHugh and Krukonis, 1994). In principle it is possible to predict the phase behavior of the multicomponent system (formed by the reactants, the near-critical fluid, and additional water for the enzyme's functioning) from the phase behavior of the binary subsystems (Chrisochoou et al., 1995).

In this paper vapor−liquid equilibria (VLE) data for the ternary system carbon dioxide + vinyl acetate + 2-butanol are presented. This system is of importance in the study of the *Pseudomonas cepacia* lipase-catalyzed reaction of vinyl acetate + 2-butanol in near-critical carbon dioxide (Stevens et al., 1997a). For this system experimental and modeling results on the binary systems with CO_2 are also known (Stevens et al., 1997b,c).

Experimental results on bubble, dew, and critical points are presented for the ternary system in the temperature range from 278 to 510 K at pressures up to 14 MPa. VLE predictions for the system investigated are carried out using two equations of state. The experimental bubble points have been predicted with the Stryjek−Vera (1986) modification of the Peng−Robinson equation of state (1976) using Wong−Sandler mixing rules (Wong and Sandler, 1992) with the NRTL-G^E model. The parameters used were obtained from fits of the binary subsystems (Stevens et al., 1997b). Also the LCVM model (Boukouvalis et al., 1994) is used for predicting the measured phase behavior. This model combines the t-mPR EOS (Magoulas and Tassios, 1990) with a linear combination of the Vidal (1978) and Michelsen (1990) mixing rules in which a modified UNIFAC model is used (Yakoumis et al., 1996).

Materials and Methods

Bubble-point pressures, some dew-point pressures, and critical points of ternary mixtures of carbon dioxide + vinyl acetate + 2-butanol of known composition were determined experimentally up to 510 K using the synthetic method in a so-called Cailletet apparatus, which is described in detail by de Loos et al. (1986). A sample of the mixture with known composition was present in a narrow glass tube, mounted in a thermostat. Bubble points and dew points were measured by observing the disappearance of the vapor phase or the liquid phase, respectively, at constant temperature with increasing pressure, which is measured with a dead-weight gauge (accuracy, $\Delta T = \pm 0.01$ K; $\Delta P = \pm 3$ kPa). The critical point could be located in that temperature interval in which the observed phase behavior changed from bubble-point behavior to dew-point behavior (accuracy interval, $\Delta T = \pm 0.03$ K, $\Delta P = \pm 5$ kPa). A detailed describtion of the experimental procedure is given by de Loos et al. (1986).

A liquid mixture of vinyl acetate and 2-butanol is prepared by weighing. The sample to be investigated is prepared by weighing an amount of this liquid mixture in the Cailletet tube, which is degassed by alternating freezing and melting under vacuum with liquid nitrogen as a cooling agent. A known volume of carbon dioxide at known temperature and pressure was added by displacement using mercury. The error in the mole fractions of the components in the mixtures is estimated to be less than ±0.003.

The carbon dioxide (Air Products) had a minimum purity of 99.95%. Its vapor pressure was checked and found to be equal to the recommended value from IUPAC (Stevens et al., 1997b). The vinyl acetate and 2-butanol (Merck) had a minimum purity of 99.0% and 99.5%. The vinyl acetate was stabilized by 10 ppm hydrochinon. The vinyl acetate and 2-butanol were stored over 3 Å molecular sieves to

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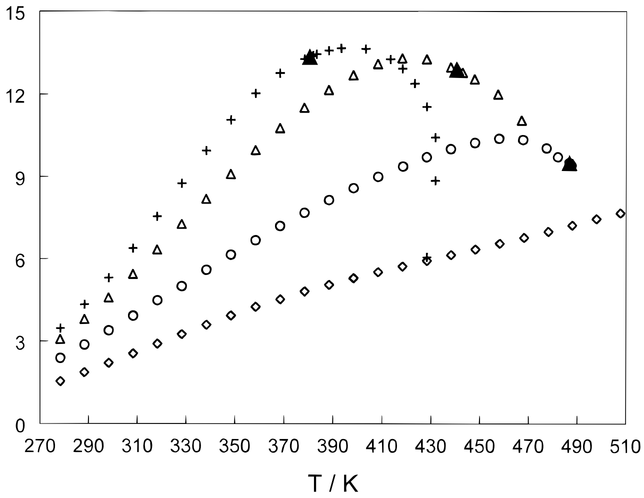

Figure 1. VLE of the system [(x_1)carbon dioxide + (x_2)vinyl acetate + (x_3)2-butanol]. Isopleths at constant (x_2/x_3) = (1/3). (x_1, x_2): +, (0.801, 0.048); △, (0.601, 0.095); ○, (0.397, 0.143); ◇, (0.200, 0.198); ▲, critical points.

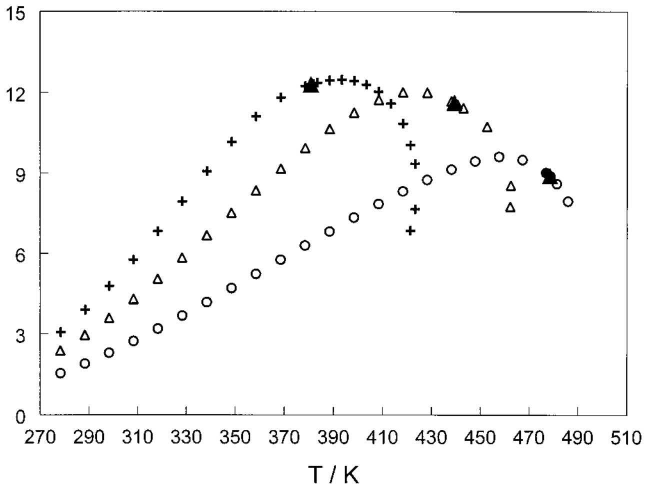

Figure 2. VLE of the system [(x_1)carbon dioxide + (x_2)vinyl acetate + (x_3)2-butanol]. Isopleths at constant (x_2/x_3) = (3/1). (x_1, x_2): +, (0.800, 0.151); △, (0.612, 0.292); ○, (0.400, 0.451); ▲, critical points.

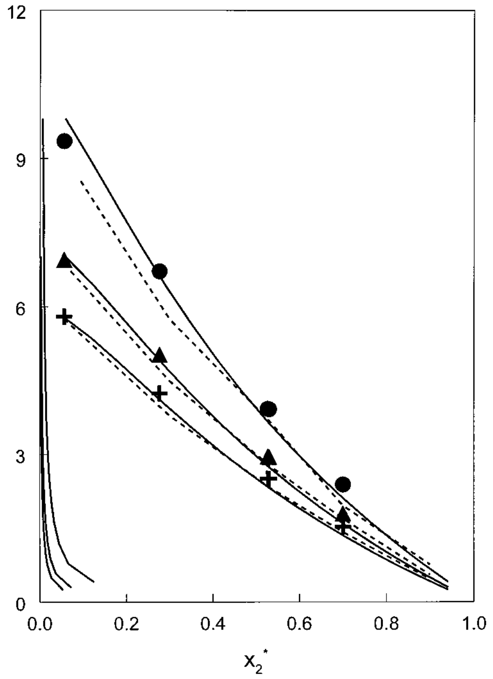

Figure 3. P, x_2* section for the ternary system [(x_1)carbon dioxide + (x_2)vinyl acetate + (x_3)2-butanol]. At constant x_3 = 0.15. x_2* is defined as $x_2/(x_1+x_2)$: +, 303.15 K; ▲, 313.15 K; ●, 333.15 K. Solid lines, LCVM model; broken lines, PRSV/WS.

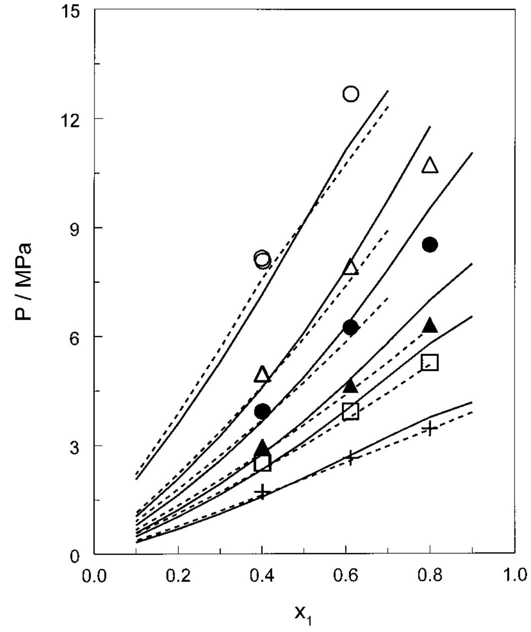

Figure 4. Quasi-binary P, x section for the ternary system [(x_1)-carbon dioxide + (x_2)vinyl acetate + (x_3)2-butanol]. Data for x_2/x_3 = 3/1: +, 283.15 K; □, 303.15 K; ▲, 313.15 K; ●, 333.15 K; △, 353.15 K; ○, 413.15 K. Solid lines, LCVM model; broken lines, PRSV/WS.

exclude moisture. The water content was less than 0.005%, as determined by Karl Fischer titration.

Results and Discussion

Experimental Results. In Table 1 the experimentally determined bubble points, dew points, and critical points are presented for the ternary system investigated. At temperatures higher than the mixture critical temperature retrograde condensation occurs, which means that at one temperature two dew points are found. The second (low-pressure) dew point is denoted with s in Table 1. For selected mole fraction ratios of vinyl acetate and 2-butanol x_2/x_3 of 1/3 and 3/1, experimental P, T data are shown graphically in Figures 1 and 2, respectively. The isopleths show a smooth behavior with a pressure maximum. Experimental data of the pure compounds, of the binary systems with CO_2, and of the binary critical lines are given elsewhere (Stevens et al., 1997b). From the experimental constant-composition data in Table 1, isothermal P, x sections can be obtained by interpolation, using third-order polynomials to represent the ternary isopleths. The maximum value of the residuals was equal to or less than the error in the pressure measurement (5 kPa). The experimental points in the Figures 3, 4, and 5 were obtained this way. Figure 3 shows three P, x_2* sections at 303.15 K, 313.15 K, and 333.15 K and at a constant value of x_3 = 0.15. x_2* is defined as $x_2/(x_1+ x_2)$, so it is the mole fraction of vinyl acetate in carbon dioxide on a 2-butanol free basis. At the chosen temperatures the solubility of the low-volatile compounds in carbon dioxide has also been determined (Stevens et al., 1997c). In Figures 4 and 5 the data of the ternary system are represented as a function of the overall mole fraction of carbon dioxide x_1 at constant ratios of the mole fractions of vinyl acetate and 2-butanol, x_2/x_3 = 3 and x_2/x_3 = 1/3, respectively, at the temperatures 283.15 K, 303.15 K, 313.15 K, 333.15 K, 353.15 K, and 413.15 K.

Table 1. Vapor−Liquid Equilibria for the System [(x_1)CO_2 + (x_2)Vinyl Acetate + (x_3)2-Butanol]: Bubble-Point Pressure P (at $T < T_c$) and Dew-Point Pressure P (at $T > T_c$) as a Function of Temperature T for Given Mole Fraction x_1 and x_2

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
$x_1 = 0.7998$, $x_2 = 0.0970$									
278.36	3.267	333.31	8.877	373.33	12.469	383.25	12.829	408.21	12.724
283.40	3.677	338.36	9.447	376.31	12.599	383.33	12.839	413.16	12.399
288.32	4.097	343.39	10.012	377.29	12.639	386.23	12.899	418.11	11.897
293.32	4.547	348.34	10.512	378.23	12.674	387.28	12.924	422.59	11.102
298.29	5.022	353.35	11.034	379.24	12.709	387.61	12.929	424.03	10.052
303.33	5.522	353.37	11.042	379.82	12.734	388.19	12.939	425.04	10.402
308.35	6.047	358.38	11.539	380.30	12.744	388.25	12.929	425.59	9.902
313.31	6.587	363.39	11.884	380.72	12.754 c[a]	393.25	12.999	425.04	8.156 s[b]
318.34	7.147	368.35	12.209	381.22	12.769	398.15	12.994	424.03	7.156 s[b]
323.29	7.717	373.32	12.474	381.35	12.779	403.21	12.904	422.59	6.156 s[b]
328.30	8.292								
$x_1 = 0.8006$, $x_2 = 0.0475$									
278.40	3.415	338.31	9.900	380.53	13.295	388.34	13.525	423.26	12.335
288.38	4.285	348.34	11.015	380.60	13.300	393.34	13.605	428.21	11.495
298.31	5.255	358.41	11.980	380.85	13.310	403.31	13.580	428.71	10.380
308.29	6.335	368.36	12.715	381.12	13.315	413.32	13.210	428.71	8.800 s[b]
318.28	7.495	378.42	13.220	381.91	13.345 c[a]	418.27	12.875	428.21	6.000 s[b]
328.35	8.705	380.36	13.290	383.34	13.395				
$x_1 = 0.7998$, $x_2 = 0.1506$									
278.42	3.066	338.32	9.076	380.85	12.306	388.38	12.451	418.19	10.849
288.40	3.896	348.41	10.166	380.90	12.306	393.31	12.478	421.23	10.050
298.36	4.781	358.36	11.111	381.06	12.311	398.28	12.438	423.15	9.351
308.29	5.761	368.47	11.821	381.32	12.316	403.24	12.298	423.15	7.652s[b]
318.28	6.826	378.43	12.241	381.85	12.331	408.24	12.039	421.23	6.853s[b]
328.30	7.946	380.75	12.301 c[a]	383.40	12.366	413.24	11.594		
$x_1 = 0.6118$, $x_2 = 0.2921$									
278.30	2.384	338.36	6.679	398.32	11.260	439.11	11.628	440.48	11.566
288.35	2.959	348.39	7.519	408.35	11.735	439.16	11.628 c[a]	442.93	11.436
298.31	3.594	358.38	8.354	418.24	12.016	439.32	11.623	452.58	10.739
308.34	4.299	368.52	9.169	428.17	12.006	439.47	11.618	462.28	8.551
318.27	5.049	378.47	9.945	438.02	11.681	439.66	11.608	462.09	7.752 s[b]
328.29	5.844	388.42	10.650	439.05	11.638	440.00	11.588		
$x_1 = 0.6014$, $x_2 = 0.0949$									
278.35	3.074	328.35	7.266	378.38	11.508	428.19	13.268	441.33	12.848
288.38	3.801	338.31	8.186	388.31	12.153	438.07	12.978	442.87	12.784
298.30	4.586	348.37	9.097	398.32	12.688	440.36	12.888	447.80	12.549
308.29	5.441	358.39	9.967	408.28	13.098	440.40	12.888 c[a]	457.35	12.000
318.28	6.336	368.40	10.772	418.22	13.299	440.81	12.873	467.00	11.050
$x_1 = 0.4003$, $x_2 = 0.4512$									
278.31	1.544	338.32	4.184	398.22	7.345	457.40	9.622	478.27	8.909 c[a]
288.31	1.899	348.40	4.709	408.22	7.855	467.03	9.507	478.49	8.894
298.24	2.299	358.37	5.239	418.16	8.330	476.68	9.028	478.51	8.859
308.35	2.734	368.40	5.770	428.06	8.760	477.36	8.979	481.14	8.610
318.34	3.194	378.35	6.300	437.96	9.146	477.91	8.934	485.73	7.957
328.35	3.679	388.33	6.825	447.67	9.452	478.21	8.914		
$x_1 = 0.3972$, $x_2 = 0.1434$									
278.39	2.383	328.33	4.993	378.40	7.676	428.15	9.716	477.13	10.041
288.37	2.868	338.36	5.593	388.33	8.141	438.04	358.41	481.77	9.721
298.34	3.383	348.37	6.143	398.35	8.581	447.90	10.236	486.52	9.511
308.33	3.918	358.36	6.673	408.31	8.996	457.75	10.391	486.82	9.501 c[a]
318.33	4.478	368.38	7.191	418.45	9.376	467.54	10.346	487.43	9.406
$x_1 = 0.1998$, $x_2 = 0.1984$									
278.40	1.545	328.31	3.245	378.42	4.807	418.25	5.722	468.03	6.772
288.33	1.865	338.36	3.590	388.37	5.047	428.22	5.927	477.96	6.992
298.30	2.200	348.38	3.925	398.32	5.282	438.16	6.142	487.84	7.222
308.35	2.545	358.42	4.245	398.37	5.297	448.10	6.347	497.80	7.457
318.32	2.900	368.46	4.517	408.33	5.512	458.05	6.557	507.66	7.667
$x_1 = 0.5939$, $x_2 = 0.2265$									
278.41	2.569	328.31	6.274	368.24	9.743	408.09	12.478	447.80	12.828
288.38	3.194	338.35	7.234	378.19	10.538	418.04	12.868	452.71	12.553
298.35	3.874	348.34	8.009	388.21	11.268	427.98	13.098	454.64	12.498 c[a]
308.34	4.629	358.41	8.879	398.16	11.938	437.89	13.113	457.67	12.333
318.33	5.434								
$x_1 = 0.3592$, $x_2 = 0.5408$									
278.38	1.334	328.35	3.199	378.15	5.539	427.95	7.876	477.38	9.119
288.36	1.639	338.36	3.649	388.11	6.024	437.94	8.277	472.76	9.198
298.37	1.984	348.38	4.114	398.14	6.509	447.87	8.642	482.65	8.995
308.35	2.364	358.37	4.584	408.07	6.984	457.75	8.953	488.44	8.647 c[a]
318.34	2.789	368.17	5.054	418.04	7.426	467.54	9.123	492.54	8.320

Table 1 (Continued)

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
				$x_1 = 0.2545$, $x_2 = 0.5954$					
278.42	0.962	298.36	1.422	318.32	1.973	338.35	2.588	358.34	3.263
288.40	1.207	308.34	1.693	328.28	2.273	348.37	2.918		
				$x_1 = 0.5979$, $x_2 = 0.0957$					
278.31	3.005	308.28	5.290	338.35	7.935	368.41	10.430	398.28	12.340
288.37	3.705	318.27	6.155	348.37	8.805	378.37	11.150	408.29	12.785
298.34	4.470	328.28	7.040	358.35	9.640	388.38	11.800		
				$x_1 = 0.4029$, $x_2 = 0.4493$					
278.32	1.543	308.35	2.733	338.33	4.197	358.41	5.252	378.40	6.333
288.25	1.898	318.34	3.198	348.37	4.717	368.40	5.793	388.33	6.858
298.29	2.303	328.35	3.692						

[a] c: critical point. [b] s: second dew point.

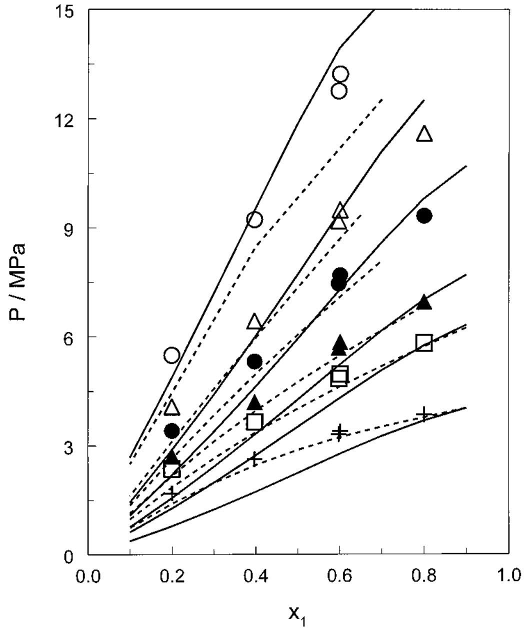

Figure 5. Quasi-binary *P*, *x* section for the ternary system [(x_1)-carbon dioxide + (x_2)vinyl acetate + (x_3)2-butanol]. Data for x_2/x_3 = 1/3: +, 283.15 K; □, 303.15 K; ▲, 313.15 K; ●, 333.15 K; △, 353.15 K; ○, 413.15 K. Solid lines, LCVM model; broken lines, PRSV/WS.

Table 2. Pure Compound Properties Used in This Study (Stevens et al., 1997b)

compound	P_c/MPa	T_c/K	ω	κ_1
2-butanol	4.226	532.63	0.6177	0.2336
vinyl acetate	4.140	519.20	0.3881	0.0260
carbon dioxide	7.394	304.34	0.2250	0.04285[a]

[a] Parameters obtained from Stryjek and Vera (1986).

Modeling. The ternary system has been modeled using the PRSV/WS EOS (Wong and Sandler, 1992) and the LCVM model (Yakoumis et al., 1996). The pure compound data and binary parameters used in the PRSV/WS EOS and LCVM model are taken from Stevens et al. (1997b) and presented in Table 2 and Table 3. The binary interaction parameter and the NRTL parameters (WS) for the system vinyl acetate + 2-butanol are obtained by fitting the VLE generated by UNIFAC (Fredenslund et al., 1977), using the experimental critical properties of the pure compounds and are given in Table 4.

Predictions of the ternary VLE at constant $x_3 = 0.15$ are presented in Figure 3 for the temperatures 303.15 K, 313.15 K, and 333.15 K. At these temperatures experimental data on the solubility of vinyl acetate and 2-butanol in CO_2 are available (Stevens et al., 1997c). In case of the varying carbon dioxide composition at constant vinyl acetate/2-butanol ratio, VLE are also predicted at 283.15 K, 383.15 K, and 413.15 K. See Figures 4 and 5.

Table 3. WS Interaction Parameter and NRTL Parameters for the PRSV/WS EOS for the Systems Investigated in This Study for α = 0.2

	CO_2 + vinyl acetate			CO_2 + 2-butanol		
T/K	k_{12}	A_{12}/ J mol^{-1}	A_{21}/ J mol^{-1}	k_{13}	A_{13}/ J mol^{-1}	A_{31}/ J mol^{-1}
283.15	0.385	4843.8	−3174.3	0.543	4454.3	170.22
303.15	0.402	−1687.1	2391.8	0.531	4243.0	139.0
313.15	0.402	1142.8	−762.8	0.524	4964.4	−393.6
333.15	0.406	569.1	−134.8	0.504	5674.9	−1058.6
353.15	0.414	3376.8	−2572.1	0.500	5486.6	−1113.0
413.15	0.470	−2583.0	3435.0	0.531	1071.2	1728.6

Table 4. NRTL and Binary Interaction Parameters for the System Vinyl Acetate (2) + 2-Butanol (3) for α = 0.2

T/K	A_{23}/J mol^{-1}	A_{32}/J mol^{-1}	k_{23}
283.15	5583.1	148.30	0.097
303.15	5277.3	746.01	0.016
313.15	5324.1	434.76	0.05
333.15	4930.0	556.72	0.05
353.15	4747.6	587.18	0.05
413.15	2105.5	2706.6	0.061

Conclusions

The experimental data show a pressure maximum in the vapor−liquid coexistence curve, which is comparable with the binary systems. The LCVM model gives a reasonable good prediction of the ternary system (Figures 3−5). The results are even slightly better than the prediction of the bubble point curve in the binary systems (Stevens et al., 1997b,c). In the binary systems the bubble point pressure in the system with vinyl acetate is overpredicted, whereas in the system with the 2-butanol the bubble point pressure is underpredicted. The PRSV/WS EOS showed good results in predicting the ternary system using only binary fit parameters. However, it must be stated that the LCVM model is a purely predictive model, but the PRSV/WS EOS uses one (PRSV/WS/UNIFAC) or three (PRSV/WS/NRTL) fit parameters per binary subsystem.

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