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Phase Behaviors, Density, and Isothermal Compressibility of Styrene + CO_2, Ethylbenzene + CO_2, and Ethylbezene + Styrene + CO_2 Systems

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The critical points, bubble points, and dew points of ethylbenzene + CO_2, styrene + CO_2, and ethylbezene + styrene + CO_2 mixtures were measured in CO_2-rich region, and the density of the mixtures were also determined. For all the mixtures, the critical temperatures and critical pressures increase with the decrease of CO_2 concentration in the concentration range studied. The phase separation pressures of the mixtures increased with increasing temperature at a fixed composition, but at constant temperature the phase separation pressures decreased as the CO_2 mole fraction in the mixtures was reduced. The Peng−Robinson equations of state was used to calculate the critical points, bubble points, and dew points parameters. The results agreed reasonably with the experimental data. The isothermal compressibility (K_T) of the mixtures was also investigated. It is demonstrated that the trend of K_T to pressure varies slowly as the pressure is far from the phase separation points. However, K_T is sensitive to pressure and reaches the maximum as the pressure approaches to the phase separation points. At the critical temperatures, K_T varies more significantly with pressure than that at bubble points and dew points.

Introduction

Supercritical fluids (SCFs) have some unique properties that make them attractive as environmentally benign media in different processes.[1,2] Supercritical (SC) CO_2 is the most commonly used solvent because its critical temperature is close to ambient temperature and its critical pressure is moderate. Additionally, it is nontoxic and inexpensive. It has been used in SC extraction,[3,4] materials preparation,[5−7] and chemical reactions.

Styrene is one of the most important raw materials of polymers. It is commercially produced by catalytic dehydrogenation of ethylbenzene, with an excess amount of steam as a diluent and a heat carrier.[8] Since the flow, including water, styrene, and unreacted ethylbenzene, needs to be cooled to avoid the polymerization of styrene, a large amount of latent heat of vaporizing water is wasted. Recently, the dehydrogenation of ethylbenzene in the presence of CO_2 instead of steam has received much attention[9−12] because it can reduce the energy required and increase the styrene yield as well. In addition, separating styrene from the incompletely reacted ethylbenzene by use of SC CO_2 as a solvent may be an attractive method because the generally employed vacuum distillation is energy consuming. High-pressure phase behaviors, density, and compressibility of the related systems are necessary for the designing of reaction and separation process, and some results have been reported. For example, pressure−composition isotherms of the styrene + CO_2 system were determined in the temperature range of (308.2 to 373.2) K.[13] Density of styrene + CO_2 solution with a wide concentration range from (0.65 to 29.9) mol % were measured isothermally at different temperatures and pressures.[14] Vapor−liquid equilibrium data of the ethylbenzene + CO_2, styrene + CO_2, and ethylbezene + styrene + CO_2 systems were studied at (308, 318, and 328) K over a pressure range from (1.4 to 8.4) MPa.[15]

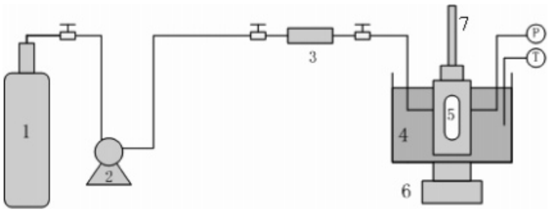

Figure 1. Schematic diagram of the apparatus measuring the critical points: 1, gas tank; 2, syringe pump; 3, sample bomb; 4, water bath; 5, high-pressure view cell; 6, magnetic stirrer; 7, piston.

In this work, we focused on the systematic investigation on the phase behaviors of the binary and ternary mixtures with the CO_2 concentration ranging from (89.6 to 97.9) mol %, including the critical points, bubble points, and dew points at different temperatures and pressures. Additionally, the density and isothermal compressibility of the mixtures were obtained. Part of the phase separation data were calculated by the Peng−Robinson equation of state (P−R EOS).[16]

Experimental Section

Materials. CO_2 was purchased from Beijing Analytical Instrument Factory, and the purity was 99.995 mol %. Ethylbenzene and styrene were supplied by Beijing Chemical Agent Corporation, and the purities were 99.0 mass % and 98.0 mass %, respectively. All the chemicals were used without further purification.

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Table 1. Comparison of the Measured and Calculated Critical Temperatures (T_c) and Critical Pressures (P_c) of Ethylbenzene + CO_2, Styrene + CO_2, and Ethylbezene + Styrene + CO_2 Systems

samples	x_{EB} mol %	x_{ST} mol %	x_{CO_2} mol %	$T_{c,meas}$ K	$P_{c,meas}$ MPa	$T_{c,cal}$ K	$P_{c,cal}$ MPa
1	0	0	100.00	304.2	7.36	304.2	7.39
2	2.11	0	97.89	317.5	8.69	318.4	8.83
3	3.84	0	96.16	326.0	9.63	326.3	9.82
4	5.12	0	94.88	332.6	10.45	330.7	10.44
5	6.37	0	93.63	335.4	10.87	334.6	11.02
6	7.51	0	92.49				
7	9.98	0	90.02				
8	0	2.25	97.75	318.8	8.90	319.8	9.10
9	0	3.63	96.37	325.7	9.75	325.9	9.92
10	0	4.88	95.12	331.0	10.44	330.2	10.56
11	0	7.42	92.58				
12	0	10.10	89.90				
13	1.68	3.29	95.03	331.0	10.41	328.7	10.31
14	1.25	3.75	95.00	330.8	10.31	328.5	10.30
15	1.70	5.10	93.20	337.2	11.19	331.7	10.86
16	2.30	4.62	93.08	338.0	11.21	332.5	10.96
17	3.24	6.62	90.14				
18	2.60	7.81	89.59				

Experimental Apparatus. The schematic diagram of the apparatus was shown in Figure 1. It was similar to that used previously.[17] It consisted mainly of a high-pressure view cell, a syringe pump, a constant-temperature water bath, a pressure gauge, a magnetic stirrer, and a gas tank.

The inner volume of the high-pressure view cell could be changed. A piston was designed in the high-pressure cell. It could be screwed in or out freely. Screwing the piston in the cell, the inner volume of the cell would change to small, while screwing the piston out, the inner volume would become large. For the cell used in this work, the inner volume of it could range from (23 to 50) cm^3, and the inner volume can be measured with an accuracy of ± 0.005 cm^3.

The view cell was immersed in the water bath, where the temperature was controlled by a Haake-E3 temperature controller with an uncertainty of the temperature ± 0.1 K. The pressure gauge was composed of a pressure transducer (FOXBORO/ICT, model 93) and an indicator. The uncertainly of the pressure gauge was ± 0.025 MPa in the pressure range of (0 to 20) MPa.

Experimental Procedures. Only the measurement of the phase behavior of the ternary systems containing CO_2, styrene, and ethylbenzene was described here. For the binary systems, the procedures were similar. In a typical experiment, the apparatus was washed thoroughly using ethanol and dried under vacuum. A known mass of the mixture with a predetermined molar ratio of styrene and ethylbenzene was charged into the cell. A low-pressure CO_2 flow was introduced to the high-pressure cell slowly to replace the air within after the styrene and ethylbenzene were charged in. Then CO_2 was charged using a 41 cm^3 sample bomb. The quantity of the CO_2 added was known by the mass difference of the sample bomb before and after charging the view cell. Therefore, the composition of the mixture in the system was known from the masses of the chemicals in the system. The water bath was maintained

Table 2. Phase Separation Points, Temperatures, and Pressures of Ethylbenzene + CO_2, Styrene + CO_2, and Ethylbezene + Styrene + CO_2 Systems[a]

T K	P MPa	ρ g/cm^3
	sample 2	
303.2	6.91	0.709
308.2	7.63	0.665
313.2	8.21	0.590
317.5^c	8.69	0.504
318.2	8.78	0.498
	sample 3	
303.2	6.67	0.741
308.2	7.25	0.715
313.2	7.98	0.673
318.2	8.65	0.633
323.2	9.32	0.583
326.0^c	9.63	0.546
328.2	9.98	0.533
	sample 4	
303.2	6.56	0.762
308.2	7.22	0.735
313.2	7.89	0.702
318.2	8.63	0.671
323.2	9.30	0.630
328.2	9.95	0.603
332.6^c	10.45	0.560
333.2	10.64	0.557
	sample 5	
303.2	6.52	0.782
308.2	7.20	0.761
313.2	7.85	0.731
318.2	8.53	0.703
323.2	9.21	0.675
328.2	9.91	0.642
333.2	10.58	0.607
335.4^c	10.87	0.590
	sample 6	
303.2	6.48	0.790
308.2	7.11	0.769
313.2	7.82	0.748
318.2	8.42	0.722
323.2	9.11	0.697
328.2	9.87	0.672
333.2	10.55	0.646
	sample 7	
303.2	6.42	0.818
308.2	7.01	0.799
313.2	7.62	0.779
318.2	8.30	0.760
323.2	9.02	0.742
328.2	9.71	0.723
333.2	10.48	0.706
	sample 8	
303.2	6.89	0.721
308.2	7.59	0.675
313.2	8.23	0.615
318.2	8.86	0.529
318.8^c	8.90	0.520
321.2	9.20	0.500
	sample 9	
303.2	6.77	0.755
308.2	7.38	0.721
313.2	8.13	0.683
318.2	8.75	0.635
323.2	9.43	0.582
325.7^c	9.75	0.545
330.2	10.30	0.527
	sample 10	
303.2	6.59	0.774
308.2	7.24	0.747
313.2	8.02	0.711
318.2	8.61	0.682
323.2	9.29	0.645
328.2	10.09	0.608
331.0^c	10.44	0.580
333.2	10.73	0.570
	sample 11	
303.2	6.54	0.805
308.2	7.15	0.781
313.2	7.84	0.758
318.2	8.53	0.734
323.2	9.26	0.711
328.2	10.03	0.685
333.2	10.72	0.663
	sample 12	
303.2	6.39	0.831
308.2	7.00	0.813
313.2	7.70	0.794
318.2	8.43	0.774
323.2	9.19	0.755
328.2	9.89	0.733
333.2	10.67	0.713
	sample 13	
303.2	6.66	0.767
308.2	7.36	0.740
313.2	8.04	0.708
318.2	8.69	0.674
323.2	9.36	0.636
328.2	10.02	0.599
331.0^c	10.41	0.570
333.2	10.72	0.558
	sample 14	
303.2	6.62	0.771
308.2	7.30	0.744
313.2	7.97	0.711
318.2	8.67	0.675
323.2	9.34	0.637
328.2	9.98	0.599
330.8^c	10.31	0.568
333.2	10.68	0.553
	sample 15	
303.2	6.56	0.798
308.2	7.16	0.777
313.2	7.78	0.752
318.2	8.52	0.729
323.2	9.24	0.700
328.2	9.94	0.670
333.2	10.56	0.647
337.2^c	11.19	0.598
341.2	11.77	0.590
	sample 16	
303.2	6.45	0.801
308.2	7.10	0.780
313.2	7.83	0.753
318.2	8.45	0.727
323.2	9.18	0.701
328.2	9.92	0.671
333.2	10.56	0.648
338.0^c	11.21	0.603
341.2	11.70	0.590
	sample 17	
303.2	6.31	0.815
308.2	7.01	0.802
313.2	7.69	0.784
318.2	8.41	0.765
323.2	9.11	0.744
328.2	9.77	0.724
333.2	10.64	0.701
	sample 18	
303.2	6.37	0.816
308.2	7.04	0.801
313.2	7.89	0.780
318.2	8.37	0.767
323.2	9.10	0.748
328.2	9.94	0.730
333.2	10.59	0.712

[a] Key: ^{c} represents the critical temperature, pressure, and density.

at a desired temperature. After thermal equilibrium had been reached, the piston of the high-pressure cell was screwed in and/or out to change the volume of the system. The experiments were carried out from low temperature to high temperature to obtain the bubble point(s), critical point, and dew point(s) at the fixed composition. It was estimated that the uncertainty of the critical temperature (T_c), critical pressure (P_c), and critical density (ρ_c) were ± 0.3 K, ± 0.04 MPa, and ± 0.01 g·cm^{-3}, respectively. The accuracies of the data at the bubble and dew points were better and were ± 0.2 K, ± 0.025 MPa, and ± 0.005 g·cm^{-3}, respectively.

Results and Discussion

Critical Parameters of Pure CO_2. To confirm the reliability of the apparatus, the critical parameters of pure CO_2 were measured. The critical temperature and critical pressure determined in this work were 304.2 K and 7.36 MPa, respectively, which are in good agreement with the literature data.

Bubble Points, Critical Points, and Dew Points of the Systems. In this work, we determined the critical points of the mixture based on two phenomena. One is the strong critical opalescence that can be observed when the fluid is at its critical points. The other is that when the homogeneous phase becomes heterogeneous at its critical point, the volume of the upper and the bottom phase is equal.[16] The former phenomenon can be obtained even when the fluid is close to but not at its critical point. Therefore, it cannot be claimed to be at critical point if the volume of the upper phase is different from that of the bottom phase when phase separation occurs even the homogeneous fluid has opalescence.

Table 1 lists the T_c and P_c of the binary and ternary systems with different concentrations of ethylbenzene, styrene, and CO_2. Because of the temperature limitation of the water bath, the highest measuring temperature was restricted to below 340 K. For all the mixtures, the critical temperatures and critical pressures increase with the decrease of CO_2 concentration in the concentration range studied.

Table 2 demonstrates the temperatures and pressures of the bubble, dew, and critical points. The compositions of the samples in Table 2 are the same as those of the corresponding samples in Table 1. The phase separation points in Table 2 are bubble points when $T < T_c$ and dew points when $T > T_c$, respectively.

It can be seen from Table 2 that the phase separation pressures increase with increasing temperature at fixed composition, but at fixed temperature, the phase separation pressures decrease as the CO_2 mole fraction in the mixtures decreases.

The critical data and the bubble point data at 308.2 K of the styrene + CO_2 system were compared to the work of Suppes and McHugh.[13] The results were shown in Figures 2 and 3. Seen from the graphs, the data are coincidence.

Figures 4−6 show the phase separation points densities of ethylbenzene + CO_2, styrene + CO_2, and ethylbenzene + styrene + CO_2 systems at different temperatures. It can be seen that the density curves decrease regularly with the increasing temperature when the temperature is far away from the critical temperatures, while they have slight changes when the temperatures are close to the critical points.

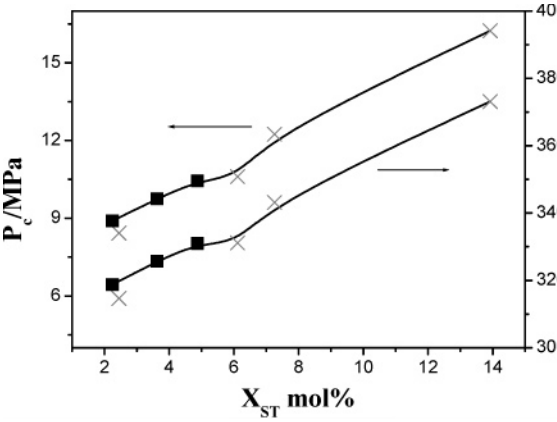

Figure 2. Comparison of the T_c and P_c of the styrene + CO_2 systems between this work and literature: ■, this work; ×, ref 13.

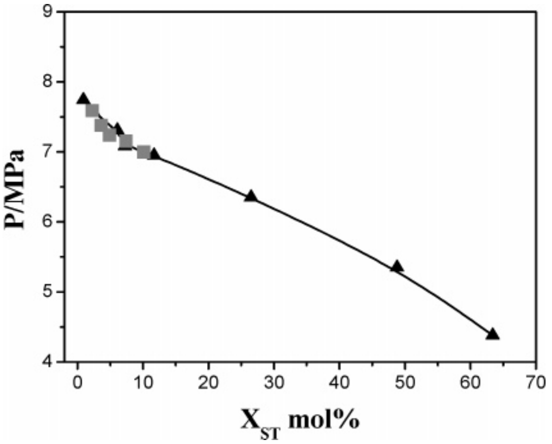

Figure 3. Comparison of the bubble points pressures of the styrene + CO_2 systems at 308.2K between this word and literature: ■, this work; ▲, ref 13.

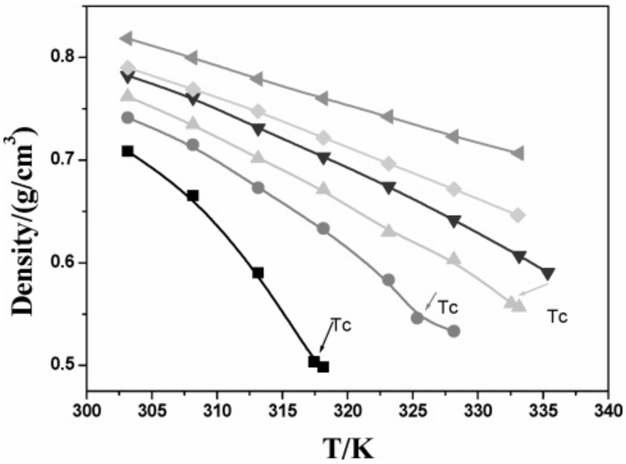

Figure 4. Dependence of the phase separation points densities on temperature of ethylbenzene + CO_2 systems: ■, ethylbenzene mol % = 2.11 mol %; ●, 3.84 mol %; ▲, 5.12 mol %; ▼, 6.37 mol %; ◆, 7.51 mol %; solid triangle pointing left, 9.98 mol %.

Isothermal Compressibility. The isothermal compressibility (K_T) of a fluid is an important characteristic parameter related to the intermolecular interaction. It can be calculated using the density data and the following equation:

$$K_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \qquad (1)$$

where ρ is the density of the mixture. As examples, Figures 7−9 show the dependence of K_T of the mixtures on

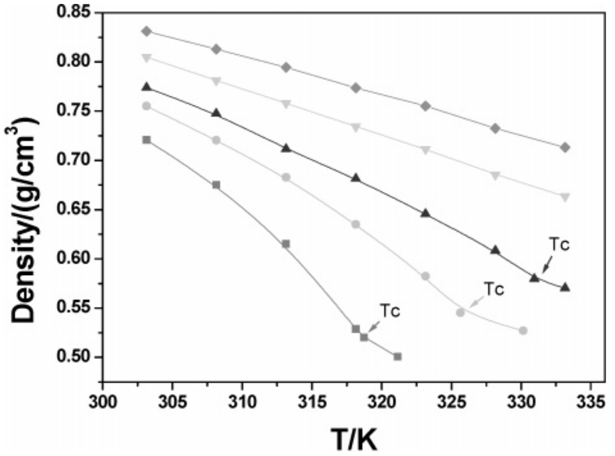

Figure 5. Dependence of the phase separation points densities on temperature of styrene + CO_2 systems: ■, styrene mol % = 2.25 mol %; ●, 3.63 mol %; ▲, 4.88 mol %; ▼, 7.42 mol %; ◆, 10.10 mol %.

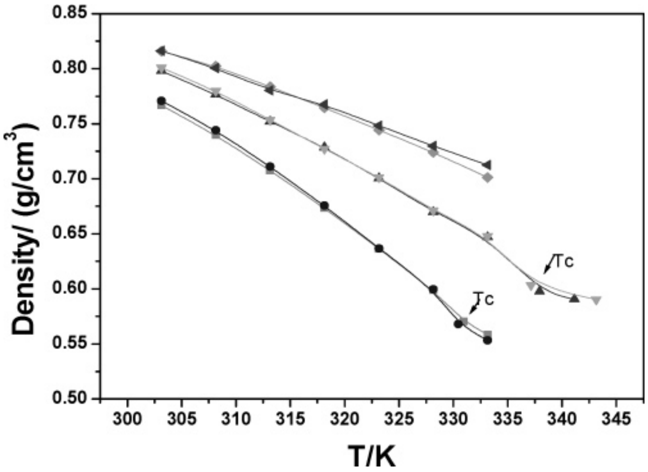

Figure 6. Dependence of the phase separation points densities on temperature of ethylbenzene + styrene + CO_2 systems: ■, ethylbenzene + styrene mol % = 4.97 mol %, r = styrene mol %/ethylbenzene mol % = 1.95; ●, 5.00 mol %, r = 3.00; ▲, 6.92 mol %, r = 2.00; ▼, 6.80 mol %, r = 3.00; ◆, 9.86 mol %, r = 2.04; solid triangle pointing left, 10.41 mol %, r = 3.00.

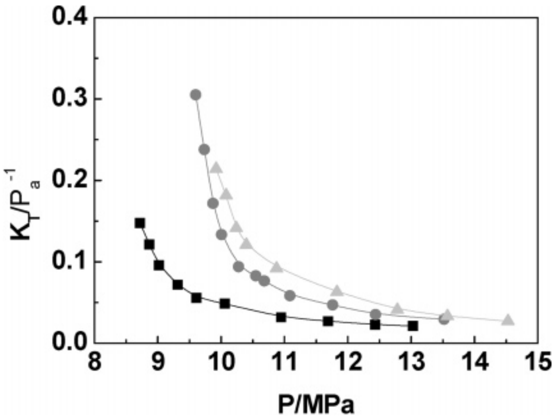

Figure 7. Plot of isothermal compressibility K_T of ethylbenzene + CO_2 systems to pressure at different temperatures (ethylbenzene is 3.84 mol %): ■, 318.2 K; ●, 326.0 K (T_c); ▲, 328.2 K.

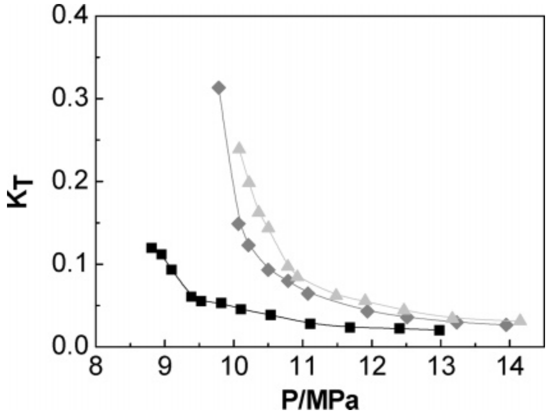

Figure 8. Plot of isothermal compressibility K_T of styrene + CO_2 systems to pressure at different temperatures (styrene is 3.63 mol %): ■, 318.2 K; ◆, 325.7 K (T_c); ▲, 328.2 K.

temperature and pressure at a selected composition for each system. The lowest pressure in each curve represents the phase separation point (CP, BP, or DP) of the mixture. Seen from the figures, the variation of K_T with pressure is limited as pressure is far from the phase separation points. However, K_T changes severely as pressure is close to the phase separation points. At the critical point, K_T changes more significantly than those at bubble or dew points.

Calculation of the Critical Points, Bubble Points, and Dew Points. The critical points, bubble points, and dew points of the mixtures were also calculated from the P−R EOS.[16] The equation can be expressed as

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \tag{2}$$

$$a = 0.457235\frac{R^2T_c^{\ 2}}{P_c}\alpha \tag{3}$$

$$b = 0.077796\frac{RT_c}{P_c} \tag{4}$$

$$\alpha = \left[1 + m\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \tag{5}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{6}$$

For a mixture, the van der Waals mixing rules are applied:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{7}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{8}$$

$$a_{ij} = (1 - k_{ij})\sqrt{a_{ii}a_{jj}} \tag{9}$$

$$b_{ij} = \frac{1}{2}(1 - l_{ij})(b_{ii} + b_{jj}) \tag{10}$$

where T_c, P_c, and ω stand for the critical temperature, critical pressure, and acentric factor, respectively. k_{ij} and l_{ij} are the binary interaction coefficients. In this work, the T_c, P_c, and ω of CO_2, ethylbenzene, and styrene are available in handbooks, which are listed in Table 3. The binary interaction parameters k_{ij} and l_{ij} of ethylbenzene + CO_2 and styrene + CO_2 were obtained by regressing the phase equilibrium $P-T$ $x-y$ data[15] and listed in Table 4. The interaction parameter between styrene and ethylbenzene was set to zero because their physical properties are similar.

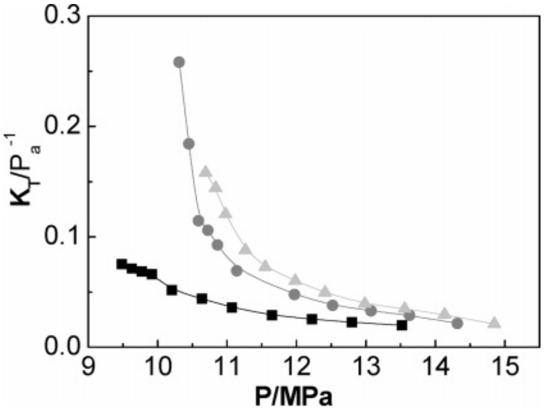

Figure 9. Plot of isothermal compressibility K_T of ethylbenzene + styrene + CO_2 systems to pressure at different temperatures (ethylbenzene is 1.25 mol %, styrene is 3.75 mol %): ■, 323.2 K; ●, 330.8 K (T_c); ▲, 333.2 K.

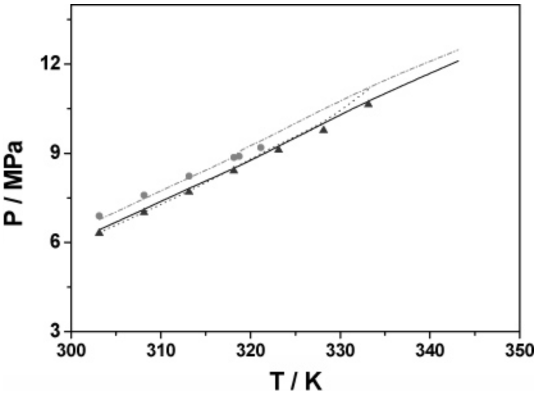

Figure 10. Comparison of part of the experimental and calculated phase separation data for ethylbenzene + CO_2, styrene + CO_2, and ethylbezene + styrene + CO_2 systems: ■, —, experimental and calculated data of ethylbenzene + CO_2 system (x_{EB} = 7.50 mol %); ●, - - -, experimental and calculated data of styrene + CO_2 system (x_{ST} = 2.25 mol %); ▲, ···, experimental and calculated data of ethylbezene + styrene + CO_2 system (x_{EB} = 3.24 %, x_{ST} = 6.62 %).

Table 3. Parameters of the Pure Components Used in This Work

	T_c/K	P_c/MPa	ω
CO_2	304.19	7.39	0.2283
ethylbenzene	617.09	3.61	0.3011
styrene	647.15	3.99	0.2572

Table 4. Binary Mixture Parameters k_{ij} and l_{ij} Used in This Study

	ethylbenzene + CO_2	styrene + CO_2
k_{ij}	0.079	0.081
l_{ij}	−0.031	−0.033

The experimental and calculated T_c and P_c are listed in Table 1 and compared to the measured data. It can be seen that for the binary systems the deviation between the experimental and calculated data is less than 0.7 % for critical temperatures and that the deviation for the ternary system is less than 2.0 %. For the critical pressures, the deviation is less than 3.0 %.

The bubble points and dew points of ethylbenzene + CO_2, styrene + CO_2, and ethylbezene + styrene + CO_2 systems were also calculated. Figure 10 illustrates the plots of the phase separation pressure versus temperature at some selected conditions. The curves in this figure were calculated using P−R EOS. The results showed that calculated results agree fairly with the calculated values.

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