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Critical Properties of the Reacting Mixture in the Esterification of Acetic Acid with Ethanol

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The critical properties of binary mixtures (acetic acid + ethanol, water + ethyl acetate, and ethyl acetate + ethanol) and ternary mixtures (acetic acid + ethanol + carbon dioxide and water + ethyl acetate + carbon dioxide) involved in the esterification of acetic acid with ethanol were measured using a high-pressure viewing cell with visual observation. Moreover, the critical properties of the nominal reacting mixtures (acetic acid + ethanol + water + ethyl acetate and acetic acid + ethanol + water + ethyl acetate + carbon dioxide) were also determined with the composition representing the extent of reaction (conversion of ethanol or acetic acid) of esterification with the initial mole ratio of acetic acid to ethanol being 1. Such information is essential for determining the reaction conditions when one intends to carry out the esterification under supercritical conditions and/or using carbon dioxide as a solvent, which could be an interesting option to enhance the reaction rate and to increase the equilibrium conversion.

1. Introduction

Ethyl acetate is generally produced through the esterification of acetic acid with ethanol in the liquid phase with an acid catalyst.¹ In practice, such a reversible reaction is limited by the low equilibrium conversion and slow reaction rate. A strong acid catalyst can enhance only the reaction rate at the expense of possible side reactions such as dehydration and isomerization, the corrosion of equipment, and the releasing of hazardous components. To improve the extent of conversion, the most effective way is to carry out this reaction using reactive distillation so as to remove one of the products; however, the components in this reaction make highly nonideal liquid mixtures with the possibility of forming several different azeotropes.^{2,3}

Supercritical fluid (SCF) technology has been developing since the 1980s in the chemical industry. Performing reactions under supercritical conditions rather than in the gas or liquid phase could be an interesting option for improving the equilibrium conversion, enhancing the reaction rate, increasing throughput, prolonging the catalyst lifetime, and making the process more environmentally benign.^{4–7} Moreover, the addition of proper SCF media can also be used to replace the environmentally undesirable solvents, improve the conversion, and avoid undesirable side products. For the synthesis of methanol and higher alcohols, the addition of proper solvents (alkanes) could improve the alcohol yield greatly under supercritical conditions;^{8–10} the selection of the solvent depends on the molecular size of intent of the alcohol and the reaction temperature and pressure. Supercritical CO₂ has received attention as an alternative solvent because of its special effects on the reaction rate, selectivity, and yield.⁶ In the esterification of acetic acid with ethanol, the presence of high-pressure CO₂ will shift the final equilibrium position significantly toward the products compared to the neat reaction;² at 333 K and 5.86 MPa, CO₂ shifted the equilibrium conversion from 63% to 72%. However, there exist

some contradictions in explaining the solvent effect because of the lack of knowledge about the critical properties of such a reacting system. With a CO₂ mole fraction of about 0.30, the equilibrium conversion increases with the pressure in the two-phase region and reaches a maximum in the critical region of the reaction system where the system just becomes one phase;^{2,11} with a higher CO₂ mole fraction (about 0.90), the solvent effect is ascribed to the local density and/or local composition enhancement or “clustering” and is sensitive to the reaction conditions, which are determined by the properties of the reacting mixture.¹²

The reacting mixture for the esterification consists mainly of acetic acid, ethanol, water, ethyl acetate, and CO₂ if it is used as a solvent. To understand the mechanism of CO₂ solvent effects on the esterification and capitalize on the unique characteristics of the reaction medium under supercritical conditions, one must be cognizant of the critical properties of the reacting mixture because the composition and related critical properties of the reacting mixture change along the reaction course. The critical properties then depend on both the original composition and the conversion. However, the reaction conditions are usually determined by the critical properties of the initial reacting mixture and sometimes even by the critical properties of one pure substance in the reactants. Ignorance of the change of the critical properties in a reacting system can cause a misinterpretation of the solvent effect. Although a series of work has focused on the critical properties of the related mixtures, experimental data for ternary and more complex mixtures are scarce,^{12–15} and more data are necessary to determine the phase behavior of the reacting mixture and the operating parameters for the reaction under supercritical conditions.

In this work, the critical properties of binary and ternary mixtures (acetic acid + ethanol, water + ethyl acetate, ethanol + ethyl acetate, acetic acid + ethanol + carbon dioxide, and water + ethyl acetate + carbon dioxide) involved in the esterification of acetic acid with ethanol were measured using a high-pressure viewing cell with visual observation. Moreover, the critical properties of the

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Table 1. Critical Properties of the Pure Substances

substance	T_c/K		P_c/MPa		$\rho_c/g\cdot cm^{-3}$	
	this work	lit	this work	lit	this work	lit
carbon dioxide	304.5	304.1 ¹⁸	7.42	7.38 ¹⁸	0.473	0.469 ¹⁸
ethanol	516.7	514.0 ¹⁹	6.27	6.14 ¹⁹	0.280	0.275 ¹⁹
ethyl acetate	523.8	523.3 ²⁰	3.90	3.87 ²⁰	0.308	0.308 ²⁰

nominal reacting mixtures (acetic acid + ethanol + water + ethyl acetate and acetic acid + ethanol + water + ethyl acetate + carbon dioxide) were also determined with the composition representing the extent of reaction (conversion of ethanol or acetic acid) of esterification with the initial mole ratio of acetic acid to ethanol being 1. On the basis of the critical properties of the reacting mixture, the CO₂ solvent effects on the esterification were clarified.

2. Experimental Section

Acetic acid (>99.5%) and ethanol (>99.7%) were purchased from Tianjin Tian-Da Chemical Corporation. Ethyl acetate (>99.5%) was purchased from Shanghai Chemical Corporation. Deionized water was supplied by Taiyuan Chemical Corporation. CO₂ (>99.95%) from the Beijing Analytical Instrument Corporation was used without further treatment. All of the reagents except CO₂ were further purified by distillation. The purity of all chemicals was checked by gas chromatography, and the results indicated that the impurities did not exceed 0.5 mass %.

The critical properties of the mixtures were measured with the same viewing cell and procedures as described previously.^{16,17} Briefly, the composition of a nominal reacting mixture was determined according to the initial reactant constituents and the extent of reaction (conversion of acetic acid or ethanol). A preevacuated cell was first charged with a known mass of a liquid mixture based on the composition of the nominal reacting mixture, and then the cell was pressurized with CO₂ through a sampling tube. The amount of the mixture in the cell was controlled in such a way that the density of the mixture should be close to or slightly higher than its critical density. The temperature and pressure readings were made by the occurrence of strong red-glow critical opalescence and the reappearance of a meniscus on slow cooling through the critical point. The critical properties of the nominal reacting mixture remained stable during the measurement, which indicated that the change in composition due to the reactions (further esterification, hydrolysis, and other side reactions) during the measurement is negligible because such reactions generally proceed very slow and need a certain catalyst. The uncertainties of the critical temperature, critical pressure, and mole fraction were estimated to be within ± 0.3 K, ± 0.03 MPa, and ± 0.003 , respectively.

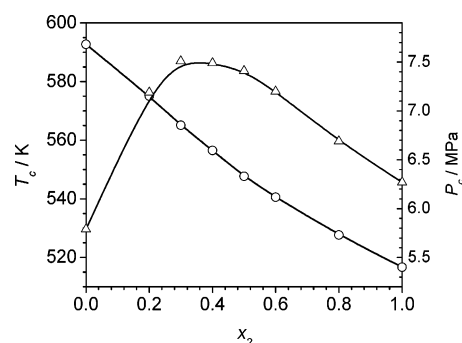
3. Results and Discussion

3.1. Pure Substances. As shown in Table 1, a comparison of the critical properties of pure ethanol, ethyl acetate, and CO₂ measured in this work with those in the literature proved that the agreement between critical temperatures and pressures was satisfactory.^{18–20} The difference between our measured density and the literature values indicated that the critical temperature and pressure could be obtained within the required uncertainty using a relatively wide range of density of the mixture provided that it was higher than the critical density. The measured critical density is the fluid density at which the critical properties were obtained; therefore, it is not very accurate (usually a

Table 2. Critical Properties of the Binary Mixtures of Acetic Acid (1) + Ethanol (2), Water (1) + Ethyl Acetate (2), and Ethyl Acetate (1) + Ethanol (2)

x_2	T_c/K	P_c/MPa	x_2	T_c/K	P_c/MPa
Acetic Acid (1) + Ethanol (2)					
0 ^a	590.7	5.78	0.500	547.7	7.41
0.200	575.1	7.19	0.600	540.6	7.20
0.300	565.1	7.51	0.800	527.7	6.69
0.400	556.5	7.49	1	516.7	6.27
Water (1) + Ethyl Acetate (2)					
0 ^a	647.3	22.12	0.580	538.4	6.17
0.210	592.5	13.71	0.810	529.8	4.73
0.380	558.5	8.84	1	523.8	3.90
Ethyl Acetate (1) + Ethanol (2)					
0	523.8	3.90	0.680	515.9	5.35
0.200	521.6	4.32	0.750	515.3	5.52
0.400	519.2	4.77	0.850	515.4	5.78
0.590	516.8	5.17	1	516.7	6.27

^a The critical properties of pure water and acetic acid are cited from refs 18 and 20 because of the endurance limit of the viewing cell.

**Figure 1.** Critical properties of the binary mixture of acetic acid (1) + ethanol (2): \circ , critical temperatures; \triangle , critical pressures.

little higher than the real value). Nevertheless, this was not addressed in the current work.

3.2. Binary Mixtures. The critical properties of the binary mixtures of acetic acid + ethanol, water + ethyl acetate, and ethyl acetate + ethanol are listed in Table 2.

For the binary mixture of acetic acid (1) + ethanol (2), as shown in Figure 1, the critical lines are continuous over the whole composition range between the critical points of the two pure components; the critical temperature decreases monotonically with the content of ethanol, and the critical pressure passes through a maximum at $x_2 \approx 0.35$. The critical point locus in the P – T projection is shown in Figure 2, which should exhibit type I fluid-phase behavior according to the classification of van Konynenburg and Scott.²¹

For the binary mixture of water (1) + ethyl acetate (2), as shown in Figure 3, both the critical pressure and temperature decrease monotonically with the content of ethyl acetate. The critical point locus in the P – T projection was shown in Figure 4, which is almost a straight line between the critical points of the two pure components.

For the binary mixture of ethyl acetate (1) + ethanol (2), as shown in Figure 5, the critical lines are continuous over the whole composition range between the critical points of the two pure components; the critical pressure increases monotonically with the molar fraction of ethanol, and the critical temperature shows a minimum at $x_2 \approx 0.75$. The critical point locus in the P – T projection was shown in Figure 6, which should exhibit type I fluid-phase behavior according to the classification of van Konynenburg and Scott.²¹

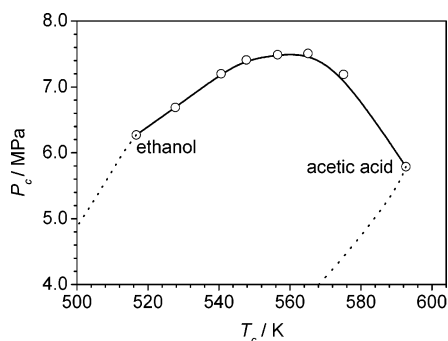


Figure 2. Projection of the critical pressure versus the critical temperature for the binary mixture of acetic acid (1) + ethanol (2): \circ , critical points in this work; \cdots , vapor pressure of each pure component below the critical temperature.¹⁸

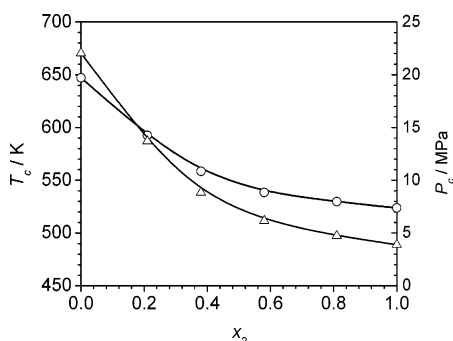


Figure 3. Critical properties of the binary mixture of water (1) + ethyl acetate (2): \circ , critical temperatures; Δ , critical pressures.

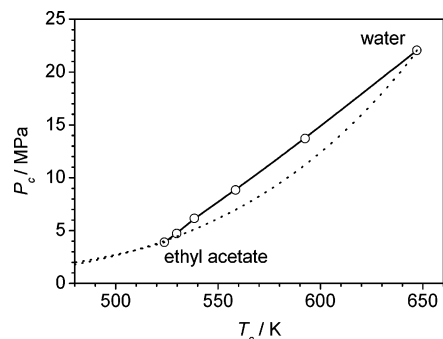


Figure 4. Projection of the critical pressure versus the critical temperature for the binary mixture of water (1) + ethyl acetate (2): \circ , critical points in this work; \cdots , vapor pressure of each pure component below the critical temperature.¹⁸

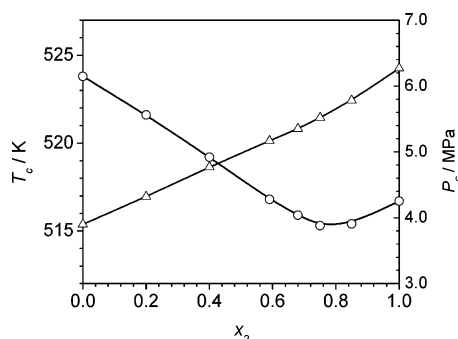


Figure 5. Critical properties of the binary mixture of ethyl acetate (1) + ethanol (2): \circ , critical temperatures; Δ , critical pressures.

For the esterification of acetic acid with ethanol, the binary mixture of acetic acid + ethanol represents the initial reacting mixture, and the final product will be a binary mixture of water + ethyl acetate provided a complete

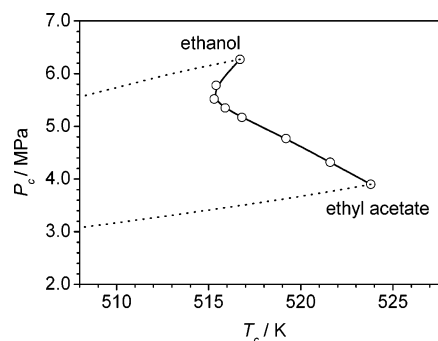


Figure 6. Projection of the critical pressure versus the critical temperature for the binary mixture of ethyl acetate (1) + ethanol (2): \circ , critical points in this work; \cdots , vapor pressure of each pure component below the critical temperature.¹⁸

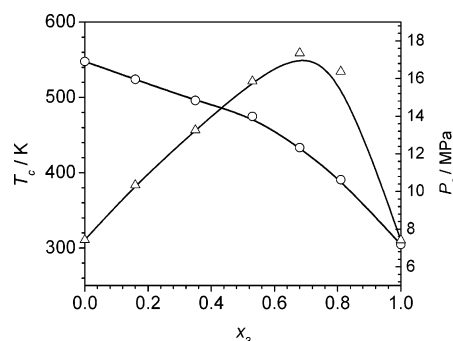


Figure 7. Critical properties of the ternary mixture of acetic acid (1) + ethanol (2) + carbon dioxide (3) ($x_1/x_2 = 1$): \circ , critical temperatures; Δ , critical pressures.

Table 3. Critical Properties of the Ternary Mixtures of Acetic Acid (1) + Ethanol (2) + Carbon Dioxide (3) and Water (1) + Ethyl Acetate (2) + Carbon Dioxide (3)

x_3	x_1	x_2	T_c/K	P_c/MPa
Acetic Acid (1) + Ethanol (2) + Carbon Dioxide (3) ($x_1/x_2 = 1$)				
0	0.500	0.500	547.7	7.43
0.160	0.420	0.420	524.0	10.34
0.350	0.325	0.325	495.8	13.26
0.530	0.235	0.235	474.8	15.86
0.680	0.160	0.160	433.2	17.36
0.81	0.095	0.095	390.8	16.38
1	0	0	304.5	7.42
Water (1) + Ethyl Acetate (2) + Carbon Dioxide (3) ($x_1/x_2 = 1$)				
0	0.500	0.500	546.2	7.10
0.220	0.390	0.390	521.5	10.90
0.400	0.300	0.300	495.2	13.20
0.600	0.200	0.200	453.2	14.90
0.680	0.160	0.160	431.6	14.60
0.810	0.095	0.095	378.5	12.50
1	0	0	304.5	7.42

conversion is realized and no side reaction is performed (though this may be impossible because of the equilibrium limits). The critical properties of the initial and final reacting mixture are strongly dependent on the ratio of acetic acid to ethanol for the esterification.

3.3. Ternary Mixtures. The critical properties of the ternary mixtures of acetic acid (1) + ethanol (2) + carbon dioxide (3) with a fixed mole ratio of acetic acid to ethanol (initial reacting mixture for the esterification, $x_1/x_2 = 1$) and water (1) + ethyl acetate (2) + carbon dioxide (3) with a fixed mole ratio of water to ethyl acetate (final resultants of the esterification, $x_1/x_2 = 1$) are shown in Table 3 and Figures 7 and 8.

The critical temperature of the ternary mixtures decreases with the increase in content of CO_2 , which indicates that the addition of CO_2 is an effective way to reduce the

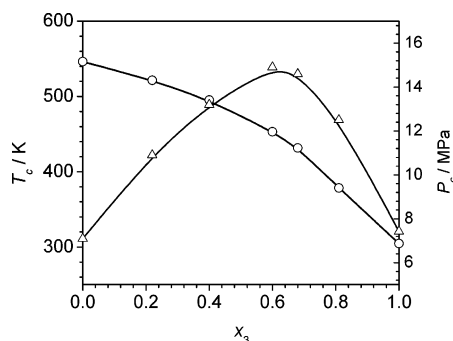


Figure 8. Critical properties of the ternary mixture of water (1) + ethyl acetate (2) + carbon dioxide (3) ($x_1/x_2 = 1$): \circ , critical temperatures; \triangle , critical pressures.

Table 4. Critical Properties of the Nominal Reacting Mixture (Acetic Acid (1) + Ethanol (2) + Water (3) + Ethyl Acetate (4)) along the Reaction Course of Esterification with the Initial Mole Ratio of Acetic Acid to Ethanol Being 1

extent of reaction	$x_1 (= x_2)$	$x_3 (= x_4)$	$T_c/^\circ\text{C}$	P_c/MPa
0	0.500	0	547.7	7.43
0.100	0.450	0.050	549.1	7.44
0.200	0.400	0.100	550.0	7.42
0.400	0.300	0.200	551.5	7.37
0.600	0.200	0.300	552.5	7.30
0.800	0.100	0.400	552.3	7.23
1	0	0.500	546.2	7.10

critical temperature of the reacting mixture. However, the critical pressure increases largely with the addition of CO_2 and shows a maximum at $x_3 \approx 0.70$ and 0.60 for acetic acid (1) + ethanol (2) + carbon dioxide (3) and water (1) + ethyl acetate (2) + carbon dioxide (3) ($x_1/x_2 = 1$), respectively, and then decreases with further increases in CO_2 content.

3.4. Critical Properties of the Nominal Reacting Mixture along the Reaction Course in the Esterification of Acetic Acid with Ethanol. For the esterification, the consumption of acetic acid and ethanol during the reaction will produce the same quantities of water and ethyl acetate if no side reaction is performed; the composition of the reacting mixture depends on the extent of reaction (conversion of acetic acid or ethanol) as well as the initial ratio of acetic acid to ethanol. Thereby, the critical properties of the quaternary mixture (nominal reacting mixture) of acetic acid (1) + ethanol (2) + water (3) + ethyl acetate (4) were measured with the composition representing the extent of reaction of esterification with the initial mole ratio of acetic acid to ethanol being 1 (Table 4). The critical temperatures and pressures of the reacting mixture along the reaction course were then shown in Figure 9. The critical properties of the reacting mixture change with the extent of reaction; with the reaction proceeding to higher conversion, the critical pressure decreases slightly, and the critical temperature shows a maximum at a conversion of about 0.70.

It was reported that carrying out a reaction under supercritical conditions near the critical point often gives special performance on the yield, selectivity, and catalyst stability,^{4–12} and this work shows that the critical properties change with the extent of reaction. Therefore, to ensure that the reaction was carried out under supercritical conditions near the critical point, the reaction conditions should be tuned according to the critical properties of the reacting media along the reaction course. The reaction conditions will be a compromise between both the initial reactants and the final products when the reaction is carried out at a fixed temperature and pressure.

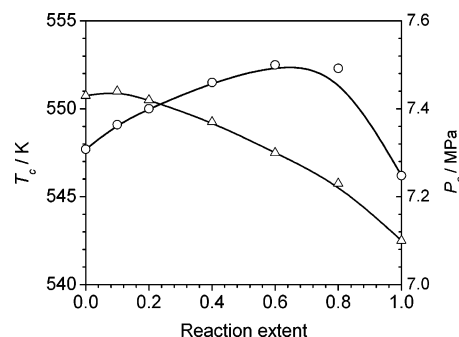


Figure 9. Critical properties of the nominal reacting mixture along the reaction course of esterification with the initial mole ratio of acetic acid to ethanol being 1: \circ , critical temperatures; \triangle , critical pressures.

It should be noted that some side reactions such as etheralization and dehydration may occur along with the esterification under the acidic environment and the reacting mixture may also contain certain side products. The critical properties of the actual reacting mixture should then be reevaluated by taking into account the side reactions.

3.5. Effects of the Addition of CO_2 on the Critical Properties of the Reacting Mixture. In recent years, many studies concerning the esterification of acetic acid with ethanol show that the addition of the proper solvent (CO_2) to the reacting mixture can improve the equilibrium conversion at a certain temperature and pressure.^{2,11,12} To clarify the variance of critical properties of the reacting mixture with the extent of reaction and the content of CO_2 , the critical properties of the quinary mixture (nominal reacting mixture with CO_2 as an additional solvent) of acetic acid (1) + ethanol (2) + water (3) + ethyl acetate (4) + CO_2 (5) were measured with the composition representing the extent of reaction (conversion of acetic acid or ethanol) of esterification with the initial mole ratio of acetic acid to ethanol being 1 and the mole fraction of CO_2 being 0.2 to 0.8 (Table 5). The critical temperatures and pressures of the reacting mixture along the reaction course were also shown in Figures 10 and 11, respectively.

With the addition of CO_2 , the critical properties of the reacting mixture depend largely on the content of CO_2 . The critical temperature decreases with the increasing content of CO_2 ; the critical pressure increases first with the content of CO_2 , reaches a maximum at $x_5 \approx 0.70$, and then decreases with more CO_2 . Comparatively, the extent of reaction has less impact on the critical properties of the reacting mixture, which may further prove that the addition of the proper solvent is an effective way to tune the critical properties of the reacting mixture.

Hou et al.¹² studied esterification with the initial mole fractions of CO_2 , acetic acid, and ethanol being 0.90, 0.05, and 0.05, respectively, at 333.2 K and under different pressures; the ethanol conversion increased to a maximum of about 0.7 at 10.33 MPa, which was near the critical point of the reacting mixture, as also shown in Figures 10 and 11 of this work. This enhancement was ascribed to the existence of density inhomogeneities, which are often referred to as local composition enhancement or “clustering”. CO_2 may aggregate with the reactants and the products, and the concentration of a reactant or a product around others may be higher than that of the bulk. The degree of clustering is normally highest under the supercritical conditions near the critical point and decreases with further increases of pressure when the density is far higher than the critical properties.

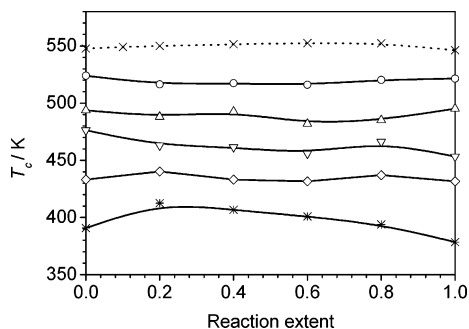


Figure 10. Critical temperature of the nominal reacting mixture along the reaction course of the esterification in the presence of CO₂ with the initial mole ratio of acetic acid to ethanol being 1 and the mole fraction of CO₂ being ×, 0; ○, 0.2; △, 0.4; ▽, 0.6; ◇, 0.7; *, 0.8.

Table 5. Critical Properties of the Nominal Reacting Mixture (Acetic Acid (1) + Ethanol (2) + Water (3) + Ethyl Acetate (4) + CO₂ (5)) along the Reaction Course of Esterification in the Presence of Carbon Dioxide with the Initial Mole Ratio of Acetic Acid to Ethanol Being 1

extent of reaction	x_5	$x_1 (= x_2)$	$x_3 (= x_4)$	$T_c/^\circ\text{C}$	P_c/MPa
0	0.200	0.400	0	524.0	10.34
0.200	0.200	0.320	0.080	516.5	11.05
0.400	0.200	0.240	0.160	517.4	10.77
0.600	0.200	0.160	0.240	516.0	11.31
0.800	0.200	0.080	0.320	520.3	11.01
1	0.200	0	0.400	521.5	10.85
0	0.400	0.300	0	493.8	13.26
0.200	0.400	0.240	0.060	488.1	13.73
0.400	0.400	0.180	0.120	492.7	12.41
0.600	0.400	0.120	0.180	481.9	14.41
0.800	0.400	0.060	0.240	485.1	13.84
1	0.400	0	0.300	495.2	13.21
0	0.600	0.200	0	476.3	14.83
0.200	0.600	0.160	0.040	462.9	15.83
0.400	0.600	0.120	0.080	461.5	15.56
0.600	0.600	0.080	0.120	445.8	16.56
0.800	0.600	0.040	0.160	469.3	14.74
1	0.600	0	0.200	453.2	14.88
0	0.700	0.150	0	433.2	17.36
0.200	0.700	0.120	0.030	440.2	17.26
0.400	0.700	0.090	0.060	433.1	16.78
0.600	0.700	0.060	0.090	431.6	17.36
0.800	0.700	0.030	0.120	437.1	16.48
1	0.700	0	0.150	431.6	14.61
0	0.800	0.100	0	390.8	16.38
0.200	0.800	0.080	0.020	412.6	16.79
0.400	0.800	0.060	0.040	406.8	16.42
0.600	0.800	0.040	0.060	400.9	16.44
0.800	0.800	0.020	0.080	394.0	15.89
1	0.800	0	0.100	378.5	12.49

Blanchard et al.² carried out the esterification with the mole fraction of CO₂ being about 0.30 at 333 K and 5.86 MPa and found that the equilibrium conversion of the esterification can be shifted from 0.63 in neat solution to 0.72. Hu et al.¹¹ also obtained similar results for the esterification of acetic acid with ethanol over HY zeolite in the presence of CO₂ at 333 K. However, with a CO₂ mole fraction of only about 0.30, the critical point of the reacting mixture will be around 505 K and 12.5 MPa. Therefore, the enhancement of the equilibrium conversion in this case cannot be ascribed to the clustering near the critical point. Actually, the reacting mixture separated into two phases, liquid and gas. The mechanism in such a case appears to involve both the preferential solubilization of one of the products, ethyl acetate, in the CO₂-rich gas phase and the pressure effects on the nonideality of the liquid phase. This also supports the opinion that CO₂ does not have to be in the supercritical state to be a viable reaction medium.

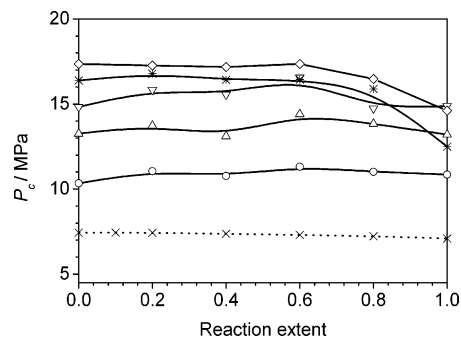


Figure 11. Critical pressure of the nominal reacting mixture along the reaction course of the esterification in the presence of CO₂ with the initial mole ratio of acetic acid to ethanol being 1 and the mole fraction of CO₂ being ×, 0; ○, 0.2; △, 0.4; ▽, 0.6; ◇, 0.7; *, 0.8.

4. Conclusions

The critical properties of the binary, ternary, quaternary, and quinary mixtures involved in the esterification of acetic acid with ethanol using CO₂ as an additional solvent were measured. Moreover, the critical properties of the nominal reacting mixtures were also determined with the composition representing the extent of reaction of esterification with the initial mole ratio of acetic acid to ethanol being 1.

The critical properties of the reacting mixture change with the extent of reaction (conversion of acetic acid or ethanol); with the addition of carbon dioxide, the critical properties of the reacting mixture depend largely on the content of carbon dioxide. Ignorance of the change in the critical properties in a reacting system can cause a misinterpretation of the solvent effect. To ensure that the reaction was carried out under supercritical conditions near the critical point, the reaction conditions should be tuned according to the critical properties of the reacting mixture along the reaction course.

The addition of the proper solvent, carbon dioxide, to the reacting mixture can enhance the equilibrium conversion at a certain temperature and pressure. This may be achieved through either the clustering at the supercritical conditions near critical point by using large amounts of carbon dioxide or the preferential solubilization of one of the products in the CO₂-rich gas phase by using moderate amounts of carbon dioxide.

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