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Study on Phase Equilibrium Properties for CO_2+ Cosolvent Binary Systems

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Abstrcact: In this study, the constant volume, visual method is used to measure the critical point of CO_2+toluene, CO_2+cyclohexane, CO_2+*n*-butyraldehyde, CO_2+*i*-butyraldehyde, CO_2+methanol and CO_2+alcohol binary systems. The relationship between critical point and the concentration of the entrainer for different substances has been discussed, and the comparison of the phase behavior of single component system and that of binary systems have been carried out.

Keywords: Critical point, supercritical, binary system, phase equilibrium.

Recently, the application of supercritical fluid technology is very interested, and it is applied in many areas for its special properties. The performance of supercritical fluid (SCF) as a solvent can be greatly affected by addition of an entrainer to the system. An entrainer can be added to a supercritical fluid to enhance its solvent strength and/or selectivity. Critical point data for these dilute supercritical fluid-cosolvent systems are imperative for the design of efficient separation and reaction processes. Despite this fact, the data of phase behavior of SCFs with typical laboratory solvents are scarce. So that, it is very important to study the phase equilibrium properties of binary and multicomponent systems.

In this study, we present the critical points of CO_2+toluene, CO_2+cyclohexane, CO_2+*n*-butyraldehyde, CO_2+*i*-butyraldehyde, CO_2+methanol and CO_2+alcohol. The concentration region of 0.4-3.2 mol% was emphasized.

Experimental Section

The apparatus used for studies of supercritical fluid-entrainer systems is a high-pressure view cell, which is similar to that used by Gurdial (1993)[1]. Pressure was measured using a pressure sensing device, and the temperature of the bath was measured with a precise thermometer readable to ±0.1°C. The temperature was controlled using a temperature relay in an agitated water bath. The system was stirred internally.

The mixtures were prepared by injecting a known mass of entrainer into the cell and then adding a known volume of CO_2 at fixed temperature and pressure. The CO_2 was delivered to the high-pressure view cell with a batcher. Then the cell was placed in the agitated water bath. The temperature of bath was increased using an immersion

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heater and circulator until only one phase could be observed. Then the temperature was decreased slowly until a phase transition occurred. Therefore, critical temperatures and pressures were recorded when the phase transition occurred. The phase transition of the mixture is very noticeable as the critical temperature and pressure are approached. Upon reaching the phase transition, the entire solution becomes cloudy and extremely opaque. The critical temperature and pressure of each mixture was observed at least three times to ensure the accuracy of the results.

Results and Discussion

The temperature range measured in this study is between 30°C and 51°C, the pressure is below 10MPa. The critical properties of six CO_2+entrainer mixtures were measured and compared to the data in the literature.

Figure 1 represents the relationship of critical temperature and mol% of the entrainer at an almost constant molar volume in binary systems. With the increase of mol% of the entrainer, critical temperature increased, and the experimental data show a linear dependence of critical temperature with mol% of the binary system over the concentration ranges studied. The critical temperature of binary system is related to the critical temperature of pure entrainers.

Figure 1 Relationship of critical temperature and mol% of entrainer

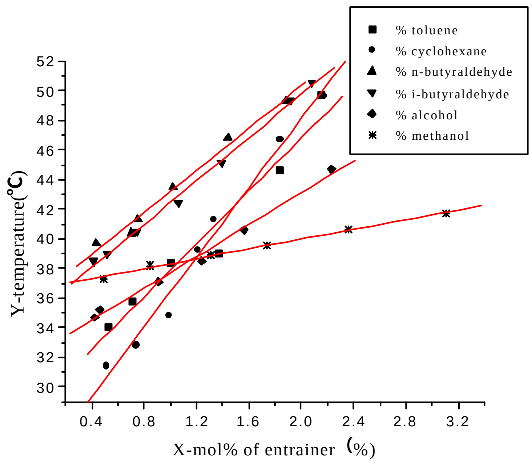


Figure 2 represents the relationship of critical pressure and mol% of entrainer at an almost constant molar volume in binary systems. Critical pressure of binary system has some relationship with that of entrainer, with the change of the critical pressure of entrainer, the critical pressure of binary system changes at the same concentration.

Figure 3 gives the critical mixture curve of several CO_2+entrainer systems over a concentration range of 0.4-3.2 mol%. We can see from **Figure 3** that the experimental data show a linear dependence of critical temperature on critical pressure over the concentration ranges studied. The critical temperature and pressure of pure entrainer have some effect on the entrainer. The slopes of the curves are different.

Figure 2 Relationship of critical pressure and mol% of entrainer

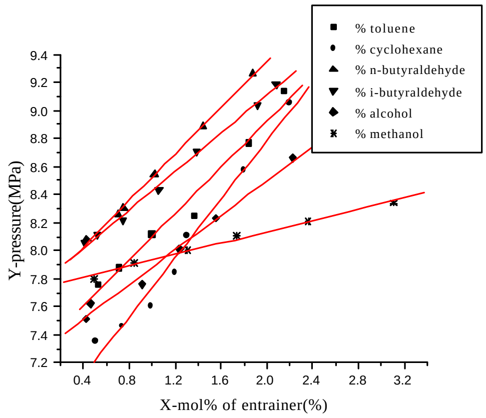
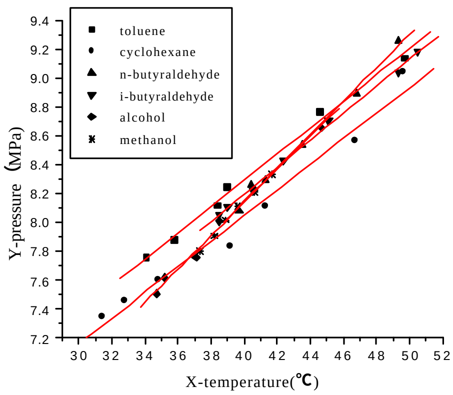


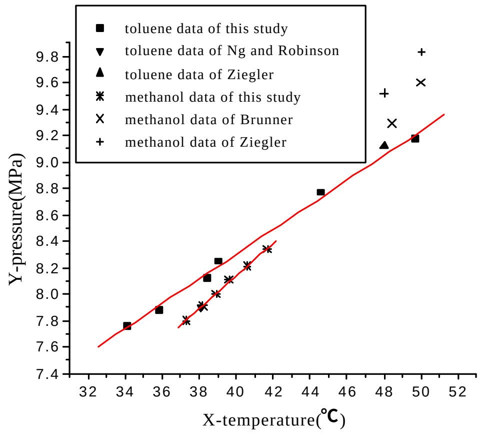
Figure 3 Relationship of critical temperature and critical pressure



In summary, the critical temperature and pressure of binary systems were higher than that of the pure CO_2, but there still exist some complicate relationship between the critical points of entrainer and binary system. It will be discussed in detail when there are more data available.

Figure 4 represents the critical point curve of CO_2+toluene and CO_2+methanol mixtures from 0.5% to 2.2% of our study, and corresponding data given by Ng, Robinson[2], Ziegler[3], Brunner[4]. The critical temperatures and pressures of CO_2+toluene system are within ±0.8°C and ±0.09MPa according to the measurement of Ng and Robinson and within ±0.5°C and ±0.07MPa according to Ziegler. The critical points of CO_2+methonal measured by Ziegler and Brunner are all above the data area measured by us. The estimated error of the measurement of Brunner and this study is very small. The critical temperatures and pressures of CO_2+methonal system are within ±0.8°C and ±0.12MPa of the measurement of Ziegler, and the difference between our measurements and the data from Ziegler is within the estimated error of the experiment. The discrepancy between the new measurements and the data of former is possibly due to the sensitivity of the CO_2+toluene system to the molar volumes used in the experiments.

Figure 4 Comparison of former toluene and methanol critical point data and this study



The critical temperatures and pressures of the binary systems presented here have an estimated experimental error of ±0.5°C and ±0.07 MPa, respectively.

Conclusion

Comparison with the former data, the new measurements show that these measurements can give a good determination of the critical mixture curve with the comparatively simple constant volume, visual method. Furthermore, the critical temperature and pressure of pure entrainers have some effects on the critical properties of binary systems.

Acknowledgments

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