J. Chem. Eng. Data **1998,** *43,* 683−686

Critical Properties of Dilute Carbon Dioxide + Entrainer and Ethane + Entrainer Mixtures

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Critical temperatures and pressures for dilute supercritical fluid−entrainer systems are imperative for the design of efficient and environmentally conscious separation processes. In this study, the constant volume, visual method is used to measure the critical point of CO_2 + acetone, CO_2 + toluene, CO_2 + propan-2-ol, CO_2 + methylene chloride, CO_2 + benzene, and ethane + benzene mixtures. The dilute entrainer concentration region is emphasized. The estimated experimental error for the critical temperature and pressure measurements is ±0.5 K and ±0.7 bar, respectively. Molar volumes are presented for all systems studied.

Introduction

The performance of a supercritical fluid (SCF) as a solvent can be greatly affected by addition of an entrainer to the system. An entrainer, or cosolvent, can be added to a supercritical fluid to enhance its solvent strength and/or selectivity. The amount of entrainer added to a supercritical solvent for many applications is usually less than 5 mol %. However, even with this small addition, solubilities of organic solutes have been observed to increase by several orders of magnitude (Eckert et al., 1986; Dobbs et al., 1987; Brennecke and Eckert, 1989). Critical point data for these dilute supercritical fluid−cosolvent systems is imperative for the design of efficient separation processes. Despite this fact, phase behavior data for SCFs combined with typical laboratory solvents is scarce (Ziegler et al., 1995). Two of the most common SCF solvents utilized are CO_2 ($T_c = 304.2$ K, $P_c = 73.8$ bar) and ethane ($T_c = 305.4$ K, $P_c = 48.8$ bar).

The solvent strength of a supercritical fluid is commonly modified by the addition of an entrainer whose critical properties can be significantly different from that of the SCF solvent. These systems typically exhibit either type I or type II phase behavior (McHugh and Krukonis, 1994; Ziegler et al., 1995) as defined by van Konynenburg and Scott (1980). A type I system is formed when the SCF and entrainer are miscible as liquids. Type II mixtures result when the two are immiscible as liquids but become miscible in the near critical region. In either case, between the critical point of the SCF solvent and the entrainer, the phase diagrams for both type I and type II mixtures exhibit the same features. That is, a critical mixture curve exists that is the locus of mixture critical points over the entire concentration range of the binary mixture.

Gurdial et al. (1993) reported the critical temperatures and pressures of several CO_2 + entrainer mixtures in the dilute entrainer concentration region by visual observation using a constant volume high-pressure view cell. However, the experimental molar volumes of the mixtures studied were not reported. Ziegler et al. (1995) used the more accurate supercritical fluid chromatography (SFC) peak shape method to determine the critical temperatures and pressures of CO_2 + acetone, CO_2 + propan-2-ol, and CO_2 + toluene mixtures. Unfortunately, only one measurement is presented in the dilute concentration range for each of these systems. Ng and Robinson (1978) also determined the critical loci of the CO_2 + toluene system in a high-pressure cell by measuring the vapor and liquid equilibrium phase compositions. Again, only one data point is available in the dilute concentration range of 5 mol % or less.

Table 1. Source and Purity of All Reagents Used

component	source	purity
carbon dioxide	Scott Specialty Gases, Inc.	SFC grade, 99.99%
ethane	BOC gases, Inc.	SFC grade, 99.99%
acetone	Fisher	99+%
propan-2-ol	Fisher	99+%
benzene	Fisher	99+%
toluene	Fisher	99+%
methylene chloride	Fisher	99+%

In this study, we present the critical points of CO_2 + acetone, + toluene, + propan-2-ol, + methylene chloride, and + benzene mixtures along with the data for an ethane+benzene system. The 0.5−7 mol % region is emphasized. Measurements for the CO_2 + toluene, + acetone, and + propan-2-ol systems are compared with the literature values. Molar volumes loaded are presented for all systems.

Experimental Section

All materials used in this study were used without further purification. The source and purity of the supercritical solvents and entrainers are given in Table 1. The apparatus used for studies of supercritical fluid−entrainer systems is similar to that used by Gurdial (1993). A Jerguson sight gauge (model 13R32) was used for visual observation of the critical points. Temperature was controlled to ±0.2 K using an immersion circulator (Cole-Parmer Polystat series 12002) in an agitated water bath. The temperature of the bath was measured using a Fisher traceable thermometer readable to ±0.1 K. Pressure was measured to within ±0.7 bar using a pressure transducer

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S0021-9568(97)00275-6 CCC: $15.00

(Omega, model PX945-10). The pressure transducer was calibrated using a Heise digital pressure indicator (901A). The system volume in each experiment was 42.2 mL (±0.5 mL). The system was agitated internally using a stir bar and a magnetic stirrer. The critical temperature and pressure of pure CO_2 and ethane measured in our system differed by less than 0.2 K and 0.2 bar from literature values listed above. The critical temperatures and pressures of the binary mixtures presented here have an estimated experimental error of ±0.5 K and ±0.7 bar, respectively.

Mixtures were prepared by injecting a known mass of entrainer into the Jerguson gauge and then adding a known volume of CO_2 or ethane at a fixed temperature and pressure. The CO_2 or ethane was delivered to the view cell using a calibrated pressure generator (Hi P Pressure Generator model 87-6-5) with a heating/cooling coil for temperature control. The mass of CO_2 or ethane delivered was calculated from density data obtained from the literature (Angus et al., 1976; Sychez et al., 1987). The appropriate masses of the solvent and entrainer were loaded into the system to give the desired mole fraction as well as a system density near that of the critical density. This was determined by observing the reappearance of the liquid−vapor interface as the critical point is approached. At the critical point of the system, the gas and liquid phases must occupy the same volumes. Therefore, critical temperatures and pressures were recorded when the interface reappeared within ±0.75 cm from the center line of the high-pressure vessel. The molar volume of a system was then calculated by dividing the view cell volume by the total number of moles loaded into the system.

To start a run, the view cell was placed in the agitated water bath. The temperature was increased using an immersion heater and circulator until only one phase could be observed. The temperature was then decreased slowly until a phase transition occurred. The temperature and pressure at which this occurred was noted. 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 clouds and is extremely opaque. The critical temperature and pressure of each mixture was observed at least four times to ensure accuracy of the results.

Results and Discussion

The critical properties of various CO_2 + entrainer and ethane + entrainer mixtures were measured and compared to the literature where available. Table 2 lists the critical temperatures and pressures for all systems measured including the molar volumes studied. In all cases, the new experimental data show a linear dependence of critical temperature with critical pressure over the concentration ranges studied. Figure 1 represents the critical mixture curve for the CO_2 + propan-2-ol system over a concentration range of 0.6−5 mol %. The critical temperatures and pressures of the mixtures are within ±0.5 K and ±0.5 bar of the measurements of Gurdial et al. (1993). The critical temperatures and pressures of the mixtures are also within ±0.5 K and ±0.5 bar of the Ziegler et al. (1995) measurement. Unfortunately, only one data point was available for comparison in this mole fraction range. The difference between the measurements and the literature is within the estimated error of the experiment. While Gurdial et al. (1993) do not report the molar volumes in their experiments, a comparison of their data with the new data in this study illustrates the sensitivity of the experiment to the molar volumes loaded. The constant volume, visual method requires that the density of the mixture studied be similar to the critical density of the mixture. Studying densities significantly different from the critical density will result in the measurement of a cloud point as opposed to a critical point. These new measurements and the data from the SFC peak shape method of Ziegler et al. (1995) show that a good determination of the critical mixture curve for the CO_2 + propan-2-ol system can be made using the constant volume visual method.

Table 2. Critical Properties of CO_2 + Entrainer and Ethane + Entrainer Mixtures

mol % entrainer	T_c/K	P_c/bar	V/cm^3·mol^{-1}
	CO_2 + toluene		
0.5	307.2	76.1	109.6
0.9	313.7	81.7	104.7
1.0	311.4	79.8	111.3
1.1	311.4	79.7	118.8
1.4	311.9	80.6	104.2
1.6	317.3	84.8	118.2
2.1	317.1	86.0	117.6
2.3	319.4	87.6	103.3
2.9	325.1	93.2	106.9
3.4	330.2	98.5	108.6
	CO_2 + Acetone		
1.1	308.6	77.8	85.4
2.3	311.8	80.4	90.8
3.5	316.2	83.0	91.3
3.5	316.8	83.9	91.1
4.2	318.2	85.0	82.1
5.4	323.2	88.9	82.8
5.8	323.2	88.3	89.8
7.0	332.2	95.8	99.2
	CO_2 + Propan-2-ol		
0.6	306.2	75.6	99.9
1.1	308.0	77.2	92.6
1.6	309.0	77.5	87.4
1.7	310.7	79.1	91.4
2.3	311.8	80.5	91.7
3.0	313.8	82.5	91.2
3.3	314.2	82.8	88.6
5.0	319.6	88.1	90.1
	CO_2 + Benzene		
0.5	306.7	76.1	99.2
1.0	308.2	77.7	96.9
1.6	310.9	79.9	101.9
2.0	311.4	79.8	94.2
2.2	313.0	81.0	103.4
2.2	314.9	83.1	105.4
2.5	314.4	82.8	95.4
3.1	316.7	84.7	98.4
3.6	319.9	87.5	97.9
4.0	319.0	86.1	94.0
4.3	324.9	91.8	101.2
4.4	325.0	92.0	103.1
5.8	333.6	99.9	109.0
	CO_2 + Methylene Chloride		
0.7	306.1	75.0	109.9
1.0	307.1	76.0	105.2
1.9	310.2	78.2	93.0
1.9	311.6	79.2	104.1
2.7	313.7	80.7	100.5
3.6	316.3	82.6	96.9
	Ethane + Benzene		
0.9	310.3	51.9	166.4
1.7	314.2	53.3	158.4
2.4	317.4	55.7	151.2
3.3	321.6	58.0	155.8
4.2	325.9	59.9	159.4
4.8	328.2	61.9	150.4
2.9	316.7	55.5	134.9
2.2	313.9	54.2	140.7
2.4	316.1	55.1	151.2
3.8	321.0	57.9	143.5

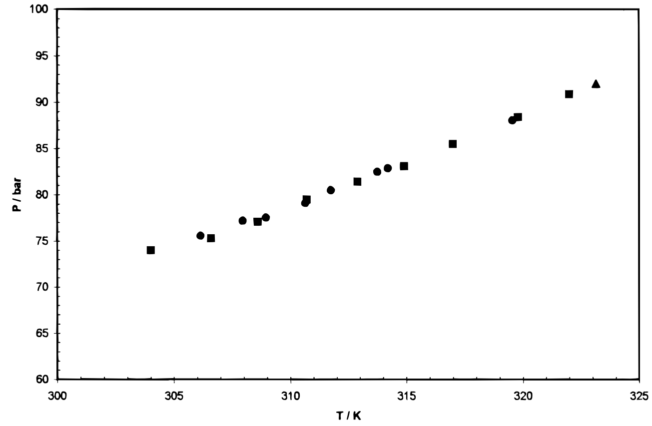

Figure 1. Critical mixture curve for CO_2 + propan-2-ol: (●) this study; (■) Gurdial et al. (1993); (▲) Ziegler et al. (1995).

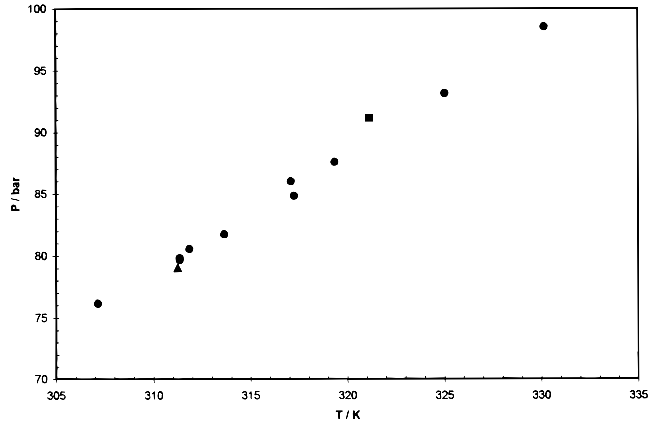

Figure 2. Critical mixture curve for CO_2 + toluene: (●) this study; (■) Ziegler et al. (1995); (▲) Ng and Robinson (1978).

Figure 2 represents the critical mixture curve of the CO_2 + toluene system for mixtures between 0.5 and 3.4 mol %. The critical temperatures and pressures of the mixtures are within ±0.5 K and ±0.5 bar of the measurement of Ng and Robinson (1978) and are within ±1.5 K and ±1.5 bar of the Ziegler et al. (1995) measurement. Again, only one point from each literature source was available for comparison in this concentration range. The difference between the new measurements and the data from Ng and Robinson (1978) is within the estimated error of the experiment. The discrepancy between the new measurements and the data of Ziegler et al. (1995) is possibly due to the sensitivity of the CO_2 + toluene system to the molar volumes used in the experiments as discussed above.

Figure 3 represents the critical point curve of the CO_2 + acetone system for mixtures between 1.1 and 7.0 mol %. The experimental data show a linear dependence of critical temperature with critical pressure over the concentration ranges studied. The critical temperatures and pressures of the mixtures are within ±1.5 K and ±2 bar of the measurements of Gurdial et al. (1993), which do not show the same degree of linearity. Again, the disagreement between the measurements is possibly due to the sensitivity of the CO_2 + acetone system to the molar volumes loaded for each run as discussed earlier. The critical temperatures and pressures are within ±0.5 K and ±0.5 bar of the single Ziegler et al. (1995) measurement and are within the estimated error of the experiment.

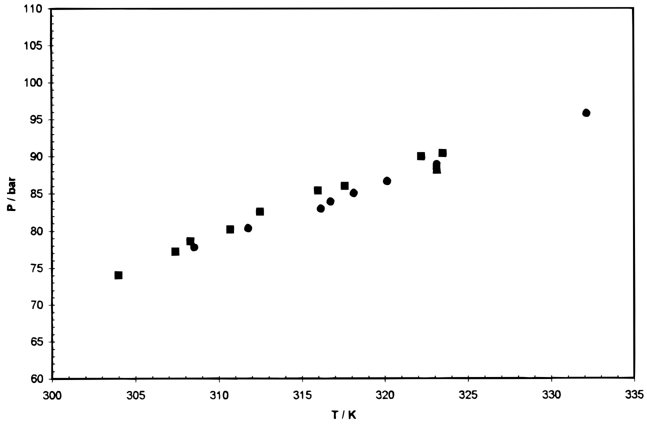

Figure 3. Critical mixture curve for CO_2 + acetone: (●) this study; (■) Gurdial et al. (1993); (▲) Ziegler et al. (1995).

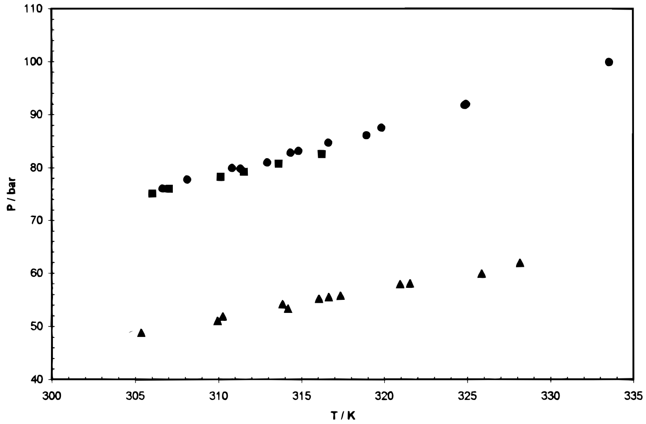

Figure 4. Critical mixture curves for (●) CO_2 + benzene, (■) CO_2 + methylene chloride, and (▲) ethane + benzene.

The data for the CO_2 + benzene, CO_2 + methylene chloride, and ethane + benzene systems show the same behavior of increasing critical temperature and pressure with increasing entrainer concentration as seen with the other systems over the dilute concentration range. The addition of benzene to CO_2 and ethane affects the mixture critical properties to a similar degree. This would be expected since both CO_2 and ethane are small, nonpolar solvents with similar critical temperatures. For instance, the addition of approximately 4 mol % benzene to CO_2 and ethane increases the critical temperatures of the mixtures by 6.7% and 6.8%, respectively, compared to their pure values. The same benzene addition increases the critical pressures of CO_2 and ethane by 24% and 23%, respectively. Figure 4 represents the critical mixture curves of the three systems.

Conclusions

The critical mixture curves for the CO_2 + toluene, CO_2 + propan-2-ol, CO_2 + acetone, CO_2 + benzene, CO_2 + methylene chloride, and ethane + benzene systems are reported. The measurements provide new data in the entrainer concentration range between 0.5 and 7 mol %. These measurements show that a good determination of the critical mixture curve can be made with the comparatively simple constant volume, visual method when mixture densities near the critical density are studied.

Acknowledgment

The authors thank Mr. Kenrick Venett for his help with the experimental apparatus.

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Received for review November 18, 1997. Accepted April 27, 1998. The authors gratefully acknowledge the financial support received for this work from the NSF-EPSCoR Program (OSR-9550480).

JE9702753