Phase Equilibrium of Ethanol + CO₂ and Acetone + CO₂ at Elevated Pressures

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Vapor-Liquid equilibria for two binary mixtures at elevated pressures were determined by a novel technique of density measurement. In this investigation using two high-pressure densitometers, phase diagrams for carbon dioxide + ethanol and carbon dioxide + acetone mixtures were established at five temperatures and pressures up to 14.39 MPa. Solubilities of carbon dioxide in both ethanol and acetone were found to increase with applied pressure but decreased with increasing temperature. The solubility for carbon dioxide in acetone was found to be greater than that of carbon dioxide in ethanol.

Introduction

Most ethanol is currently obtained by acid-catalyzed hydration of ethylene (Peters, 1993). One commercial process of acetone manufacture involves dehydrogenation of 2-propanol (McMurry, 1992). Vapor-liquid equilibria of carbon dioxide with hydrocarbons at elevated pressures are commonly used in the design and operation of separation equipment in the petroleum industry. However, limited data are available for carbon dioxide + alcohol mixtures at elevated pressures (Chang and Huang, 1994).

Panagiotopoulos and Reid (1987), Shibata and Sandler (1989), and Kato et al. (1991) recently measured the density of a high-pressure system using the vibrating-tube density meters with circulation in their vapor—liquid equilibrium apparatus. Panagiotopoulos and Reid studied the phase behavior of carbon dioxide + ethanol at different temperatures. Kato and Tanaka (1995) used the new density apparatus to measure high-pressure phase compositions of a carbon dioxide + ethanol mixture at 308.15 K. The authors (Chang, 1992; Chang et al., 1995) recently proposed volume expansion coefficients and activity coefficients of carbon dioxide + organic liquids at 298 K, and the solubilities of carbon dioxide and nitrous oxide in three liquid solvents were measured under phase equilibria at several temperatures at elevated pressures.

Experimental Section

Ethanol (Merck, 99.8+%), acetone (Merck, 99.5+%), carbon dioxide (Air Product local branch, 99.5+%), and nitrogen (Air Product local branch, 99.5+%) were purchased without further purification. Liquid and vapor densities were individually measured by using a system containing two vibrating tube densitometers (Anton Parr, DMA 512 and 512P and DMA60); pressure-related constants of two densitometers were determined from the period of vibrations of deionized water and nitrogen of accurately known densities, the information could be found elsewhere in the earliest study of Chang (1992).

The experimental system is illustrated schematically in Figure 1. At the beginning of an experiment, the residual solvent was evacuated from the equilibrium system. After degassing and evacuation of the whole system, carbon dioxide gas from a high-pressure cylinder was bubbled to an equilibrium cell up to the desired pressure and the circulation started. Recirculation was continued until reaching a stable density reading. The required time to attain equilibrium ranged from approximately 15 min at lower pressure to 30 min at higher pressure. The vapor and liquid compositions (*y* and *x*) at fixed temperature and pressure can be evaluated by combining a set of data, based on overall mass balances and the phase rule, which were used in the studies of Chang (1992), Chang et al. (1995), Kato et al. (1991), and Kato and Tanaka (1995). The sensitivity and absolute reliability of the equilibrium compositions appeared to be 0.0005 mole fraction, based on the accuracy of the density measurement. The absolute standard deviation of the temperature was within 0.015 K.

Results and Discussion

Figures 2 and 3 show the P-x-y diagrams of CO_2 + ethanol at 308.11 K and 313.14 K. Compared with the data of Kato and Tanaka (1995) and Panagiotopoulos and Reid (1987), the differences of the vapor and liquid compositions were found to be within 2%. The P-x-y diagrams at 291.15, 298.17, and 303.12 K are shown in Figure 4. At low pressures, the solubility of carbon dioxide (x_1) was relatively low and increased linearly with pressure, obeying Henry's law closely. At high pressures, x_1 could be up to 0.8 and decreased with temperature. Figures 5 and 6 represent the P-x-y diagrams for CO_2 + acetone at 298.16 K and 313.13 K. The differences of *x* and *y* were found to be within 2%, when compared with data in the literature (Kato et al., 1991; Katayama et al., 1975; Panagiotopoulos, 1987). Figure 7 shows three P-x-y diagrams at 291.15, 303.13, and 308.15 K. The solubility of CO₂ in acetone is similar to that of CO_2 + ethanol at low pressure, but larger than that of the CO_2 + ethanol system at high pressure. Tables 1 and 2 show the experimental results of coexisting phase compositions at every temperature, respectively. The difference of vapor and liquid densities between this study and Kato and Tanaka (1995) is 3% and 11%, respectively. Figures 8 and 9, respectively, show that the equilibrium constant of CO_2 + ethanol and CO_2 + acetone systems increases with temperature and decreases with pressure. The K value of carbon dioxide converged to 1 at each temperature, indicating that these two binary mixtures approached the critical state of carbon dioxide at high pressure. As the pressure approached the vicinity of the critical pressure of the mixture, the expansion of the liquid phase increased dramatically as a result of a nonlinear

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Figure 1. Experimental apparatus of V–L composition measurement for CO_2 + ethanol and CO_2 + acetone: (1) gas cylinder; (2) filter; (3) metering pump; (4) refrigerator; (5) pressure gauge; (6) relief valve; (7a,7b) needle valve; (8) air bath; (9) equilibrium cell; (10) check valve; (11) circulation pump; (12) digital thermometer; (13) digital pressure transducer; (14) wet gas meter; (15) line printer; (16) densitometer [a, DMA60; b, DMA512; c, DMA512P]; (17) high-precision thermometer.



Figure 2. Vapor−liquid equilibria for carbon dioxide (1) + ethanol (2) at 308.11 K: (●) liquid; (▲) vapor; (−) Kato and Tanaka (1995); (- - -) Panagiotopoulos and Reid (1987).

increase of the solubility of carbon dioxide. The equilibrium constant is represented as a function of relative volatility, which provides a measure of the chemical affinity



Figure 3. Vapor-liquid equilibria for carbon dioxide (1) + ethanol (2) at 313.14 K: (\bullet) liquid; (\blacktriangle) vapor; (\diamond) Jennings et al. (1991) at 314.5 K.

of the gas to the liquid for comparison. In this study, carbon dioxide was found to have a larger affinity to acetone than ethanol.

| x ₁ 0.1593 0.2138 0.2560 0.2985 0.3463 0.3923 0.4423 0.1296 0.1865 0.2622 0.3268 0.4095 0.0978 0.1412 0.2077 0.2753 0.3644 0.4179 0.1160 0.1591 | <i>y</i> 1 0.9893 0.9889 0.9888 0.9925 0.9940 0.9940 0.9948 0.9850 0.9872 0.9910 0.9933 0.9953 0.9953 0.9754 0.9880 0.9930 0.9921 0.9939 0.9934 | $\rho^{\rm V/kg \cdot m^{-3}}$ 12.2 19.1 28.7 37.4 43.7 52.9 59.8 30.4 44.6 58.1 73.0 90.5 11.9 26.1 41.4 51.8 | $\rho^{L/kg \cdot m^{-3}}$ $T = 29$ 683.6 687.8 692.2 697.0 700.8 703.7 707.4 $T = 29$ 678.4 684.3 688.6 692.2 697.3 $T = 30$ 668.6 672.6 676.3 | <i>P</i> /MPa 91.15 K 3.84 4.36 4.97 5.30 5.45 98.17 K 4.34 5.39 5.82 6.13 03.12 K 4.95 5.58 | <i>x</i> ₁ 0.4963 0.5587 0.6315 0.7405 0.7981 0.8301 0.5139 0.6357 0.7400 0.8302 | <u>y</u> 1 0.9950 0.9932 0.9966 0.9957 0.9916 0.9952 0.9969 0.9976 0.9983 0.9994 | $ ho^{V}$ /kg·m ⁻³ 68.9 79.9 96.7 121.8 137.0 147.6 109.7 147.0 168.0 285.0 | $\rho^{L/kg \cdot m^{-3}}$ 711.4 713.6 720.2 728.2 733.3 739.0 704.4 715.4 720.9 724.9 |
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| 0.3644 0.4179 0.1160 0.1591 | 0.9939 0.9934 | | 685.4 | 6.27 | 0.7173 | 0.9907 | 161.6 | 707.4 |
| 0.4179 0.1160 0.1591 | 0.9934 | 75.6 | 687.8 | 6.48 | 0.7700 | 0.9916 | 173.6 | 710.6 |
| 0.1160 0.1591 | 0.0001 | 85.6 | 691.2 | 6.63 | 0.8280 | 0.9916 | 183.9 | 712.0 |
| 0.1160 0.1591 | | 00.0 | 001.2 | 0.00 | 0.0200 | 0.5510 | 105.5 | 116.4 |
| 0.1160 0.1591 | | | T=30 | 08.11 K | | | | |
| 0.1591 | 0.9838 | 18.8 | 670.6 | 5.16 | 0.4017 | 0.9919 | 123.5 | 697.7 |
| 0 10 5 7 | 0.9882 | 30.0 | 675.1 | 5.68 | 0.4589 | 0.9914 | 140.5 | 699.5 |
| 0.1957 | 0.9884 | 42.7 | 678.6 | 6.01 | 0.5287 | 0.9947 | 153.2 | 732.3 |
| 0.2239 | 0.9936 | 62.5 | 684.1 | 6.31 | 0.5819 | 0.9939 | 166.2 | 703.9 |
| 0 2593 | 0 9913 | 82.2 | 687 | 6 66 | 0 6370 | 0 9913 | 183.3 | 706.4 |
| 0.2000 | 0.0010 | 90.8 | 689 5 | 6 89 | 0 72/9 | 0.9926 | 196.9 | 707 7 |
| 0.2304 | 0.0002 | 101.3 | 602.3 | 7.01 | 0.7243 | 0.0020 | 204 7 | 707.7 |
| 0.3324 | 0.9932 | 101.3 | 092.3 | 7.01 | 0.7713 | 0.9969 | 204.7 | 708.7 |
| 0.3000 | 0.9941 | 114.7 | 094.4 | 7.17 | 0.6237 | 0.9909 | 210.1 | 706.6 |
| | | | T=31 | 13.14 K | | | | |
| 0.0529 | 0.9878 | 8.40 | 657.8 | 5.90 | 0.4697 | 0.9969 | 122.8 | 685.7 |
| 0.1009 | 0.9883 | 24.9 | 663.6 | 6.31 | 0.5268 | 0.9925 | 137.2 | 688.6 |
| 0.1418 | 0.9917 | 33.7 | 666.1 | 6.65 | 0.5881 | 0.9965 | 150.7 | 690.5 |
| 0 1718 | 0.9925 | 45.8 | 668.8 | 7.02 | 0.6356 | 0.9962 | 167.3 | 693.1 |
| 0.1710 | 0.0028 | 54.0 | 672 8 | 7.02 | 0.6678 | 0.0054 | 170.1 | 604 7 |
| 0.2155 | 0.9928 | J4.3 69 1 | 676.0 | 7.00 | 0.0078 | 0.9934 | 170.1 | 605 5 |
| 0.2430 | 0.9941 | 00.1 | 070.0 | 7.51 | 0.7133 | 0.9972 | 102.2 | 095.5 |
| 0.3074 | 0.9939 | 82.2 | 6/8.1 | 7.60 | 0.7607 | 0.9977 | 198.5 | 696.2 |
| 0.3636 | 0.9960 | 94.4 | 680.1 | 7.73 | 0.7999 | 0.9985 | 207.8 | 696.6 |
| 0.4117 | 0.9963 | 109.5 | 682.7 | 7.92 | 0.8208 | 0.9989 | 221.4 | 697.2 |
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 Table 1. Experimental Data for Carbon Dioxide (1) + Ethanol (2) at Various Temperatures

Figure 4. Vapor−liquid equilibria for carbon dioxide (1) + ethanol (2) at different temperatures: (+) liquid/(+) vapor at 303.12 K; (▲) liquid/(△) vapor at 298.17 K; (♠) liquid/(◇) vapor at 291.15 K.

Conclusions

Two densitometers were used for the determination of high-pressure phase equilibria for mixtures of CO_2 + ethanol and CO_2 + acetone at five temperatures and

Figure 5. Vapor-liquid equilibria for carbon dioxide (1) + acetone (2) at 298.16 K: (\bullet) liquid; (\blacktriangle) vapor; (\diamond) Kato et al. (1991); (-) Katayama et al. (1975).

pressures up to 14.39 MPa. A recirculation device for the liquid phase proved to be efficient for phase equilibrium studies. The result of this investigation showed that the mole fraction of carbon dioxide in the liquid phase is high

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| Fable 2. | Experimental Data for | Carbon Dioxide | (1) + Acetone | (2) at | Various Ten | nperatures |
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|-------|------------|------------|---------------------------------|---------------------------------|---------|------------|------------|-----------------------------------|---------------------------------|
| P/MPa | <i>X</i> 1 | <i>y</i> 1 | $ ho^{ m V}/ m kg{\cdot}m^{-3}$ | $ ho^{ m L}/ m kg{\cdot}m^{-3}$ | P/MPa | <i>X</i> 1 | <i>Y</i> 1 | $ ho^{ m V}/ m kg{f \cdot}m^{-3}$ | $ ho^{ m L}/ m kg{\cdot}m^{-3}$ |
| | | | | T = 29 | 1.15 K | | | | |
| 0.87 | 0.2150 | 0.9528 | 11.4 | 687.9 | 3.45 | 0.7119 | 0.9847 | 68.5 | 717.2 |
| 1.18 | 0.2885 | 0.9655 | 17.2 | 692.8 | 3.84 | 0.7670 | 0.9888 | 79.7 | 720.3 |
| 1.73 | 0.4027 | 0.9729 | 28.1 | 698.7 | 4.34 | 0.8177 | 0.9902 | 95.9 | 723.4 |
| 2.41 | 0.5208 | 0.9789 | 42.8 | 703.3 | 4.94 | 0.8662 | 0.9869 | 119.7 | 725.9 |
| 2.81 | 0.5940 | 0.9815 | 52.1 | 707.4 | 5.27 | 0.9100 | 0.9866 | 136.1 | 727.7 |
| 3.10 | 0.6545 | 0.9839 | 59.5 | 713.1 | | | | | |
| | | | | T = 29 | 8 16 K | | | | |
| 0.88 | 0.1699 | 0.9646 | 11.0 | 673.9 | 3.65 | 0.6409 | 0.9869 | 70.6 | 721.9 |
| 1.27 | 0.2460 | 0.9751 | 18.2 | 684.0 | 4.00 | 0.6945 | 0.9891 | 85.0 | 728.5 |
| 1.62 | 0.3125 | 0.9782 | 25.0 | 688.9 | 4.34 | 0.7465 | 0.9909 | 95.3 | 730.7 |
| 1.96 | 0.3701 | 0.9791 | 31.8 | 695.7 | 4 69 | 0 7912 | 0.9918 | 106.3 | 732.9 |
| 2.28 | 0 4190 | 0.9826 | 38.2 | 699 7 | 5.00 | 0.8368 | 0.9906 | 119.6 | 734.9 |
| 2.20 | 0.4687 | 0.9842 | 45.2 | 703.6 | 5 39 | 0.8917 | 0.9850 | 137.6 | 737.0 |
| 2.00 | 0.5291 | 0.9855 | 53 5 | 710.4 | 5.82 | 0.0017 | 0.9687 | 157.0 | 739.3 |
| 2.00 | 0.5890 | 0.9868 | 62.0 | 716.6 | 5.62 | 0.0000 | 0.3007 | 157.4 | 755.5 |
| 0.00 | 0.0000 | 0.0000 | 02.0 | 710.0 | 0 10 17 | | | | |
| 0.07 | 0 4055 | 0.0774 | | T = 30 | 3.13 K | 0.0000 | 0.0004 | 00.0 | 710.1 |
| 0.87 | 0.1655 | 0.9751 | 9.6 | 669.5 | 4.25 | 0.6886 | 0.9891 | 83.2 | 712.4 |
| 1.31 | 0.2360 | 0.9782 | 17.4 | 676.0 | 4.56 | 0.7314 | 0.9909 | 92.6 | 715.1 |
| 1.65 | 0.2927 | 0.9791 | 23.6 | 682.4 | 4.95 | 0.7738 | 0.9918 | 104.7 | 719.4 |
| 2.01 | 0.3482 | 0.9826 | 30.5 | 687.2 | 5.31 | 0.8167 | 0.9906 | 116.9 | 723.4 |
| 2.43 | 0.4191 | 0.9842 | 38.8 | 691.5 | 5.58 | 0.8502 | 0.9850 | 127.4 | 725.6 |
| 2.91 | 0.4823 | 0.9855 | 49.1 | 697.1 | 5.93 | 0.8870 | 0.9687 | 142.2 | 727.0 |
| 3.42 | 0.5695 | 0.9868 | 61.3 | 703.4 | 6.27 | 0.9197 | 0.9767 | 159.1 | 728.4 |
| 3.89 | 0.6330 | 0.9869 | 73.2 | 709.1 | | | | | |
| | | | | T = 30 | 8.15 K | | | | |
| 0.82 | 0.1620 | 0.9317 | 4.0 | 664.0 | 4.87 | 0.7026 | 0.9894 | 96.6 | 705.1 |
| 1.32 | 0.2252 | 0.9467 | 13.3 | 668.5 | 5.16 | 0.7497 | 0.9892 | 105.5 | 706.9 |
| 1.57 | 0.2649 | 0.9651 | 18.4 | 675.6 | 5.68 | 0.8017 | 0.9904 | 122.8 | 709.7 |
| 2.09 | 0.3349 | 0.9723 | 29.4 | 679.8 | 6.01 | 0.8319 | 0.9902 | 135.2 | 742.7 |
| 2.58 | 0.4080 | 0.9790 | 40.2 | 683.4 | 6.31 | 0.8630 | 0.9900 | 148.0 | 713.4 |
| 3.13 | 0.4787 | 0.9824 | 52.1 | 693.2 | 6.66 | 0.8920 | 0.9826 | 164.7 | 714.9 |
| 3.65 | 0.5476 | 0.9846 | 64.2 | 695.0 | 7.01 | 0.9256 | 0.9748 | 184.4 | 716.2 |
| 4.00 | 0.6006 | 0.9845 | 72.9 | 697.2 | 7.17 | 0.9336 | 0.9734 | 195.4 | 716.8 |
| 4.39 | 0.6516 | 0.9854 | 83.1 | 701.1 | | | | | |
| | | | | T = 31 | 3.13 K | | | | |
| 0.78 | 0.1428 | 0.9109 | 7.0 | 655.4 | 4.60 | 0.6368 | 0.9880 | 85.0 | 695.3 |
| 1.18 | 0.1882 | 0.9259 | 13.7 | 664.1 | 5.17 | 0.7022 | 0.9872 | 100.4 | 698.9 |
| 1.56 | 0.2468 | 0.9571 | 20.5 | 667.8 | 5.48 | 0.7471 | 0.9891 | 109.7 | 700.3 |
| 2.03 | 0.3078 | 0.9692 | 29.0 | 671.5 | 5.91 | 0.7964 | 0.9912 | 123.7 | 701.7 |
| 2.47 | 0.3634 | 0.9713 | 37.4 | 675.8 | 6.2 | 0.8153 | 0.9915 | 133.5 | 702.6 |
| 2.80 | 0.4068 | 0.9789 | 43.8 | 679.3 | 6.44 | 0.8464 | 0.9907 | 142.8 | 702.6 |
| 3.24 | 0.4663 | 0.9749 | 53.0 | 683.5 | 6.90 | 0.8670 | 0.9754 | 161.8 | 702.8 |
| 3.59 | 0.5369 | 0.9837 | 61.1 | 687.5 | 7.12 | 0.8920 | 0.9830 | 172.3 | 702.3 |
| 4.06 | 0.5762 | 0.9721 | 71.6 | 691.4 | 7.39 | 0.9083 | 0.9867 | 186.8 | 701.6 |



Figure 6. Vapor−liquid equilibria for carbon dioxide (1) + acetone (2) at 313.13 K: (●) liquid; (▲) vapor; (−) Katayama et al. (1975); (- - -) Panagiotopoulos and Reid (1987).



Figure 7. Vapor−liquid equilibria for carbon dioxide (1) + acetone (2) at different temperatures: (+) liquid/(+) vapor at 291.15 K; (▲) liquid/(△) vapor at 303.13 K; (●) liquid/(○) vapor at 308.15 K.



Figure 8. Equilibrium constants of carbon dioxide for ethanol CO₂ (1) at different temperatures: (●) 291.15 K; (▲) 298.17
■) 303.12 K; (◆) 308.11 K; (+) 313.14 K.

even at moderate pressure. The solubility of CO_2 in acetone is larger than that of CO_2 in ethanol, because ethanol is polar and is also self-associated, while acetone is polar but not associated. The use of equilibrium values provides computational convenience in material balance calculations and also indicates the critical point of these two binary mixtures. It is evident that the asymmetric binary mixture approaches the critical state of carbon dioxide when the system pressure is high enough.

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Figure 9. Equilibrium constants of carbon dioxide for acetone $(2) + CO_2$ (1) at different temperatures: (**•**) 291.15 K; (**•**) 298.16 K; (**•**) 303.13 K; (**•**) 308.15 K; (+) 313.13 K.

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