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Phase Behavior of Carbon Dioxide + 1,2-Epoxycyclohexane Mixtures

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The two-phase boundaries of mixtures of carbon dioxide and 1,2-epoxycyclohexane (cyclohexene oxide) were determined at 343 K, 363 K, 383 K, and 405 K for cyclohexene oxide mole fractions of $0.02 < x_2 < 0.65$. The bubble/dew points were determined visually in a windowed, variable volume, high-pressure cell during isothermal expansions and compressions of mixtures of known overall composition. Pressure−composition diagrams were constructed from the experimental data, and the critical points of the mixtures were determined for each temperature from these phase diagrams. Although the Peng−Robinson equation of state slightly overestimated the critical pressure, an excellent fit of the remainder of the bubble and dew point data was obtained with a binary interaction parameter of 0.05. Anomalous phase behavior, in the form of remarkably high dew point data, was observed at 383 K and 405 K. ^{1}H NMR results of the cyclohexene oxide from these experiments suggest that this was due to the formation of poly(cyclohexene ether). The formation of this polymer may have been catalyzed by trace amounts of water in the system. This polymer has a low solubility in CO_2; therefore, its presence increased the dew point pressure.

Introduction

There has been a trend in the chemical industry toward green chemistry and chemical processing. As a result, carbon dioxide has recently received attention as a solvent replacement. In contrast to conventional solvents, carbon dioxide is nontoxic, nonflammable, environmentally benign, and readily available. Carbon dioxide has already been successfully used to replace conventional organic solvents in extractions (McHugh and Krukonis, 1986), emulsions (Hoefling *et al.*, 1991; Newman *et al.*, 1993), inverse emulsion polymerizations (Adamsky and Beckman, 1994), and homogeneous polymerizations (DeSimone *et al.*, 1992).

Our recent work (Super *et al.*, 1977) describes the copolymerization of carbon dioxide with 1,2-epoxycyclohexane (cyclohexene oxide) to make polycarbonates. Reactions of carbon dioxide with epoxides have been extensively studied (Inoue, 1976; Rokicki and Kuran, 1981; Super and Beckman, in press). Some of the difficulties encountered by past researchers include poor catalyst activity, highly polydisperse copolymers, and low incorporation of carbon dioxide into the copolymer. In an attempt to address some of these problems, it was desired to perform this reaction in a one-phase system. This single-phase mixture was to be composed of supercritical carbon dioxide, cyclohexene oxide, and a catalyst designed to exhibit carbon dioxide solubility. Supercritical carbon dioxide, present in excess, would serve as the solvent and as a reactant. Supercritical carbon dioxide and cyclohexene oxide are not completely miscible at all conditions. The phase behavior of supercritical carbon dioxide and cyclohexene oxide at conditions relevant to our copolymerization reaction needed to be determined to define the limits of the single-phase region.

The objective of this study was to determine the phase behavior of carbon dioxide/cyclohexene oxide mixtures at conditions required for the copolymerization reaction. An initial study of the copolymerization of cyclohexene oxide and carbon dioxide using only carbon dioxide as the solvent showed that the best results were achieved between 343 K and 405 K; therefore, the phase behavior experiments were completed over this temperature range.

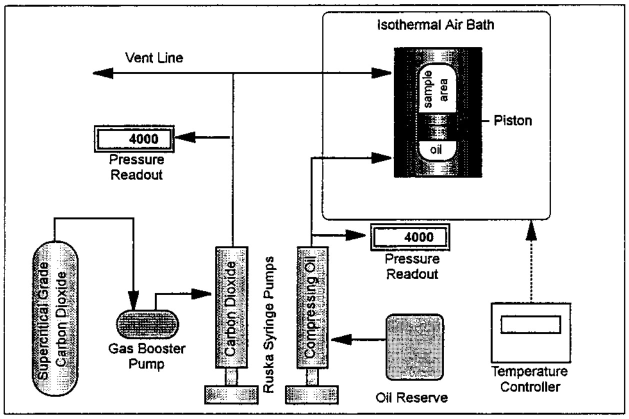

Figure 1. High-pressure, isothermal, variable volume view cell.

Experimental Section

The phase behavior of the mixtures was determined visually at isothermal conditions over a range of mole fractions. The mixtures were composed of cyclohexene oxide (Aldrich Chemicals, Milwaukee, WI), which was distilled under reduced pressure over calcium hydride, and bone dry carbon dioxide (99.9%, Liquid Carbonic, Oak Brook, IL), which was used without further purification. Mixtures of carbon dioxide and cyclohexene oxide were observed in a variable volume, high-pressure view cell (D. B. Robinson and Associates; Edmonton, Alberta, Canada). A simplified schematic of this apparatus is shown in Figure 1. The Robinson Cell is rated to 473 K and 70 MPa. Mixing is accomplished by mechanically rocking the entire cell. The main component of the Robinson Cell is a thick-walled, hollow, Pyrex cylinder into which a movable piston is introduced. The piston is equipped with an O-ring which seals off the contents of the sample volume above the piston from the transparent, overburden silicone oil below the piston. This seal maintains its integrity as the piston moves vertically within the cylinder. This overburden oil also surrounds the outside of the tube, eliminating any pressure gradient across the cylinder's wall. The sample volume is isolated from the silicone oil on the outside of the cylinder by O-rings on top of the glass tube. Since the glass tube and the oil are both transparent, the contents

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of the sample area can be viewed under high pressures through borosilicate windows on each side of the high-pressure cell. This high-pressure cell is mounted on a mechanical rocker inside a constant temperature air bath and a J-type thermocouple (accuracy to ±0.1 K) is located in direct contact with the outside of the glass tube's wall, adjacent to the sample volume, for temperature measurements. Pressure readings are taken from a Heise gauge with 0.14 MPa increments (readings can be taken with an accuracy of ±0.07 MPa).

In a typical experiment, the sample volume of the cell is loaded with the desired volume of cyclohexene oxide using graduated, glass syringes with 2% accuracy. The cell is then sealed, and compressing oil (overburden fluid) is added to the system to move the piston to the top of the cell. This is continued until all of the air initially present in the sample volume is displaced out of the cell through the vent. The cell is then heated to the desired operating temperature. Once the desired temperature is reached, carbon dioxide at 13.8 MPa and room temperature (~296 K) is added to the sample area of the cell using a graduated, high-pressure Ruska syringe pump with an accuracy of 0.05 cc (maximum error of 0.5%). The maximum error in mole fraction associated with making the cyclohexene + CO_2 mixtures is then 2.5%. The overburden oil is simultaneously removed using a second Ruska syringe pump running at the same speed, but in the opposite direction. This results in an easily controlled, isobaric, isothermal injection of carbon dioxide into the sample volume. Once the desired amount of carbon dioxide is added, the overburden oil is reintroduced using the Ruska syringe pump in order to increase the cell pressure to 41.4 MPa. The cell is rocked with a Scotch-yoke mechanism for 20 min at 41.4 MPa to achieve equilibrium of the cell contents. Small glass balls can be placed within the sample volume to enhance mixing during the rocking. The compressing oil is slowly removed, resulting in the sample volume's expansion. The pressure of the carbon dioxide + CO_2 mixture is lowered in this manner until a bubble is observed at the top of the sample area. The cell is again rocked to achieve equilibrium. If the bubble is still present, the pressure is slowly increased by compressing the sample volume. This is accomplished by adding the overburden oil to the cell in increments corresponding to pressure increases of 0.14 MPa to 0.34 MPa. The system is equilibrated by mixing after each addition. The bubble grows smaller and smaller after each pressure increase until it disappears. The highest pressure at which the bubble (vapor or fluid phase) is observed is referred to as the bubble point pressure for that mole fraction and temperature and is accurate to ±0.7MPa. The error associated with these readings is a result of the reproducibility of these visual observations. A ±0.7 MPa difference in bubble point determinations is associated with repeated measurements.

The pressure in the cell is then returned to 13.8 MPa, and carbon dioxide is once again injected into the sample area of the cell to achieve the next desired mole fraction. This is continued in decreasing increments of 0.01−0.05 mole fraction until no more carbon dioxide can be added to the sample area of the cell due to the piston approaching the bottom of the cell.

Table 1. Dew (dp) and Bubble (bp) Points of CO_2 (1) + 1,2 Epoxycyclohexane (2)

T/K	x_2	P/MPa	T/K	x_2	P/MPa
343	0.65	5.6 (bp)	383	0.25	15.7 (bp)
343	0.60	6.3 (bp)	383	0.23	15.5 (bp)
343	0.55	6.8 (bp)	383	0.21	16.2 (bp)
343	0.50	7.4 (bp)	383	0.20	15.9 (bp)
343	0.45	8.1 (bp)	383	0.20	16.2 (bp)
343	0.40	8.8 (bp)	382	0.20	16.1 (bp)
343	0.35	9.4 (bp)	383	0.19	16.2 (bp)
343	0.30	9.9 (bp)	382	0.18	16.1 (bp)
343	0.30	10.8 (bp)	383	0.18	16.1 (bp)
343	0.25	11.2 (bp)	382	0.16	16.2 (bp)
343	0.20	12.1 (bp)	382	0.14	16.3 (dp)
343	0.15	11.6 (bp)	383	0.12	16.2 (dp)
343	0.10	11.9 (bp)	383	0.10	16.1 (dp)
343	0.08	11.9 (dp)	383	0.08	16.0 (dp)
363	0.65	6.6 (bp)	383	0.08	17.1 (dp)
363	0.60	7.4 (bp)	383	0.08	17.0 (dp)
363	0.55	8.3 (bp)	383	0.06	17.6 (dp)
363	0.50	9.1 (bp)	383	0.06	18.5 (dp)
363	0.45	10.0 (bp)	383	0.05	18.6 (dp)
363	0.40	11.0 (bp)	383	0.05	18.9 (dp)
363	0.35	11.9 (bp)	383	0.03	21.9 (dp)
363	0.30	12.6 (bp)	383	0.03	18.6 (dp)
363	0.30	12.9 (bp)	383	0.02	20.6 (dp)
363	0.25	13.5 (bp)	383	0.02	17.9 (dp)
363	0.20	13.9 (bp)	405	0.65	9.2 (bp)
363	0.15	14.1 (bp)	405	0.60	10.6 (bp)
363	0.10	14.1 (dp)	405	0.55	11.7 (bp)
363	0.07	14.1 (dp)	405	0.50	13.0 (bp)
382	0.63	8.1 (bp)	406	0.45	14.1 (bp)
382	0.60	8.6 (bp)	405	0.40	15.8 (bp)
382	0.55	9.9 (bp)	405	0.35	16.2 (bp)
382	0.50	11.3 (bp)	405	0.30	16.9 (bp)
382	0.45	12.3 (bp)	404	0.30	17.4 (bp)
383	0.45	12.4 (bp)	404	0.25	17.8 (bp)
382	0.44	12.1 (bp)	404	0.20	18.1 (bp)
382	0.43	12.2 (bp)	404	0.15	18.3 (dp)
383	0.41	12.4 (bp)	405	0.10	19.3 (dp)
383	0.40	13.5 (bp)	404	0.10	22.6 (dp)
383	0.39	12.7 (bp)	404	0.08	31.6 (dp)
383	0.38	13.1 (bp)	405	0.06	34.2 (dp)
383	0.35	14.2 (bp)	405	0.04	34.4 (dp)
383	0.31	15.0 (bp)			

When x_2 decreased to below the critical point for a particular temperature, the phase behavior of the mixture changed from a bubble point to a dew point at the phase boundary. When a dew point is reached tiny droplets of liquid "dew" form throughout the solution, clouding it drastically, and then very slowly settle forming a tiny drop of a cyclohexene oxide-rich phase at the bottom of the cell. When a dew point is being observed, the pressure in the cell is dropped very slowly until the droplet formation and subsequent settling is observed; this point is considered to be the dew point pressure. The critical point of the mixture is located between the last observed bubble point and the newly observed dew point.

Results and Discussion

Experimental Data. The phase behavior of carbon dioxide (1) + cyclohexene oxide (2) was determined at 343 K, 363 K, 383 K, and 403 K. The experimental data are presented in Table 1. In this table, bubble and dew points are denoted by (bp) and (dp) respectively. The critical points for the mixtures occur between the last bubble point and the first dew point as the mole fraction is decreased. Therefore at 343 K, the critical point of the mixture is between $x_2 = 0.1$ and 0.08. At 363 K, the critical point is located between $x_2 = 0.15$ and 0.1. The phase behavior of the mixture at 343 K and 363 K from $x_2 = 0.65$ and 0.07 is shown graphically in Figure 2. The error bars reflect the inaccuracy associated with visually determining phase boundaries on a viewable cell like the Robinson Cell, which we have found previously to be ±0.7 MPa. (As x_2 decreased, the fluid changed from clear to a yellowish color with decreasing pressure. This color change became more evident in the near-critical region.)

The continuous curves depict the shape of the phase boundary as predicted by the Peng−Robinson equation of

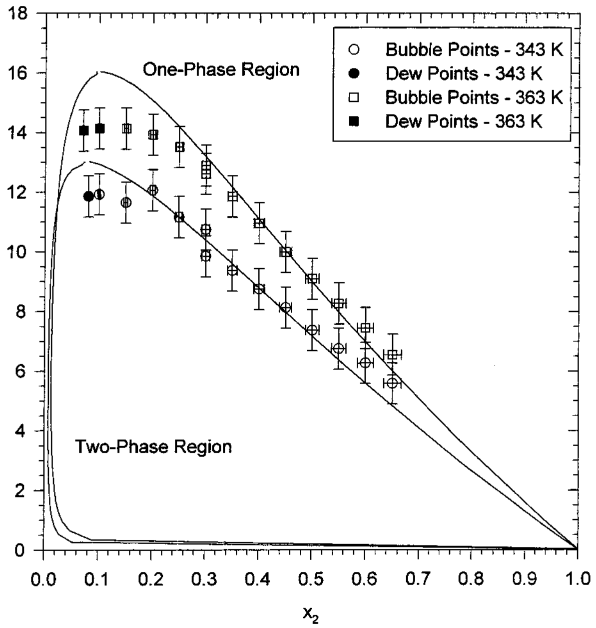

Figure 2. *Px* diagram for binary mixtures of cyclohexene oxide (2) + carbon dioxide (1) at 343 K and 363 K.

Table 2. Critical Properties for CO_2 and Cyclohexene Oxide (Reid *et al.*, 1987)

	CO_2	cyclohexene oxide (Ambrose)	cyclohexene oxide (Joback)
T_c (K)	304	635	622
P_c (MPa)	7.38	4.79	4.34
V_c (cm^3/mol)	93.9	317	298
mol wt (g/mol)	44.0	98.1	98.1

state (PR-EOS) (Peng and Robinson, 1976). Two different group contribution methods (the Ambrose method and the Joback modification of Lyderson's method) (Reid *et al.*, 1987) were used to estimate the critical temperature, pressure, and volume of cyclohexene oxide, Table 2. The critical values generated by the Joback method were used in the PR-EOS modeling of our results. AspenPlus 9.2 was used to determine the value of the binary interaction parameter that minimized the absolute average percent deviation of the liquid and vapor phase compositions. The best fit was obtained by setting the binary interaction parameter, k_{ij}, equal to 0.05. The PR-EOS slightly overestimated the mixture critical pressure.

Unlike the experiments at 343 K and 363 K, the experiments at 383 K and 405 K show the presence of anomalous phase behavior at low cyclohexene oxide mole fractions. The phase behavior of the mixtures at 383 K and 405 K is displayed graphically in Figure 3 (the solid lines are generated using the PR-EOS with $k_{ij} = 0.05$). A significant and unexpected increase in the dew point pressure was observed at low mole fractions of cyclohexene oxide.

After the low mole fraction phase behavior experiments were performed, a sample of the liquid phase was collected and analyzed using ^{1}H NMR. A sample of cyclohexene oxide prior to running the experiment was also analyzed. The ^{1}H NMR results, Table 3, suggest that the anomalous behavior is due to the formation of poly(cyclohexene ether), possibly owing to catalysis by trace amounts of water introduced from the atmosphere or the carbon dioxide (Adkins, 1996). This polymer has a low solubility in carbon dioxide; therefore, its presence will dramatically increase the bubble/dew point pressure of the mixture. NMR analysis of the cyclohexene oxide from higher mole fraction experiments did not indicate the presence of poly(cyclohexene ether). It appears that the polymerization proceeds to an equilibrium extent which depends upon the x_2 initially present in the mixture.

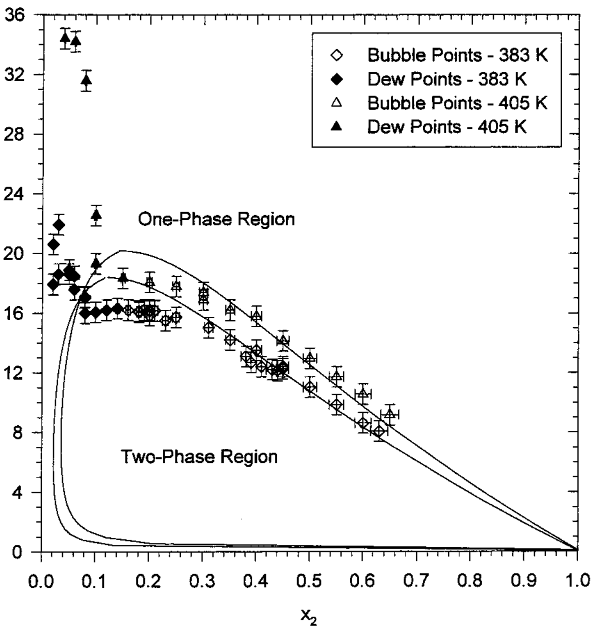

Figure 3. *Px* diagram for binary mixtures of cyclohexene oxide (2) + carbon dioxide (1) at 383 K and 405 K.

Table 3. ^{1}H NMR Spectra of 1,2-Epoxycyclohexane and of the Sample from the Robinson Cell Taken after the Phase Behavior Experiment at 405 K

Cyclohexene Oxide Peak Assignments			
doublet, 2H 1.3 ppm (ring protons)	doublet, 2H 1.9 ppm (ring protons)	triplet, 2H 3.1 ppm (epoxy protons)	
Peak Assignments for Sample Taken from Robinson Cell			
singlet, 2H 1.2 ppm (ring protons)	singlet, 2H 1.6 ppm (ring protons)	singlet, 2H 1.9 ppm (ring protons)	singlet, 2H 3.3 ppm (−CH−O−)

The initial phase behavior runs at 383 K and 405 K were performed prior to knowledge of the polymerization. Therefore, temperature equilibration was achieved, but polymerization equilibrium may not have been attained in some runs. The wide scatter in the data at low x_2 at these temperatures may be due to differing extents of polymerization. To test the hypothesis that the presence of atmospheric water is necessary to initiate polymerization, an attempt was made to repeat the poly(cyclohexene ether) formation under dry conditions. Cyclohexene oxide and carbon dioxide were loaded (under nitrogen) into a high-pressure reactor at $x_2 = 0.034$, and the mixture was stirred at 34.5 MPa and 403 K for 24 h. The product from this reaction was analyzed by ^{1}H NMR, and the presence of the poly(cyclohexene ether) was not detected. This suggests that a small amount of moisture from the air leads to polyether formation.

Conclusions

Experiments displaying the phase behavior of cyclohexene oxide in carbon dioxide were completed. Although the phase behavior of this system could be correlated with the PR-EOS and critical property estimates of cyclohexene, conditions leading to the formation of poly(cyclohexene oxide) were observed. Cyclohexene oxide and carbon dioxide will form a one-phase system under a wide variety of conditions, yet under certain conditions cyclohexene oxide will homopolymerize in the presence of carbon dioxide to form the corresponding polyether. Not only is this information vital in designing a one-phase reaction system which includes mixtures of cyclohexene oxide and carbon dioxide but it also makes possible the extraction of unreacted monomer from the synthesized polycarbonate using carbon dioxide resulting in a truly organic solvent-free system.

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ASPEN PLUS is a trademark of Aspen Technology, Inc.: Cambridge, MA. The phase boundary modeling and Peng−Robinson mixture critical temperature predictions were generated using ASPEN PLUS, Release 9, 1994.

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