Phase Behavior and Its Effects on Reactions in Liquid and Supercritical CO_2

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Introduction

Carbon dioxide, either as an expanded liquid or as a supercritical fluid, may be a viable replacement for a variety of conventional organic solvents in reaction systems. Numerous studies have shown that many reactions can be conducted in liquid or supercritical CO_2 (sc CO_2) and, in some cases, rates and selectivities can be achieved that are greater than those possible in normal liquid or gas phase reactions (other chapters contained herein; Savage et al. 1995; Noyori 1999). Nonetheless, commercial exploitation of this technology has been limited.

One factor that contributes to this reluctance is the extremely complex phase behavior that can be encountered with high pressure multicomponent systems. Even for simple binary systems, one can observe multiple fluid phases, as shown in Figure 1. Shown in the figure is the PT projection of the phase diagram of a binary system, where the vapor pressure curve of the light component (e.g., CO_2) is the solid line shown at temperatures below T_B. It is terminated by its critical point, which is shown as a solid circle. The sublimation curve, melting curve and vapor pressure curve of the pure component 2 (say, a reactant that is a solid at ambient conditions) are the solid lines shown at higher temperatures on the right side of the diagram; i.e., the triple point of this compound is above T_E. The solid might experience a significant melting point depression when exposed to CO_2 pressure (the dashed-dotted SLV line, which terminates in an upper critical end point - UCEP). For instance, naphthalene melts at 60.1ºC under CO_2 pressure (i.e., one might observe a three-phase solid/liquid/fluid

system), even though the normal melting point is 80.5ºC (McHugh and Yogan 1984). To complicate things even further, there will be a region close to the critical point of pure CO_2 where one will observe three phases as well, as indicated by the dashed SLV line that terminates at the lower critical end point - LCEP. The dashed line connecting the critical point of the light component and the LCEP is a vapor/liquid critical point locus. A much more detailed discussion of systems of the type shown in Figure 1 can be found in Xu et al. (2000). Systems of compounds that are liquid at room temperature can also be complicated by the formation of additional liquid phases when placed in equilibrium with CO_2 (see, for example, the binary phase diagrams as classified by van Konynenburg and Scott 1980).

Figure 1 near here

Nonetheless, understanding high pressure phase behavior is vitally important to evaluating CO_2 as a potential replacement solvent for reactions. Certainly, commercial reactions are not run at dilute conditions so the solubility of the reactants, products and catalysts in the CO_2 (if one desires to run the reaction as a single phase system) will frequently be the key factor in determining the economic viability of the CO_2-based reaction system.

An additional difficulty in evaluating CO_2 as a potential replacement solvent for reactions is the problems that one may encounter with conventional flash algorithms when attempting to calculate high pressure phase behavior for any particular equation of state model. Conventional algorithms, even in commercial implementations, may fail to converge or converge to an incorrect solution (Stradi et al. 1999a). Although conventional algorithms may have difficulties with the modeling of normal liquid solutions, this is especially a

problem for any supercritical fluid system. This is because convergence near critical points, where there is very little difference in the density and compositions of the two phases, and near three-phase lines is especially challenging. This can be a serious impediment to the design, optimization and evaluation of a high pressure reaction system that uses CO_2 as the solvent.

To address these limitations to the commercial evaluation and implementation of CO_2 as a substitute solvent we 1) present a methodology to measure and model high pressure phase behavior of CO_2-based reaction systems using minimal experimental data and 2) present a new computational technique for high pressure phase equilibrium calculations that provides a guarantee of the correct solution to the flash problem.

Systems Studied

We have applied the methodology and newly developed computational techniques to two model reaction systems. Both examples represent classes of reactions that are of significant commercial interest and are reactions that have been shown to occur with good rates and selectivities in CO_2 by researchers at Los Alamos National Laboratories (Pesiri et al. 1998; Tumas, personal communication). The first reaction is the epoxidation of *trans*-2-hexen-1-ol, in which the double bond of the allylic alcohol is converted into an epoxy group by addition of an oxygen atom. This is an example of Sharpless chemistry, which produces a high-value, stereospecific product. It constitutes a good target for solvent substitution by carbon dioxide since epoxidation reactions are traditionally performed in organic solvents. The second reaction is an acylation, which is an example of a class of commercially important Friedel-Crafts reactions. The naphthalene and acetyl chloride react to form isomers of acetonaphthone. The full reaction would also require the presence of stoichiometric amounts of $AlCl_3$ or other appropriate catalyst. These reactions are shown in Figure 2.

Figure 2 near here

Methodology

As mentioned above, we will present a two-pronged approach to understanding the multicomponent high pressure phase behavior of potential reaction systems. First, we seek to model the multicomponent phase behavior using limited experimental data. For this effort we have chosen to use the Peng-Robinson equation of state (Peng and Robinson 1976) with conventional van der Waals mixing rules as described below. There are many different models that can be used to correlate and predict high pressure phase behavior, including more complex, and more fundamental models. These include other cubic equations of state like the Soave-Redlich-Kwong equation and models like the statistical associating fluid theory (SAFT). While some may work better for certain types of systems, in general, the more adjustable parameters, the better the fit one will achieve. However, larger numbers of fit parameters tends to decrease the predictive power of the model. A discussion of the benefits and drawbacks of various models can be found in several reviews (Johnston et al. 1989; Brennecke and Eckert 1989; McHugh and Krukonis 1990). We have chosen the Peng-Robinson equation since it is known to give reasonably good representations of solubilities in sc CO_2 (Brennecke and Eckert 1989; Johnston et al. 1989), because it is relatively simple to use, and because it is readily available for use in industry. The Peng-Robinson equation requires inputs of critical temperatures and pressures, acentric factors (w) and binary interaction parameters, k_{ij}. The pure component properties can be taken from the literature or estimated (Reid et al. 1987; Stradi et al. 1998, 1999a,b) but the binary interaction parameters must be fit to experimental data. Thus, our methodology is to measure binary phase behavior

if it is not already available in the literature, to find the best-fit k_{ij}'s to that data, and to use those binary interaction parameters to estimate the multicomponent phase equilibria.

The completely reliable computational technique that we have developed is based on interval analysis. The interval Newton/generalized bisection technique can guarantee the identification of a global optimum of a nonlinear objective function, or can identify all solutions to a set of nonlinear equations. Since the phase equilibrium problem (i.e., particularly the phase stability problem) can be formulated in either fashion, we can guarantee the correct solution to the high pressure flash calculation. A detailed description of the interval Newton/generalized bisection technique and its application to thermodynamic systems described by cubic equations of state can be found in a variety of publications (Hua et al. 1996, 1998a, b, 1999; Xu et al. 2000). In these same publications can be found a discussion of work by other researchers who apply global optimization techniques to phase stability and phase split calculations, in an effort to guarantee correct solution to the thermodynamic models. However, thus far the method described here is the only general purpose method that can be applied to any equation of state model, i.e., the types of models that are needed to described high pressure phase equilibria of CO_2-based systems.

Experimental Techniques

A discussion of a variety of techniques to measure high pressure phase equilibria can be found in a review by Dohrn and Brunner (1995). Here we use two different apparatuses. The first is a static high pressure equilibrium apparatus, which has been described previously (Stradi et al. 1998). It consists of a high pressure glass tube, in which a liquid sample can be loaded. CO_2 is carefully metered into the glass cell and, by assuming that the gas phase is essentially pure CO_2, one can determine the composition of the liquid phase as a function of pressure and temperature. It can also be used to investigate vapor/liquid/liquid equilibria and

solid/liquid/vapor equilibria. The second apparatus is a standard dynamic flow ISCO 220 SX extractor, which is used to determine compositions in the CO_2-rich vapor or fluid phase. Either a solid or liquid solute can be loaded in the extractor, through which CO_2 is passed from an ISCO 260 syringe pump. The saturated solution is passed through a restrictor and the precipitated solute collected, usually in a liquid collection solvent that is analyzed by UV-visible spectrometry. Thus, these two apparatuses are used in a complementary fashion to obtain full information about the high pressure phase behavior. The chemicals used were obtained from Aldrich and were used as received (purities: acetyl chloride – 99+%, 1′-acetonaphthone - 98%, 2′-acetonaphthone - 99%). CO_2 was Coleman Instrument Grade with a minimum purity of 99.99% and was obtained from Mittler Gas Supply.

Modeling

As mentioned above, we have chosen to model the high pressure phase behavior with the Peng-Robinson equation (Peng and Robinson 1976) with standard van der Waals mixing rules:

$$P = \frac{RT}{(v-b)} - \frac{a}{[v(v+b)+b(v-b)]}$$

where,

$$a = \frac{0.45724 R^2 T_c^2}{P_c}[1+(0.3764+1.54226w-0.2699w^2)(1-T_r^{0.5})]^2$$

$$b = 0.07780\frac{RT_c}{P_c}$$

and w is the acentric factor. T_c and P_c are the critical temperature and pressure of the compound, respectively, and $T_r = \frac{T}{T_c}$. To extend this equation to mixtures, the conventional van der Waals mixing rules were used:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}, \quad b = \sum_{i=1}^{n} x_i b_i, \quad \text{and} \quad a_{ij} = (a_{ii}a_{jj})^{0.5}(1-k_{ij})$$

where the sums extend over all components, and a_{ii} and b_i indicate the pure component values for component i.

The key to obtaining good representation of experimental data is fitting a single binary interaction parameter, k_{ij}, to each set of binary data. In most of the modeling described below, we are most concerned with the binary interaction parameters between each of the components and CO_2 since CO_2 introduces the most asymmetry (i.e., difference in size and energy parameters) into the system. In a few cases, we include nonzero binary interaction parameters for some of the other components.

Computational Techniques

The phase equilibrium problem consists of two parts: the phase stability calculation and the phase split calculation. For a particular total mixture composition, the phase stability calculation determines if that "feed" will split into two or more phases. If it is determined that multiple phases are present, then one performs the phase split calculation, assuming some specified number of phases. One must then calculate the stability of the solutions to the phase split to ascertain that the assumed number of phases was correct. The key to this procedure is performing the phase stability calculation reliably. Unfortunately, this problem, which can be formulated as an optimization problem (or the equivalent set of nonlinear equations), frequently has multiple minima and maxima. As a result, conventional phase equilibrium algorithms may fail to converge or converge to the wrong solution.

We have applied a global optimization technique, based on interval analysis, to the high pressure phase equilibrium problem (INTFLASH). It does not require any initial guesses and is guaranteed, both mathematically and computationally, to converge to the correct

solution. The interval analysis method and its application to phase equilibria using equation of state models has been described elsewhere (Hua et al. 1996, 1998a,b, 1999; Xu et al. 2000). It is a general-purpose technique that can be applied to any equation of state or excess Gibbs free energy model, and it guarantees correct solution to the phase equilibrium problem.

In addition to the interval method developed, we also used standard modeling tools from Aspen Plus (Aspen Technology, Inc.), including a routine to fit binary interaction parameters and two flash algorithms – the FLASH3 module and the RGIBBS module. We also used the two-phase flash routine LNGFLASH, which employs Michelsen's well-known approach, from the IVC-SEP package (Hytoft and Gani, 1996).

Results and Discussion

1. Epoxidation Reaction

For the epoxidation of *trans*-2-hexen-1-ol to (2R,3R)-(+)-3-propyloxiranemethanol we have measured the high pressure phase behavior of each of the reactants, products and catalysts in CO_2 and modeled them quite well with the Peng-Robinson equation, even in the cases where we observed vapor/liquid/liquid equilibria (Stradi et al. 1998).

Unfortunately, even in modeling these binary systems we experienced some computational difficulties when attempting to use Aspen Plus and LNGFLASH (Stradi et al. 1999a). This was especially pronounced at conditions close to the formation of three phases (vapor/liquid/liquid). For instance, for the *trans*-2-hexen-1-ol/CO_2 system at a feed composition of 0.8 mole fraction CO_2, a temperature of 303.15K and a pressure of 71.00725 bar, LNGFLASH and both Aspen Plus modules converged, but to incorrect solutions. At just a slightly higher pressure (71.00826 bar), LNGFLASH converged correctly but the Aspen Plus modules still converged to the wrong answer. At a feed composition of 0.7 mole fraction CO_2, T=303.15K, and P=70.09 bar, LNGFLASH and both Aspen Plus modules indicate no

phase split when, in fact, correct solution to the model yields two phases. In all cases, the newly developed routine, INTFLASH, identified the correct solutions to the model without any difficulty.

Based on the binary measurements and modeling, we estimated the multicomponent high pressure phase behavior for the reaction mixture, extending the entire way from all reactants to full conversion (Stradi et al. 1999a). These calculations suggested that at 40ºC and 150 bar, the reaction mixture would remain single phase. However, if the reaction were run at 100 bar, the reactant mixture would be two phase and at 50 bar the system would be two phase all the way from reactants to full conversion. Thus, by maintaining the pressure above just 125 bar one would expect the reaction mixture to remain single phase throughout the reaction. This pressure is significantly below the 346 bar used originally for this reaction. Subsequent investigations by researchers at Los Alamos showed high conversions and selectivities at lower pressures. Thus, by using modeling tools to interactively guide experimental work, an improved design was achieved that uses a much lower pressure than originally proposed.

2. Friedel-Crafts reaction

Friedel-Crafts alkylation and acylation reactions are ubiquitous in industrial practice and are conducted in a variety of volatile organic solvents, since solvent polarity can be used to control product distribution. Tumas and coworkers (Tumas, personal communication) conducted successful preliminary investigations of the acylation of naphthalene with acetyl chloride in sc CO_2. We have measured the binary phase behavior of acetyl chloride and each of the products, 1′-acetonaphthone and 2′-acetonaphthone, with CO_2 over a wide range of pressures at temperatures of 40ºC and 50ºC. Data for naphthalene is available in the literature (Tsekhanskaya et al. 1964; Najour and King 1966; McHugh and Paulaitis 1980; McHugh and

Yogan 1984). For this demonstration, we have not included the catalyst, $AlCl_3$; however, its impact on the mixture phase behavior will be discussed later.

Naphthalene is a solid at room temperature (melting point of 80.5ºC (Weast 1983)) so it is likely to exhibit solid/fluid equilibria at 40ºC and 50ºC; i.e. these are likely to be temperatures like T_D shown in Figure 1, which are above the LCEP and below the UCEP. In fact, the UCEP for naphthalene/CO_2 is 60.1ºC (McHugh and Yogan 1984; Lamb et al. 1986) and this is adequately modeled by the Peng-Robinson equation of state using a k_{ij} of 0.0974. This is the value that provides the best fit to the solid/fluid equilibria data at 55ºC. A detailed description of the modeling of this particular system with the Peng-Robinson equation can be found in Xu et al. 2000.

Acetyl chloride is a liquid at room temperature so we measured the solubility of CO_2 in the acetyl chloride rich liquid phase as a function of pressure at both 40ºC and 50ºC and these results are shown in Figure 3. Also shown in the figure is the modeling done with the Peng-Robinson equation of state. Using binary interaction parameters of 0.0196 at 40ºC and –0.0138 at 50ºC, we are able to obtain very good representation of the liquid phase compositions. Also shown on the graph are the predicted values of the vapor phase compositions that would be in equilibrium with the liquid phases measured. As shown in the graph, a binary mixture of CO_2 and acetyl chloride of any composition at 50ºC would produce a single phase mixture at pressures above around 90 bar.

Figure 3 near here

1′-Acetonaphthone is a liquid at room temperature (melting point 10.5ºC) and our measurements of the solubility of CO_2 in 1′-acetonaphthone liquid at 40ºC and 50ºC are

shown in Figure 4. As with acetyl chloride, these measurements were taken with the static high pressure phase equilibrium apparatus. However, for this system, we also measured the solubility of the 1′-acetonaphthone in the CO_2-rich vapor phase using the dynamic extraction apparatus at pressures up to 340 bar. Also shown in the figure is the Peng-Robinson equation of state modeling using a binary interaction parameter of 0.0687 at 40ºC and 0.0715 at 50ºC. These values gave the best fit to the liquid phase composition data; i.e., we did not use the vapor phase measurements in obtaining this value. Yet, the Peng-Robinson equation, with a k_{ij} determined from liquid phase compositions, gives remarkably good estimates of the vapor phase compositions, as shown in the figure. The model suggests, and the experimental measurements support, that there is an extremely large two-phase envelope that extends to very high pressure. In other words, to obtain a single phase system for CO_2/1′-acetonaphthone mixtures over the whole composition range at 40ºC or 50ºC, one would have to operate at prohibitively high pressures of greater than about 700 bar.

Figure 4 near here

2′-Acetonaphthone is a solid at room temperature, with a melting point of 53-55ºC. However at 40ºC or 50ºC it is very likely to melt under CO_2 pressure; i.e., these temperatures are likely to be above the UCEP, as shown by T_E in Figure 1. Moreover, equimolar mixtures of 1′- and 2′-acetonaphthone are liquid even at room temperature. Thus, we sought to measure the vapor/liquid equilibrium of 2′-acetonaphthone with CO_2. This was easily achieved using both the static and dynamic apparatuses. For instance, 2′-acetonaphthone was melted to introduce it into the glass cell of the static apparatus. It did not resolidify when the cell was cooled to 50ºC; this type of subcooling is quite common. We then added CO_2 and

measured its solubility in the liquid at 50ºC and these data are shown in Figure 5. Also shown are the solubilities of 2′-acetonaphthone in the CO_2-rich vapor phase. Once again, the Peng-Robinson equation was fit to just the liquid phase compositions (k_{ij}=0.0695), yet it provided excellent estimates of the vapor phase compositions. Once again, the model indicates the existence of a large two phase envelope; pressures of 680 bar would be required to achieve single-phase mixtures across the whole composition range.

Figure 5 near here

Based on these binary measurements (and the k_{ij}'s determined from them), we have performed phase equilibrium computations for the multicomponent mixtures that would result in the course of this reaction system. Assuming feed compositions consisting of 90 mole % CO_2, 5 mole % naphthalene and 5 mole % acetyl chloride, we estimate that pressures greater than about 165.5 bar would be required to achieve a single phase reactant mixture at 50ºC. However, if the reaction proceeded to 100% conversion at this pressure and temperature, assuming formation of equal amounts of the two isomers, the system would clearly be two phase. In fact, modeling suggests that pressures greater than 603.3 bar would be required to solubilize a mixture of 10 mole% 1′- and 2′-acetonaphthone in CO_2. Phase equilibrium calculations indicate that the mixture would have split into two phases (vapor and liquid) even at 50% conversion if one were to operate at 50ºC and 306.8 bar and start with 5 mole % of each of the reactants. The critical temperatures, pressures, acentric factors for all of the components, as well as their binary interaction parameters with CO_2, that were used in these calculations, are shown in Table1. Note that in performing the multicomponent modeling, we used binary interaction parameters for each component with CO_2 but assumed

that all other binary interaction parameters were zero, except the one for the 1′-acetonaphthone/2′-acetonaphthone pair. A value of 0.2013 provided a best fit to ternary 1′-acetonaphthone/2′-acetonaphthone/CO_2 vapor/liquid equilibrium data (not shown here).

Table 1 near here

Thus, the reaction of naphthalene with acetyl chloride to form acetonaphthone in CO_2 would require either prohibitively high pressures (>600 bar) or extremely dilute (well less than one mole percent reactants and products) concentrations if single phase operation was desired. Since both extremely high pressure and very large moderate pressure vessels would require significant capital investment, these options are not likely to be economically attractive. Two phase operation would require excellent mixing to eliminate mass transfer resistances. It should be noted that in the real reaction system, two phase operation would probably be unavoidable. In this example, we have neglected to include the $AlCl_3$ catalyst. The $AlCl_3$ actually forms a complex with the acetyl chloride and is required to be present in greater than stoichiometric amounts. We attempted to measure the phase behavior of the acetyl chloride/$AlCl_3$ complex with CO_2. Preliminary investigations revealed that the complex is highly insoluble in CO_2 and, when a 1.3/1 $AlCl_3$/acetyl chloride ratio is used, actually forms two liquid phases when exposed to CO_2 pressure. Since all of the components of this reaction can be solubilized in various liquid solvents, this work suggests the Friedel-Crafts acylation of naphthalene may not be a good candidate for solvent substitution with CO_2 due to the complex, multiphase system that would result.

Conclusions

Phase behavior is an extremely important issue in designing and evaluating processes that use CO_2 as a replacement solvent. Evaluation of systems that might exhibit complex high pressure phase behavior is further frustrated by the inability of conventional flash algorithms and process modeling tools to reliably compute the phase behavior given a particular model. Here we have presented a methodology to model and compute complex high pressure phase behavior for reaction systems, taking a limited amount of binary experimental data. We have developed a completely reliable computational technique for performing the flash calculations, based on interval mathematics. We have demonstrated this methodology for two systems: the allylic epoxidation of *trans*-2-hexen-1-ol and the Friedel-Crafts acylation of naphthalene. Based on model calculations, we recommend that the epoxidation reaction could be run efficiently as a single phase system in CO_2 at pressures as low as 125 bar. Conversely, it appears that the Friedel-Crafts reaction would have to be performed under multiphase conditions, which is likely to make it a poor candidate for solvent substitution with CO_2.

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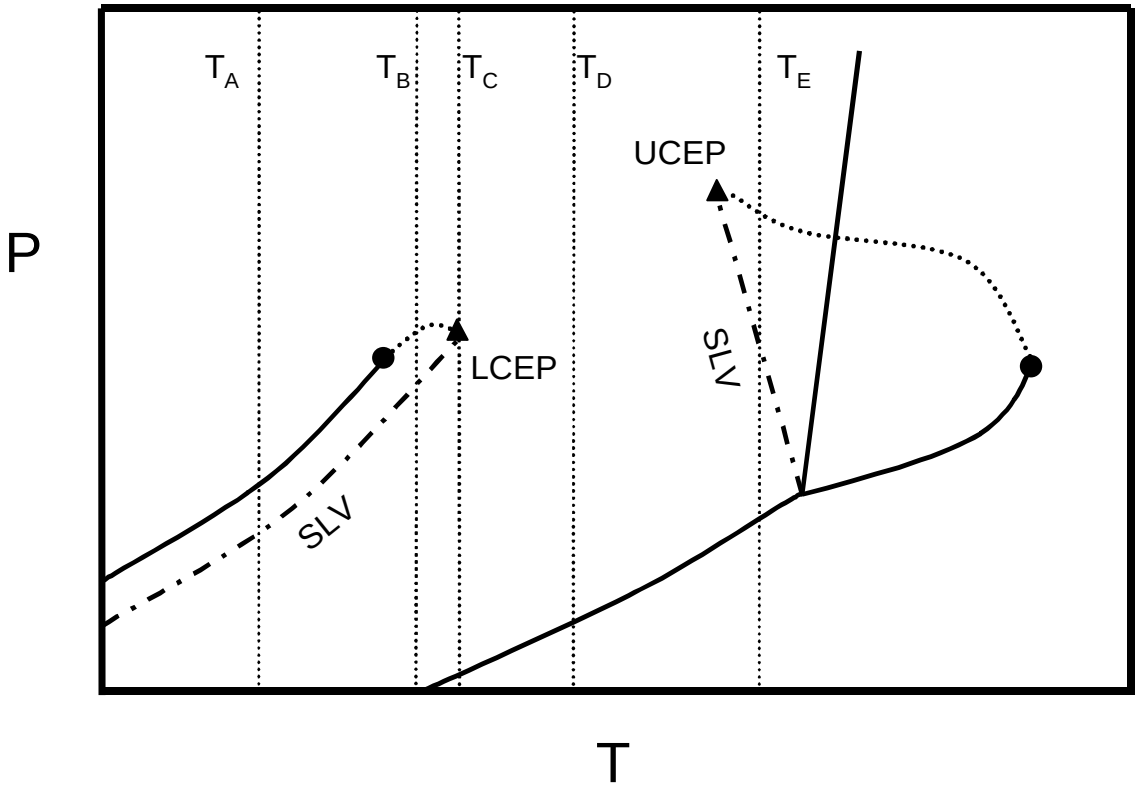
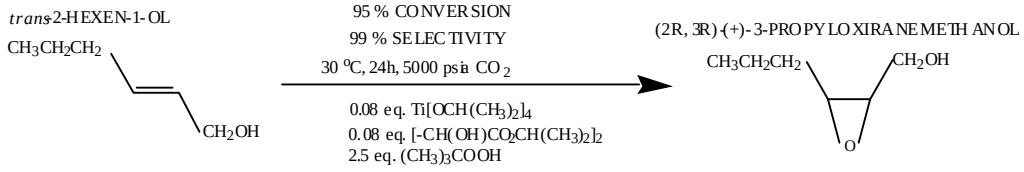
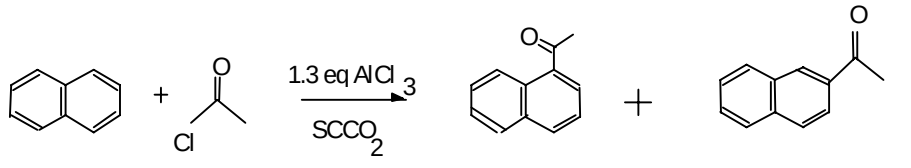


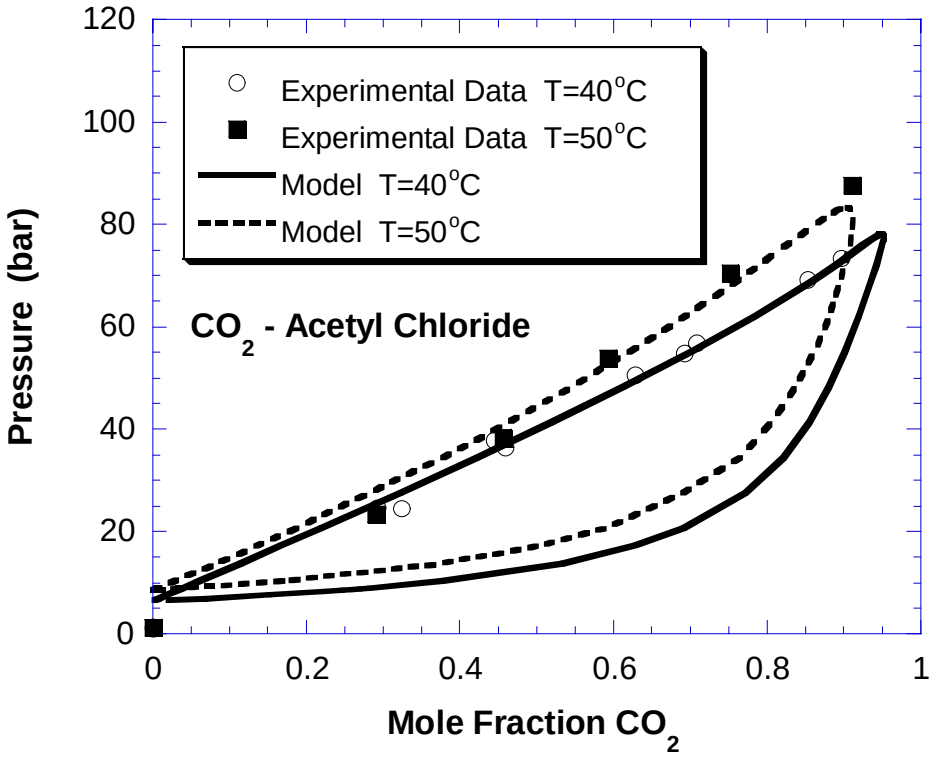
Epoxidation Reaction



Friedel-Crafts Acylation Reaction



Naphthalene Acetyl Chloride 1' - Acetonaphthone 2' - Acetonaphthone


Experimental Data T=40°C
Experimental Data T=50°C
Model T=40°C
Model T=50°C
CO2 - Acetyl Chloride
Pressure (bar)
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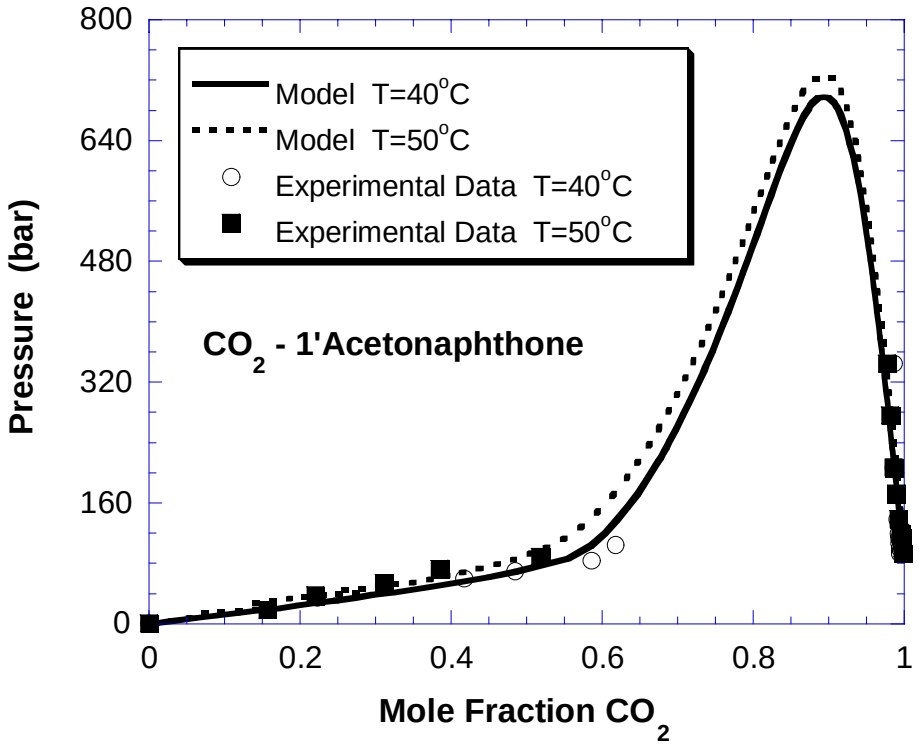
40
60
80
100
120
0.2
0.4
0.6
0.8
1


Model T=40°C
Model T=50°C
Experimental Data T=40°C
Experimental Data T=50°C
CO2 - 1'Acetonaphthone
Pressure (bar)
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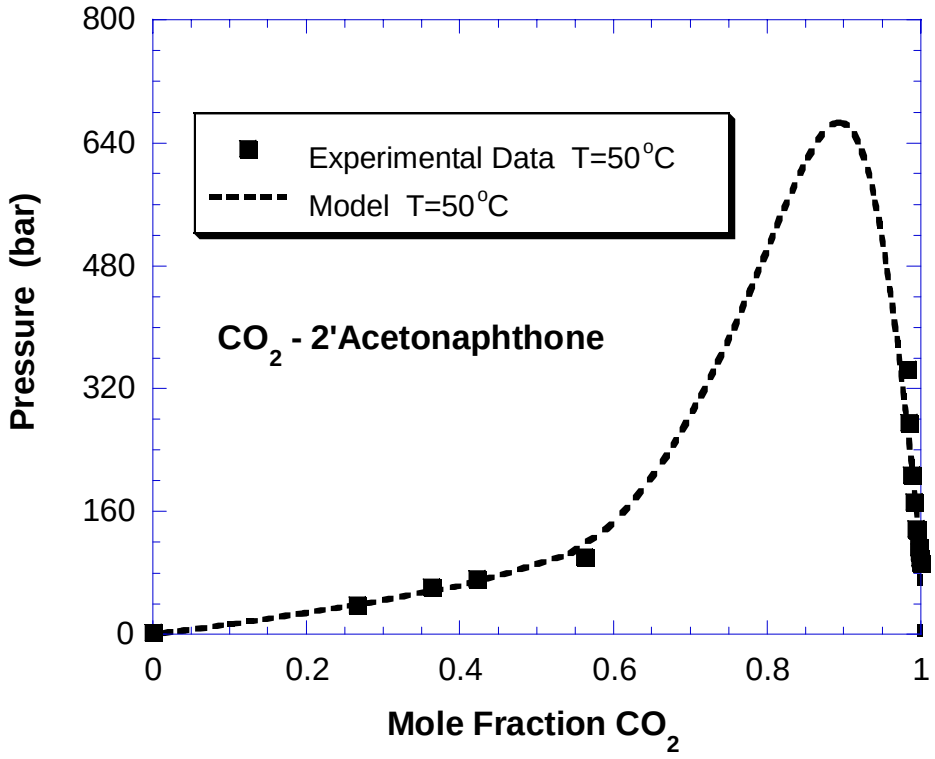
0
160
320
480
640
800
0.2
0.4
0.6
0.8
1


800
640
480
320
160
0
Pressure (bar)
0
0.2
0.4
0.6
0.8
1
Mole Fraction CO2
Experimental Data T=50°C
Model T=50°C
CO2 - 2'Acetonaphthone