Process Synthesis Concepts for Supercritical Gas Extraction in the Crossover Region

A procedure is presented for designing supercritical gas extraction processes using a pure solvent fluid to effect the separation. The necessary conditions for the procedure to be applicable are the existence of crossover behavior and separable crossover pressures in the fluid phase mixture. Data are presented to support the existence of such phenomena in ternary systems, and an actual separation process has been designed and operated based upon the data. For systems exhibiting this behavior, process synthesis principles are developed to illustrate the evolution of a process flowsheet for the separation of a mixture into its pure components.

E. H. Chimowitz, K. J. Pennisi
Department of Chemical Engineering
University of Rochester
Rochester, NY 14627

Introduction

Extraction using supercritical fluids is a separation technique that has aroused much interest. In the food processing industry the advantage of using nontoxic supercritical carbon dioxide for conventional extractions has been recognized and a number of processes have been patented in recent years (Hubert and Vitzhum, 1978; HAG A. G. (1973). Process engineering applications have been suggested in various papers: coal extraction (Maddocks et al., 1979), the regeneration of activated carbon beds used for extracting organic pollutants from wastewater streams (Modell et al., 1979), recovery of carboxylic acids from dilute aqueous solutions of their alkali-metal salts by mixed solvents (Shimshick, 1981), ethanol-water separations (McHugh et al., 1981). Much of the experimental data in supercritical systems has been assembled by Paulaitis et al. (1982). In general there is much data available for binary systems, i.e., a single pure solid or liquid in equilibrium with a supercritical component. Data for multicomponent systems is more scarce, the only ternary solubility data currently available in the literature being that of Van Gunst (1950) for the system hexachloroethane-naphthalene-supercritical ethylene, the data published by Kurnik and Reid (1982), and the recent work of Gopal et al. (1985).

Our purpose here is to present new data for both a binary and a ternary solid-fluid system with a supercritical fluid phase. In particular data are presented in the ternary crossover region for a model system, which we believe to be the first such data published. In presenting the data the major objective has been to encourage development of process synthesis concepts for use in the design of supercritical extraction processes using crossover phenomena to effect the separation. Process synthesis involves the original conception of a chemical process. For supercritical extraction this means providing a procedure for systematically identifying operating temperatures and pressures for the process, constituents of the supercritical solvent phase, number of stages in the cascade, and related factors.

Optimal answers to these synthesis questions could determine the economic feasibility of processes. Recent work underscores the importance of these issues. Van Alsten et al. (1984) studied various solute solubility enhancements in supercritical fluids. For pure supercritical fluid phases their data showed that the ratios of enhancement factors for various solutes were nearly constant over the entire supercritical fluid density range studied. They concluded that this was a major stumbling block for the use of pure supercritical fluids as extractants since pure solvents were not very selective. Similar conclusions were reached by Kurnik and Reid (1982) in their study on mixed solute systems. Van Alsten et al. also studied entrainer-doped supercritical phases and showed that selectivity control was somewhat improved, however more work remains to be done in this area before conclusions can be drawn.

Many important processes where our concepts are likely to apply involve the separation of solid mixtures into pure components. One such isomeric system is the 7-methoxy 1-tetralone, 6-methoxy 1-tetralone, 5-methoxy 1-tetralone separation, an important intermediate step in the synthesis of oestrane and 19-

nor-steroids (Chang and Morrell, 1984). We begin with a description of the experimental work performed.

Experimental

Solubilities of pure 1,10-decanediol and a solid mixture of benzoic acid and 1,10-decanediol were measured in supercritical carbon dioxide. Experimental data were obtained using a flow apparatus similar to the system used by Kurnik et al. (1981); a schematic diagram of the apparatus is shown in Figure 1. Liquid carbon dioxide (99.8% pure, Air Products & Chemicals) was compressed to the desired operating pressure by a Milton Roy liquid pump. Pressure was controlled to within ±1.5 bar (150 kPa) with a backpressure regulator valve manufactured by Haskel Engineering and Supply Co. The high-pressure carbon dioxide flowed through the preheated section of tubing and into the vertical extraction tube.

The preheater consisted of 4 ft (1.2 m) of heating tape wrapped around the tubing carrying the fluid flow. Temperature regulation was provided by a Variac transformer and an Omega temperature controller set in on-off mode. The temperature measured at the preheater outlet was controlled to within ±1 K.

The extraction tube was packed with a uniform mixture consisting of equal volumes of the solid and 3 mm glass beads. The glass beads were used primarily to reduce caking of the solid during operation of the system. In the case of solid mixtures, equal weights of the two solids were combined in a uniform mixture with an equal volume of glass beads. A glass wool plug at the outlet of the extraction tube prevented entrainment of the solid.

The extraction tube was 1.75 cm ID and 30.5 cm long. It was wrapped with heating tape that was connected to a Watlow on-off temperature controller. The controller's reference thermocouple was mounted on the outside wall of the extractor vessel under the heating tape. The internal temperature was monitored with a type J thermocouple located in the center of the extraction tube. The internal temperature was controlled to within approximately ±0.5 K. A calibrated Heise gauge accurate to ±5 psi (±34.5 kPa) was used to measure the pressure in the extractor vessel.

The supercritical carbon dioxide and dissolved solid flowed out of the extraction tube into a short length of tubing. For experiments in the crossover region where an increase in temperature causes solute to deposit from the fluid phase it became necessary to control the temperature on this section of tube. This part of the line was therefore wrapped with heat tape and its temperature controlled at the extractor vessel temperature. The dense fluid was expanded across a heated micrometering valve (manufactured by Autoclave Engineers) to 1 bar (100 kPa) pressure. The solids were precipitated in two consecutive tared U-tubes which were immersed in an ice-brine solution. The extractant gas flow rate was measured by a rotameter. The total extractant gas volume passed through the system was measured by a calibrated Singer dry-test meter.

The mass of solid collected was found by weighing the tared U-tubes on a Mettler balance accurate to ±1 mg. In the case of a pure solid, knowledge of the total gas volume and weight of the solid collected was sufficient to determine the mole fraction of solid in the supercritical fluid. When dealing with solid mixtures, the composition of the precipitated solid must also be known. NMR spectroscopy was used to determine mixture compositions. The NMR solvent used was deuterated chloroform (99.8% pure, Aldrich Chemical Co.).

Accurate thermodynamic modeling of solid mixtures requires knowledge of the composition of any solid solutions that may exist in the system. Temperature-composition-melting point curves were obtained for the benzoic acid 1,10-decanediol system to determine the existence of solid solutions. The melting behavior indicated that solid solutions did not form for this system at the conditions of interest. These results are well described elsewhere (Pennisi, 1985).

Before experiments with new chemical components were done it was necessary to test the reliability of the equilibrium mea-

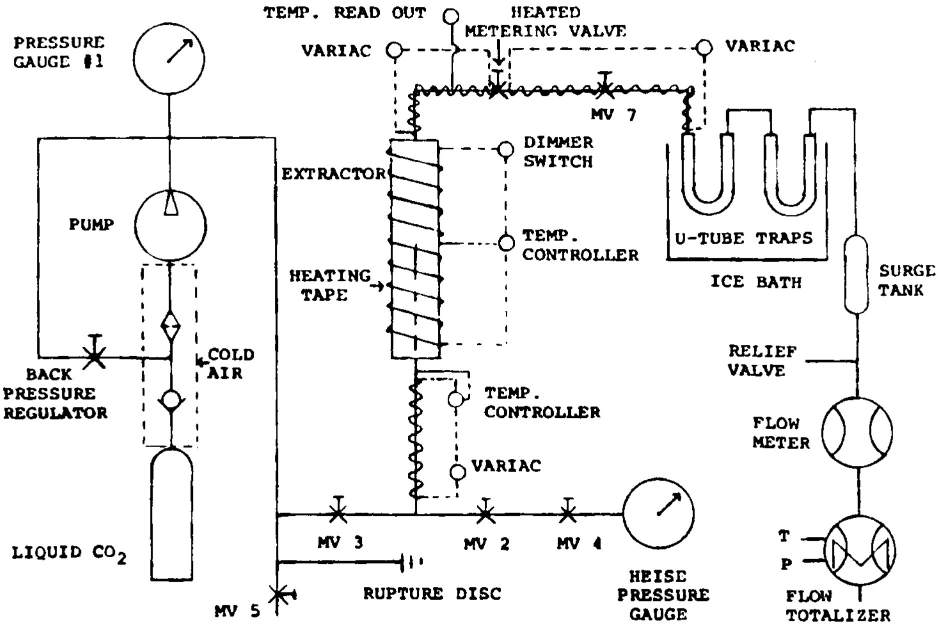

Figure 1. Experimental apparatus.

Table 1. Equilibrium Solubilities of 1,10-decanediol (1) in Supercritical Carbon Dioxide (2)

Temperature	Pressure Bar	$y(\times 10^4)$ Mol Frac* 1,10-decanediol	95% Conf. Limits
318 K	205.3	2.992	Single data points
k_{12} = 0.14252	253.7	3.577	confidence limits
	307.1	3.949	not available.
323 K	138.2	1.888	± 1.734**
k_{12} = 0.14292	154.5	2.597	± 0.154
	185.5	3.622	± 0.318
	224.4	4.482	± 0.251
	263.7	5.429	± 0.063
	305.9	6.169	± 0.306
328 K	133.7	1.994	± 0.277
k_{12} = 0.14211	164.7	3.965	± 0.188
	195.8	5.238	± 0.158
	222.8	5.985	± 0.188
	262.8	7.040	± 0.315
	307.3	7.891	± 0.277

*Mean values
**Only two data points
SI conversion: kPa = bar × 100.

surements made by the apparatus. Solubilities of napthalene in carbon dioxide were measured and found to compare well with the solubility data of Tsekhanskaya et al. (1964); the average deviation was 4.6%. The tests performed with napthalene also included determinations of suitable flow rates for our experiments. Experiments were done with flow rates varying from 0.020 SCFM (0.034 m^3/h) to 0.052 SCFM (0.087 m^3/h) with no change in results over this range.

Results

Extensive data were taken for the low vapor-pressure solid 1,10-decanediol at three different temperature levels and pressures of the carbon dioxide ranging between 130–310 bar (13–31 MPa). Table 1 shows equilibrium solubilities of the decanediol in supercritical carbon dioxide for three different isotherms as a function of pressure. Figure 2 shows these data graphically displayed with the familiar crossover pressure (the pressure around which the various isotherms converge) occurring at approximately 130 bar (13 MPa).

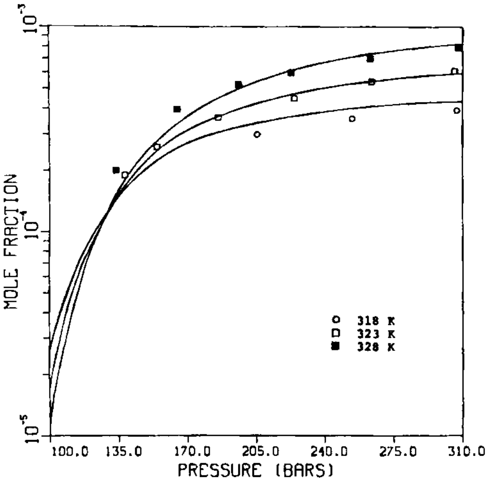

Figure 2. Solubility isotherms of 1,10-decanediol in supercritical carbon dioxide.

Table 2. Equilibrium Solubilities of a 1,10-decanediol (1)–Benzoic Acid (2) Mixture in Supercritical Carbon Dioxide (3)

Temperature	Pressure Bar	$y\ (\times 10^4)$ 1,10-decanediol	$y\ (\times 10^3)$ Benzoic Acid
308 K	163.8	1.814 ± 0.130	2.338 ± 0.150
	186.4	2.360 ± 0.139	2.689 ± 0.163
k_{13} = 0.14252	230.9	2.542 ± 0.228	3.246 ± 0.138
k_{12} = −0.14176	265.1	2.882 ± 0.146	3.425 ± 0.172
k_{23} = 0.018723	306.4	3.064 ± 0.240	3.874 ± 0.173
318 K	163.8	3.411 ± 0.102	2.755 ± 0.075
	186.8	3.486 ± 0.424	3.195 ± 0.067
k_{13} = 0.14252	226.1	4.107 ± 0.189	3.843 ± 0.119
k_{12} = 0.14368	267.6	4.125 ± 0.205	4.582 ± 0.112
k_{23} = 0.010457	307.1	5.335 ± 0.311	4.840 ± 0.182

SI conversion: kPa = bar × 100.

Table 2 shows equilibrium solubilities for the binary solid mixture consisting of 1,10-decanediol (*1*) and benzoic acid (*2*) in supercritical carbon dioxide (*3*) at two temperature levels as a function of pressure. In Figure 3 the solubility of 1,10-decanediol (from the binary solid mixture) in supercritical carbon dioxide is shown. Figure 4 shows the solubility of benzoic acid in the ternary mixture. The solubility of decanediol in the ternary mixture increases by a maximum of 35% over that when no benzoic acid is present. The corresponding increase for benzoic acid is 16%. Kurnik and Reid (1982) also reported this effect in a number of ternary systems, whereby large solubility increases are apparent for a component extracted from a binary solid mixture as opposed to the pure-component situation. The data points in

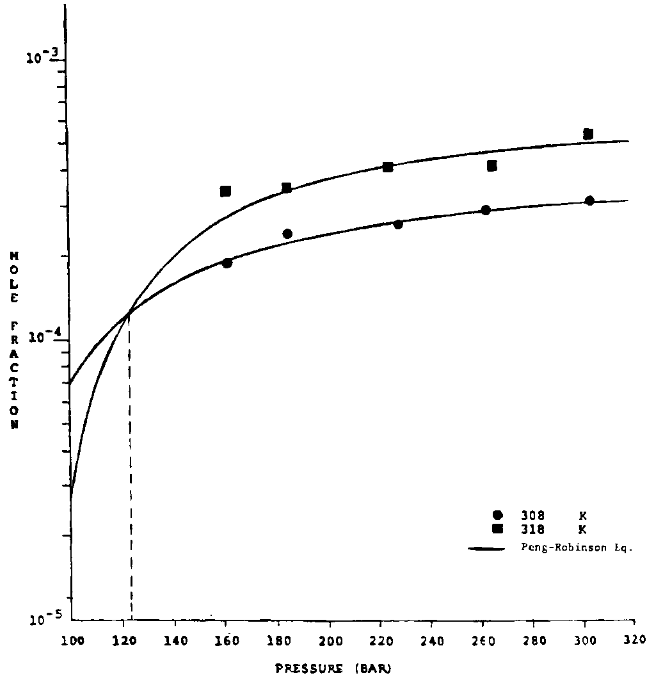

Figure 3. Solubility isotherms of 1,10-decanediol in supercritical carbon dioxide from a binary solid mixture of decanediol and benzoic acid.

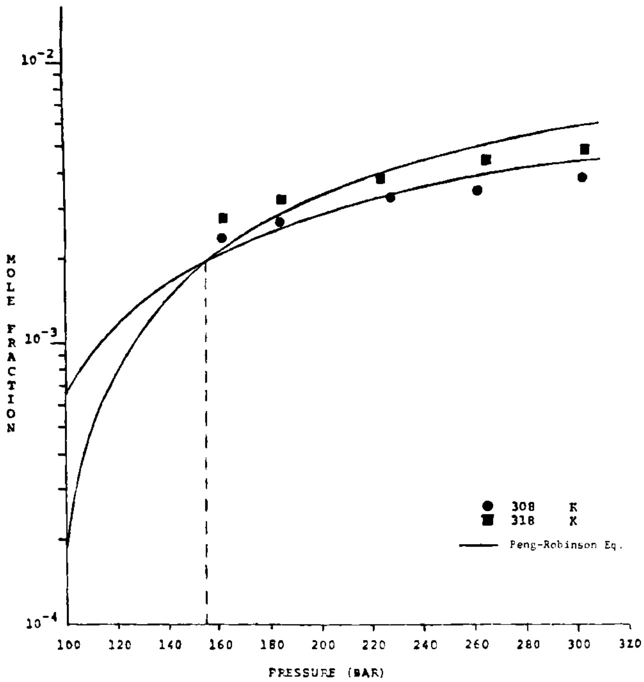

Figure 4. Solubility isotherms of benzoic acid in supercritical carbon dioxide from a binary solid mixture of decanediol and benzoic acid.

Figures 3 and 4 for the two components 1,10-decanediol and benzoic acid, show well-defined trends including the convergence of the isotherms toward what appear to be crossover pressures in the ternary system. The crossover pressure is the pressure at which the isotherms intersect. Data specifically taken in the crossover region for this system are discussed later. The existence of crossover pressures in multicomponent systems has important implications for our process synthesis ideas.

Data Correlation

Previous approaches in the literature for modeling the thermodynamic properties of the vapor phase have generally involved the application of semiempirical cubic equations of state. Mackay and Paulaitis (1979) used the Redlich-Kwong (1949) equation of state to model the vapor phase, and reported a satisfactory correlation of their data. Kurnik et al. (1981) and Kurnik (1981) used the Peng-Robinson (1976) equation of state to correlate the equilibrium solubilities of both pure solids and binary solid mixtures in the supercritical fluid. Dieters (1983) proposed a three-parameter equation of state derived from square-well potential models and compared it to the Redlich-Kwong and Peng-Robinson equations in a number of systems. At very high pressures (greater than 500 bar [50 MPa]) the Deiters equation was superior at correlating data. At lower pressures (less than 400 bar [40 MPa]) all three equations were roughly equivalent in their ability to represent data. More sophisticated equations based upon statistical mechanical considerations have been tested in supercritical systems by Johnston et al. (1982) for binary systems, and by Marouschek and Peter (1985). The latter work successfully used the mean-field lattice-gas model proposed by Kleintjens (1983) to represent the solubility of salts in supercritical steam. Because of its ease of use and reasonable success in representing the solid-fluid equilibrium data of Kurnik and Reid (1982), we chose to use the Peng-Robinson equation in this work. Solid solubilities in high-pressure fluids have been treated by Prausnitz (1969). The resulting thermodynamic relationships are given below for the sake of completeness.

For component i, present in the gas phase,

$$y_i = (P_{vp_i}/p)(1/\phi_i)\exp\left[(P - P_{vp_i})V_i^s/RT\right] \qquad (1)$$

where y_i denotes the gas phase mole fraction of component i; P_{vp_i} is the vapor pressure of i; P is the total system pressure; ϕ_i is the fugacity coefficient of i in the gas phase; V_i^s is the pure component solid molar volume; T is the temperature; and R is the gas constant. The equation of state is used to find the vapor phase fugacity coefficient ϕ_i. For the Peng-Robinson equation this is given by

$$\ln \phi_i = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{2^{1.5}B}\,2\sum_j (1-K_{ij}) \cdot \frac{(a_i a_j)^{1/2}}{a} \cdot y_j - \frac{b_i}{b}\ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \qquad (2)$$

Here Z is the compressibility factor of the gas mixture found from the solution to the cubic equation

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \qquad (3)$$

The other quantities in Eq. 2 are found from the usual pure-component properties (critical temperature and pressure, acentric factor) and mixing rules. These are summarized below.

$$a_i = \Omega_a \frac{R^2 T_{c_i}^2}{P_{c_i}}\left[1 + \kappa_i(1 - T_{r_i}^{1/2})\right]^2 \qquad (4)$$

$$b_i = \Omega_b \frac{R T_{c_i}}{P_{c_i}} \qquad (5)$$

$$\kappa_i = 0.37464 + 1.54226\,\omega_i - 0.26992\,\omega_i^2 \qquad (6)$$

where $\Omega_a = 0.45724$ and $\Omega_b = 0.0778$

$$a = \sum_i \sum_j y_i y_j a_i^{1/2} a_j^{1/2}(1 - k_{ij}) \qquad (7)$$

$$b = \sum_i y_i b_i \qquad (8)$$

$$A = aP/(RT)^2 \qquad (9)$$

$$B = bP/(RT) \qquad (10)$$

The binary interaction parameter k_{ij} in Eq. 7 is introduced to account for interactions between species i and j (with $k_{ii} = 0$ and

$k_{ij} = k_{ji}$). It is a purely empirical factor and has to be evaluated by regressing Eq. 1 against experimental data. For a ternary system consisting of solid mixture components *2* and *3* in a supercritical gas component *1*, the following k_{ij} factors must be determined: k_{12} from binary data for components *1* and *2*; k_{13} from binary data for components *1* and *3*; and k_{23} from ternary data for the gas phase. All of these factors were found for the data presented in this work and are shown in Tables 1 and 2. The k_{ij} factors for the benzoic acid-carbon dioxide system were found by regressing the data for this system presented by Kurnik et al. (1981). This approach yielded the equation of state curves drawn in Figures 2, 3, and 4. For the 1,10-decanediol–carbon dioxide system the model fit well to within an average of 6.2%. However, for the ternary system the fit was less satisfactory, the disparity between the data and the equation of state predictions reaching as high as 25% for some points. These results are similar to those given by Kurnik and Reid (1982) showing that cubic equations of state such as the Peng-Robinson equation can only be expected to give semiquantitative estimates of phase equilibrium in these systems. The pure-component properties for 1,10-decanediol, benzoic acid, and carbon dioxide used in our analysis are shown in Table 3. The properties of benzoic acid and carbon dioxide were available in the literature. For 1,10-decanediol the critical properties were estimated using Lydersen's method (Reid et al., 1977). The vapor pressures were predicted using the Riedel equation in conjunction with actual vapor pressure measurements taken in our laboratory using an apparatus similar to that used for the supercritical solubility experiments. The details of these experiments are given by Pennisi (1985).

The k_{ij} binary interaction parameter for the 1,10-decanediol-carbon dioxide system was found to be independent of temperature over the temperature range considered and hence was kept constant at this value for ternary calculations. Kurnik and Reid (1982) reported a weak temperature dependence of the binary interaction parameters in the systems they studied. For the 1,10-decanediol-benzoic acid interaction parameter in carbon dioxide (found from regressing ternary data) we found a stronger dependence on temperature.

Process Synthesis Concepts in Supercritical Extraction

By process synthesis we mean the formulation of a process for transforming a raw material (or input stream) into desired products. A review of various activities within the process synthesis area was provided by Nishida et al. (1981). Some of the major successes in the field have been in strategies for energy recovery design (heat exchanger network synthesis, Linnhoff and Flower 1978), and design of separation trains (Rudd et al., 1973). A synthesis approach for supercritical extraction processes has not been presented previously in the literature. Here we address this topic from a novel perspective, one that applies to systems exhibiting crossover solubility behavior. One of the tasks of synthesis is to provide a process configuration based upon the inherent physical and chemical phenomena of the process. Our proposed principles will guide the choice of temperature and pressure operating regimes, solvent selection, solvent flow rates, and cascade size and structure for a class of supercritical separations.

Table 3. Pure-Component Properties for Ternary System

Property	Benzoic Acid	1,10-decanediol	CO_2
T_c, K	725.0	720.4	304.2
P_c, bar	45.6	23.7	73.8
ω	0.62	1.325	0.225
V, (m^3/kmol)	0.096473	0.1584	—

	Vapor Pressure, Pa	
Temp., K	Benzoic Acid	1,10-decanediol
308	0.264	2.97 E-3
318	0.780	1.62 E-2
323	—	3.64 E-2
328	2.16	7.96 E-2

SI conversion: kPa = bar × 100.

In some of the previously proposed applications of supercritical extraction the motivations for using the process are quite clear. A good example of this is in the food processing industry where there are obvious advantages to using a nontoxic solvent such as carbon dioxide as an extraction agent, in place of previously used toxic solvents. The decaffeination of coffee is an example of this situation. However, the use of a supercritical fluid to effect the separation of a mixture into its pure component is not currently a widely used process. At present we are unaware of any commercial processes using this technology for mixture separations into pure components.

What are promising candidate separations for the technology? Paulaitis et al. (1981) proposed using supercritical carbon dioxide to separate ethanol-water mixtures. They stated that the supercritical process would be less energy-intensive than conventional distillation. No flowsheet was provided in that paper and the operating conditions suggested were a countercurrent cascade with the extraction taking place at higher pressures

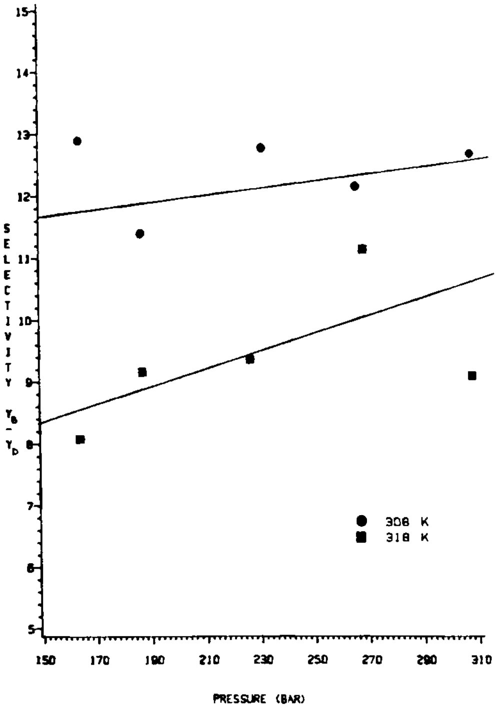

Figure 5. Selectivity of benzoic acid to 1,10-decanediol in supercritical carbon dioxide.

where greater solvent loadings are possible. However, even at high fluid densities (carbon dioxide at 308 K and 2,500 psi [17 MPa]) ethanol loadings are low (less than 0.1 mole fraction), leading to a cascade with large gas flow rates. In the process suggested by McHugh et al. (1981) using supercritical ethane to separate ethanol-water mixtures, ethanol loadings were less than 2 mol %. The data in both of these studies are in accord with the conclusions of Van Alsten et al. (1984), namely, that selectivities in the supercritical phase are rather insensitive to the supercritical fluid density. This, coupled with the low gas phase loadings and the fact that it was not possible to enrich beyond the azeotropic composition, would appear to be severe disadvantages in the development of a competitive supercritical extraction alternative to more conventional processes such as pressure-swing distillation. Furthermore, capital costs associated with a cascade at such elevated pressures are bound to be large compared to the conventional low-pressure process. Another point raised in both of these papers suggested that the three-phase liquid-liquid-vapor region must be of interest because of the high selectivity for ethanol between the liquid phases. However, the operability problems associated with a three-phase countercurrent process at high pressures are probably severe. At present no commercial processes are operational using supercritical extraction for liquid mixture separations, although patents on some potential processes have been issued (de Fillipi and Vivian, 1980).

Separation of solid mixtures was considered by Kurnik and Reid (1982). For the carbon dioxide-naphthalene-phenanthrene system at low pressures, their calculations showed the selectivity of naphthalene to phenanthrene to be the ratio of the pure solid vapor-pressures. At higher pressures the selectivity decreased and essentially flattened out at a value of approximately 7 for pressures greater than 100 bar (10 MPa). Our data for the carbon dioxide-decanediol-benzoic acid system exhibits similar features. A plot of selectivity in this system at various pressures is given in Figure 5, showing the selectivity to be almost constant beyond 160 bar (16 MPa). This is a rather disappointing situation, since for the design of a cyclic separation process using high-pressure gas to extract solids before depositing them at low pressure it would be preferable to have selectivity be a strong function of pressure. In fact, with no difference in selectivity at the high- and low-pressure ends of the process the deposited solids are in the same ratio as they appeared in the gas phase, no refining having occurred. These considerations led Kurnik and Reid (1982) to argue that an azeotropic situation arises in such a process and that cascade processing would not be a viable technique unless the solvent properties (and selectivity) can be modified in some other way. In the following section we propose a new perspective on synthesis concepts for supercritical extraction processes which exploits crossover phenomena that can occur in such systems.

Crossover Regions in the Gas Phase

One of the interesting features of data for the solubility of pure components dissolved in the supercritical phase is the existence of crossover points. This is a high-pressure region on the solubility diagram around which the various isotherms converge, and for many pure substances experimental data show the crossover point to be focused around a distinctive pressure. Furthermore, the crossover pressure for a specific solute can vary considerably with different solvent supercritical phases (see data presented by Eckert et al., 1985). Kurnik et al. (1981) show solubility isotherms for various substances. For 2,3 dimethylnaphthalene in ethylene the crossover pressure is 120 bar (12 MPa), while in carbon dioxide the crossover pressure is 145 bar (14.5 MPa; note that the critical pressure of ethylene is 50.4 bar [5 MPa] while that of carbon dioxide is 73.8 bar [7.1 MPa]).

For pure components the crossover point is rather unique with respect to temperature. Below the crossover pressure an increase in temperature causes a decrease in solubility in the gas phase, while above the crossover pressure the opposite effect occurs. This is an unusual phenomenon that does not exist in liquid solvents at usual liquid extraction conditions. The accepted explanation for this phenomenon is that at pressures below the crossover pressure the density of the gas is more sensitive to temperature changes than at higher pressures. A temperature decrease in this region affects the solubility in two ways. The vapor pressure of the solid decreases while the density of the gas (related to its solvent power) increases. The density effect predominates and the solubility increases. At pressures above the crossover pressure a temperature increase causes the vapor pressure of the solid to increase while the density of the gas decreases. The vapor pressure effect predominates and the solubility increases.

The important question that arises is whether or not crossover points persist in multicomponent mixtures and if so, can they be related to the crossover points in the constituent binaries in even an approximate way? Our computer modeling of the phase equilibria in the carbon dioxide-decanediol-benzoic acid system showed that indeed crossover points do persist in the ternary system and that they can be related fairly closely to the crossover points in the constituent binaries (i.e., carbon dioxide-benzoic acid, carbon dioxide-decanediol systems, respectively). It is not surprising that this should be the case in this system since the gas phase is extremely dilute in the solids, and it seems reasonable that the dominant interactions should be solute-solvent interactions as opposed to solute-solute interactions. The convergence of isotherms toward crossover points in the ternary carbon dioxide-decanediol-benzoic acid mixture can be seen from the equation of state extrapolations of our data as shown in Figures 3 and 4. Moreover, the same effect can be observed in some of the ternary data presented by Kurnik and Reid (1982).

This observation prompted further experimentation with the carbon dioxide-decanediol-benzoic acid mixture in an attempt to verify a crossover region in the ternary system. Based upon the equation of state predictions shown in Figures 3 and 4, experiments were done in the 120–140 bar (12–14 MPa) pressure range. The data obtained are shown in Table 4 and plotted in Figures 6 and 7. Each data point represents an average value obtained from at least three experiments, and there is clearly a crossover region in this ternary system in the 120–140 bar pressure range.

Upon further examination of the data presented by Kurnik and Reid it became clear that for certain of their ternary systems, experimental data were taken in the ternary crossover region. In particular the ternary system carbon dioxide-2,3 dimethylnaphthalene-2,6 dimethylnaphtalene was examined. In their previous work Kurnik et al. (1981) published data for the constituent binaries. In carbon dioxide, the crossover pressure reported for the 2,3 isomer was approximately 145 bar (14.5 MPa) and for the 2,6 isomer somewhat lower, which we esti-

Table 4. Experimental Data in Ternary Crossover Region for Carbon Dioxide–1,10-decanediol–Benzoic Acid System

Temp. K	Pressure Bar	$y_d \times 10^4$	$y_b \times 10^3$	Loading g/mol CO_2
308	119.4	1.27 ± 0.06	1.43 ± 0.14	0.20 ± 0.02
318	119.4	1.25 ± 0.12	1.00 ± 0.15	0.145 ± 0.02
308	125.5	1.42 ± 0.06	1.61 ± 0.08	0.22 ± 0.01
318	125.0	1.63 ± 0.08	1.35 ± 0.13	0.19 ± 0.02
308	131.9	1.53 ± 0.04	1.79 ± 0.12	0.25 ± 0.02
318	132.9	2.03 ± 0.28	1.72 ± 0.12	0.25 ± 0.02

SI conversion: kPa = bar × 100.

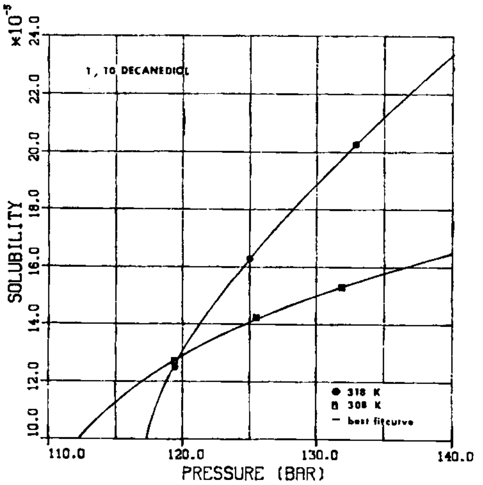

Figure 6. Solubility isotherms of 1,10-decanediol in ternary crossover region.

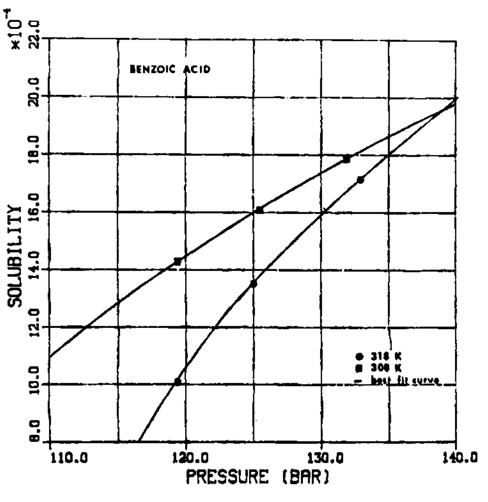

Figure 7. Solubility isotherms of benzoic acid in ternary crossover region.

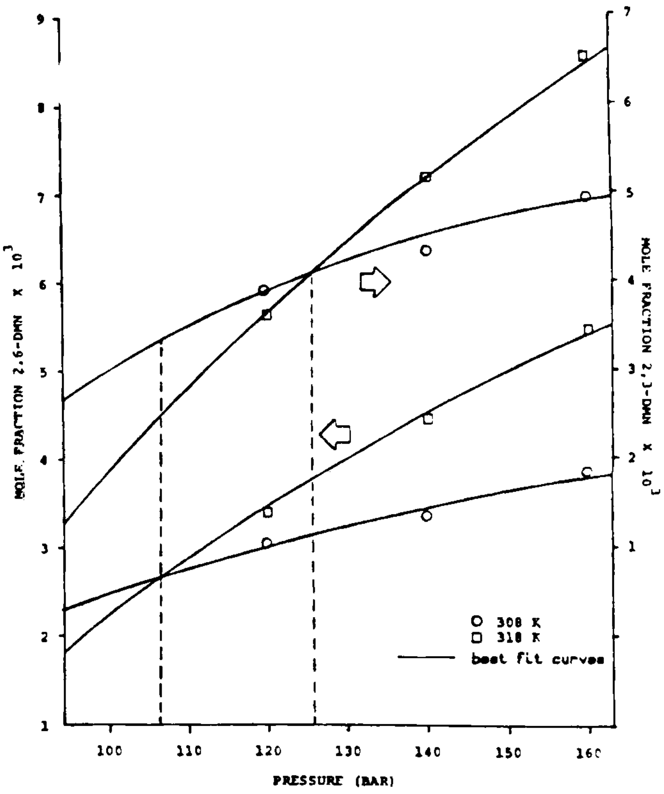

Figure 8. Crossover regime for a mixture of solid isomers in supercritical carbon dioxide.

Data of Kurnik and Reid (1982).

mated at between 100–120 bar (10–12 MPa). A plot of the ternary data presented by Kurnik and Reid (1982) is shown in Figure 8, showing crossover behavior in the ternary system. At a pressure of 120 bar (12 MPa), a temperature decrease from 318 to 308 K causes the solubility of 2,3-DMN to increase while that of 2,6-DMN decreases.

The implications of these two sets of data showing crossover regions in ternary systems are very interesting. Figure 9 illustrates this graphically for two compounds dissolved in a supercritical solvent. The crossover pressures, assumed to be separate for each component in the gas phase, are clearly shown at pressures P_1^* and P_2^*. It is the middle pressure regime between P_1^* and P_2^* (the crossover regime) that is of significance as far as our synthesis concepts are concerned. This regime is shown in an expanded form in Figure 10. At a pressure P_O, intermediate to P_1^* and P_2^*, consider that the gas phase is initially at a temperature T_H (with $T_H > T_L$) and then cooled to a temperature T_L. For component 2 this is a process from A to B in Figure 10, and clearly the equilibrium solubility of component 2 in the gas phase increases while the solubility of component 1 decreases in going from A to B. Hence, it is possible to conceive of a process where a mixture of components 1 and 2 is extracted at a pressure P_O and temperature T_H, and by a simple temperature decrease to T_L, pure component 1 would drop out of the gas phase.

Tables 5 and 6 show yield-purity characteristics for separation processes for both the data in Tables 2 and 4 and the isomeric data of Kurnik and Reid. At a pressure in the crossover regime one of the components from the mixture is obtained in a pure state. In a later section we present data for an actual pro-

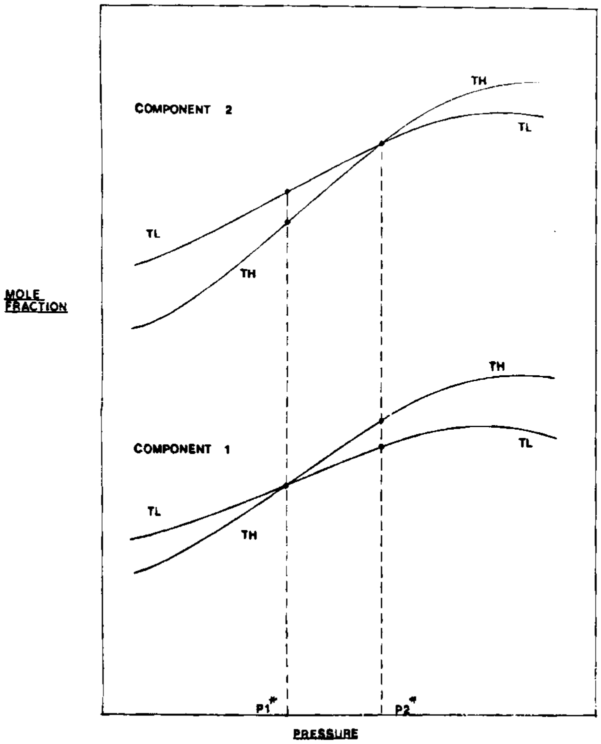

Figure 9. Separable crossover points with two solutes dissolved in a supercritical solvent.

cess run in our laboratory corresponding to the path *A-B* in Figure 10 for the 1,10-decanediol, benzoic acid, carbon dioxide system.

Multicomponent Fractionations

The ideas for a binary separation process can be extended to encompass more components. The referent solubility diagram for a quaternary mixture exhibiting separable crossover regimes is shown in Figure 11 for three components, *A*, *B*, and *C*. A process can be formulated and understood by tracing the cascade path in Figure 11. Supercritical fluid at temperature T_H and pressure P_2 is contacted with a mixture of *A*, *B*, and *C*. In the

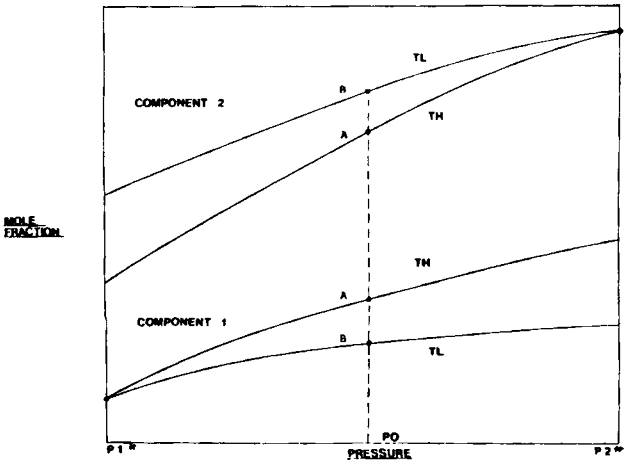

Figure 10. Crossover regime with two solutes dissolved in a supercritical solvent.

Table 5. Yield and Purity Enhancement Factors for 1,10-decanediol, Benzoic Acid in Supercritical Carbon Dioxide at Various Pressures

Pressure Bar	1,10-decanediol Yield** ($\times 10^4$)	Benzoic Acid Yield** ($\times 10^4$)	Purity Enhancement Factor* for Decanediol in Deposited Phase
306.8	2.28	9.71	2.13
228.5	1.57	5.97	2.46
163.8	1.59	4.20	3.08
132.2	0.497	0.00	∞†

*Purity enhancement factor: ratio of mol frac decanediol/benzoic acid in deposited phase to that in feed.

**Yield: ratio of mol solid deposited/mol CO_2 in feed.

†Crossover regime, pure decanediol deposited.

SI conversion: kPa = bar × 100.

Table 6. Yield-Purity Characteristics for Isomeric Separation in Supercritical Carbon Dioxide Using Temperature Cycling from 318 to 308 K

Pressure Bar	2,6 Isomer Yield ($\times 10^3$)	2,3 Isomer Yield ($\times 10^3$)	Purity Enhancement Factor for 2,6 Isomer in Deposited Phase
280	3.40	3.76	1.13
140	1.12	0.848	1.53
120*	0.362	0.00	∞*

*Crossover regime, pure 2,6 isomer deposited.

SI conversion: kPa = bar × 100.

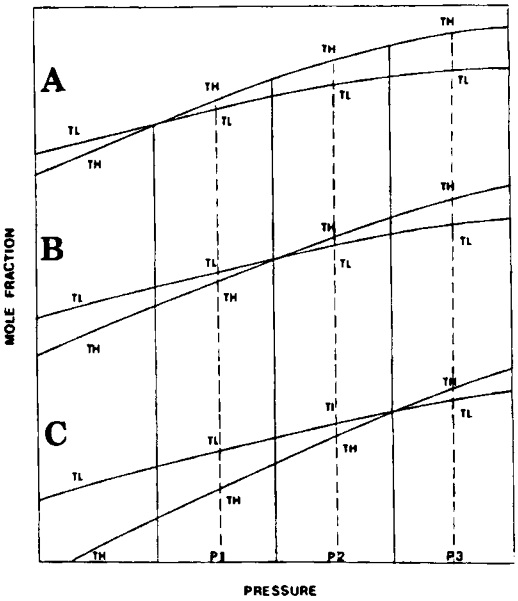

Figure 11. Crossover regimes in a quaternary system.

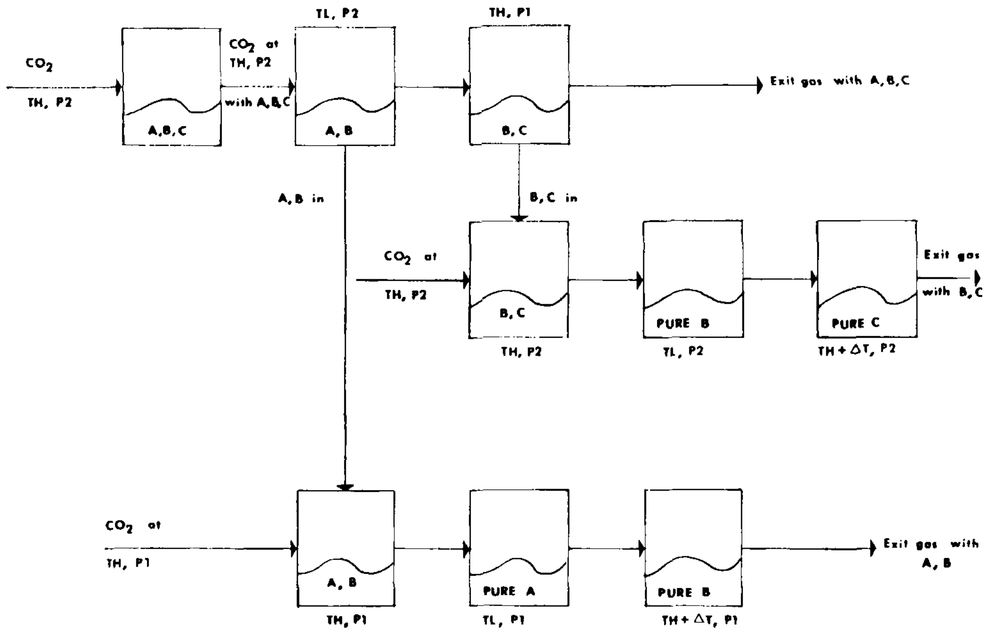

Figure 12. Flowsheet for separating ternary solid mixture of components *A*, *B*, *C*.

first stage, the fluid phase is cooled to T_L. From Figure 11, since P_2 is in the crossover regime separating components (A, B) and C, a mixture of A and B will precipitate out of the first stage. The exit fluid from this stage is then decompressed to a pressure P_1 and heated to temperature T_H (or greater than T_H). Under these conditions it can be seen from Figure 11 that a mixture of B and C will precipitate out in the second stage. Exit fluid from the second stage with remaining quantities of A, B, and C can be recycled for further processing. The mixtures from stages one and two are binary mixtures and can be purified in isobaric cascades by temperature-cycling as described in the previous section for binary mixture separations. These sections of the cascade are shown in Figure 12 and can be formulated on the basis of Figures 9 and 10. In order to get pure B and C from these sections of the cascade, the temperature of the end stages will have to be above T_H (i.e., $T_H + \Delta T$, where ΔT is some prespecified temperature change). Generally T_L will be a temperature slightly higher than the critical temperature of the solvent, with $T_H > T_L$.

Alternative process flowsheets for separating a mixture of A, B, and C can be conceived of, based on Figure 11. An interesting one is shown in Figure 13. Supercritical fluid at T_H and P_2 is contacted with the A, B, C mixture. The fluid is cooled to T_L in the first stage, where a binary mixture of (A, B) precipitates. The exit fluid from this stage with remaining A, B, C is then heated to a temperature $T_H + \Delta T_1$, (ΔT_1 is some prespecified temperature) causing pure C to deposit in the end stage. The exit fluid with remaining A, B, and C can then be recycled for further processing. The binary mixture consisting of A and B can then be separated by temperature-cycling at a pressure P_1, giving rise to the bottom section of the cascade shown in Figure 13 where both pure A and pure B can be obtained. Hence the process shown in Figure 13 consists of two parallel isobaric cascades with temperature-cycling in each one. This process has fewer stages than the process shown in Figure 12, but the process in Figure 12 produces pure B at two stages in the cascade (as opposed to just one stage in Figure 13). To compare the two processes, detailed design calculations should now be done showing comparative yields, solvent flow rates, capital costs, and other factors affecting the process economics.

The flowsheet in Figure 13 represents a generic process for separating multicomponent mixtures into their pure compo-

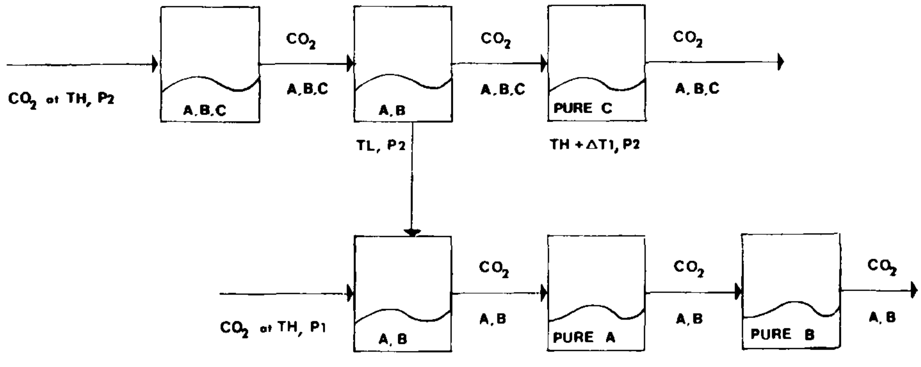

Figure 13. Alternative flowsheet for separating ternary solid mixture of components *A*, *B*, *C*.

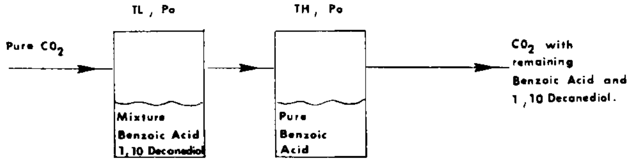

Figure 14. Diagram of laboratory-run separation process to separate two solids in crossover region.

nents. By operating the first section of the cascade at a pressure within the highest crossover regime it is possible to produce a pure component and a mixture of lower order (i.e., with one less component). By repeating this process on the lower order mixture, a flowsheet of parallel isobaric cascades can be conceived of which will eventually give the pure components. The pressures in each isobaric cascade lies within successive crossover regimes of the mixtures. The exit fluid streams from the isobaric sections can be recycled for further processing. The guiding principles for the process synthesis will be solubility diagrams similar to that shown in Figure 11.

An Actual Process in the Crossover Region

Once a system exhibits a crossover region the separation process conception is straightforward, as described in the previous sections. Here we present data for an actual process run in our laboratory for producing pure benzoic acid from a mixture of 1,10-decanediol and benzoic acid using pure supercritical carbon dioxide. A diagram of the process constructed is shown in Figure 14, which corresponds to the path *B-A* in Figure 10. The pressure P_O in the ternary crossover regime (from the data in Table 4) was specified to be 125 bar (12.5 MPa). Table 7 shows the actual process yield data compared to the expected results, based upon the data shown in Table 4. Agreement between the actual and expected results is good, showing the operability of the process—an encouraging result. If a binary mixture is required to be split into two components, the process shown in Figure 15 is preferable, where the temperature is cycled down to T_L and then up to T_H, dropping out pure component at each stage. Calculations (shown in the Appendix) for such a process for the 2,3-DMN, 2,6-DMN system based upon the data of Kurnik and Reid show that a carbon dioxide flow rate of approximately 3–4 m^3/h will yield 1 kg/h of the 2,6 isomer and 2.52 kg/h of the 2,3 isomer. The current price of the 2,6 isomer is $3,000/kg, showing that when high-value products are to be separated the crossover process could be a promising alternative.

Table 7. Results of Separation Process Operating in Ternary Crossover Region for 1,10-decanediol–Benzoic Acid–Carbon Dioxide System at 125 Bar

	Range of Expected Values*	Actual Process Yields
Stage 1		
Loading, g/mol CO_2	0.221 ± 0.01	0.23
$y_d \times 10^4$	1.361–1.485	1.59
$y_b \times 10^3$	1.532–1.684	1.67
Stage 2		
Expected mass of pure benzoic acid, g	0.2453 ± 0.19	0.19

*Based on data in Table 4.

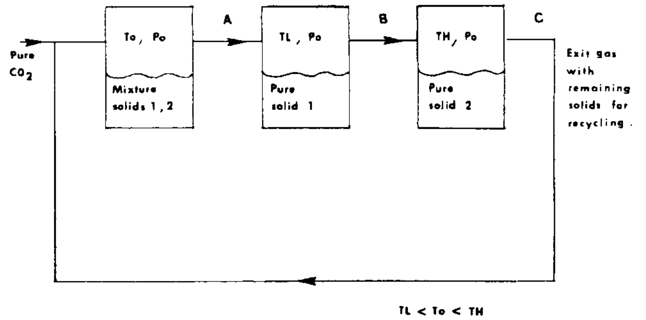

Figure 15. Process flowsheet yielding both solids from a binary mixture.

Discussion

The novel synthesis principles postulated here take advantage of separable crossover regions in the multicomponent fluid phase. These appear to be unique in supercritical fluids, and when present provide interesting possibilities for designing extraction processes. Presently, data in the crossover region for multicomponent systems are virtually nonexistent except for the ternary systems cited in this study. This is probably due to the fact that previous work has generally been directed at the high-pressure region where solubilities are higher (however, in this region such phenomena are absent). A theory for the crossover effect in supercritical fluids is given in a recent work (Munoz and Chimowitz, 1986).

For the system used in this paper, where data were presented showing a ternary crossover region, a separation was demonstrated to be feasible in accordance with the process concepts described. Clearly the best candidate separations for the process will be high-value, low vapor-pressure specialty chemicals. Even with low solubilities in such systems the process could be economically viable if the products are expensive. In comparison with competitive processes such as solution recrystallization, the supercritical process will have a number of advantages: ease of solvent regeneration, straightforward operation in a continuous manner, and virtually no contamination of the products by the solvent. If the solids form solutions or melt, modeling of the phase equilibria becomes more complex; however, the data recently published by Gopal et al. (1985) show crossover behavior in the fluid phase in such a system. Once this crossover behavior is present the separation process should still be feasible. Current research is examining this situation in an attempt to extend the range of application for the concepts.

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The authors wish to acknowledge an equipment grant from Autoclave Engineers, Inc. in support of this research. We are also grateful for the comments offered by R. Reid, which enhanced the preparation of the final manuscript.

Notation

a_i = parameter in equation of state, component i
b_i = parameter in equation of state, component i
k_{ij} = binary interation parameter, components i-j

P = pressure
T = temperature
V_i^s = solid phase molar volume, component i
y_i = gas phase mole fraction, component i
Z = compressibility factor

Greek letters

κ_i = parameter in equation of state, component i
ϕ_i = fugacity coefficient, component i
ω_i = acentric factor, component i

Subscripts

vp = vapor pressure
c = critical property
r = reduced property

Appendix: Process Yields Based on Isomeric Data of Kurnik and Reid (1982)

Pressure of cascade 115 bar (11.5 MPa), flowsheet as in Figure 15.

$$\text{2,6-DMN} = 1$$

$$\text{2,3-DMN} = 2$$

$$T_H = 318$$

$$T_L = 308$$

$$T_O = 313 \text{ (say)}$$

$$y_{1H} = 3.1 \times 10^{-3} \quad y_{2H} = 3.4 \times 10^{-3}$$

$$y_{1L} = 2.9 \times 10^{-3} \quad y_{2L} = 3.9 \times 10^{-3}$$

Choose T_O such that $T_L < T_O < T_H$, giving an average of the above concentrations.

At A: $y_1 = 3.0 \times 10^{-3}$
$y_2 = 3.65 \times 10^{-3}$
At B: $y_1 = 2.9 \times 10^{-3}$
y_2 = slightly higher than 3.65×10^{-3}
At C: y_1 = slightly higher than 2.9
$y_2 = 3.4 \times 10^{-3}$

Say CO_2 flow rate is 10^3 mol. (Under these process conditions this corresponds to a volume of $CO_2 \approx 64$ L.)

At A we have:

$$\left.\begin{array}{l} \dfrac{M_1}{M_1 + M_2 + 10^3} = 3.0 \times 10^3 \\[2ex] \dfrac{M_2}{M_1 + M_2 + 10^3} = 3.65 \times 10^{-3} \end{array}\right\} \frac{M_1}{M_2} = \frac{3.0}{3.65}$$

$$\frac{\dfrac{3.0}{3.65}}{\dfrac{3.0}{3.65} + 1 + \dfrac{10^3}{M_2}} = 3.0 \times 10^{-3}$$

$$\frac{0.82192}{1.82192 + \dfrac{10^3}{M_L}} = 3.0 \times 10^{-3}$$

$$273.97 = 1.82192 + \frac{10^3}{M_L}$$

$$272.15068 = \frac{10^3}{M_2}$$

$$=> M_2 = \xrightarrow{3.67444 \text{ mol}}$$

$$M_1 = \xrightarrow{3.02008 \text{ mol}}$$

At B:

$$M_2 = 3.67444$$

$$\frac{M_1}{M_1 + M_2 + 10^3} = 2.9 \times 10^{-3}$$

$$M_1 = 2.9 \times 10^{-3}(M_1 + M_2 + 10^3)$$

$$0.9971\, M_1 = 2.91066$$

$$M_1 = \xrightarrow{2.91912 \text{ mol}}$$

Dropping out in 1 = $\xrightarrow{0.10096 \text{ mol}}$ 2,6 DMN.

in two passes we get = $\xrightarrow{0.20192 \text{ mol}}$

Now into vessel 2:

$$M_1 = 2.91912$$

At D:

$$\frac{M_2}{M_1 + M_2 + 10^3} = 3.4 \times 10^{-3}$$

$$M_2 = 3.4 \times 10^{-3}(2.91912 + M_2 + 10^3)$$

$$0.9966\, M_2 = 3.40993$$

$$M_2 = 3.42156$$

. . . dropping out in 2 = 3.67444 − 3.42156 = $\xrightarrow{0.25288 \text{ mol}}$

2,3-DMN

in two passes we get

$$M_2 = \xrightarrow{0.50576\ \text{mol}}$$

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