# Experimental Data for the Crossover Process in a Model Supercritical System

This paper presents the experimental technique and data acquired in the evaluation of a separation process in the crossover region of a model supercritical fluid system consisting of benzoic acid, 1-10 decanediol, and carbon dioxide. The results show that by exploiting the crossover effect it is possible to obtain essentially pure benzoic acid (>99.5% purity) with a single temperature cycle. A number of other issues are also discussed including the tradeoff between yield and purity and the manner in which the process variables are specified, which involves the interplay of experiment and model calculations.

**F. D. Kelley**
**E. H. Chimowitz**
Department of Chemical Engineering
University of Rochester
Rochester, NY 14627

## Introduction

This paper provides details of the experimental apparatus and technique as well as results achieved in the evaluation of a separation process that makes use of the crossover effect in a binary solid mixture dissolved in a supercritical fluid. Crossover regions in supercritical fluids and their potential use for separations were discussed by Chimowitz and Pennisi (1986). A theoretical analysis leading to a set of both necessary and sufficient conditions delineating these regions was recently given by Chimowitz et al. (1988). The crossover process concept essentially exploits the fact that there may be "window" regions of temperature and pressure in the near-critical fluid state, where one solute is retrograde while the other is either partially or wholly outside of its respective retrograde region. Based upon the existence of this phenomenon, novel separation schemes can readily be devised. The regimes of interest are in the near-critical state of the supercritical fluid. The extraordinary solution properties that pertain in these regions have been discussed in a number of recent papers (Eckert et al., 1986; Dibenedetti and Kumar, 1988).

At present, such regions have been observed experimentally in two ternary systems, the benzoic acid, 1,10-decanediol, carbon dioxide (BDC) system (Chimowitz and Pennisi, 1986) and the 2,3-dimethylnaphthalene, 2,6-dimethylnaphthalene, carbon dioxide (DMN) system (Johnston et al., 1987). The regions in the latter system are narrow, making it difficult to obtain a completely pure separation in one temperature cycling step. Nevertheless, Johnston et al. (1987) reported a 4:1 enhancement from a 50:50 mixture of the DMN isomers in one step. This is considerably better than would be suggested by the ratio of vapor pressures of these two isomers (approximately 1.25) at the conditions of the experiment. The crossover regions in the BDC system are larger suggesting that this system provides a good analogue for evaluating the process concept. In this paper we use the BCD system and attempt to experimentally vindicate some of the theoretical ideas put forward by Chimowitz et al. (1988).

## Choice of Experimental Conditions for the Two-Stage Process

In the absence of the extensive data required to completely characterize multicomponent crossover regions, one must resort, at least initially, to model calculations for choosing feasible experimental operating conditions for the two-stage process suggested by Chimowitz et al. (1988). These model calculations were done using a perturbed hard-sphere equation of state which had been fitted to the ternary BCD solubility data of Chimowitz and Pennisi (1986). These solubility calculations are shown in Figures 1 and 2 for 1,10-decanediol and benzoic acid, respectively. Three pressures were chosen at 126, 127 and 128 bar, since the experimental pressure was taken to be 127 bar with an allowance of ± 1 bar to account for pressure fluctuations during the experiment. Based upon these calculations and the process aim of achieving pure benzoic acid in the second (condenser) vessel, the extractor (first vessel) temperature $T_E$ was chosen to be 302 K. From Figure 1 it is shown how the upper limit (at 126-bar pressure) for the condenser temperature was established. Any condenser temperature above this would cause 1,10-decanediol to be forced into a region causing undesired precipitation. The condenser temperature for the initial series of experiments was therefore conservatively chosen to be 335 K (denoted by $T_c$ in Figures 1 and 2). Given an accurate model, these calculations show that no 1,10-decanediol should condense in the condenser under the conditions established.

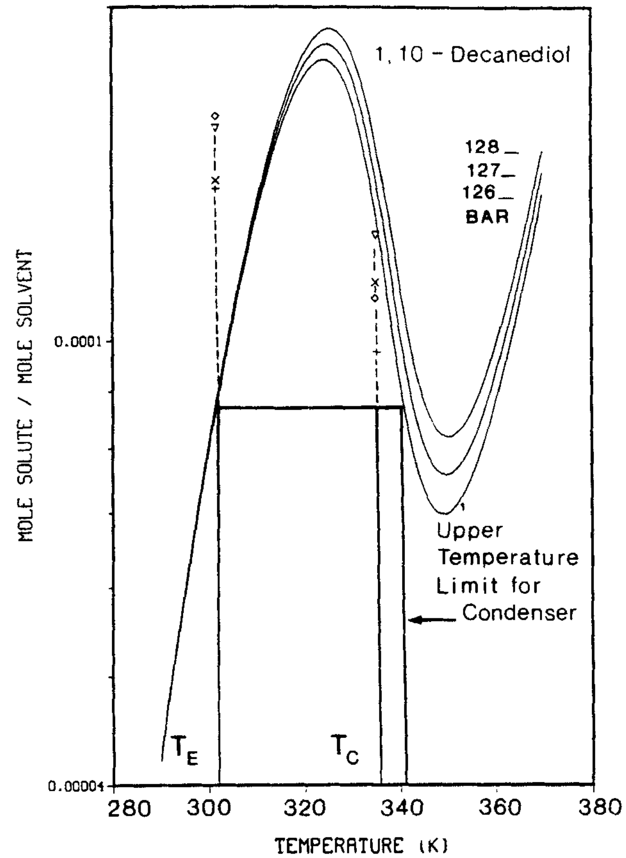

**Figure 1. Solubility calculations of 1,10-decanediol in the BCD ternary (solid line).**

◇, ▽, x, + represent data for the first series of experiments.

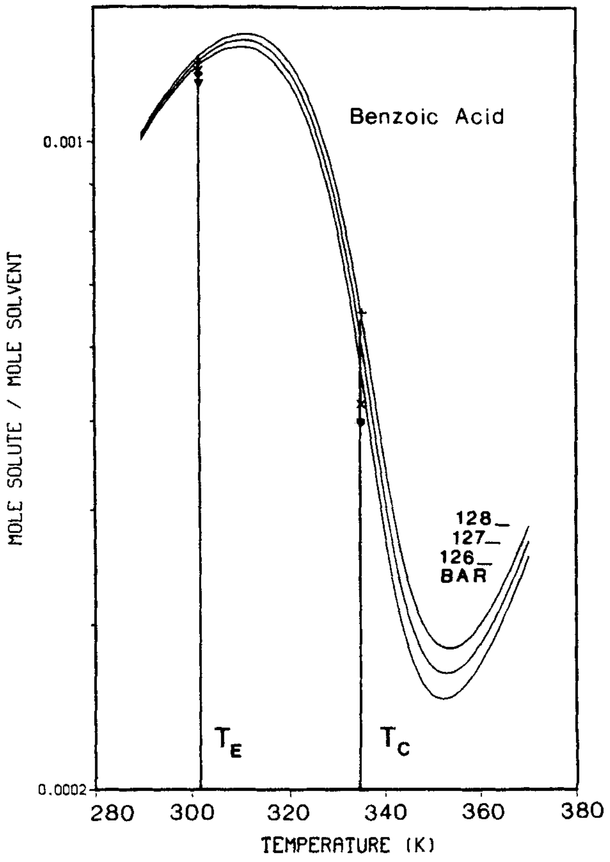

**Figure 2. Solubility calculations of benzoic acid in the BCD ternary (solid line).**

◇, ▽, x, + represent data for the first series of experiments.

## Experimental System Description

The equipment used for the separation experiments was similar to the extraction apparatus used by Chimowitz and Pennisi (1986); a schematic diagram is shown in Figure 3. This system differs in that it can be operated as two parallel extractor vessels for solubility studies or, in this work, as two vessels in series, one functioning as the extractor and the other as the condenser. During operation, liquid $CO_2$ (99.8% pure, Air Products & Chemicals) was compressed to the desired operating pressure by a Milton Roy piston pump. The line between the tank and pump was cooled to ensure that only liquid solvent reached the pump head. A back pressure regulator (Haskel Engineering and Supply Co.) controlled the system operating pressure within ±1.5 bar of set point. For these experiments, the extractor was packed with a uniform mixture of benzoic acid (99.5% pure, by Mallinckrodt Chemical Works), 1,10-decanediol (99% pure, by Aldrich Chemical) and 3 mm glass beads. The glass beads were used to prevent caking of the solid mixture during operation. A glass wool plug at the outlet of the extractor prevented entrainment of fine particles. The fluid entering the extractor was preheated in 3 ft (0.9 m) of tubing submerged in a water bath along with the extractor. The water bath temperature was controlled within $\pm 1°F \longrightarrow \pm 5/9°C \approx .55°C$ of the setpoint using an Omega Engineering, Inc. controller. A calibrated Heise gauge accurate to ±5 psi (±34.5 kPa) was used to measure the inlet pressure at the extractor vessel.

The condenser was also submerged in a controlled temperature water bath. The water was level with the top of the vessel so that the inlet line could be kept colder to avoid plugging. The line between the extractor vessel and inlet to the condenser was wrapped with electrical heat tape. This line was maintained manually using a variac at +1 to +3°C higher than the extractor temperature. The line temperature was maintained using a Type J thermocouple (Omega Engineering, Inc.) and a Beckman temperature readout monitor. The carbon dioxide flow rate was regulated by using a heated micrometering valve (Autoclave Engineers). The fluid expanded across this valve to approximately 1 bar. Glass U-tubes, partially packed with glass wool, functioned as final filters for any materials passing out of the collection vessel, and as "explosion" relief devices to protect the flowmeter and dry-test meter in case of micrometering valve failure. The gas flow rate was monitored by a flowmeter (Fisher-Porter) and the total gas volume was measured by a Singer dry-test meter. Teflon inserts were used to reduce the volume of the vessels and to act as filter holders for the collection of condensed solids. Figure 4 provides details of the various vessel internals. The extractor, condenser, and collection vessels were all Autoclave Engineering pressure vessels with a 1.75 cm internal diameter and a 30.0 cm internal length.

An experiment began with all manual valves closed. The two water baths were filled and heated to the desired temperatures. The liquid pump was primed by opening and closing valve V3.

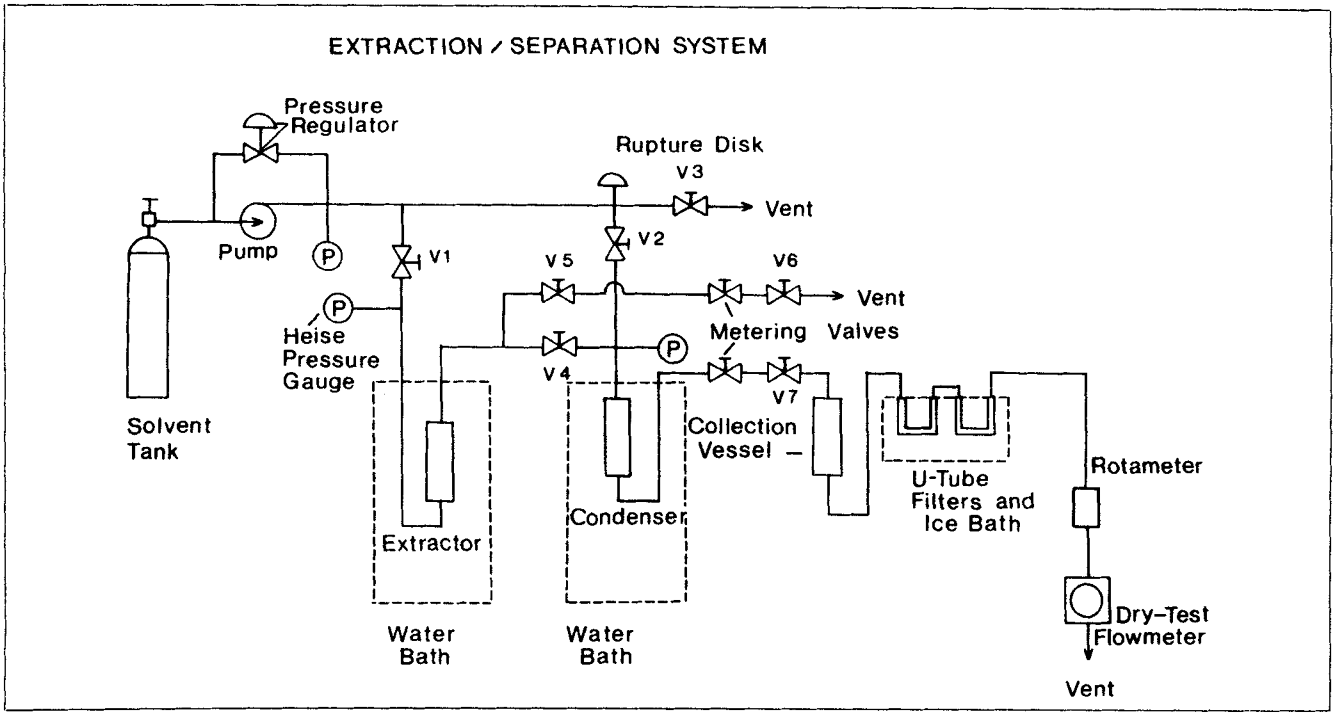

**Figure 3. Experimental system description**

The system operating pressure was crudely adjusted using the backpressure regulator and the first pressure gauge. Valve V1 was opened and the extractor pressurized. Fine adjustment of the system pressure was then made using the Heise pressure gauge and the backpressure regulator. Valve V1 was closed and valve V2 opened, bringing the condenser up to pressure. When the condenser achieved the correct operating pressure, the outlet valve V7 was opened and the flow rate adjusted using the micrometering valve. The flow rate was normally adjusted to be approximately 1 std. $ft^3/h$ (28.3 L/h). Once flow was stabilized,

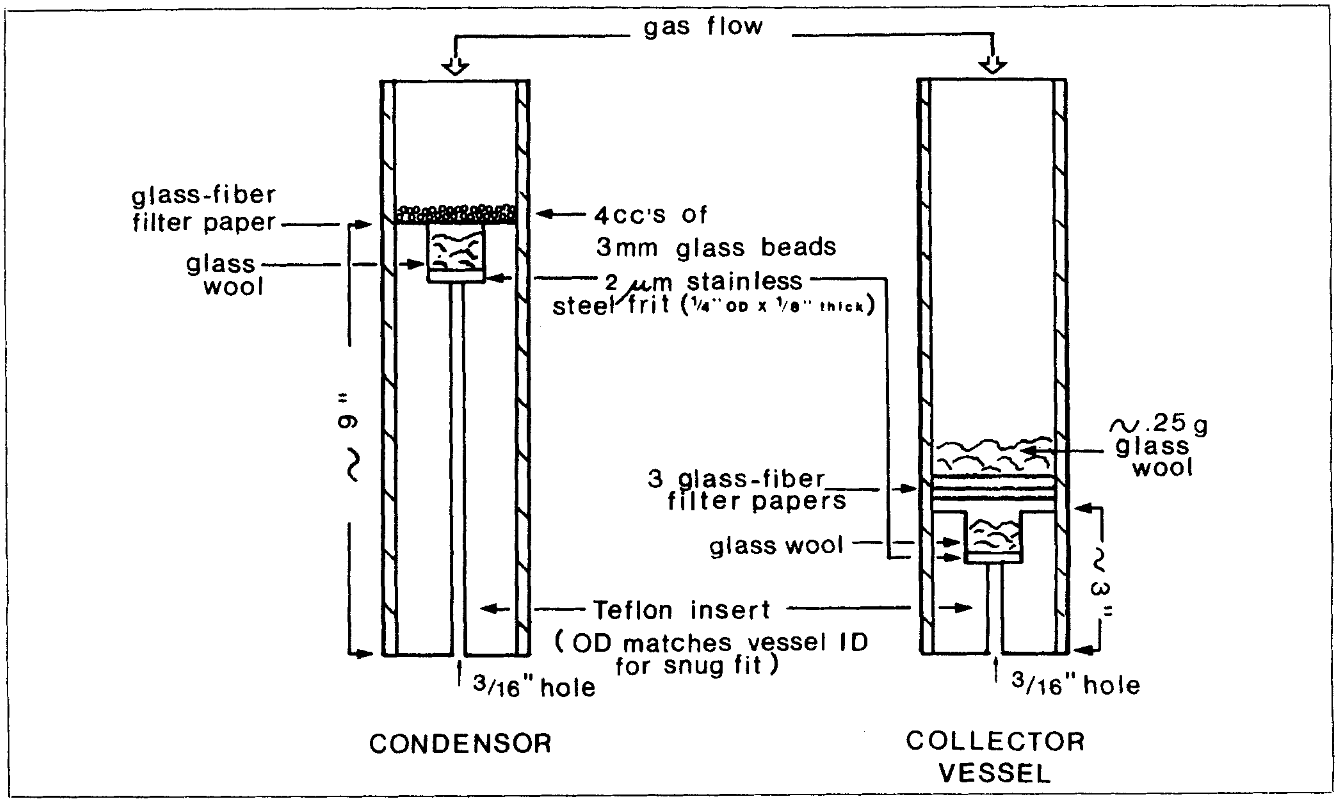

**Figure 4. Crosssection of extractor and condenser vessels.**

Table 1. Experimental Results for Series #1

| Run | System Pres. bar | Moles of $CO_2$ Used | Extractor Temp. K | Condenser Temp. K | Condenser Mass g | Condenser Benzoic Acid Mole Fraction | Collector Mass g | Collector Benzoic Acid Mole Fraction |
|---|---|---|---|---|---|---|---|---|
| 4 | 128.1 | 14.7789 | 301.9 | 335.3 | 1.1170 | 0.9352 | 1.3673 | 0.8636 |
| 5 | 127.5 | 11.7763 | 301.9 | 335.0 | 1.0212 | 0.9621 | 0.9807 | 0.8222 |
| 6 | 127.1 | 12.8674 | 301.9 | 335.0 | 1.1912 | 0.9322 | 1.0277 | 0.8204 |
| 7 | 126.9 | 13.6066 | 301.9 | 335.0 | 1.1675 | 0.9550 | 1.1210 | 0.8007 |

valve V1 was opened, and valve V2 was closed. The system was then allowed to operate until sufficient gas volume passed through the system to dissolve approximately 2 g of material from the extractor. The system was shut down by closing valve V4, opening valve V2 for a short duration to purge extractor gases (some collected product was lost as a result of this), and then finally valve V2 was closed allowing the system to depressurize at constant temperature. After depressurization, the material in the condenser and collector vessel was removed and any residual materials flushed from the walls using acetone (99.7% pure J. T. Baker Chemical), which was then evaporated. All dried solids were weighed using a Mettler balance, with a precision of ±1 mg.

For the first series of experiments (series 1 data), the determination of the solids composition was done by an outside laboratory using gas chromatography. They reported some difficulty in obtaining accurate, reproducible areas for the 1,10-decanediol peaks, since it was present in small amounts in the condenser material, relative to benzoic acid. The main purpose of these data was to evaluate how accurate the initial process operating conditions were (established based upon equation of state model predictions) and to ascertain whether or not significant amounts of 1,10-decanediol precipitated in the condenser. If this were the case (and it turned out to be so, see data for these experiments shown in Figures 1 and 2), then the process conditions had to be iteratively adjusted in order to find conditions that did not violate the solubility boundary for 1,10-decanediol as discussed earlier. This led to a second series of experiments (series 2 data). Here the solids composition was analyzed inhouse using nuclear magnetic resonance spectroscopy. The samples were prepared by extracting the condenser mass from the glass wool using acetone. The acetone was distilled off and a small amount of the residual solid was dissolved in deuterated chloroform (99.8% pure, Aldrich Chemical) prior to use in the NMR analysis.

## Results and Discussion

The results of the first series of experiments are summarized in Table 1. From those results, it can be seen that 1,10-decanediol was detected in the condenser material at levels exceeding our expectations. This implies that the condenser temperature chosen from Figures 1 and 2, $T_C$, was too high. The 1,10-decanediol solubility at $T_C$ is lower than at $T_E$. The reverse situation is required to obtain pure benzoic acid in the condenser material. These experiments established the important fact that the condenser temperature used was too high if pure benzoic acid is the objective in the condenser material.

The condenser temperature for the second series of experiments was reduced to 326 K, close to the predicted 1,10-decanediol solubility peak shown on Figure 1. The results of the second series of experiments are summarized in Table 2. The experimental data are shown in Figures 5 and 6 together with the model calculations for 1,10-decanediol and benzoic acid respectively. Runs 9, 10 and 11 uniformly showed the mole fraction of benzoic acid in the condenser material to be greater than 99.6% purity.

The chemical analyses of the materials for these series 2 runs were done using nuclear magnetic resonance spectroscopy. Outputs from the instrument for various material samples are shown in Figure 7. All of the protons that resonate between 1 to 4 ppm are associated with 1,10-decanediol and the protons resonating between 7 to 9 ppm are associated with the benzoic acid. The hydroxyl protons of both benzoic acid and 1,10-decanediol resonate farther down field than 10 ppm and are not shown in these figures. The peak at 1.3 ppm is specifically associated with the 12 chemically similar methylene protons in the center of the 1,10-decanediol molecule and is the strongest signal when present. Figure 7a is an NMR trace of a control mixture of benzoic acid and 1,10-decanediol with a known benzoic acid mole fraction of 0.9954. Figure 7b is an NMR trace of condenser material taken from a series 2 experiment. A comparison of Figures 7a and 7b shows that the purity of benzoic acid collected from the condenser for the series 2 experiment (run #11) is greater than that of the 99.54% standard shown. The other runs (9 and 10) looked virtually identical. Figure 7c shows the NMR trace of the material collected in the collection vessel for run #11. Significant amounts of 1,10-decanediol are present.

Although we purged the system at the end of each experiment to minimize 1,10-decanediol contamination by the remaining

Table 2. Experimental Results for Series #2

| Run | System Pres. bar | Moles of $CO_2$ Used | Extractor Temp. K | Condenser Temp. K | Condenser Mass g | Condenser Benzoic Acid Mole Fraction | Collector Mass g | Collector Benzoic Acid Mole Fraction |
|---|---|---|---|---|---|---|---|---|
| 9 | 126.9 | 15.1138 | 301.9 | 326.5 | 0.4251 | 0.9969 | 2.4468 | 0.9344 |
| 10 | 127.6 | 14.8131 | 302.2 | 326.5 | 0.3751 | 0.9971 | 2.2835 | 0.9389 |
| 11 | 127.4 | 14.7386 | 302.2 | 326.5 | 0.3852 | 0.9969 | 2.3889 | 0.9323 |

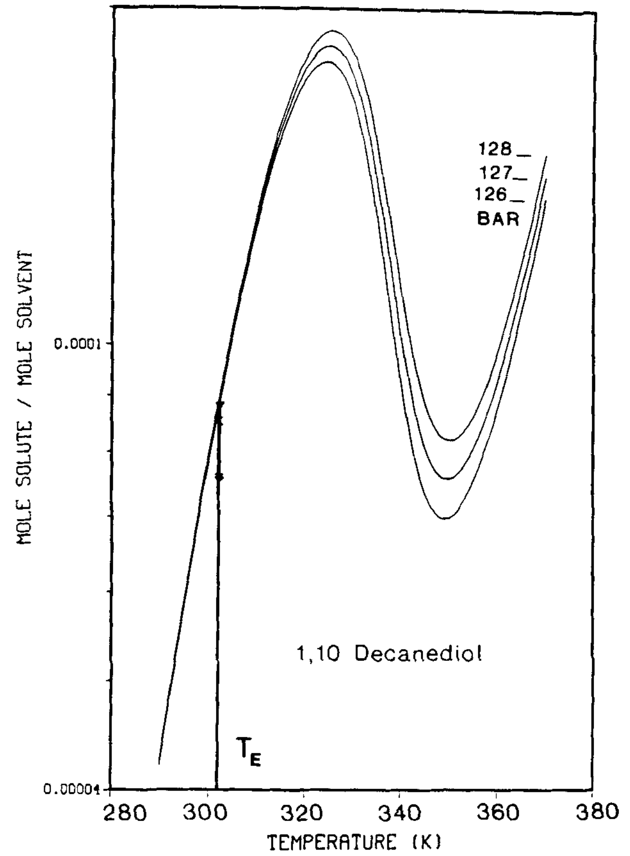

**Figure 5. Model calculations (solid line) and data for the second series of experiments.**

◇, ▽, x, + represent data for 1,10-decanediol

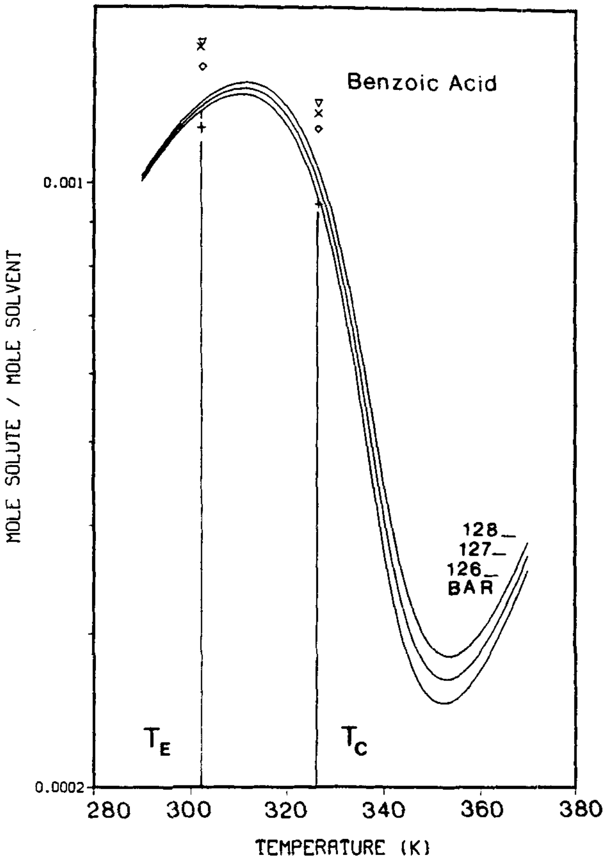

**Figure 6. Model calculations (solid line) and data for the second series of experiments.**

◇, ▽, x, + represent data for benzoic acid

fluid in the condenser, there are other possible sources for further contamination. The line from valve V4 and the pressure gauge line both contain stagnant fluid with some 1,10-decanediol. Upon depressurization, this fluid expands and passes over the condensed material, possibly leaving some 1,10-decanediol behind. From a qualitative viewpoint, the samples collected in the condenser from series 1 and series 2 experiments were also different. In the first series (condenser temperature 335 K), the condenser solids collected were white and appeared as a mixture of fine particles and small needle-like crystals. In the second series (condenser temperature 326 K), the material collected was completely transparent with large "quartz-like" crystal spars.

From Tables 1 and 2, it can be seen that much less mass was collected in the condenser for the series 2 experiments than for the series 1. Table 3 shows equation of state calculations for the percentage of extracted mass that ends up in the condenser and the purity of this material. These calculations were done for various condenser temperatures in the BDC system with the extractor temperature at 302 K and 127 bar pressure. The equation of state calculations show that the percentages of extracted mass that end up in the condenser for series 1 and series 2 experiments are 45.32% and 15.05%, respectively. These should be compared to the experimental average values of 50.17% and 14.94%. As the condenser tmperature increases, a point is reached at which the benzoic acid becomes retrograde. Beyond this point, pure benzoic acid is deposited and the yield of material in the condenser increases. At a higher temperature, 1,10-decanediol begins to deposit; and while the yield of condensed material increases with temperature, the purity of benzoic acid progressively decreases with temperature so that there is a tradeoff between the two quantities—yield and purity. Exactly where to make this tradeoff, thereby establishing the condenser operating temperature, will depend upon the requirements of the particular separation at hand. Obviously at high enough temperatures there will be no deposition of material in the condenser, but clearly this situation is of no practical interest.

## Conclusion

This paper describes the experimental apparatus and technique used to study a chemical separation process using cross-

**Table 3. Calculated Yield-Purity Factors in the BCD System**

| Condenser Temp. g | Mass Condensed/ mol $CO_2$ g | mol Fraction Benzoic Acid % | % Yield of Mass Extracted/mol $CO_2$ |
|---|---|---|---|
| 317 | 0 | — | — |
| 326 | 0.0248 | 1.0 | 15.05 |
| 335 | 0.0746 | 1.0 | 45.32 |
| 344 | 0.1110 | 0.9946 | 67.43 |
| 353 | 0.1187 | 0.9888 | 72.13 |
| 362 | 0.1129 | 1.0 | 68.57 |

$T_E$ = 302 K, Pressure 127 bar.

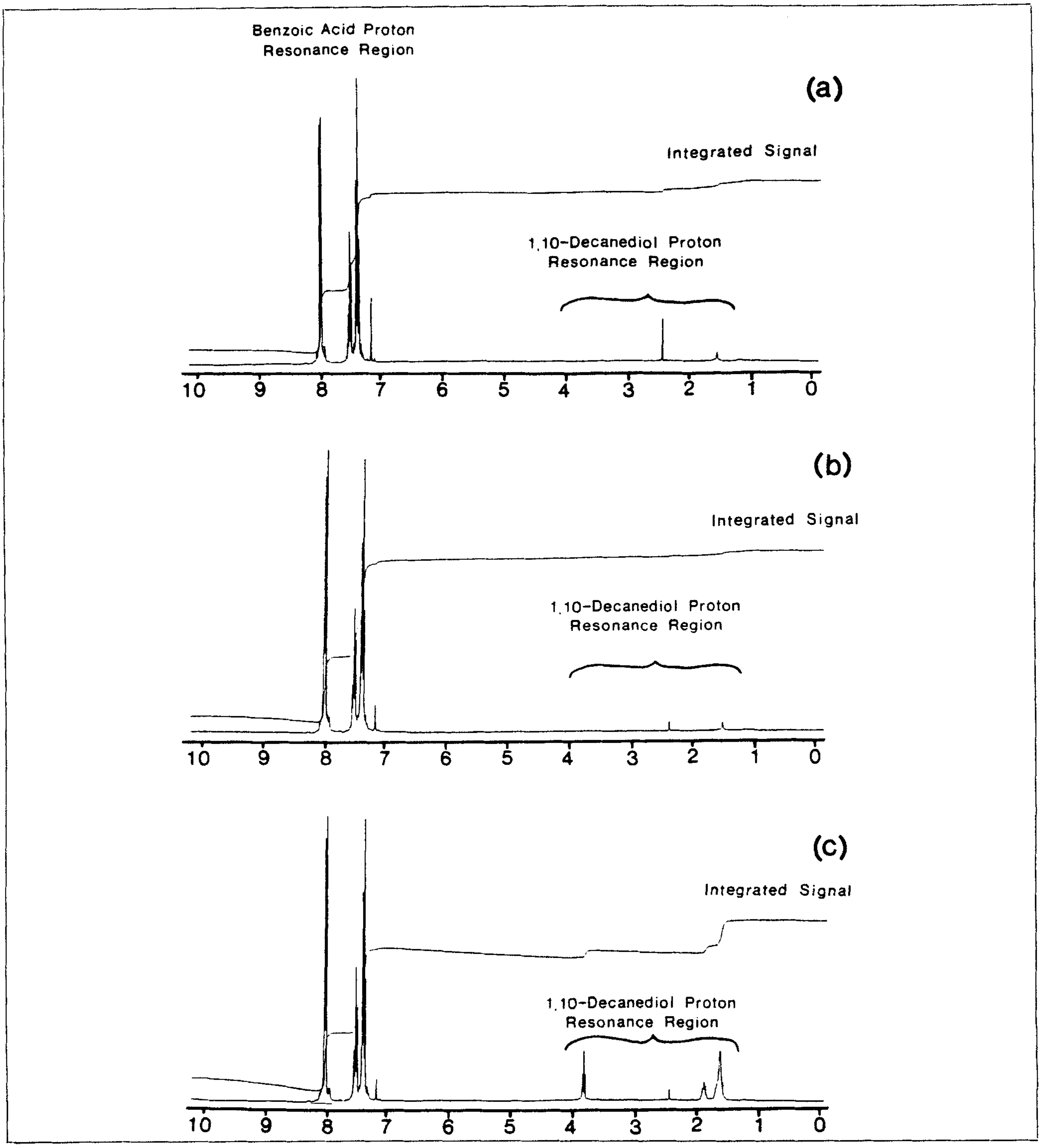

**Figure 7. Comparative NMR traces of mixtures of benzoic acid and 1,10-decanediol.**

over phenomena in a supercritical fluid. The BCD system served as the paradigm, since it has fairly wide crossover regions. The data presented establish that it is possible to separate essentially pure benzoic acid from a solid mixture of benzoic acid and 1,10-decanediol in one temperature cycle. The initial process operating conditions were estimated based upon equation of state calculations using a perturbed hard sphere model. However, these equations are not sufficiently accurate in the near critical region and process data are ultimately required to fix suitable operating conditions. This is an iterative procedure, as described in this paper, involving the interplay between both theoretical calculations and experiments.

Based upon these results, the crossover concept should in principle be applicable to other systems displaying analogous behavior to the BCD system. In the quest for a practical technology based upon the crossover idea, we feel that very high-value product separations represent the most likely areas of success.

## Acknowledgment

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## Literature Cited

Chimowitz, E. H., F. D. Kelley, and F. M. Munoz, "Analysis of Retrograde Behavior and the Crossover Effect in Supercritical Fluids," *Fluid Phase Equil.* **44,** 23 (1988).

Chimowitz, E. H., and K. P. Pennisi, "Process Synthesis Concepts for Supercritical Gas Extraction in the Crossover Region," *AIChE J.*, **32,** 1665 (1986).

Dibenedetti, P. G., and S. K. Kumar, "The Molecular Basis of Temperature Effects in Supercritical Extraction," *AIChE J.*, **39,** 645 (1988).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and S. Kim, "Solute Partial Molal Volumes in Supercritical Fluids," *J. Phys. Chem.*, **86,** 2738 (1986).

Johnston, K. P., S. E. Barry, N. K. Read, and T. R. Holcomb, "Separation of Isomers Using Retrograde Crystallization from Supercritical Fluids," *Ind. Eng. Chem. Res.*, **26,** 2372 (1987).

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