DISCUSSION

Computer simulations were used to analyze the isothermal stability behavior of a CSTBR using a simple empirical growth model. Phase-plane analysis showed that when the reactor was controlled to a naturally unstable steady state and the manipulated variable was sufficiently constrained, as many as five steady states were possible. Two new unstable steady states appeared corresponding to those at each of the controller constraints. The consequence of this was to change the nature of the control at the desired point from one which is globally stable without constraints, to one which is only locally stable.

Using a digital computer for control and a laboratory continuous flow reactor in which methanol-utilizing organisms were cultured, this behavior was investigated experimentally. Results showed that PI control with constraints was possible and that the closed-loop system was not globally stable. Cascade control was implemented to demonstrate the existence of the unstable steady states at the constraints. The metastable nature of these points was indicated.

The steady state results were in good agreement with predictions from the simple model and were consistent with results expected from a conceptual model of methanol metabolism discussed elsewhere (DiBiasio et al., 1981b). The difference between experimental and simulation controller constants is a reflection of model deficiencies in predicting transient behavior. Other interesting dynamic behavior was observed which was not predicted, and this will be discussed in a later report.

NOTATION

D = dilution rate (volumetric flow rate/reactor volume) 1/h
D^- = lower dilution rate constraint, 1/h
D^+ = upper dilution rate constraint, 1/h
K_{c_i} = proportional control constant ($i = 1,2$)
S = substrate (methanol) concentration, W/V %
S_f = feed substrate concentration, W/V %
X = cell concentration, W/V %
X_{sp} = setpoint to inner control loop, W/V %
X_d = setpoint to cascade control loop, W/V %

Subscripts

s = denotes steady state value

Greek Letters

μ = specific growth rate, 1/h
$\sigma\cdot$ = specific substrate consumption rate, 1/h
τ_I = integral control constant, h

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Supercritical Fluid Extraction with Mixed Solvents

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In recent years there has been a revival of interest in supercritical fluid extraction, i.e., in the separation of condensed-phase mixtures by extraction, using a compressed gas (rather than a liquid) as the selective solvent (Schneider et al., 1980). Pertinent phase equilibria have been reported by numerous authors, including, for example, Mackey and Paulaitis (1979), Johnston and Eckert (1981), Kurnik and Reid (1981), and Kurnik et al. (1981). Since the density of a fluid near its critical point is sensitive to small changes in pressure and temperature and since solubility is strongly dependent on the solvent's density, it is sometimes attractive to use a fluid near its critical state as an extraction solvent because solvent regeneration is then easily achieved.

Most phase-equilibrium studies related to supercritical extraction have been restricted to single-solvent systems. However, under certain conditions, it may be advantageous to use a mixed solvent. This paper discusses some of the fundamental considerations leading to such advantages and presents a few examples.

ADVANTAGES OF MIXED SOLVENTS

To minimize operating costs in a continuous extraction process, it is desirable to keep solvent flows as low as possible. Low solvent flows require high solubility of the solute in the gaseous solvent.

Since the vapor pressure of a condensed component always rises with temperature, it is frequently desirable to operate supercritical extraction at as high a temperature as possible, subject to other considerations such as thermal stability. However, for maximum solubility it is also desirable to operate at a temperature close to (usually slightly above) the critical temperature of the solvent because it is in the critical region of the solvent where the particular advantages of supercritical extraction are maximized. Using a single solvent, it is not often possible to meet both desired operating conditions.

For example, suppose we have a condensed component whose thermal-stability properties are such that the maximum allowable operating temperature is 341 K. We would then want to use a solvent whose critical temperature is about 335 K. There is no suitable single solvent which meets that requirement but it is possible to use a solvent mixture whose effective critical temperature is at the desired level. The critical temperature of carbon dioxide is 304 K; that of propane is 370 K. Depending on composition, a mixture of carbon dioxide and propane could provide an optimum solvent at 341 K.

Another advantage of a mixed solvent may be achieved through the entrainer effect where a relatively small amount of a second solvent is added to a primary solvent to raise the solute's solubility through preferential intermolecular forces, such as hydrogen-bonding. For example, suppose we want to extract benzoic acid at 394 K. A possible primary solvent is propane. (Butane is not suitable because its critical temperature is too high, 425 K.) To enhance the solubility of benzoic acid, it is advantageous to add to propane a small amount of some volatile fluid which can hydrogen-bond with benzoic acid. Particularly desirable would be a fluid which hydrogen-bonds with benzoic acid but not with itself. Possible candidates are ammonia, sulfur dioxide and dimethyl ether. These fluids cannot be used as primary solvents because their critical temperatures are too high.

THERMODYNAMIC ANALYSIS

Consider a solid material i which is to be dissolved in a dense-gas solvent at temperature T and pressure P. Assuming that the solvent is not soluble in the solid phase, the only equation of equilibrium is

$$f_i^{s} = f_i^{v} \tag{1}$$

where f is fugacity and where superscripts s and v denote solid phase and vapor phase, respectively.

If solid i is pure and incompressible,

$$f_i^{s} = P_i^s \phi_i^s \exp\left[v_i^{s} \frac{(P - P_i^s)}{RT}\right] \tag{2}$$

where P_i^s is the saturation (vapor) pressure, ϕ_i^s is the fugacity coefficient at saturation (ϕ_i^s is often very close to unity) and v_i^{s} is the molar volume, all at system temperature T.

The fugacity of i in the vapor phase is given through fugacity coefficient ϕ_i and vapor-phase mole fraction y_i,

$$f_i^v = \phi_i y_i P \tag{3}$$

The fugacity coefficient is obtained from an equation of state for the gas-phase mixture containing component i and any number of gaseous solvents as discussed elsewhere (Prausnitz 1969). (If component i is not a pure solid but in a condensed-phase mixture, well-known modifications in Eq. 2 are required. Further, if component i is in a liquid phase, consideration must be given to the solubilities of the gaseous solvents in that liquid phase. In that event there are m equations of equilibrium in addition to Eq. 1, where m is the number of gaseous solvents.)

ILLUSTRATIVE EXAMPLES

While experimental data are now available for a variety of solutes in single gaseous solvents (mostly carbon dioxide or ethylene), such data are rare in solvent mixtures. To illustrate possible advantages of mixed solvents, we present some calculated results. Lacking experimental verification, these calculated results are necessarily approximate but the trends, which are of importance here, are probably reliable.

We calculate fugacity coefficient ϕ_i using Chueh's modification of the Redlich-Kwong equation (Chueh and Prausnitz, 1967):

$$\ln\phi_i = \ln\frac{v}{v-b} + \frac{b_i}{v-b} - \frac{2}{RT^{3/2}b}\left(\sum_{l=1}^{m+1} y_l a_{il}\right)\ln\frac{v+b}{v} + \frac{ab_i}{RT^{3/2}b^2}\left(\ln\frac{v+b}{v} - \frac{b}{v+b}\right) - \ln\frac{Pv}{RT} \tag{4}$$

where v is the molar volume of the mixture at P and T and where the summation is for all components, including i. Constants a and b, given by conventional mixing rules, are evaluated using the procedure described by Chueh.

Figure 1 shows calculated solubilities for phenanthrene at 341 K. Since the normal melting point is 374 K, we expect that at 341 K and at the pressures indicated, no liquid phase is present, consistent with the results of Johnston and Eckert (1981) who reported the solubility of solid phenanthrene in ethylene at 343 K. Figure 1 shows that, at high pressures, the solubility of phenanthrene in mixtures of carbon dioxide and propane is one order of magnitude larger than that in carbon dioxide alone. Gaseous propane alone cannot be used as a solvent at high pressures because propane condenses at 341 K.

Figure 2 shows similar results for phenanthrene in mixtures of ethylene and propylene.

Figures 3 and 4 show calculated solubilities of benzoic acid at 394 K in mixtures of propane and a suitable entrainer. Since polar components are now included, Chueh's method can be used only for evaluating pure-component constants a and b. For all cross coefficients a_{ij} and a_{jk} (where j and k are solvents), we use the approximations

$$a_{ij} = \mathfrak{z}_{ij}(a_i a_j)^{1/2};\ a_{jk} = \mathfrak{z}_{jk}(a_j a_k)^{1/2} \tag{5}$$

For $\mathfrak{z}_{jk}$ we use unity. For $\mathfrak{z}_{ij}$ we use unity when j is propane and we use 2 when j is the entrainer.

Calculated results are sensitive to the choice of $\mathfrak{z}_{ij}$ when j is the entrainer, as shown in Table 1. We use a conservative value ($\mathfrak{z}_{ij} = 2$) which reflects the desirable property of the entrainer: the en-

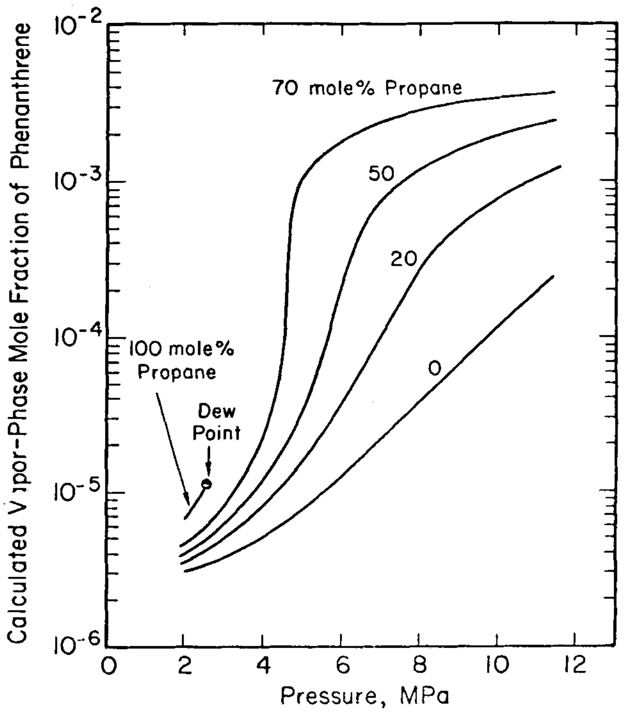

Figure 1. Calculated solubilities of phenanthrene in carbon dioxide and in mixtures of carbon dioxide and propane at 341 K.

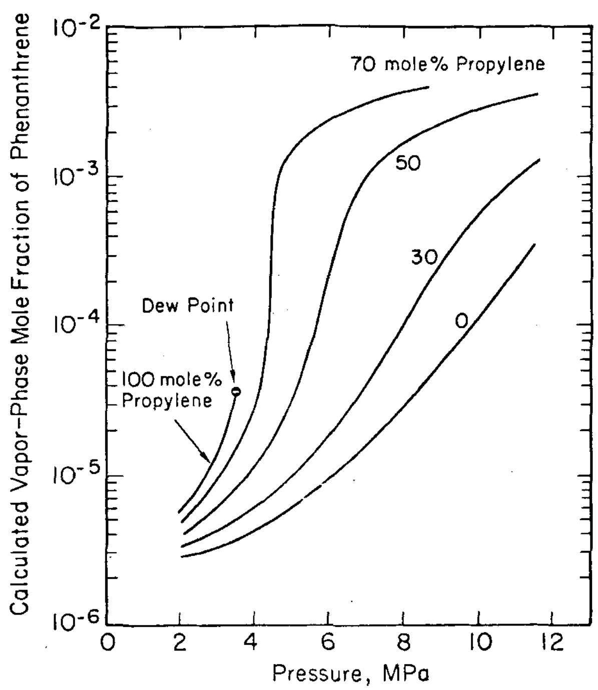

Figure 2. Calculated solubilities of phenanthrene in ethylene and in mixtures of ethylene and propylene at 341 K.

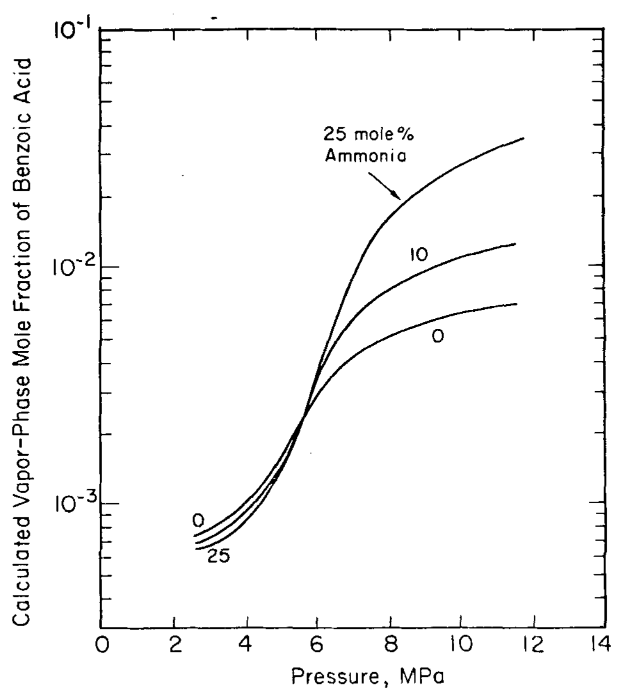

Figure 4. Calculated solubilities of benzoic acid in propane and in mixtures of propane and ammonia at 394 K.

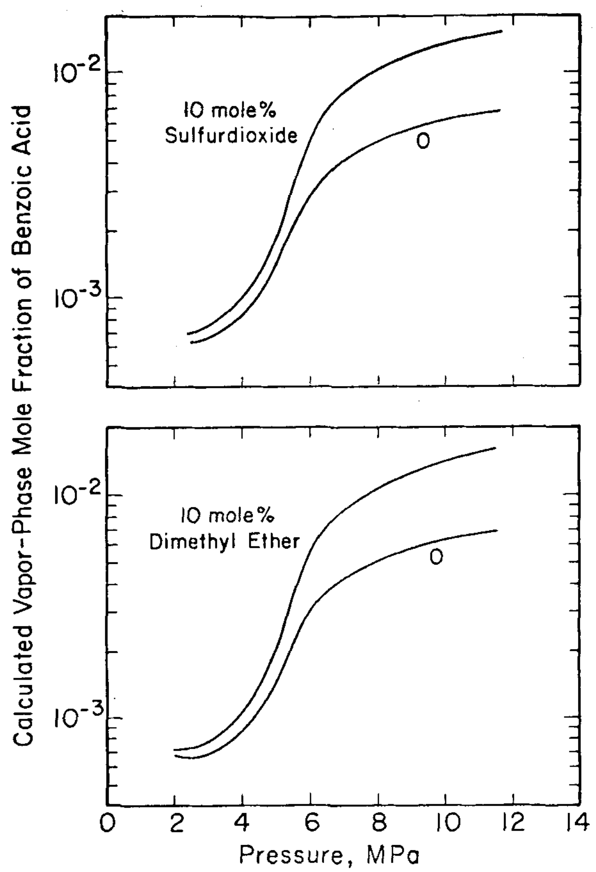

Figure 3. Calculated solubilities of benzoic acid in propane and in mixtures of propane with sulfur dioxide or dimethyl ether at 394K.

TABLE 1. EFFECT OF $\mathfrak{z}_{ij}$ ON CALCULATED VAPOR-PHASE MOLE FRACTION OF BENZOIC ACID (i) IN A 90–10 MOL % MIXTURE OF PROPANE-SULFUR DIOXIDE (j) AT 394 K

Pressure, MPa	Mole Fraction Benzoic Acid in Vapor·10^3		
	$\mathfrak{z}_{ij}$ = 1.5	2.0	2.5
4	0.918	1.02	1.13
5	1.59	1.87	2.19
6	4.06	5.20	6.67
7	6.26	8.41	11.3

trainer does not hydrogen-bond with itself but it does hydrogen-bond with benzoic acid. When j is the entrainer, it is likely that $\mathfrak{z}_{ij}$ is much larger than 2. Solubility rises rapidly with $\mathfrak{z}_{ij}$ as indicated in Table 1.

The calculations shown here assume that, at the conditions indicated, the only phases present are a (pure) solid and a gas. That assumption may not be valid because, at high pressures, the phase diagram of a binary (or ternary) system (containing one solid and one or two gases) may become complex, including a liquid phase. Little is known about these phase diagrams but a striking example has been presented by Van Welie and Diepen (1961) who showed that for ethylene-naphthalene a liquid phase appears at high pressure and 320 K, 33° below the normal melting point of naphthalene. Paulaitis (1982) indicates that for carbon dioxide-naphthalene at high pressures, a liquid phase appears at 325 K.

In our calculations we have estimated the dew point of the (subcritical) solvent k from the relation

$$\phi_k y_k P = [P^s \phi^s \exp(v^L(P - P^s)/RT)]_{\text{pure } k} \qquad (6)$$

where v^L is the molar liquid volume and P^s is the saturation (vapor) pressure.

The examples presented here suggest that, in a continuous extraction process, solvent flows can be significantly decreased by careful selection of mixed solvents. Since solvent flow is often a critical design parameter, mixed solvents may offer important economic advantages in supercritical fluid extraction.

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NOTATION

a,b = constants in the Redlich-Kwong equation of state for the mixture

f = fugacity
m = number of solvents
P = total pressure
R = gas constant
T = temperature
v = molar volume
y = mole fraction in gas phase
$\mathfrak{z}_{ij}$ = binary constant

Greek Letters

ϕ = fugacity coefficient

Superscripts

L = liquid phase
$\mathscr{s}$ = solid phase
s = saturation
v = vapor phase

Subscripts

i = solid component
j = gaseous solvent
k = gaseous solvent
l = any component

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