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M. Tietz, D. Dimitrelis, and J.M. Prausnitz

November 1986

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**THE EFFECT OF AN AQUEOUS ENTRAINER ON PHASE EQUILIBRIA FOR
SUPERCRITICAL EXTRACTION OF HEAVY FOSSIL FUELS WITH PROPANE**

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ABSTRACT

For many years, extraction with propane has been applied in the petroleum industry at conditions near propane's critical. Efficient design of this process requires knowledge of pertinent phase equilibria. For this purpose, continuous thermodynamics and the Perturbed-Chain equation of state provide suitable tools.

We present here calculations giving the effect of small amounts of water on the phase equilibria for supercritical extraction of heavy fossil fuels with propane. It is shown that water is not a suitable entrainer, since it decreases separation efficiencies in most cases.

Further, we indicate that in some cases, supercritical-fluid extraction may provide advantages for solvent recovery. In other cases, common liquid-liquid extraction is superior.

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I. INTRODUCTION

1. Supercritical-Fluid Extraction

Supercritical-fluid extraction is a separation process that has attracted wide attention in recent years. This process operates at a temperature and pressure slightly above the critical of the solvent. In the critical region, the solvent's properties are sensitive to slight changes in temperature or pressure. This sensitivity may be useful for minimizing energy requirements and may facilitate solvent recovery.

Supercritical-fluid extraction was first mentioned by Hannay and Hogarth in 1879. But it was not applied on an industrial scale until many years later.

The most common supercritical solvents are carbon dioxide, ethylene and propane. Well-known applications are decaffeination of coffee, upgrading of residual oils, and extraction of hops for beer production.

For our purposes, the critical region exists in the temperature range $0.9 < T/T_{crit} < 1.2$ and at pressures greater than the critical pressure. In this critical region, the density and the solvent power of the fluid are liquid-like whereas the viscosity and the mass-transfer resistance resemble those in gases rather than those in liquids (McHugh and Krukoni, 1986). Therefore, supercritical-fluid extraction requires smaller extraction columns than those used in common liquid extraction.

In the critical region, a small change in pressure and/or temperature changes fluid properties drastically, sometimes by more than one order of magnitude. As an example, Figure (1.1) shows the solubility of naphthalene in carbon dioxide. At low pressures, the solubility is poor similar to that in a gas. At high pressures, the solubility is about one hundred times greater and reaches values that are typical for liquid solvents.

Solubility increases sharply within a small pressure range. At higher temperatures, this increase moves to higher pressures. Hence it is possible to recover the solvent easily by a slight increase in temperature or by slight

decrease in pressure, or both. Small changes in temperature and/or pressure allow a simpler separation step following the extraction and also may help to conserve energy. Figure (1.2) shows schematically a simple supercritical-extraction process.

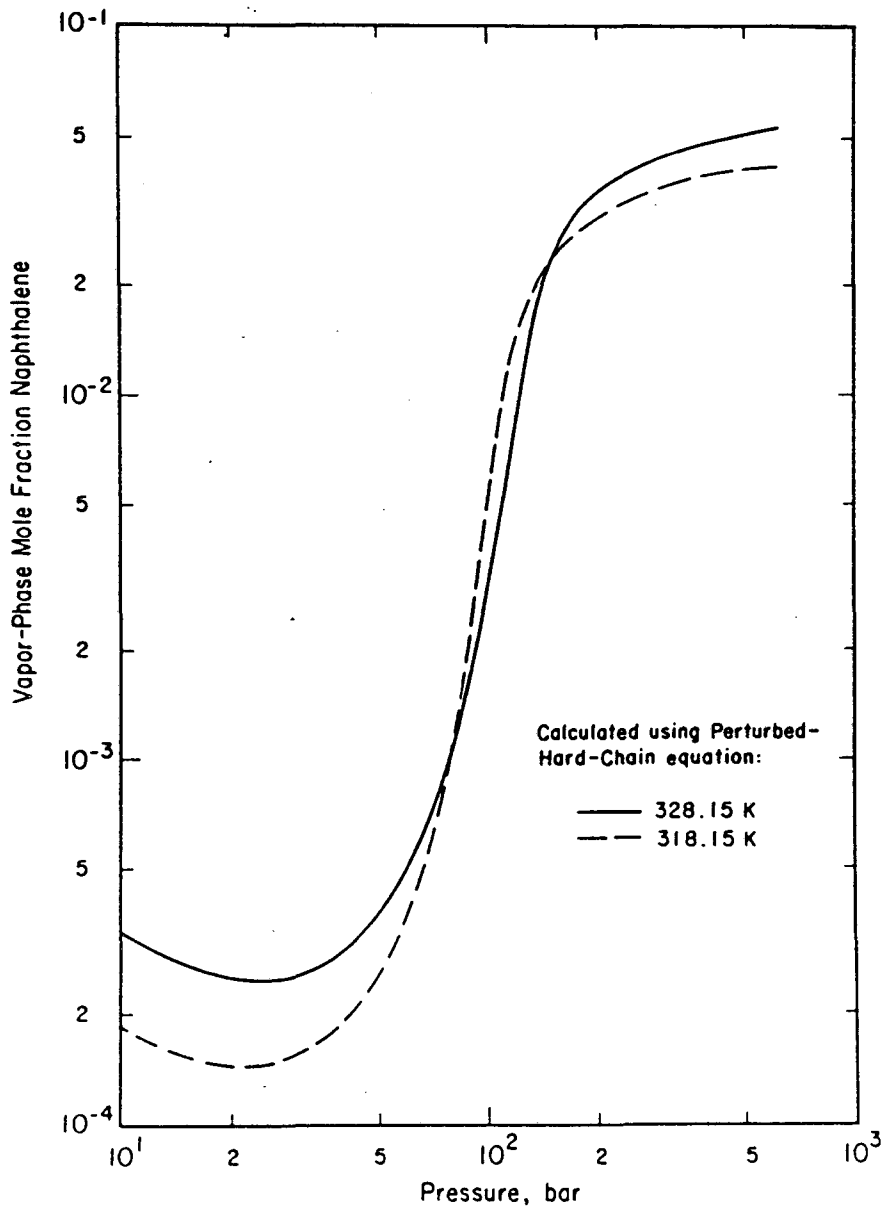


Figure (1.1): Solubility of naphthalene in carbon dioxide.

2. Scope

Supercritical-fluid extraction has found application in the petroleum industry. Efficient design and operation of this separation process require phase equilibria for the pertinent fluid mixtures.

This work studies phase equilibria for heavy fossil fuels with propane. The novel feature of this work is a critical examination of the use of water as an entrainers. Here, the most important issues are the change of capacity (solubility) and selectivity by adding small amounts of water to propane.

Since oils contain very many components, it is not possible to determine the concentration of each component. Therefore, we use continuous thermodynamics to calculate phase equilibria for mixtures containing oils. The Perturbed-Hard-Chain equation of state is used. The necessary binary parameters are obtained from data reduction. Finally, two examples are shown to illustrate the use of continuous thermodynamics and the Perturbed-Hard-Chain equation of state for process design.

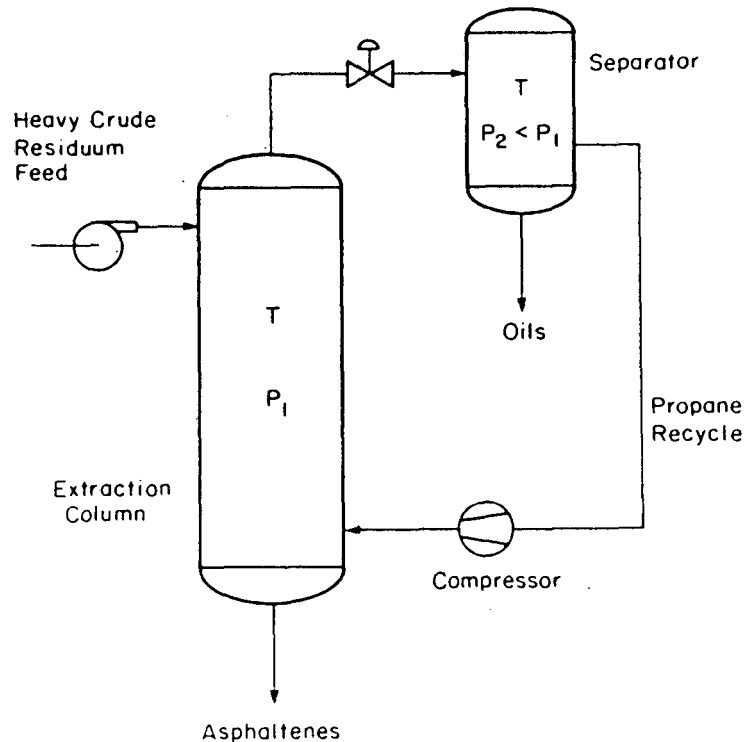


Figure (1.2): Supercritical extraction process.

II. THERMODYNAMIC ANALYSIS

1. Phase-Equilibrium Problems

We consider two coexisting phases in equilibrium. Temperature T , pressure P and chemical potential μ_i for each component i must be equal for both phases ' and ":

$$T' = T'' , \quad (1.1)$$

$$P' = P'' , \quad (1.2)$$

$$\mu_i' = \mu_i'' , \text{ for all } i. \quad (1.3)$$

Instead of the chemical potential we can express equation (1.3) in terms of fugacities:

$$f_i' = f_i'' , \text{ for all } i. \quad (1.4)$$

Provided we have an expression for the fugacity as a function of temperature, pressure and composition \underline{x} , $f = f(T, P, \underline{x})$, we can calculate the composition of a phase " that is in equilibrium with a given phase '.

Given T and \underline{x} , for a mixture containing n components, we have n equations (1.4) to calculate the $n-1$ unknown concentrations y_i and the pressure P ; here x is the mole fraction in the liquid phase and y is the mole fraction in the vapor phase. For vapor-liquid equilibria this is a bubble-point calculation.

However, we can also consider a mixture with concentration \underline{z} that will separate into two phases at fixed T and P and ask for the compositions of both phases. In addition to the n equations (1.4) we have $n-1$ mass balances of the form

$$z_i = \xi \cdot y_i + (1-\xi) \cdot x_i \quad (1.5)$$

where ξ is the vaporized fraction.

With these $2n-1$ independent equations we can calculate the $2n-2$ unknown

concentrations ($n-1$ for each phase) and the vaporized fraction ξ . These equations have to be solved simultaneously. This is called a flash calculation, shown in Figure (1.1).

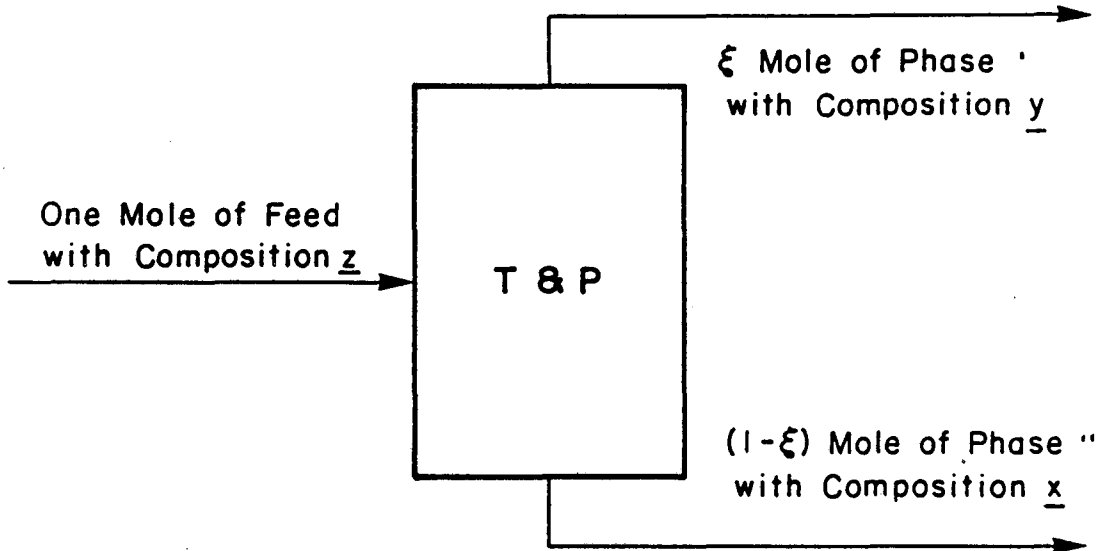


Fig. (1.1): Isothermal, isobaric flash

2. Continuous Thermodynamics

In conventional (discrete) thermodynamics, a multicomponent mixture is characterized by the mole fractions x_i for all components i . If the mixture, however, contains very many components (e.g. 50 or more, as in heavy fossil fuels regarded in this work), it becomes difficult or impossible to obtain all mole fractions. In this case it may be advantageous to describe the mixture by a continuous distribution function F . For the concentrations x_i ($i = 1 \dots n$) we substitute the distribution function $F(I)$ as shown in Figure (2.1). Here I is the distribution variable that replaces the component number i .

The normalization condition $\sum_{i=1}^n x_i = 1$ becomes $\int_I F(I) dI = 1$.

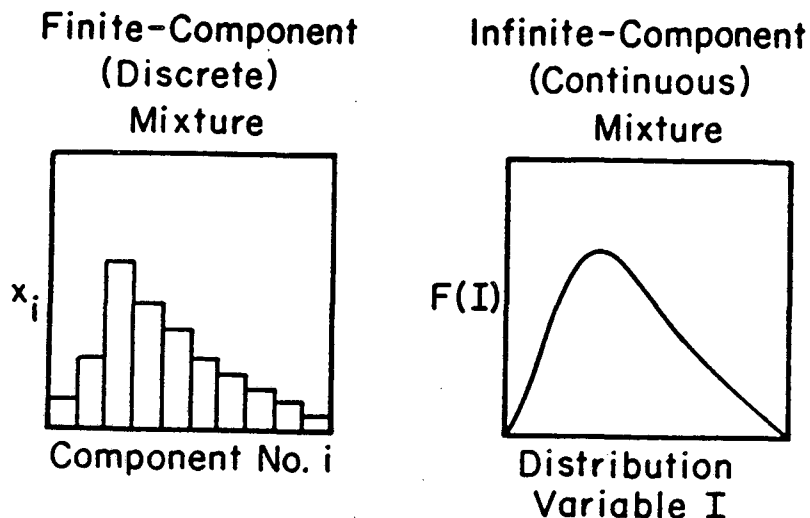


Fig. (2.1): Discrete and continuous mixtures.

The equilibrium condition (1.4) becomes

$$f'(I) = f''(I) , \quad \text{for all } I, \quad (2.1)$$

where f is now a function of pressure, temperature and the distribution function:

$$f = f(T,P,F(I)) . \quad (2.2)$$

We have to choose an appropriate distribution variable I . This might be the normal boiling point, the molecular weight, the aromaticity, or any other physical property that distinguishes the components. It might be necessary to choose more than one distribution variable, e.g. the molecular weight and the aromaticity, to characterize a mixture sufficiently. But that does not change the fundamental equations.

Having chosen the distribution variable I (or all distribution variables I, J, \dots) we must next determine the function $F(I)$. For a given I , $F(I)\Delta I$ is the fraction of molecules of the mixture that are characterized by the range I to $I+\Delta I$. Here F is the probability density function.

The flash calculation, however, stays the same. The material balance has to be satisfied for all I:

$$F^{\text{Feed}}(I) = \xi \cdot F''(I) + (1-\xi) \cdot F'(I) \quad (2.4)$$

Equations (2.2) and (2.4) determine the two distribution functions F' and F'' . In general, these distribution functions can only be obtained numerically.

3. Equation of State

To solve phase-equilibrium problems using Equation (1.4) we must calculate the fugacity coefficient ϕ for each component and each phase, since $f_i = y_i \cdot P \cdot \phi_i$. The fugacity coefficients can be obtained from an equation of state.

An equation of state is a function that relates pressure P to temperature T , molar volume v , and mole fractions x_i . These mole fractions x_i can be replaced by the mole numbers n_i , since $x_i = n_i/n_T$, where n_T is the total number of moles. Provided we have an expression for the residual Helmholtz energy, we obtain the equation of state by differentiating with respect to the volume:

$$P(T, V, \underline{n}) = \frac{n_T \cdot R \cdot T}{V} - \left(\frac{\partial A^R}{\partial V} \right)_{T, \underline{n}} \quad (3.1)$$

where V is the total volume. The residual Helmholtz energy is the difference between the Helmholtz energy of the real fluid and that of an ideal gas at the same temperature, density and composition.

We then can calculate the fugacity coefficient of component i by differentiating with respect to the mole number of this component:

$$\ln \phi_i = \left(\frac{\partial A^R / (R \cdot T)}{\partial n_i} \right)_{T, V, n_j} - \ln Z \quad (3.2)$$

where

$$Z = \frac{P \cdot V}{n_T \cdot R \cdot T} \quad (3.3)$$

For continuous mixtures, we replace the concentration by the distribution function. Hence, Equation (3.2) becomes

$$\ln \phi(I) = \left(\frac{\delta A^F / (R \cdot T)}{\delta (n_T \cdot F(I'))} \right)_{T, V, F(I'=I)} - \ln Z, \quad (3.4)$$

where δ indicates the functional derivative.

The chemical potential can also be obtained from the residual Helmholtz energy. This is shown in Appendix 6.

4. Solid-Fluid Equilibrium

We consider two examples of phase-equilibrium calculations. The simplest case is the solubility of a pure solid in a supercritical fluid.

The fugacity for component i in the fluid phase (F) is

$$f_i^F = y_i \cdot \phi_i^F \cdot P \quad (4.1)$$

where ϕ_i is the fugacity coefficient and y_i the mole fraction in the fluid phase.

The solid phase is assumed to be pure, i.e. the solubility of the volatile component in the solid component is zero. The fugacity of the solid component is

$$f_2^S = P_2^{\text{sat}} \cdot \phi_2^{\text{sat}} \cdot \exp \left\{ \int_{P_2^{\text{sat}}}^P \frac{v_2^S}{R \cdot T} dP \right\} \quad (4.2)$$

Here 2 stands for the solid component. P_2^{sat} is the saturation (sublimation) pressure of component 2 at the given temperature T , ϕ_2^{sat} is the fugacity coefficient in that state and v_2^S is the molar volume of the solid.

The exponential term in Equation (4.2) is often called the Poynting correction. If we assume the solid to be incompressible, the correction becomes

$$\exp \left\{ \frac{v_2^S \cdot (P - P_2^{\text{sat}})}{R \cdot T} \right\} .$$

At moderate pressures (say $P < 20$ bar) the Poynting correction is close to unity. However, at elevated pressures (or very low temperatures) the Poynting correction becomes important.

Since the sublimation pressure of the solid component is often very small, fugacity coefficient ϕ_2^{sat} is close to unity. Hence equation (1.4) becomes

$$y_2 \cdot \phi_2^F \cdot P = P_2^{\text{sat}} \cdot \exp \left\{ \frac{v_2^S \cdot (P - P_2^{\text{sat}})}{R \cdot T} \right\} . \quad (4.3)$$

Here T and P are given and v_2^S and P_2^{sat} are temperature-dependent properties of the solid. ϕ_2^F is obtained from an equation of state as shown in chapter 3. Solubility y_2 is then found from Equation (4.3).

5. Liquid-Fluid Equilibrium

Next we consider the more general case of the solubility of a liquid in a supercritical fluid. We can no longer assume that the more volatile component does not dissolve in the liquid phase, since this solubility is often considerable. We use equation (4.1) for both phases and both components:

$$y_1 \cdot \phi_1^F \cdot P = x_1 \cdot \phi_1^L \cdot P$$

or

$$y_1 \cdot \phi_1^F = x_1 \cdot \phi_1^L \quad (5.1)$$

where superscript L and mole fraction x refer to the liquid phase.

In this case, for a binary mixture, we require four fugacity coefficients from an equation of state, two for each component. Then we can calculate the compositions of the liquid and fluid phases.

The fugacity coefficients are a function of temperature, pressure and composition. Equation (5.1) must be solved by iteration.

III. THE PERTURBED-HARD-CHAIN EQUATION OF STATE

1. Perturbed-Hard-Chain Theory for Pure Components

The Perturbed-Hard-Chain Theory was developed by Beret and Prausnitz (1975) and extended to mixtures by Donohue and Prausnitz (1977, 1978). Cotterman, Schwarz, and Prausnitz (1986) included polar effects and suggested a separation into low-density and high-density contributions.

In 1873, van der Waals separated the residual Helmholtz energy into a reference term that accounts for repulsive intermolecular forces and a perturbation term that accounts for attractive forces:

$$a^r = a^{\text{ref}} + a^{\text{pert}} \quad (1.1)$$

The lower case a indicates a molar Helmholtz energy.

For the reference term, the Perturbed-Hard-Chain Equation uses a generalized form of the hard-sphere Carnahan-Starling (1972) equation:

$$\frac{a^{\text{ref}}}{R \cdot T} = c \cdot \frac{(3 \cdot \tau / \tilde{v} - 4) \cdot (\tau / \tilde{v})}{(1 - \tau / \tilde{v})^2} \quad (1.2)$$

where $\tau = (\pi/6) \cdot \sqrt{2} = 0.7405$ is a constant obtained from void fraction of the hexagonal-closed packing and \tilde{v} is the reduced volume.

To define the reduced volume, a temperature-dependent, soft-core diameter d is used:

$$\frac{d}{\sigma} = \frac{1 + 0.29770 \cdot \tilde{T}}{1 + 0.33163 \cdot \tilde{T} + 0.0010477 \cdot \tilde{T}^2} \quad (1.3)$$

Here σ is the hard-core diameter of a segment in a chain molecule and \tilde{T} is the reduced temperature. The volume is reduced by

$$\tilde{v} = \frac{v}{v^+} \quad (1.4)$$

where v is the molar volume and

$$v^+ = v^* \cdot \left(\frac{d}{\sigma}\right)^3, \quad (1.5)$$

$$v^* = r \cdot \sigma^3 \cdot N_{Av} / \sqrt{2}, \quad (1.6)$$

with the hard-core diameter σ and Avogadro's number N_{Av} .

The temperature is reduced using the characteristic temperature T^* :

$$\hat{T} = \frac{T}{T^*}, \quad (1.7)$$

$$T^* = \frac{\epsilon \cdot q}{c \cdot k} \quad (1.8)$$

with the external surface area per mole q . c and ϵ/k are characteristic parameters for the pure compound.

The perturbation term of the residual Helmholtz energy is separated into low-density and high-density contributions using a temperature-dependent interpolation function F with $F=0$ for $\rho \rightarrow 0$ and $F=1$ for $\rho \rightarrow \infty$:

$$a^{\text{pert}} = (1-F) a^{\text{sv}} + F a^{\text{df}}. \quad (1.9)$$

Here sv stands for second-virial (limit of low densities) and df for dense-fluid. Both terms contain dispersion and polar contributions.

For the dense-fluid dispersion term we use a perturbation expansion in reciprocal temperature for a Lennard-Jones intermolecular potential, truncated after the second-order term:

$$a^{\text{df}}_{\text{disp}} = \frac{a_1}{\hat{T}} + \frac{a_2}{\hat{T}^2}. \quad (1.10)$$

where a_1 and a_2 are universal functions of c and ϑ .

Polar contributions arise from dipolar, quadrupolar and dipolar-quadrupolar interactions:

$$a_{\text{polar}}^{\text{df}} = a^{\mu\mu} + a^{\text{QQ}} + a^{\mu\text{Q}} \quad (1.11)$$

where μ and Q are the experimental dipole and the quadrupole moments, respectively. Induction effects and higher-order polar moments are neglected.

For the low-density region, a virial expansion is used for a^{sv} , truncated after the second-virial coefficient. Thus we have

$$a^{\text{sv}} = \frac{R \cdot T}{v} \cdot (B^{\text{disp}} + B^{\mu\mu} + B^{\text{QQ}}) \quad , \quad (1.12)$$

where v is the molar volume. Induction forces and dipolar-quadrupolar forces are neglected.

To each pure compound four characteristic parameters are assigned: characteristic temperature T^* , characteristic volume v^* , Prigogine's parameter c , and potential energy per surface area ϵ/k , where k is the Boltzmann constant. Prigogine's parameter is one third of the number of external degrees of freedom.

These parameters are obtained from data reduction. T^* , v^* and c are listed for a large number of compounds by Cotterman and Prausnitz (1986). They can be estimated well within a homologous series.

2. Perturbed-Hard-Chain Theory for Discrete Mixtures

To extend the Perturbed-Hard-Chain equation of state to mixtures, we use the same equations as those for a pure component. For the parameters, we have to use suitable mixture values. They are obtained from the pure-component parameters using mixing rules. Some of these mixing rules, however, are arbitrary. They give average values for the parameters that depend on the mole fractions.

Following Cotterman and Prausnitz (1986), for the reference term (1.2), we use a mixing rule linear in mole fractions. The second-virial contribution of the perturbation term (1.12) uses a quadratic rule. An expression cubic in

mole fraction is used for the dense-fluid term (1.10). The mixing rules are listed in Appendix 1.

These mixing rules include three adjustable binary parameters, two in the dense-fluid term, k_{ij} and k_{ji} , and one in the second-virial term, k_{ij}^B . The former are fitted to binary equilibrium data; the latter, however, is determined independently from experimental second-virial cross coefficients.

Like all other equations of state of the van der Waals form, the Perturbed-Hard-Chain equation cannot describe the critical region well. Since this work describes phenomena close to the critical point of the solvent (or the mixture), it was necessary to fit pure-component parameters of the solvent to data in the critical region, as shown in Appendix 2. As a result, the accuracy of the equation decreases somewhat away from the critical region, but the critical region is described better.

3. Perturbed-Hard-Chain Theory for Continuous or Semicontinuous Mixtures

To use the Perturbed-Hard-Chain equation of state for continuous mixtures (e.g. oils), we relate the PHC parameters c , T^* and v^* to the molecular weight. For a given class of hydrocarbons, Cotterman (1985) found that v^* and $c \cdot T^*$ are linear with molecular weight and that T^* is an exponential function of the molecular weight:

$$v^* = a^{(1)} + a^{(2)} \cdot MW \quad (3.1)$$

$$c \cdot T^* = \frac{\epsilon \cdot q}{k} = a^{(3)} + a^{(4)} \cdot MW \quad (3.2)$$

$$T^* = a^{(5)} - a^{(6)} \cdot \exp(-a^{(7)} \cdot \sqrt{MW}) \quad (3.3)$$

Parameters $a^{(1)} \dots a^{(7)}$ for two classes of hydrocarbons (used to describe the oils, as shown in Chapter 3, part IV) are given in Table (3.1):

Class	a(1)	a(2)	a(3)	a(4)	a(5)	a(6)	a(7)
n-Paraffins	8.6855	0.71820	120.72	5.8408	419.86	643.89	0.19945
Fused-ring arom.	10.1030	0.51714	180.04	5.6413	1351.4	1522.3	0.04939

Table (3.1): Parameters for equations (3.1) ... (3.3).

These relations allow us to calculate $\mu(I)$ or $\phi(I)$ using the Perturbed-Hard-Chain equation of state, where $I = MW$.

IV. REPRESENTATION OF MIXTURE PROPERTIES

1. Fitting of Pure-Component Parameters

The Perturbed-Hard-Chain equation has three adjustable parameters for each pure component. These parameters have to be fitted to pure-component data. For this purpose, Cotterman and Schwarz (1986) wrote the program 'PURFIT' which uses experimental vapor-pressure, liquid-density and second-virial-coefficient data. The program uses a maximum-likelihood method. It takes into account deviations within the uncertainty of the experimental data.

For our purposes here, parameters for water and hydrocarbons do not have to be fitted to the critical point, since the region of interest is far away from their critical points. The values given by Cotterman were used. But the parameters for the solvent (propane) have to be fitted to its critical point.

For calculations in the critical region, we included the critical point as an additional experimental datum. Routine 'ECRITS' (Topliss, 1985) calculates the critical point from the equation of state. The predicted critical point is given by the conditions

$$\frac{\partial P}{\partial \rho} = \frac{\partial^2 P}{\partial \rho^2} = 0 \quad . \quad (1.1)$$

Extensive experimental data for propane are given by the National Bureau of Standards (1982). The experimental (Reid, Prausnitz and Sherwood, 1977) and predicted critical data for propane are shown in Table (1.1).

The parameters for propane in the critical region are

$$T^* = 245.69 \quad \text{K} \quad (1.2)$$

$$v^* = 0.04316 \quad \text{l/mol} \quad (1.3)$$

$$c = 1.5115 \quad (1.4)$$

Appendix 2 gives details for fitting to the critical point. Appendix 3 gives an introduction to the revised program 'PURFIT'.

	T_c , K	P_c , bar	v_c , l/mol
experimental	369.8	42.46	0.203
calculated	369.7	42.94	0.228
deviation	0.02 %	1.1 %	12 %
calc. w/o fitting to crit. pt.	376.6	47.53	0.211
deviation	1.83 %	11.9 %	4 %

Table (1.1): Calculated and experimental critical point of propane.

2. Fitting of Binary Parameters

The Perturbed-Hard-Chain equation of state uses up to three binary parameters for each binary mixture, as shown in chapter 2 of part III. These parameters are fitted to equilibrium data of the binary mixture. However, the low-density binary parameter k_{ij}^B is best fitted to second-virial-cross-coefficient data. Since this work does not include calculations in the low-density region, k_{ij}^B was set to zero unless other values were found in the literature.

Binary parameters for the dense-fluid limit can be fitted to bubble-point or dew-point data, to vapor-liquid or liquid-liquid equilibrium data or to Henry's coefficients.

Cotterman and Prausnitz (1986) give a program 'MIXFIT' that gives binary parameters. However, for this work, we changed the program.

If experimental phase-equilibrium data were to be fitted, the original program uses only first estimates of the compositions. This is satisfactory well away from critical points. But for our purposes a more reliable routine had to be used. Whenever phase-equilibrium data are fitted, a flash calculation is done, i.e. for the given temperature and pressure, the mole fractions of both phases are calculated iteratively. This routine 'FLASH' was taken from Topliss (1985). Further, to solve the equation of state for the density, routine 'DENS' (Topliss, 1985) was used. Special precautions have to be taken to obtain convergence in the critical region.

A routine was included that allows fitting of solubility data for a solid in a fluid, as indicated in chapter 4 of part II. This routine is necessary for the calculations given in Appendix 1.

An introduction of the revised program 'MIXFIT' is given in Appendix 4. With this program we fit binary parameters k_{ij} and k_{ji} to experimental data for a binary mixture.

To calculate the solubilities of oils in propane, we need binary parameters for propane with the continuous fractions of the oil. We expect the binary parameters to be a function of molecular weight.

To calculate also the effect of an entrainer, we need the binary parameters of the entrainer with propane, with paraffins and with fused-ring aromatics. The next chapters discuss procedures for fitting these parameters.

3. Characterization of Oils

As indicated in chapter 2, part II, we must first choose distribution variable I. In this work we use the molecular weight. But that is not sufficient, since there are many components with a similar molecular weight but different properties, e.g. benzene and hexane. Therefore, we consider the oil as a mixture of two continuous fractions, a fused-ring aromatic fraction and a paraffinic fraction.

Next, we have to determine the distribution functions $F(I)$ for both fractions as a function of the molecular weight. It is much easier to obtain the distribution function as a function of the boiling point, since a distillation or chromatographic analysis provides this distribution.

Using the known relation between boiling point and molecular weight, we can calculate the molecular-weight distribution from the boiling-point distribution. For a homologous series, this relation can be obtained easily. It is shown in Figure (3.1) for both fractions.

Cotterman gives the function

$$T_b/K = b^{(1)} - b^{(2)} \cdot \exp(- b^{(3)} \cdot \frac{MW}{g/mol}) \quad (3.1)$$

with the parameters given in Table (3.1).

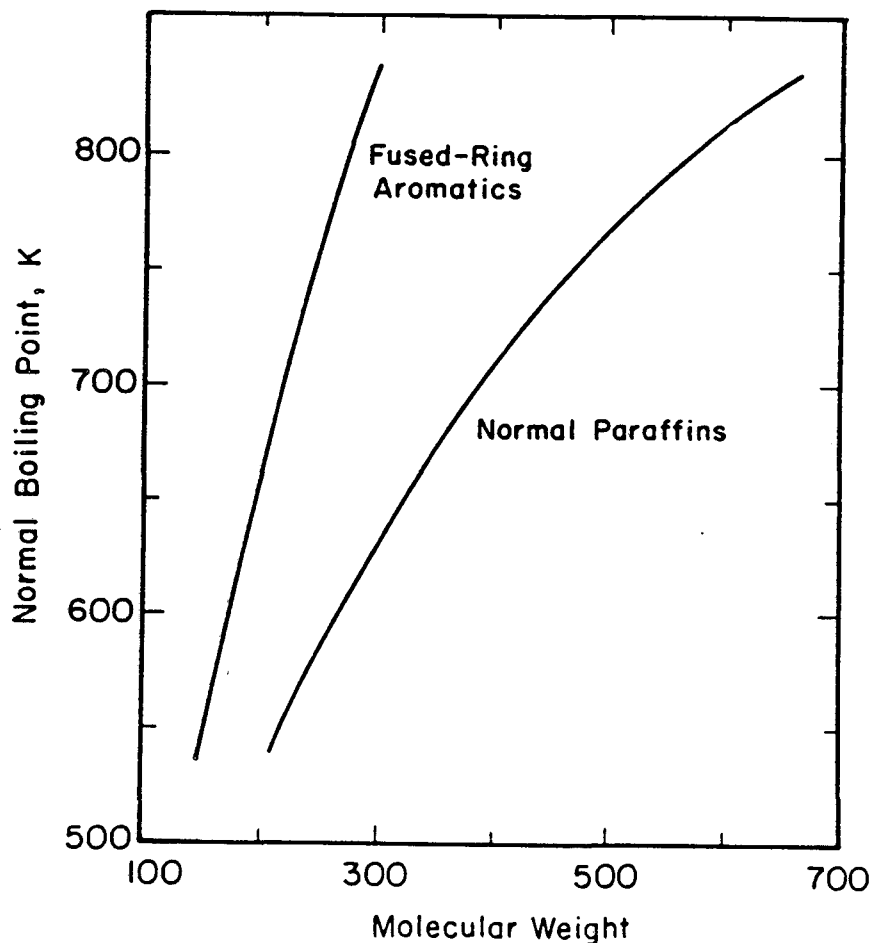


Fig. (3.1): Normal boiling point as a function of molecular weight

Class	$b^{(1)}$	$b^{(2)}$	$b^{(3)}$
Normal paraffins	962.3	733.6	0.0026580
Fused-ring aromatics	1537.5	1417.3	0.0023889

Table (3.1): Parameters for equation (3.1).

Distribution function F is usually given numerically, e.g. as a number of data points. It is desirable to have this distribution function analytically, since the equations may then be solved analytically. One has to find a compromise between mathematical simplicity and accuracy for representing the mixture. More often than not, a numerical procedure is unavoidable.

In this work the beta distribution is chosen, since that distribution provides a good approximation for the experimental data. The beta distribution is

$$F(u) = \frac{\Gamma(\alpha+\beta)}{\Gamma(\alpha)\cdot\Gamma(\beta)} \cdot u^{\alpha-1} \cdot (1-u)^{\beta-1} \quad (3.2)$$

with the gamma function Γ and the distributed variable u normalized for the interval $0 < u < 1$;

Parameters α and β are related to mean θ and variance σ by

$$\theta = \frac{\alpha}{\alpha + \beta} \quad (3.3)$$

and

$$\sigma^2 = \frac{\alpha \cdot \beta}{(\alpha + \beta)^2 \cdot (\alpha + \beta + 1)} \quad (3.4)$$

The upper and the lower boundary needed to normalize the distribution variable are the highest and the lowest boiling point or molecular weight, respectively. Parameters α and β are fitted to the mean and variance of the measured distribution. We have

$$F(I) = F(MW) \quad (3.5)$$

4. Oil Samples Used

Two petroleum-derived oils are used, one rich in saturates (paraffins and naphthenes), the other rich in aromatics. These oil samples were provided by Exxon Research and Engineering Company (1984). Some properties are listed in Table (4.1).

Property	Oils: Saturates-rich	Aromatics-rich
Specific Gravity at 60°C	0.8355	0.9237
Carbon/Hydrogen Ratio	6.25	7.56
Saturates, Wt%	88.6	37.9
Aromatics, Wt%	11.4	62.1
Boiling Range, K	575.5-744.2	581.5-746.9
Number-Average Molecular Weight	340	310

Table (4.1): Thermodynamic properties for the two oils.

A boiling-point analysis was determined from a gas-chromatographic simulated distillation. Both oils have a similar boiling range. Using relation (4.1), we obtain the mass distribution as a function of the molecular weight:

$$F_M(T_B) = F_M(MW(T_B)) = F_M(MW), \quad (4.1)$$

where F_M indicates the mass-distribution function.

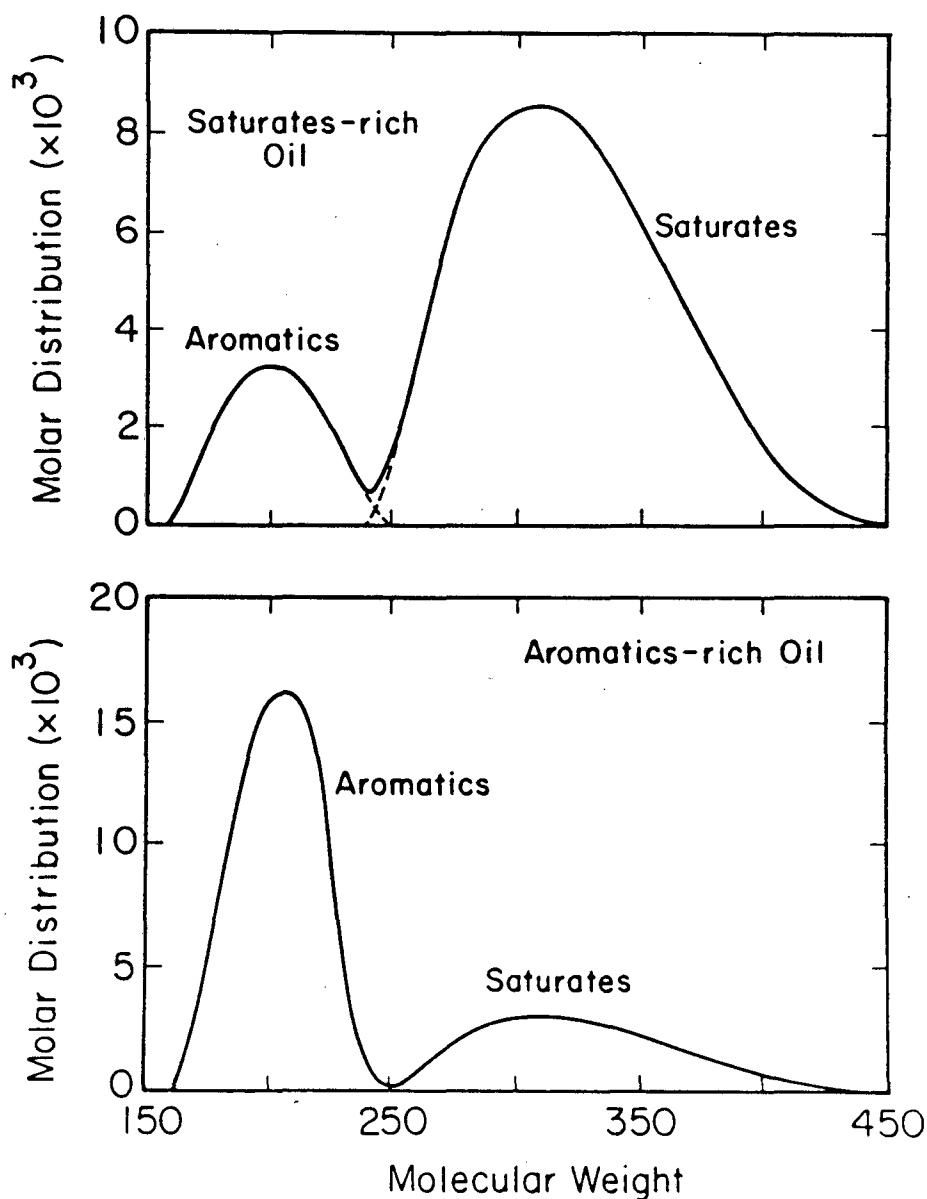
We obtain the molar distribution from the mass distribution, since the molecular weight is known for each mass fraction.

Parameter	Oils: Saturates-rich		Aromatics-rich	
	Fractions: Sat	Arom	Sat	Arom
θ	321.8	202.0	321.4	202.5
σ^2	1532.0	341.0	1256.0	253.8
min. MW	241.9	158.7	241.9	158.7
max. MW	462.4	250.7	462.4	250.7

Table (4.2): Parameters for the two oils.

However, as indicated in chapter 7, we represent the oil as the sum of two homologous series, one for paraffins and one for fused-ring aromatics. Figures (4.1) and (4.2) show the molar distributions for both oils. The molecular weights for both fractions are very different, but the boiling range is similar, since they are obtained by distillation.

These distribution functions are described by the beta function, as indicated in chapter 3. We obtain parameters θ and σ^2 and the minimum and maximum molecular weight for both fractions in each oil as shown in Table (4.2).



Figures (4.1) and (4.2): Molar distribution function for the saturates-rich (top) and the aromatics-rich oil (bottom).

5. Systems Propane/Oil

First, we consider interactions between the different oil components. Binary parameters for the system paraffins/fused-ring aromatics may be a function of molecular weight. Many data are required to determine these functions reliably but fortunately, the results are not sensitive to these parameters. We can set them to zero without significant error.

To obtain the binary parameters as a function of molecular weight for the systems propane/saturates and propane/fused-ring aromatics, Cotterman fitted the binary systems of propane with several paraffins and several fused-ring aromatics. He found the parameters to be constant, independent of molecular weight. But when he tried to describe experimental solubility data of an oil in propane with these binary parameters, he found the parameters unsuitable, probably because he made a major simplification in assuming the oil to contain only paraffins and fused-ring aromatics. Now we can either diversify our model of the oil or we can fit the binary parameters directly to the propane/oil equilibrium data. Cotterman tried the latter option. He gives binary parameters for propane/saturates and propane/fused-ring aromatics fitted to propane/oil equilibrium data measured by Radosz (1985).

Since we changed our pure-component parameters for propane, and because the binary parameters depend on the choice of pure-component parameters, we have to repeat this fitting. No suitable program was available for this purpose; therefore, this fitting was done by trial and error. The parameters for both systems are different for the two oils, due to simplifications in the oil model. The best parameters are given in Table (5.1).

Propane with:	<u>Saturates</u>		<u>Fused-ring aromatics</u>	
	k_{ij}^B	k_{ij}	k_{ij}^B	k_{ij}
Saturates-Rich	-0.040	-0.020	-0.080	-0.060
Aromatics-Rich	0.000	-0.015	0.000	-0.015

Table (5.1): Binary parameters for propane/oil.

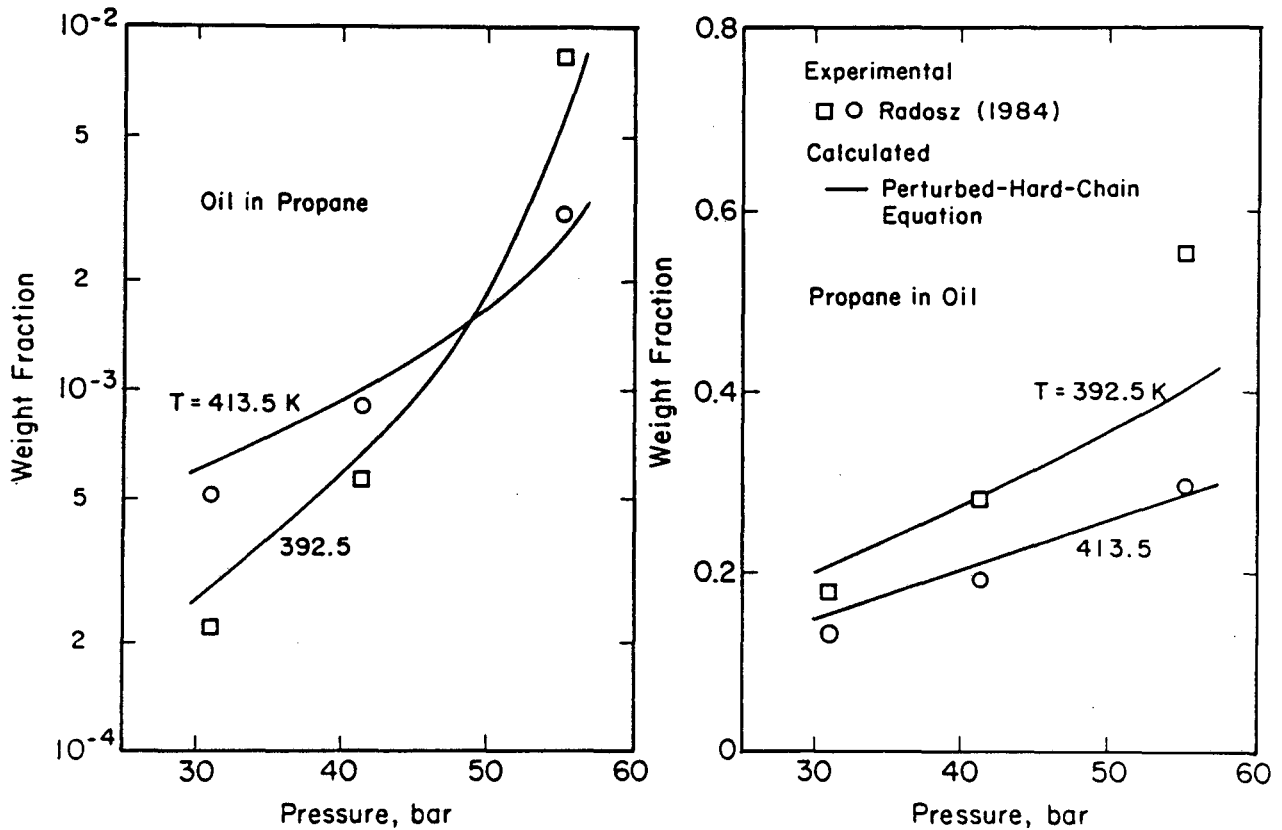


Figure (5.1): Calculated and experimental mutual solubilities of propane and saturates-rich oil.

This fitting requires some assumptions. The measured data give overall solubilities in weight fractions. Our program, on the other hand, calculates mole fractions. To convert mole fractions of a continuous component into weight fractions, the first statistical moment has to be known. To avoid the moment calculation, the number average of the molecular weight was used for the conversion.

Since the experimental data do not give information about the fractions of aromatics or saturates, it is possible that we predict the right overall solubility with the obtained parameter set, but that the ratio of the two continuous mixtures is not described properly. Further, only six data points are available per oil, too few for a good fitting of four parameters.

Finally, the highest measured pressure was 55.14 bar. The following calculations of supercritical solubilities include pressures to 120 bar. We expect that the accuracy is lower in the high pressure region, since the binary parameters are not fitted to those pressures.

Figures (5.1) and (5.2) give calculated and experimental mutual solubilities of propane and both oils. The experimental data were obtained at slightly different solvent-to-solute ratios in the feed.

Having fitted the binary parameters to the oils, we can describe the solubilities of these oils in supercritical propane. The results are given in part V. Next, we want to study the effect of adding a co-solvent (an entrainer). In this work we study the effect of water. We need the binary parameters for water with all components of the oil and with propane.

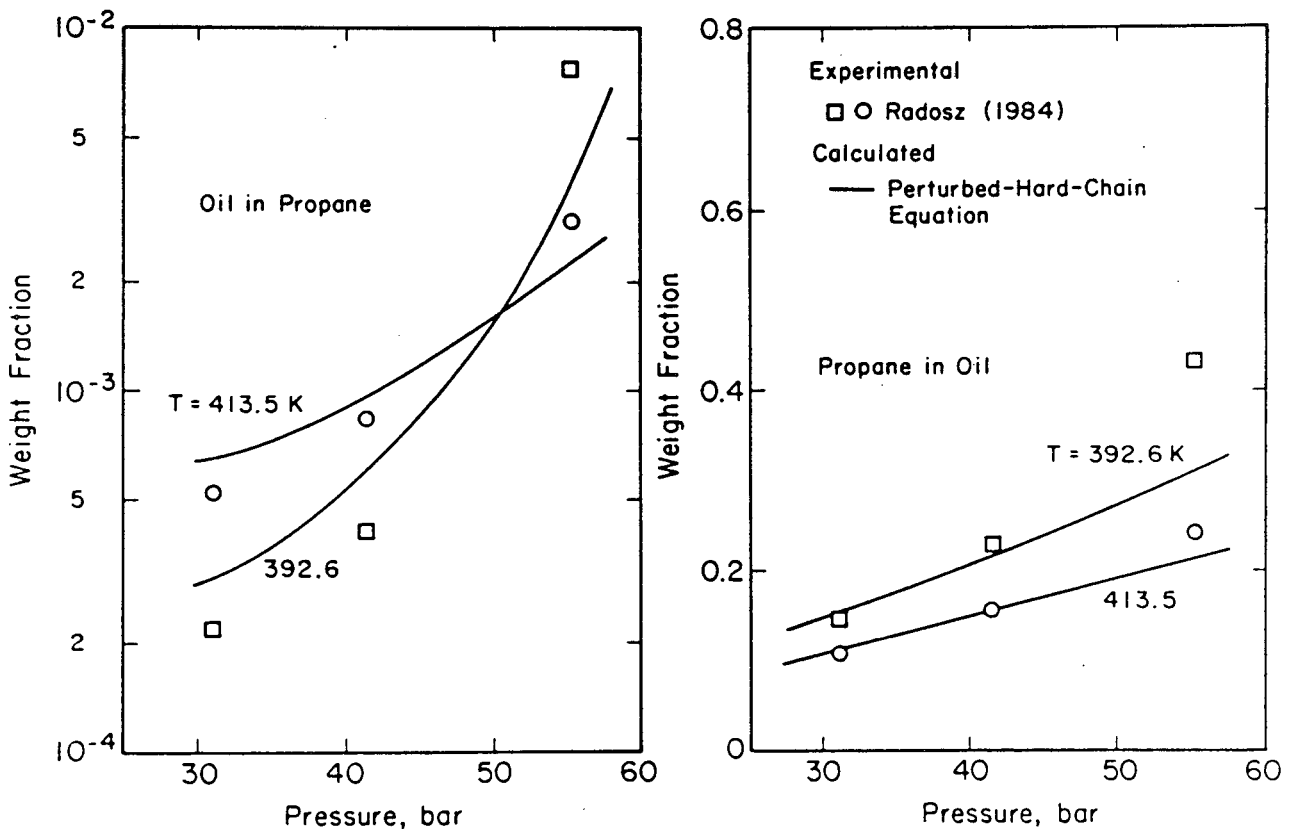


Figure (5.2): Calculated and experimental mutual solubilities of propane and aromatics-rich oil.

6. System Propane/Water

Kobayashi and Katz (1953) give extensive equilibrium data for the system propane/water between 289 and 427 K and 6.9 and 207 bar.

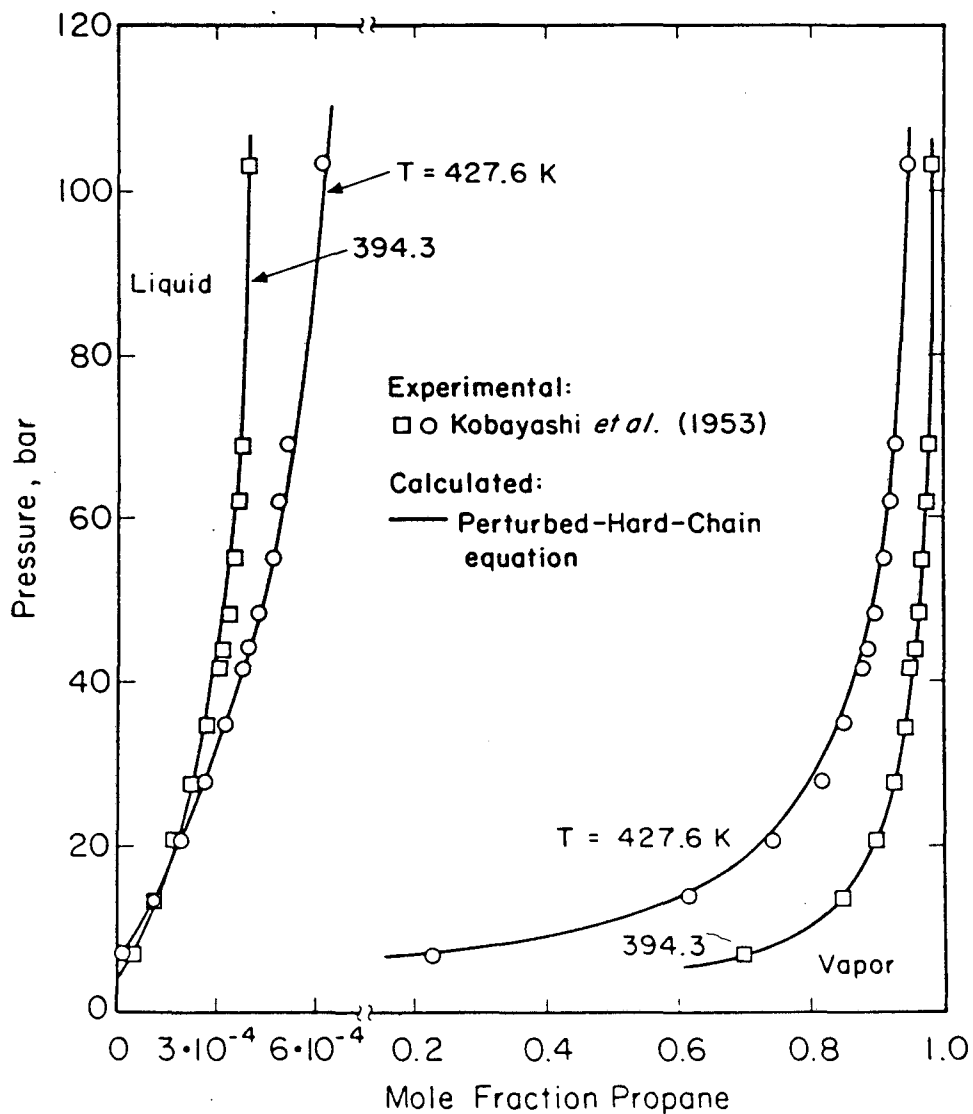


Figure (6.1): Calculated and experimental vapor-liquid equilibria for propane/water.

To obtain binary parameters from these data, it was necessary to include a temperature dependence for k_{21} , where 1 stands for hydrocarbon and 2 for water. Parameter k_{21} is determined from data where 1 is dilute in an excess of 2.

$$k_{21} = 0.417 - \frac{230}{T/K} \quad (6.1)$$

Parameter k_{12} is independent of temperature:

$$k_{12} = 0.385 \quad (6.2)$$

The fitted range is $310 < T < 430$ K and $6.9 < P < 138$ bar. The average deviation between calculated and experimental values is less than 3%.

Figure (6.1) shows vapor-liquid equilibria for propane/water at 394.3 and 427.6 K. Calculated results agree well with experiment.

7. Systems n-Alkanes/Water

Binary parameters for water with n-butane, n-pentane, n-hexane, n-octane, and n-decane, respectively, were fitted to vapor-liquid or liquid-liquid equilibrium data. The n-butane/water data were measured by Reamer et al. (1952). The Gas Processors Association (1982) gives data for water with n-pentane and n-octane. Solubility data for water/n-hexane, n-octane, and n-decane data are obtained from Tsonopoulos et al. (1983, 1985, 1986).

Again it was necessary to allow k_{21} to be temperature dependent. However, k_{21} is the same for all n-alkane/water systems, indicating that the correction for the interactions in the water-rich phase does not depend on the length of the n-alkane.

Parameter for the n-alkane-rich phase was found to be between 0.3 and 0.5 for all fitted n-alkane/water systems. It fluctuates with the temperature and the molecular weight, but no trend is evident. We use:

$$k_{12} = 0.400 \tag{7.1}$$

$$k_{21} = 0.417 - \frac{230}{T/K} \tag{7.2}$$

These parameters are expected to be valid for $310 < T < 480$ K and $8 < P < 140$ bar.

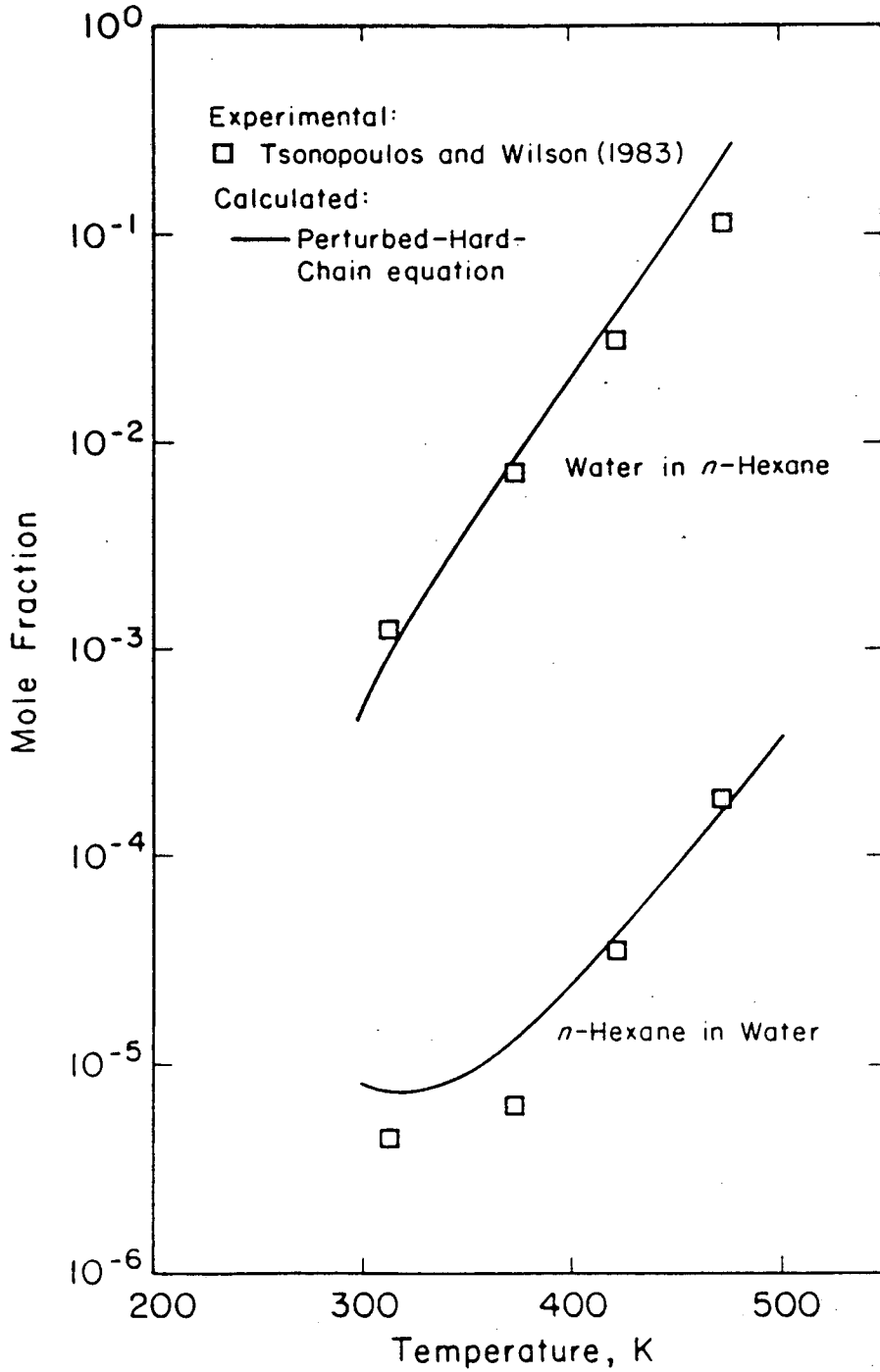


Figure (7.1): Mutual solubilities of n-hexane and water at the three-phase pressure.

Figure (7.1) shows the mutual solubilities of n-hexane and water as a function of temperature at the three-phase pressure. The solid line shows calculated results using parameter interpolations (7.1) and (7.2). The quality of the fit is good.

8. Systems Fused-Ring Aromatic Hydrocarbon/Water

Benzene/Water equilibria were measured by Tsonopoulos and Wilson (1983), the Gas Processors Association (1982), Rebert and Webster (1959), and Burd and Braun (1968). Their data were used to fit the binary parameters. Again, k_{21} is temperature dependent:

$$k_{12} = 0.280 \quad (8.1)$$

$$k_{21} = 0.379 - \frac{186}{T/K} \quad (8.2)$$

The range for these parameters is $310 < T < 615$ K and $0.3 < P < 350$ bar. The average deviation is about 1% for the benzene-rich phase and less than 10% for the water-rich phase.

Figure (8.1) shows mutual solubilities of benzene and water as a function of temperature at the three-phase pressure.

Data for fused-ring aromatic hydrocarbons/water systems are scarce. The system methylnaphthalene/water was measured by the Gas Processors Association (1982). The data at 311 and 366.5 K were fitted giving parameters identical to those for benzene/water. Therefore, we assume that these parameters are applicable for all fused-ring aromatic hydrocarbon/water systems.

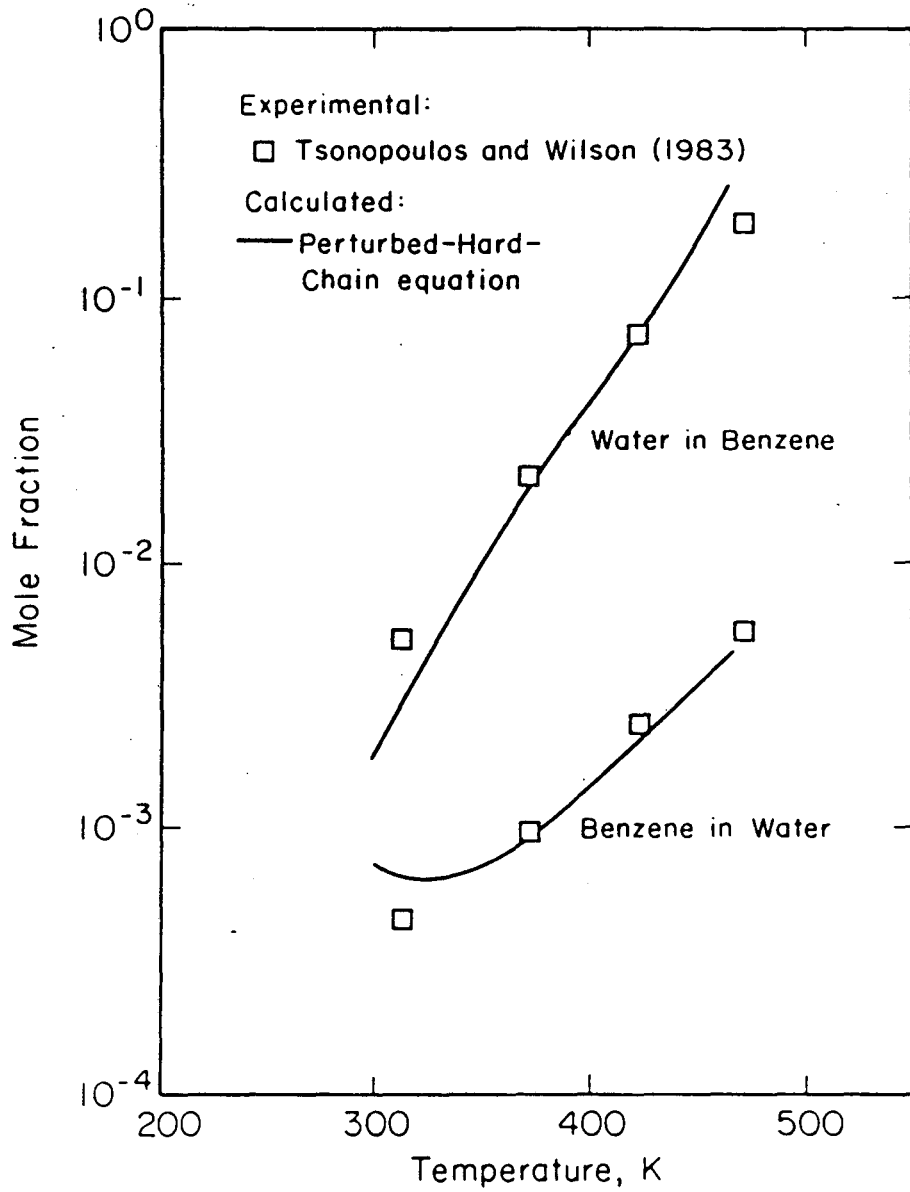


Figure (8.1): Mutual solubilities of water and benzene at the three-phase pressure.

V. APPLICATION OF CONTINUOUS THERMODYNAMICS TO THE DESIGN OF SUPERCRITICAL-FLUID EXTRACTION PROCESSES

1. Introduction

In the previous chapters we reviewed continuous thermodynamics and the Perturbed-Hard-Chain equation of state. They provide powerful tools to calculate phase equilibria, necessary for an efficient design of supercritical-fluid extraction processes. We now study the influence of the different process parameters on phase equilibria. Then we illustrate the use of calculated equilibria with two process-design examples. As a new feature, we discuss the effect of an entrainer in supercritical-fluid extraction.

For a critical examination of separation processes, it is useful to define a yield as the fraction of a fixed component that is evaporated from the feed:

$$Y_i = \frac{\xi \cdot y_i}{z_i} \quad (1.1)$$

for a discrete component, or for a continuous component:

$$Y_i(I) = \frac{\xi \cdot \eta_i^V \cdot F_i^V(I)}{\eta_i^F \cdot F_i^F(I)}, \quad (1.2)$$

where η_i^V and η_i^F are the overall mole fractions of continuous component i in the vapor or the feed, respectively.

It is the goal of an extraction to obtain a high yield (close to unity) for some components and a low yield (close to zero) for others. An efficiency of separation can then be defined by

$$E = Y_P \cdot (1 - Y_R), \quad (1.3)$$

where Y_P is the yield of those components we want in the vapor phase (product) and Y_R that of those desired in the liquid phase (residuum).

2. K-Factors

Figure (2.1) shows K-factors for the saturates-rich oil as a function of the molecular weight at 390 K and 40 bar and at 120 bar.

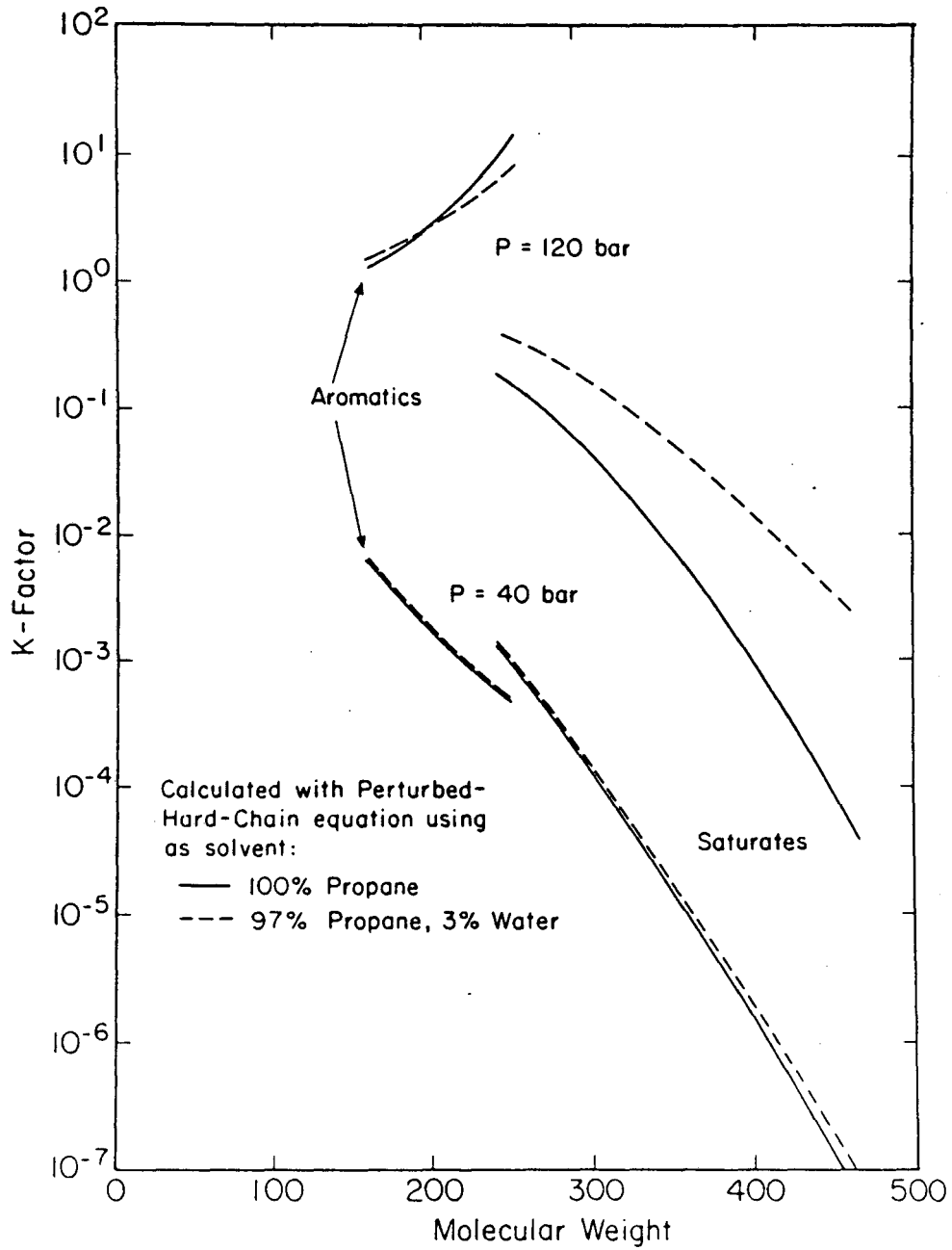


Figure (2.1): K-factors for the saturates-rich oil in the system saturates-rich oil/propane/water at 390 K.

At 40 bar, the K-factor is always smaller than unity; it decreases with rising molecular weight, since the volatility decreases with the molecular weight. At higher pressures, the K-factor is larger, because the solubility of the hydrocarbons in the vapor phase is higher. However, the K-factor for the aromatics is larger than unity, and it rises with increasing molecular weight. This effect may be useful to separate aromatics from paraffins.

The dotted lines show K-factors for the case where 3 mole % water is added to the propane. At low pressures, this does not have any significant effect. At higher pressures, however, the K-factors for the saturates are higher with increasing water concentration. Addition of water lowers the ratio of K-factors for aromatics and saturates. Hence, the separation effect is worse; water does not help the separation.

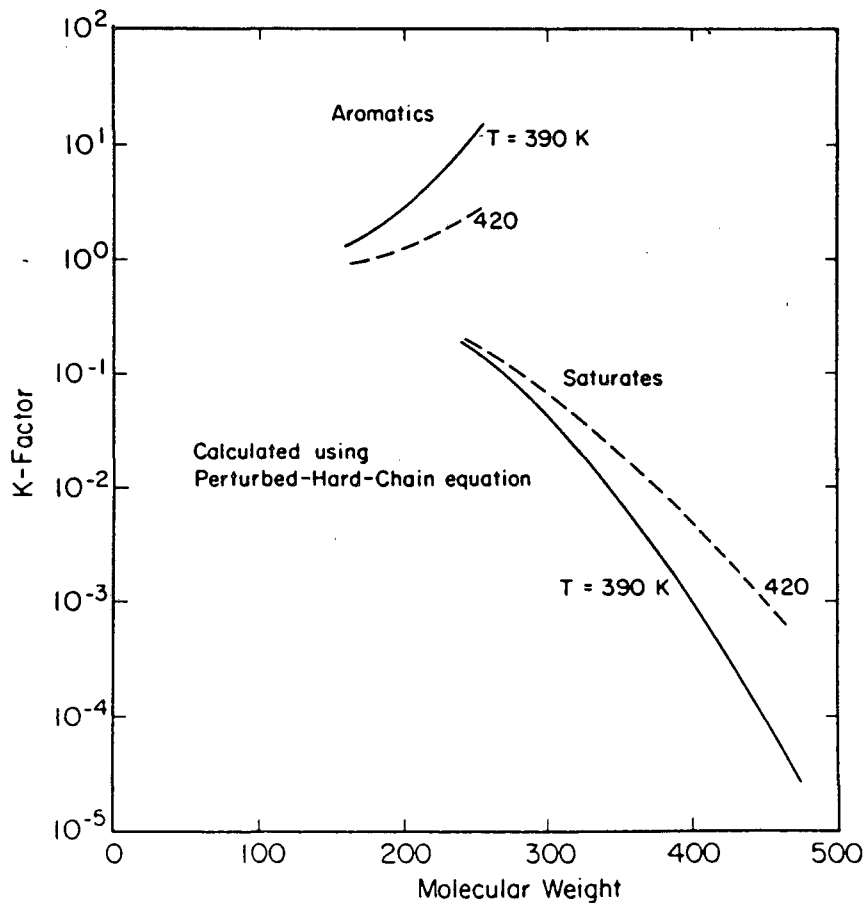


Figure (2.2): K-factors for the saturates-rich oil in the system saturates-rich oil/propane at 120 bar.

Figure (2.2) shows the effect of the temperature on the K-factor at 120 bar. With increasing temperature the K-factor for aromatics falls and that for saturates rises. These results indicate that lower temperatures are desirable for a good separation.

3. Separation of Aromatics and Saturates

We now try to optimize a process that separates aromatics from saturates, and we study whether adding water provides a suitable method to increase the efficiency of the separation. We have:

$$E = Y_{\text{Aromatics}} \cdot (1 - Y_{\text{Saturates}}), \quad (3.1)$$

since we expect the aromatics to concentrate in the vapor phase and the saturates in the liquid phase.

We give a mixture of saturates-rich oil and propane as feed and we do a flash calculation under the given conditions (temperature, pressure). The computer program gives compositions of both phases and the fraction vaporized. We can then determine the yields from Equations (1.1) and (1.2).

In this case, we choose a solvent-to-solute weight ratio of four, i.e. we add 4 kg propane for each kg oil. This ratio must also be optimized.

Figure (3.1) shows the vapor-phase mole fraction of heavies and the efficiency as a function of pressure for three temperatures. The efficiency has an optimum pressure for each temperature. With lower temperatures, the optimum pressure is lower and the maximum efficiency is higher. However, at temperatures of 360 K and lower, a phase split occurs. In that case, the optimum extraction conditions resemble those of common liquid-liquid extraction with propane. If high yields are required for the process, liquid-liquid extraction is recommended. However, some advantages of supercritical-fluid extraction are lost in that region. The subsequent separation steps require evaporation; also, an expensive compression with condensation is necessary for solvent recovery. Hence, supercritical-fluid extraction may be cheaper. In some cases that is more important than high efficiency of separation.

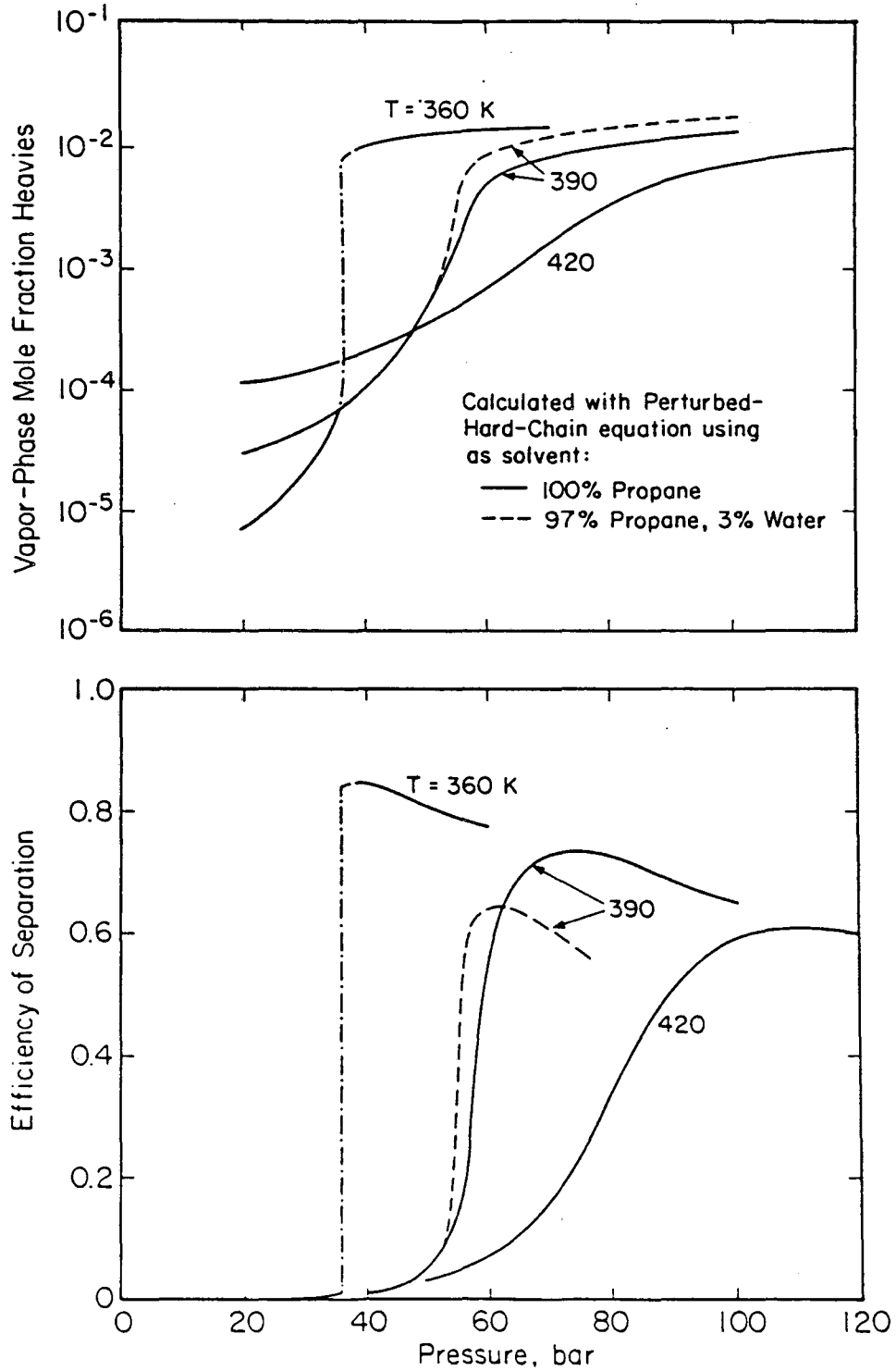


Figure (3.1): Vapor-phase mole fraction of heavies and efficiency of separation.

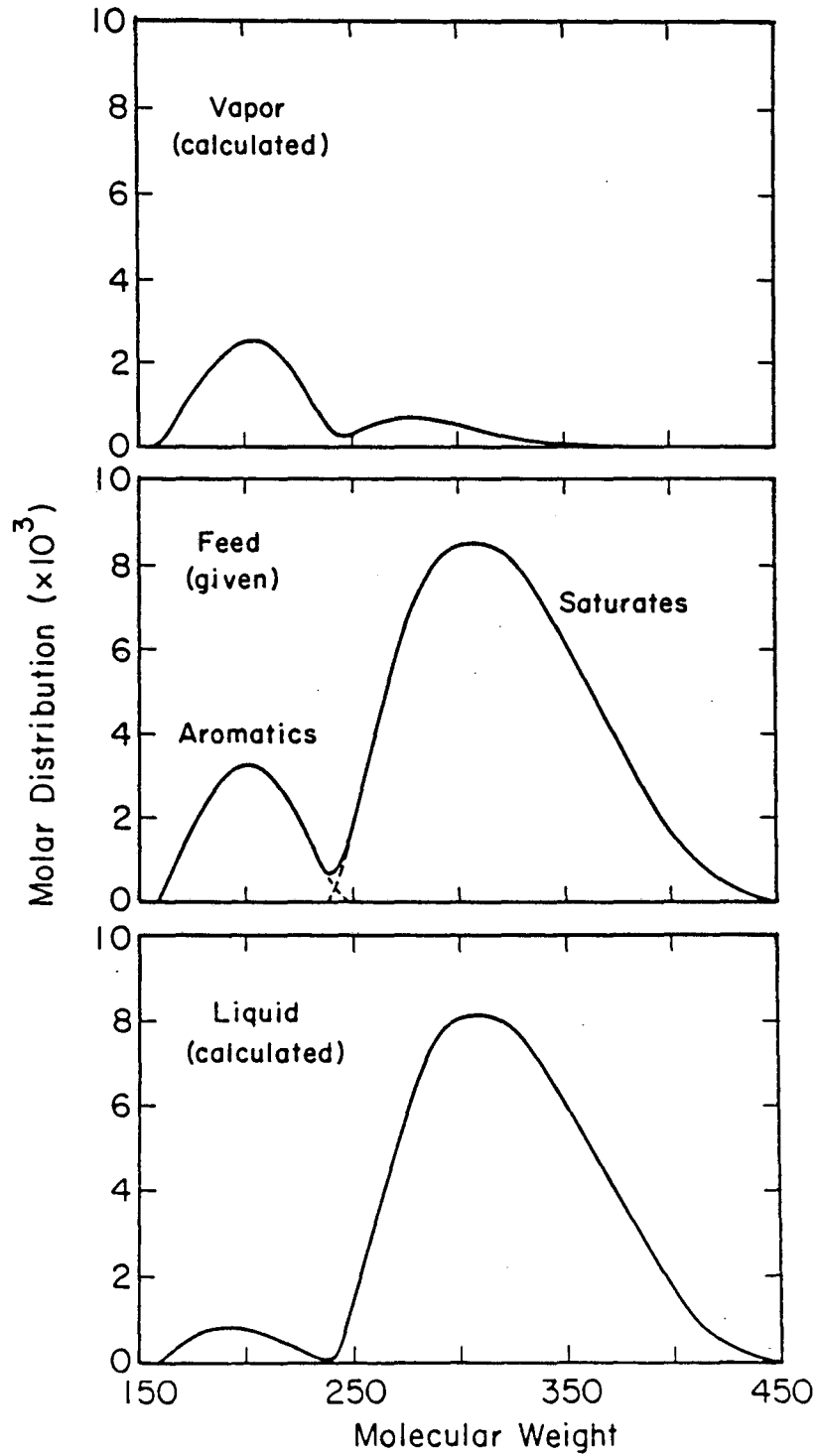


Figure (3.2): Molar distributions for the saturates-rich oil in feed, vapor and liquid for a flash at 390 K and 75 bar.

The dotted line in Figure (3.1) indicates the behavior of the system at 390 K containing 3 mole % water. The maximum efficiency is much lower than that for the water-free system. This lower efficiency is, in part, due to the fact that the presence of water lowers the vaporized fraction; hence less aromatics go into the vapor phase.

It appears advantageous to choose the slightly supercritical temperature of 390 K. At a pressure of 75 bar, we reach an efficiency of 73.5%. Under those conditions, 77.1% of the aromatics accumulate in the vapor phase and 95.3% of the saturates remain in the liquid phase.

Figure (3.2) shows the molar distributions for the saturates-rich oil in feed, vapor and liquid. The separation effect is evident.

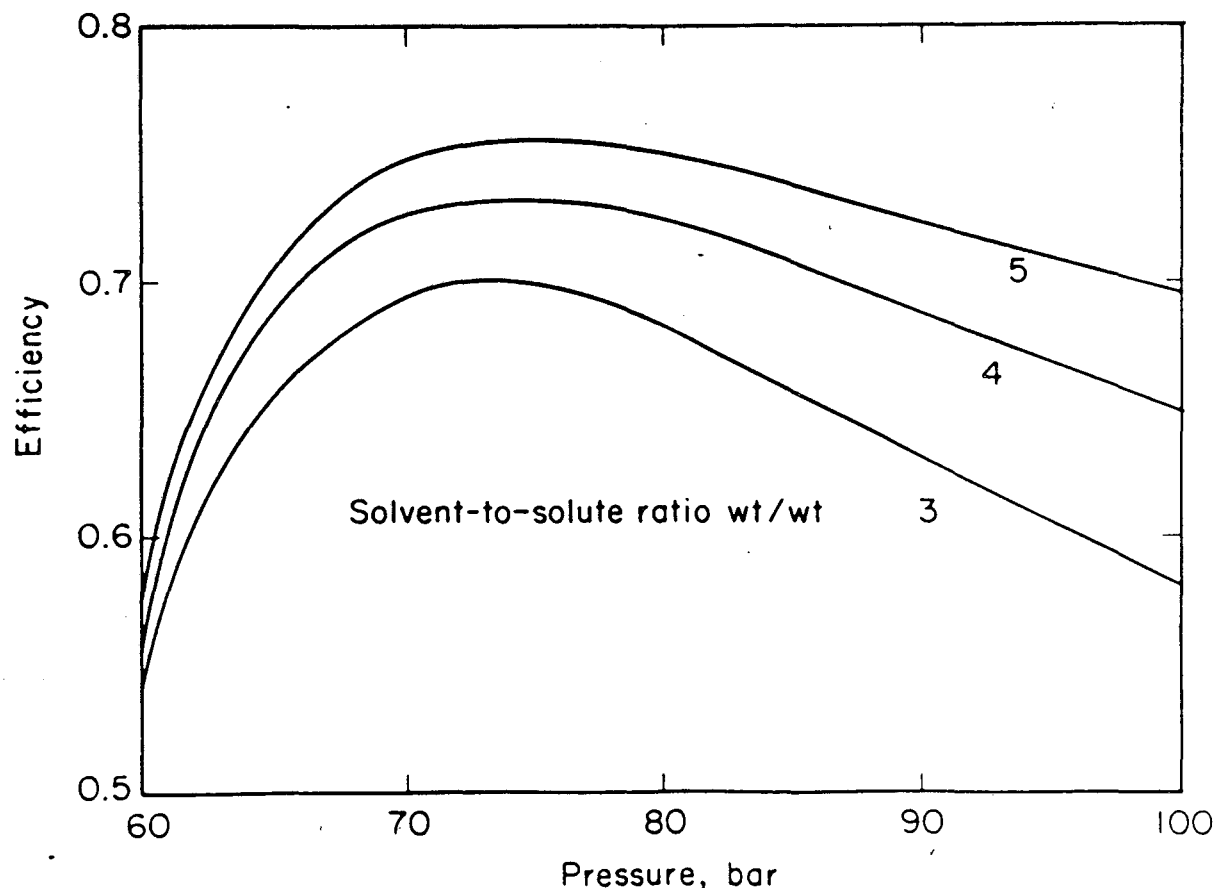


Figure (3.3): Effect of the solvent-to-solute ratio on the efficiency of separation.

The solvent-to-solute ratio in the feed also has an influence on the efficiency. Figure (3.3) shows the efficiency for three different solvent-to-solute ratios at 390 K. The efficiency increases with rising solvent concentration. But the costs of operation also increase. Again, the optimum ratio depends on the goal, on whether a good separation or an inexpensive solvent recovery step is more important. However, very often, the solvent-to-solute ratio is not determined by these arguments; instead, it is given by the process. For example, a deasphalting step may be upstream of the supercritical-fluid extraction. Then, the output composition of the first extraction determines the feed for the supercritical-fluid extraction. The ratio four, chosen here, is typical for the output of a deasphalting step.

4. Separation of the Aromatics-rich Oil

In the preceding chapters we discussed the effect of water on phase equilibria for the saturates-rich oil. For the aromatics-rich oil, however, the conditions are different. The calculated phase split occurs up to much higher temperatures. That means, a liquid-liquid equilibrium is obtained with a propane-rich liquid phase rather than a vapor-liquid or supercritical fluid-liquid equilibrium. The efficiency of the separation of aromatics and saturates is very high in the regime of the liquid-liquid equilibrium. But this has been well known for many years. However, ordinary liquid-liquid extraction does not have some of the advantages of supercritical-fluid extraction.

The upper critical end point (UCEP) for propane-rich liquid-vapor equilibrium is predicted by the Perturbed-Hard-Chain equation of state at around 450 K and 110 bar. But at such high temperatures, propane is far away from its critical point (369.8 K, 42.5 bar). Therefore, the increase in the solvent power within a narrow pressure range is less steep. To increase the solubility of heavies in propane 50 fold, the pressure has to increase from 40 to 110 bar, whereas a change from 40 to 60 bar is sufficient for the same enhancement with the saturates-rich oil. We conclude that supercritical-fluid extraction is not a suitable separation process for the aromatics-rich oil. Hence, liquid-liquid extraction is recommended in that case.

Again it does not help to add small amounts of water. Water increases the upper critical end point for the propane-rich liquid-vapor equilibrium. Hence, the region for the supercritical-fluid extraction shifts to higher temperatures, further away from the critical point of propane. Water decreases the yield of aromatics, since less propane (containing aromatics) is evaporated.

5. Separation of Heavies and Lights

For some purposes, it is desirable to separate hydrocarbons not according to their class (aromatics or saturates) but according to their molecular weights. Therefore we consider as a second process-design example whether water helps to separate hydrocarbons with high molecular weights from oils with supercritical-fluid extraction.

As we saw in chapter 3, the aromatics, which have a lower molecular weight than the saturates, concentrate in the vapor phase under supercritical conditions. Hence, our goal is to get a high yield for light saturates and a low yield for the heavy saturates.

Figure (5.1) shows the yield for both fractions of the saturates-rich oil as a function of molecular weight. As discussed in chapter 3, adding water decreases the yields. For a separation of the very heavy saturates, we need the saturates curve as steep as possible. This is reached for a given temperature at that pressure which gives the highest yield for the lightest saturates. To extract more of the light paraffins in the vapor phase, a higher temperature is desirable. At higher temperatures, however, the yield of aromatics decreases, so that more aromatics remain in the liquid. We conclude that liquid-liquid extraction is preferable.

Adding water decreases the yield at all molecular weights. However, for our purposes, we desire an increase. Hence, water is not a suitable entrainer.

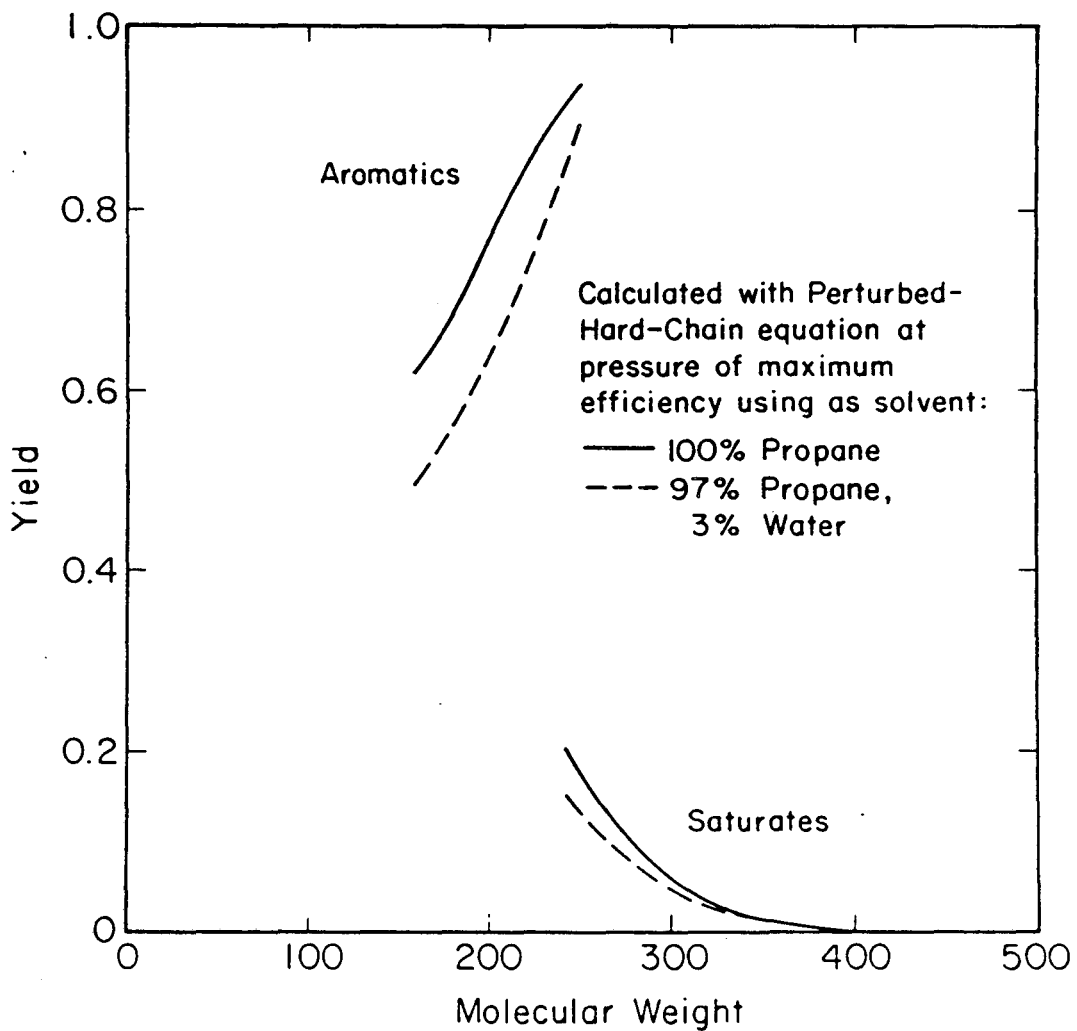


Figure (5.1): Yield of saturates-rich oil in the vapor phase at 390 K

VI. EXPERIMENTAL

1. Apparatus for Measuring Solubilities

Figure (1.1) shows schematically the apparatus for measuring solubilities in supercritical propane.

Propane is pumped by a positive-displacement pump from a cylinder through the apparatus. The desired pressure can be adjusted by a back-pressure regulator. The propane flows through the equilibrium cell. In this cell, the propane becomes saturated with the solute that has previously been put into the cell. The cell is placed in a fluidized sand-bath that provides the desired temperature. The saturated propane is expanded to a much lower pressure, low enough to ensure that no solute precipitates. A gas chromatograph takes samples of this stream and indicates whether there is any solute in the propane. Having passed the sampling valve, the solute condenses in a cooling trap. The propane flows through a volume meter which is upstream from a vacuum pump.

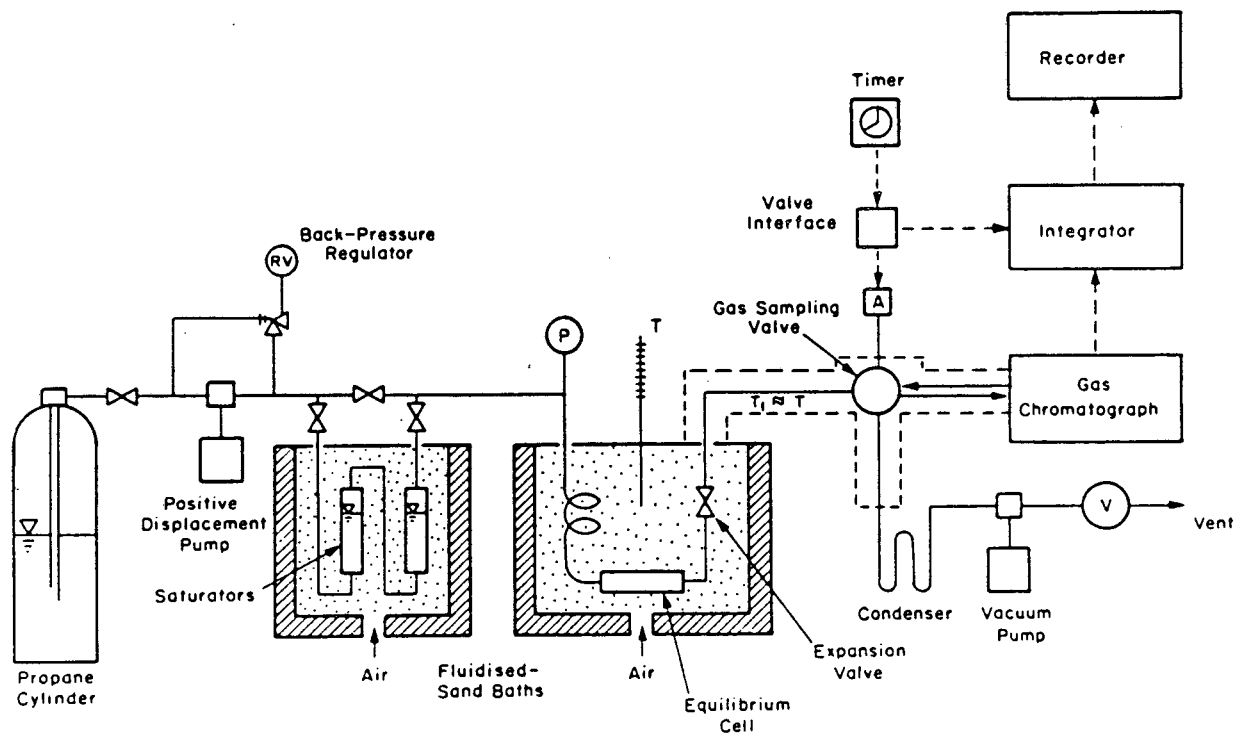


Figure (1.1): An apparatus for measuring solubilities.

Two parallel sections are downstream from the equilibrium cell. Therefore, we are able to do simultaneously two experiments at the same temperature and pressure but at different flow rates. This allows us to check whether equilibrium is reached, since the equilibrium concentration should not depend on the flow rate.

A saturator can be placed upstream of the equilibrium cell. This allows us to add an entrainer such as water. In this saturator the propane saturates with the entrainer. The output concentration can be adjusted by the temperature of the saturator, which is maintained by another fluidized-sand bath.

At the start of each experiment, the cells are filled with a solid support material and an exactly weighed amount of solute. The temperature and pressure are adjusted and the volume meter is set to zero. Propane flows through the cells and becomes saturated with the solute. The gas chromatograph indicates the presence or absence of solute. The volume meter measures the propane volume at standard temperature and pressure. After some time, when the gas chromatograph indicates no solute, all the solute is dissolved in propane and the experiment is finished. The volume meter shows the volume of propane that was required to dissolve the known amount of solute. Hence the equilibrium concentration can be calculated from the measurements.

2. Equilibrium Cell

The equilibrium cell is a 100-mm long tube with an inner diameter of ca. 4 mm. It is filled with a column support and with the solute. 'Chromosorp P 30/60' by Varian is used as support material. The particle diameter is in the range 0.250 to 0.595 mm.

The oils are put into the cell using a syringe. This syringe is weighed before and after filling the cell, giving the amount of oil in the cell.

Typical flow rates during an experiment are about $1.6 \cdot 10^{-4}$ g/s propane. With a critical density of 217 kg/m^3 , the volumetric flow is $7.5 \cdot 10^{-10} \text{ m}^3/\text{s}$.

Assuming a void fraction of the packed bed of $\psi=0.4$, we obtain an average gas-velocity of $1.5 \cdot 10^{-4}$ m/s. The diffusivity of a gas close to the critical point is about 10^{-8} m²/s (McHugh, Krukonis, 1986). Assuming the particle diameter to be $d_p=4.0 \cdot 10^{-4}$ m, we obtain a Peclet number of $Pe=(u \cdot d)/\delta=6$.

As shown by Martin (1978), the Nusselt number (and therefore the Sherwood number) decreases sharply in the range of low Peclet numbers. For $L/d_p=250$ and $Pe=6$, Martin gives $Sh=(\beta \cdot d_p)/\delta=0.1$. We have $\beta=2.5 \cdot 10^{-6}$ m/s. Assuming that we reach equilibrium if $NTU=(\beta \cdot A)/\dot{V} > 5$ (i.e. 99% equilibrium), we require a surface for mass transfer $A_{req}=1.5 \cdot 10^{-3}$ m².

The volumetric surface area of spheres is $a_v=6/d_p \cdot (1-\psi)$. For $d_p=4 \cdot 10^{-4}$ m and $\psi=0.4$, we have $a_v=9 \cdot 10^3$ m⁻¹. Hence, $V_{req}=A_{req}/a_v=1.67 \cdot 10^{-7}$ m³ and $L_{req}=V/(\pi \cdot r^2)=13$ mm. Therefore, 13% of the support material must be covered with oil.

This calculation is on the conservative side, since it assumes hydrodynamic conditions for a 13-mm cell. If the mass-transfer surface is distributed over a longer cell, the mass transfer is better, because the concentration profiles can equalize within the 'inactive' sections of the cell.

Nevertheless, we are not sure that the mass transfer is sufficient to reach equilibrium, since the oil may not properly wet the particles but may also form clusters or drops. To check whether equilibrium is reached, additional experiments must be performed with two equilibrium cells in series. Further, two experiments with different flow-rates are run simultaneously. For all cases, the output concentrations should be identical.

If we do not reach equilibrium, another cell design is necessary. It is, perhaps, possible to use a much higher amount of oil in the cell and to determine the dissolved amount by weighing the condenser.

3. Expansion

An expansion valve is placed downstream of the equilibrium cell. In this expansion valve, the propane (saturated with solute) expands from the pressure in the equilibrium cell to about 0.1 bar. The temperature remains constant.

Figure (3.1) shows the expansion in a phase diagram for the system carbon dioxide/naphthalene. In addition, the expansion valve is indicated. The flow rate can be adjusted with the compression fittings. The gas expands in a small slit between piston and tubing.

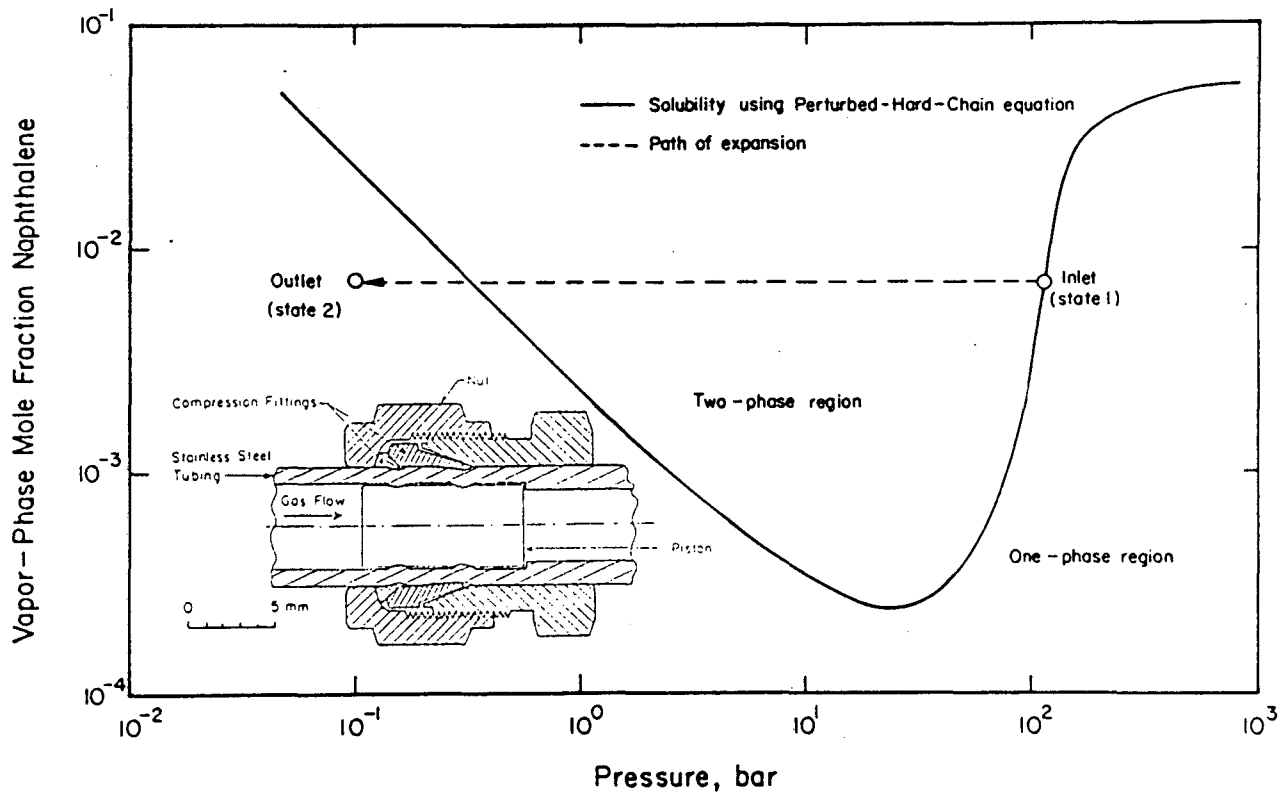


Figure (3.1): Isothermal expansion in the retrograde region for the system carbon dioxide/naphthalene at 328.15 K.

In the region of high pressures, we see the solubility curve as indicated in Fig. (1.1) part I. At low pressures, however, the solubility is determined by the ideal-gas law, i.e. the partial pressure of the solute is constant.

We expand from the pressure of the equilibrium cell (state 1) to the lower pressure of the sampling part (state 2). Figure (3.1) shows the expansion for a concentration of $7 \cdot 10^{-3}$; the gas passes the two-phase region. Hence, we expect that solute precipitates in the expansion valve. This is not desirable, since we want to be sure that the composition of the flow is the same before and after the expansion valve.

During some preliminary experiments using anthracene as solute, anthracene precipitated and plugged the valve; the flow rate decreased from the adjusted value to zero. This precipitation is not due to the Joule-Thompson-Effect, because the flow rate is so low that we can assume sufficient heat transfer to ensure isothermal conditions.

To avoid precipitation in an expansion valve, a common procedure is to heat the valve to a temperature high enough to attain total solubility. But, as shown in Figure (1.1) of part I, the solubility decreases with increasing temperature in the high-pressure range. This decrease would lead to precipitation before the expansion valve and we would measure a different equilibrium. It appears that our design of the expansion valve is not appropriate.

It may be possible to use an orifice, that is, a tiny hole for the expansion. Provided that the hole is small enough to ensure sonic flow, the flow rate depends on the inlet state only. For our purposes, the hole diameter should be around 3 μm . The resulting flow rate is not adjustable. Hence, for different equilibrium conditions and different flow rate, the holes have to be changed.

Since the velocity in the hole is very high, we do not expect precipitation in the hole. Downstream we have again conditions corresponding to the one-phase region. Current efforts are directed toward using an orifice for the expansion.

4. Limitations of the Apparatus

The concentration range to be measured is limited by the apparatus. The

lower limit is given by the detectibility of the gas-chromatograph. It is $z_{\min}=10^{-4}$ for a pure component. Since oils contain very many components, the overall concentration must be higher to ensure detection by the gas-chromatograph. We estimate $z_{\min}=5 \cdot 10^{-4}$.

The upper limit is given by the condition that no oil shall precipitate in the low-pressure section. That condition is met if the partial pressure of oil is less than its vapor pressure (dew point). The pressure after the expansion valve is about 0.1 bar and the temperature is the same as that in the equilibrium cell, for the expansion valve is located in the fluidized-sand bath. The upper limit of the concentration depends primarily on the temperature. We obtain $z_{\max} = 1 \cdot 10^{-3}$ for $T=390$ K, $z_{\max} = 3 \cdot 10^{-3}$ for $T=420$ K, and $z_{\max} = 1.5 \cdot 10^{-2}$ for $T=450$ K. At the last temperature, the maximum concentration will be reached at a pressure of about 170 bar. This is the maximum pressure allowed for the apparatus. Hence, at temperatures above 450 K, there is no upper concentration limit but there is an upper pressure limit.

To add an entrainer, a second equilibrium cell (a saturator) is used. The concentration of the entrainer in propane is adjusted by choosing the temperature corresponding to the desired equilibrium vapor-phase concentration at the given pressure.

When methanol is the entrainer, temperatures below the upper critical solution temperature of 294.3 K must be used. For this purpose, the fluidized-sand bath is not suitable. Instead, a cooling device is necessary, but it is not yet available. Hence, with the current design of the apparatus it is not possible to measure phase equilibria using methanol as entrainer in propane.

When water is the entrainer, the saturator can be used. The fluidized-sand bath requires a minimum temperature of 50° C. At this temperature and a pressure of about 70 bar, the equilibrium vapor-phase concentration is about 0.1 mol-% water in propane. At 160° C and the same pressure, we reach 7 mole %. This range includes all concentrations of interest, since we must have enough entrainer to obtain an effect, but the water concentration must be low enough to avoid formation of a condensed water-rich phase. Hence, experiments using water as entrainer are possible.

VII. CONCLUSIONS

Calculations have been performed to study the effect of small amounts of water on the phase equilibria for supercritical-fluid extraction of heavy fossil fuels with propane. The results show that water is not a useful entrainer to enhance the efficiency of the extraction.

The Perturbed-Hard-Chain equation of state in its current form cannot describe the phase equilibria of systems containing methanol. Further modifications are required, e.g. inclusion of terms that account for dimerisation and formation of clusters.

Experiments have to be performed to verify the calculation, given here. Since this work predicts properties in the critical region, verification by experiment is particularly important.

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NOTATION

a) Lower Case

a	J/mol	molar Helmholtz energy
a ⁽ⁱ⁾	-	constants
a _{ij}	-	see equation (2.6) of part III
a _v	m ² /m ³	surface area per unit volume
c	-	Prigogine's parameter
d	m	diameter
f	bar	fugacity
k	-	adjustable parameter
k	J/K	Boltzmann's constant
n	mol	mole number
q	m ²	external surface area
r	-	number of segments per molecule
u	-	normalized distribution variable
u	m/s	velocity
v	m ³ /mol	molar volume
x	-	liquid or solid-phase concentration
y	-	vapor or fluid-phase concentration
z	-	feed concentration

b) Upper Case

A	J	Helmholtz energy
A_{ijk}	-	see equation (2.4) of part III
A	m^2	surface area
B	bar	second virial coefficient
E	-	efficiency of separation
F	-	interpolation function
F	-	distribution function
I	-	distribution variable
L	m	length
MW	kg/mol	molecular weight
N_{Av}	1/mol	Avogadro's number
NTU	-	number of transfer units
P	bar	pressure
Pe	-	Peclet number
R	J/(mol K)	universal gas constant
Sh	-	Sherwood number
T	K	temperature
V	m^3	total volume
\hat{V}	m^3/s	volumetric flow rate
Y	-	yield
Z	-	compressibility factor

c) Greek Symbols

$\alpha \beta \gamma$	-	parameters in the beta distribution function
β	m/s	mass-transfer coefficient
Γ	-	gamma function
δ	m ² /s	diffusivity
ϵ	J/m ²	potential energy per surface area
η	-	overall concentration of continuous components
θ	-	mean
μ	J/mol	chemical potential
ϕ	-	fugacity coefficient
ρ	kg/mol	density
σ	m	hard-core diameter
σ^2	-	variance
τ	-	constant
Ψ	-	void fraction
ξ	-	vaporized fraction

d) Sub- and Superscripts

c	critical
crit	critical
df	dense fluid
F	fluid
i	1, 2, ... component
L	liquid
o	reference
P	particle
pert	perturbation
Q	quadrupole moment
r	residual
ref	reference
req	required
S	solid
sat	saturation
sv	second virial
T	total
V	vapor
u	dipole moment
' "	phases
*	characteristic
~	reduced
+	see equation (1.5) of part III

APPENDIX 1

Mixing Rules for the Perturbed-Hard-Chain Equation of State

For the reference term (1.2) in part III linear rules are used:

$$\langle c \rangle = \sum_i x_i \cdot c_i \quad (1.1)$$

$$\langle v^+ \rangle = \sum_i x_i \cdot v_i^+ \quad (1.2)$$

The dense-fluid dispersion term (1.10) of part III contains two parameters $a_1(\langle cT^*v^+ \rangle, \langle v^+ \rangle)$ and $a_2(\langle cT^{*2}v^+ \rangle, \langle v^+ \rangle)$. Cotterman and Prausnitz give a cubic mixing rule:

$$\langle c \cdot T^{*m} \cdot v^+ \rangle = \sum_i \sum_j \sum_k x_i \cdot x_j \cdot x_k \cdot A_{ijk}^{(m)} \quad (1.3)$$

where

$$A_{ijk}^{(m)} = 1/2 [a_{ij}^{(m)} \cdot (1 - \tilde{k}_{ij}) + a_{ik}^{(m)} \cdot (1 - \tilde{k}_{ik})] \quad (1.4a)$$

$$A_{iij}^{(m)} = 1/2 [a_{ii}^{(m)} + a_{ij}^{(m)} \cdot (1 - k_{ji})] \quad (1.4b)$$

$$A_{iji}^{(m)} = 1/2 [a_{ij}^{(m)} + a_{ji}^{(m)}] \cdot (1 - k_{ji}) \quad (1.4c)$$

$$A_{jii}^{(m)} = 1/2 [a_{ii}^{(m)} + a_{ji}^{(m)} \cdot (1 - k_{ji})] \quad (1.4d)$$

Here \tilde{k}_{ij} is the average of the two binary parameters

$$\tilde{k}_{ij} = 1/2 (k_{ij} + k_{ji}) \quad (1.5)$$

and $a_{ij}^{(m)}$ represents the expression

$$a_{ij}^{(m)} = c_i \cdot \left[\frac{\sqrt{\epsilon_i \cdot \epsilon_j} \cdot q_i^m}{c_i \cdot k} \right] \cdot \frac{r_j \cdot d_{ij}^3 \cdot N_{av}}{\sqrt{2}} \quad (1.6)$$

with

$$d_{ij} = 1/2 (d_i + d_j) \quad (1.7)$$

k_{ij} and k_{ji} are adjustable parameters that are fitted to binary equilibrium data. If $k_{ij} = k_{ji}$, equation (1.3) reduces to a quadratic mixing rule.

The second-virial perturbation term is

$$a^{sv} = \frac{R \cdot T}{v} \cdot \sum_i \sum_j x_i \cdot x_j \cdot (B_{ij}^{disp} + B_{ij}^{\mu\mu} + B_{ij}^{QQ}) \quad (1.8)$$

The dispersion-contribution term needs cross parameters. They are given by

$$c_{ij} = 1/2(c_i + c_j) \quad (1.9)$$

$$(c \cdot v^+)_{ij} = c_i \cdot v_j^+ + c_j \cdot v_i^+ \quad (1.10)$$

$$T_{ij}^* = \left(\frac{c_i \cdot T_i^* \cdot c_j \cdot T_j^*}{c_{ij}^2} \right)^{1/2} \cdot (1 - k_{ij}^B) \quad (1.11)$$

The binary adjustable parameter k_{ij}^B is fitted to experimental second-virial cross coefficients for binary mixtures.

Cotterman (1985) gives details as well as mixing rules for polar terms and interpolation function **F**.

APPENDIX 2

Perturbed-Hard-Chain Equation of State in the Critical Region

To study the quality of the Perturbed-Hard-Chain equation of state in the critical region, the system carbon dioxide/naphthalene was chosen since extensive data are available for this system (Tsekhanskaya et al 1964).

The parameters for carbon dioxide given by Cotterman are fitted to a large data set, but away from the critical point. As in all other common equations of state, the critical pressure is overpredicted more than 20%, the critical temperature over 4 K.

To obtain a parameter set that better describes the critical region, the critical point was included in the fitting. The result is shown in figure (2.1). The critical temperature and pressure are fitted very well. However, the liquid side of the two phase region is now less accurate.

The effect on the calculated phase equilibrium is shown in figure (2.2). Especially in the high-pressure region, the improvement is large. But, more important, only the parameter set fitted in the critical region yields results at temperatures between 308 and 320 K. Calculation with the original parameter set does not converge in that temperature range since the equation of state predicts subcritical conditions in that temperature range.

The Perturbed-Hard-Chain equation has been chosen since it describes the solubility best, especially if the parameters are fitted to the critical region.

Other equations of state cannot describe solubilities at temperatures close to the solvent's critical point. At higher temperatures they are inferior to the Perturbed-Hard-Chain theory.

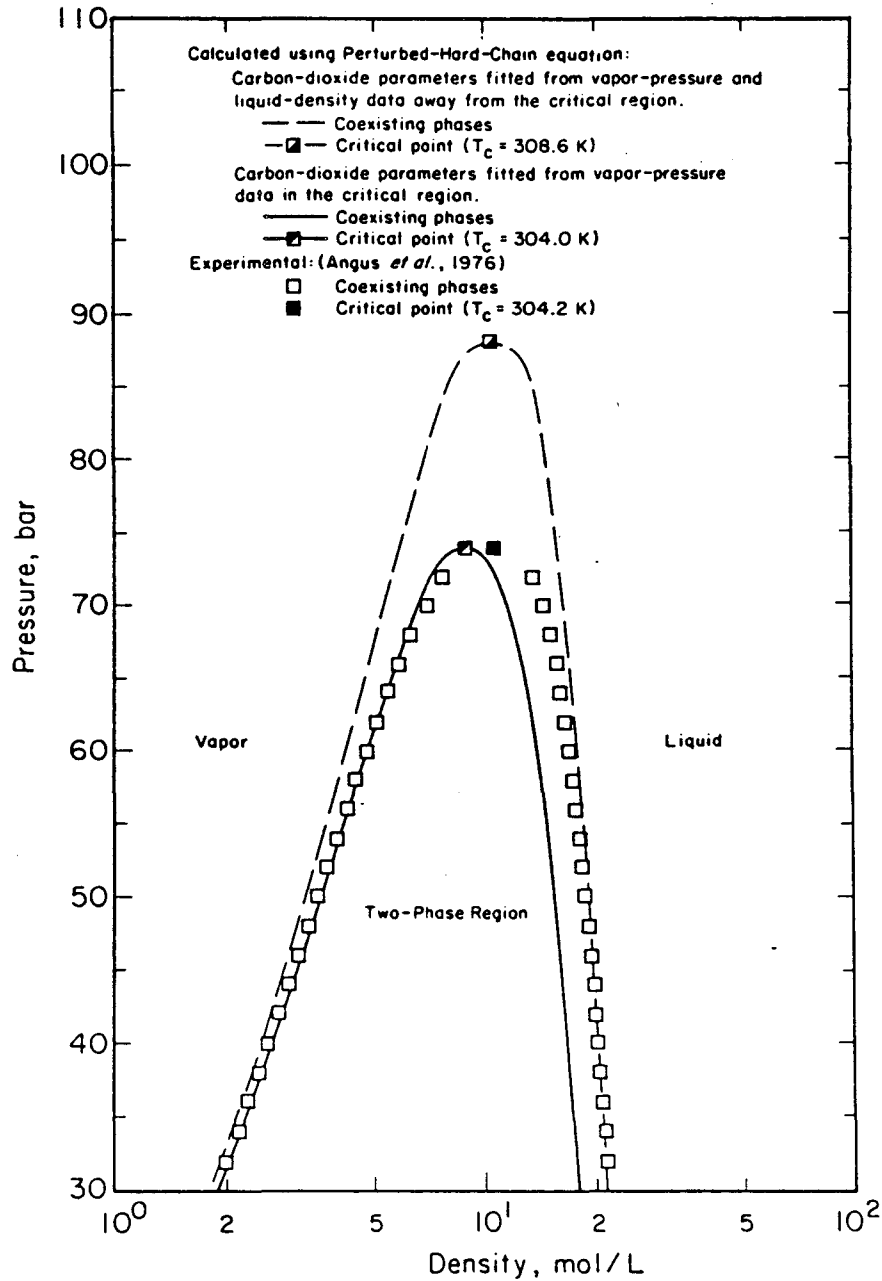


Figure (2.1): Calculated and experimental two phase region for carbon dioxide.

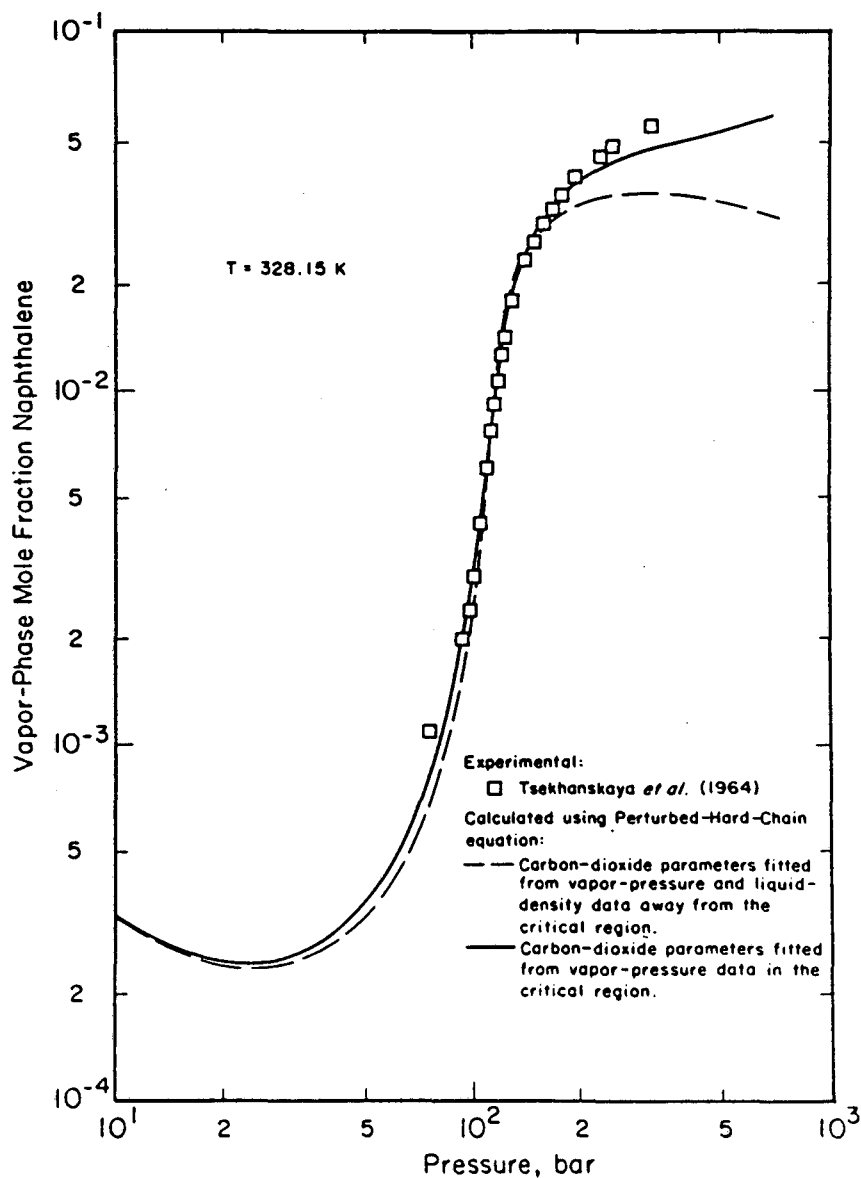


Figure (2.2): Effect of carbon dioxide parameters on the solubility of naphthalene in supercritical carbon dioxide at 328.15 K.

Figure (2.3) compares the Perturbed-Hard-Chain equation with the Boublik-Mansoori-van der Waals equation at 55°C. The Peng-Robinson equation shows the same results as the Boublik-Mansoori-van der Waals equation and is omitted in Figure (2.3). At lower temperatures the calculations for the Peng-Robinson and the Boublik-Mansoori-van der Waals equation did not converge.

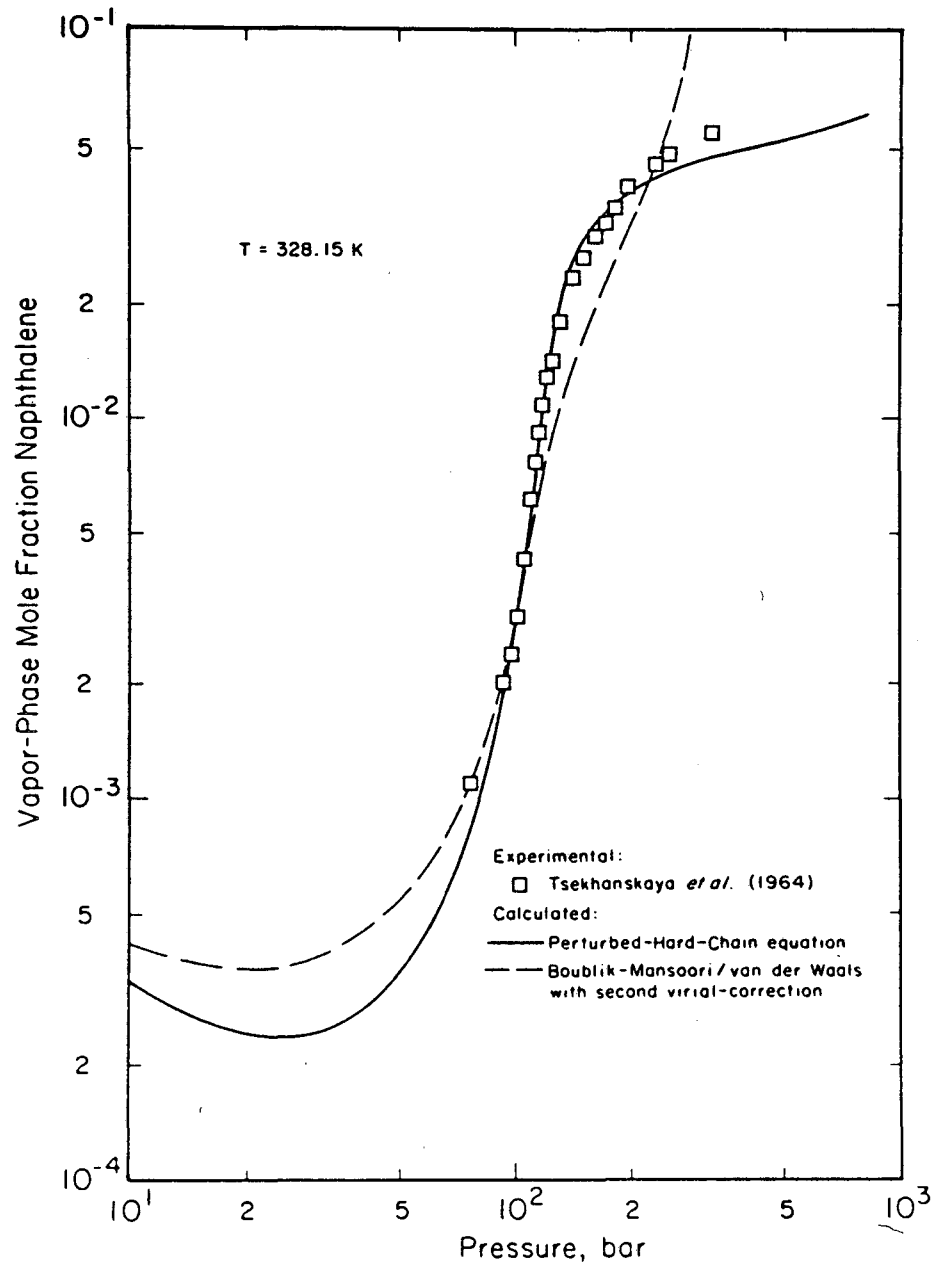


Figure (2.3): Solubility of naphthalene in supercritical carbon dioxide at 328.15 K.

APPENDIX 3

Description of Computer Program PURFIT

Program PURFIT fits the pure-component parameters of the Perturbed-Hard-Chain equation of state to experimental vapor-pressure, density and second-viariial-coefficient data. It also may be used to fit the critical point. The routine GRESS by Anderson is used, which uses a maximum-likelihood method. This routine takes into account uncertainties in the experimental data.

To fit the parameters to the critical point, the program calculates the critical point predicted by the Perturbed-Hard-Chain equation of state from the condition

$$\frac{\partial P}{\partial \rho} = \frac{\partial^2 P}{\partial \rho^2} = 0 \quad \text{at } T = T_c . \quad (3.1)$$

The literature value of the critical point is then used; there are three experimental data (critical temperature, pressure, and volume). If fitting to the critical point is not desired, data within a range of $\pm 5\%$ of the critical point are removed from the dataset, since in that region the accuracy of the equation of state decreases.

Copies of the program are available in Gilman Hall on the Berkeley Campus of the University of California.

APPENDIX 4

Description of Computer Program MIXFIT

Program MIXFIT fits the binary parameters of the Perturbed-Hard-Chain equation of state (k_{ij} , k_{ji} , and k_{ij}^B) to experimental phase-equilibrium data of the binary mixture, such as vapor-pressure, Henry's coefficient, solubility, liquid-liquid-equilibrium, or vapor-liquid-equilibrium data. For the regression, the REGRES routine is used. It is basically identical with routine GRESS by Anderson, used in program PURFIT. A maximum-likelihood method is used, which takes into account uncertainties of the experimental data.

To provide convergence close to critical points, the program uses the DENS routine by Topliss (1985), which solves the equation of state for the density using a method that is also reliable in critical regions. The FLASH routine (Topliss, 1985) is used to determine the compositions of phases in equilibrium.

Fitting solubility data for a solid in a fluid, it is possible to choose either the total pressure or the vapor concentration as independent variable.

Copies of the program are available in Gilman Hall on the Berkeley Campus of the University of California.

APPENDIX 5

Systems Containing Methanol

To study the effect of methanol as an entrainer, we need the binary parameters for the hydrocarbon/methanol systems.

Galivel-Solastiouk et al. (1986) measured vapor-liquid equilibria (VLE) for propane/methanol at 313.1, 343.1 and 373.1 K and at pressures between 0.35 and 43 MPa. This range is close to that regarded in this work. Therefore, an attempt was made to fit the binary parameters to these data. However, it was not possible to obtain a set of parameters that describes the system with sufficient accuracy. In some regions, the equilibrium is not even described qualitatively.

The experimental system propane/methanol has a liquid-liquid equilibrium (LLE). Figure (5.1) shows the pressure-temperature diagram for this system. Kuenen (1903) reports an upper critical solution temperature of 294.3 K. Galivel-Solastiouk's data do not show a liquid-liquid equilibrium, since they were obtained at temperatures higher than the upper critical solution temperature.

All equations of state have difficulties in describing critical phenomena correctly. The Perturbed-Hard-Chain equation of state predicts an upper critical solution temperature that is too high. Fitting the 313.1 K isotherm, the Perturbed-Hard-Chain equation erroneously shows liquid-liquid equilibria. The predicted upper critical solution temperature cannot be adjusted with the binary parameters.

Since the temperature range of interest for supercritical-fluid extraction with propane is close to the predicted upper critical solution temperature, it is not possible to describe quantitatively the phase equilibria containing methanol. Hence, no further calculations were performed for methanol as entrainer.

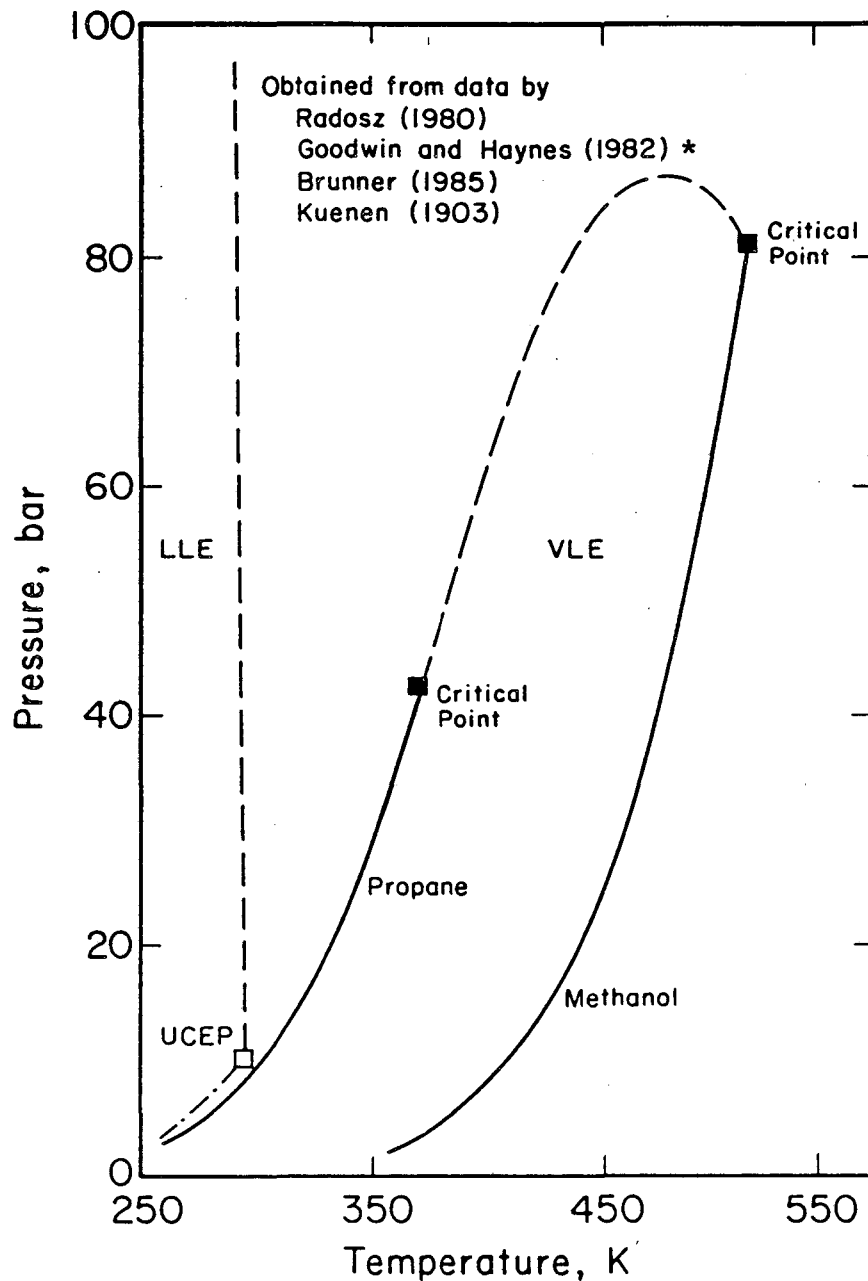


Figure (5.1): Pressure-temperature diagram for propane/methanol

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APPENDIX 6

Chemical Potential from an Equation of State

The chemical potential is obtained from an equation of state:

$$\mu_i = \int_V^{\infty} \left\{ \left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_j} - \frac{R \cdot T}{V} \right\} dV - R \cdot T \cdot \ln \frac{P^0 \cdot V}{n_i \cdot R \cdot T} + \mu_i^0(T) \quad (6.1)$$

or from an expression for the residual Helmholtz energy:

$$\mu_i = \left(\frac{\partial A^r}{\partial n_i} \right)_{T, V, n_j} - R \cdot T \cdot \ln Z + \mu_i^0(T) \quad , \quad (6.2)$$

where the superscript ⁰ indicates a reference state.

For continuous mixtures, Equation (6.1) changes to

$$\mu(I) = \int_V^{\infty} \left\{ \left(\frac{\partial P}{\partial (n_T \cdot F(I'))} \right)_{T, V, F(I'=I)} - \frac{R \cdot T}{V} \right\} dV - R \cdot T \cdot \frac{P^0 \cdot V}{n_T \cdot R \cdot T} + \mu^0(T, I) \quad (6.3)$$

and Equation (6.2) becomes

$$\mu(I) = \left(\frac{\partial A^r}{\partial (n_T \cdot F(I'))} \right)_{T, V, F(I'=I)} - R \cdot T \cdot \ln Z + \mu^0(T, I) \quad . \quad (6.4)$$

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