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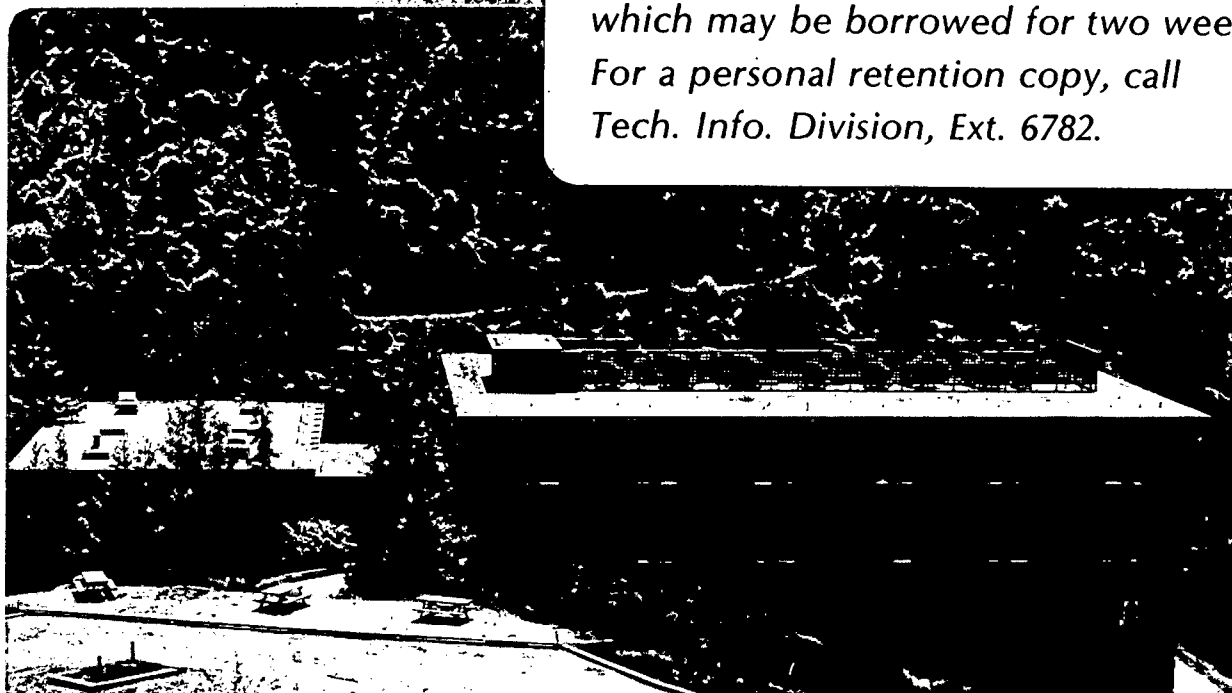
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DISCLAIMER

HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIA IN TERNARY SYSTEMS

CONTAINING TWO MISCIBLE LIQUIDS AND ONE SUPERCRITICAL GAS

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ABSTRACT

For process design in supercritical fluid extraction, it is desireable to use a molecular-thermodynamic model to calculate phase equilibria as a function of temperature, pressure and composition. A recently developed equation of state, applicable to mixtures of polar and nonpolar fluids, provides the desired model. The equation of state, using only pure-component and binary parameters, holds for gas-like and liquid-like densities; its extension to mixtures is based on the local-composition concept.

A reliable and efficient computer programm has been developed for calculating vapor-liquid, liquid-liquid or vapor-liquid-liquid equilibria in multi-component systems using the equation of state.

To illustrate, calculations are presented for the ternary system water-ethanol-carbon dioxide at temperatures and pressures slightly higher or lower than carbon dioxide's critical. Calculated distribution coefficients are sensitive to the choice of equation-of-state parameters.

INTRODUCTION

Supercritical-fluid extraction is a separation process wherein a fluid at supercritical temperatures and pressures is used for extraction of a solid or liquid. This separation process is attractive because, compared to conventional separation methods, it may have important advantages including energy savings, efficient recovery and high mass transfer rates.

Process design, computer simulation and optimization require a molecular-thermodynamic model that describes the pertinent phase equilibria. A physically reasonable, yet simple, model can improve our simulating capabilities and thereby reduce extensive experimental studies. A model does not eliminate the need for experimental data but it can reduce that need to a few reliable measurements.

Several authors have discussed models for phase-equilibrium calculations useful in supercritical-fluid extraction. Most notable among these are Professor R.C. Reid at MIT (1), Professor C.A. Eckert at Illinois (2) and especially, Professor M.E. Paulaitis at Delaware (3). The model we discuss here differs from those used previously not only in our choice of equation of state but, perhaps more important, in our choice of mixing rules, suitable for polar systems. We find that our model appears to be applicable to ternary systems containing polar components when we use only pure-component and binary parameters. Ternary parameters are not needed. However for good quantitative results, care must be exercised in the selection of binary parameters. Toward that end, we require only a few ternary data.

MOLECULAR-THERMODYNAMIC MODEL

Figure 1 shows the schematic essentials of supercritical-fluid extraction. Since the solvent is a supercritical fluid, we cannot easily use the conventional activity-coefficient models for calculating phase equilibria. We therefore use an equation of state, as indicated in Figure 2. Fugacity coefficients are calculated from the equation of state as indicated in Figure 3. While our proposed model is general, we illustrate it for the system water(1)-ethanol(2)-carbon dioxide(3).

Our equation of state for mixtures is described in in Figures 4-8. It is an equation of state of the van der Waals form, modified for non-spherical molecules upon using Prigogine's parameter c_i, where $3c_i$ is the number of external degrees of freedom for molecule i.

Figure 6 indicates a new method for extending an equation of state to mixtures. The essential novelty is that the mixing rules are density-dependent such that desireable boundary conditions are attained, as indicated in Figure 7. The Appendix gives the Helmholtz energy as a function of temperature, density and composition.

DATA REDUCTION AND PARAMETER ESTIMATION

Pure-component parameters are obtained from data reduction using experimental vapor pressures, liquid densities, and fugacities at high densities in the superheated region. Experimental and calculated vapor pressures for water are shown in Figure 9. The fit is excellent but, as commonly observed for equations of state of the van der Waals form, the calculated critical temperature and pressure are too high.

For each binary, there are two binary parameters, k_{ij} and l_{ij}, as indicated in Figures 5 and 8. Parameter α is the same for all binaries. These binary parameters are found from a few experimental, binary, phase-equilibrium data. Calculated binary phase diagrams are shown in Figures 10, 11 and 12. In these calculations $\alpha=0.2$. Figure 11 for water-carbon dioxide correctly reproduces the complex behavior at 25 °C and very high carbon dioxide concentration; it also correctly reproduces retrograde behavior at 50 °C.

Experimental data are not plentiful for ethanol-carbon dioxide; to fix binary parameters with confindence, we need some reliable measurements at high pressures (60-120 bars). A small change in the binary parameters can produce a large effect on the upper part of the diagram shown in Figure 12.

RESULTS AND DISCUSSION

Unfortunately, binary data, even extensive binary data, do not yield a unique set of a binary parameters. For a given binary, several sets of binary parameters may give nearly the same fit of the experimental data. This is an important matter because, when calculating the ternary phase diagram, small changes in the binary parameters can have a significant effect, especially in the size of the two-phase region, as shown in Figure 13.

Therefore, a few ternary phase-equilibrium data are needed to guide us in selecting the best binary parameters. This need for a few ternary data has been convincingly shown by T.F Anderson (4) using conventional activity-coeffi-cient models. That need is common to all existing models, regardless of whether they represent activity coefficients or PVT properties (equation of state).

With proper choice of binary parameters, it appears that our equation of

state can represent ternary phase equilibria, including vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibria. However, in the immediate critical region, it is difficult to obtain good agreement with experiment. Fortunately that region is of little interest in engineering because phase-contacting equipment cannot operate well in the immediate critical region because the difference in phase densities is too small.

When the equation of state and all parameters are fixed, corresponding phase equilibria are also fixed, in principle. However, the computer programs for calculating phase equilibria are far from trivial. We have developed such programs which are both efficient and reliable.

Our programs require 20-50 P-T flash calculations to define a phase diagram. The P-T flash routine generally converges after 5-10 fugacity-coefficient evaluations per phase. One evaluation is defined as the computation of the fugacity coefficient of each component in a given phase where the pressure, temperature and composition are specified. Each evaluation requires 0.1 CPU second on a VAX/VMS computer system.

CONCLUSIONS

Our conclusions are shown in Figure 14. While our present set of equation-of-state parameters is only fair, we are optimistic that calculated equilibria can be significantly improved by further small adjustment in these parameters. All our parameters are independent of temperature.

The essential achievement in this work is that we have established a promising model (and pertinent software) for calculating phase equilibria as required for process design for multicomponent supercritical fluid extraction.

The quantitative success of this model depends strongly on choice of model parameters. To obtain the optimum choice, we require only a _few_ reliable experimental measurements for the multicomponent system and for its constituent binaries.

ACKNOWLEDGEMENTS

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(1)   R.T. Kurnik, R.C. Reid, Fluid Phase Equilibria <u>8</u>, 93 (1982)

(2)   K.P. Johnston, D.H. Ziger, C.A. Eckert, IEC Fundam. <u>21</u>, 191 (1982)

(3)   M.E. Paulaitis, M.L. Gilbert, C.A. Nash,

      "Separation of Ethanol-Water Mixtures with Supercritical Fluids"

      2. World Congress of Chemical Engineering

      Montreal, Canada

      October 1981

(4)   J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R.Hsieh, J.P.

      O'Connell,

      "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid

      Equilibria"

      Prentice Hall, NJ 1980 (pg. 63-72)

APPENDIX

The Helmholtz energy of a mixture at given density, temperature and composition is given by

$$A(T,\rho,\zeta_i) - A^{id}(T,\rho,\zeta_i) = A^{ref} + A^{pert}$$

with

$$A^{ref} = n_T RT\ \tau\rho\ \langle cv^* \rangle\ (4 - 3\tau\langle v^* \rangle\rho)/(1 - \tau\langle v^* \rangle\rho)^2$$

$$A^{pert} = -(n_T RT/\alpha) \sum_i \zeta_i\ \ln \sum_j \zeta_j\ \exp(-\alpha q_i \eta_{ij}/RT)$$

$$\eta_{ij} = 0.5\ (RT/\sqrt{q_i q_j})\ (A_{ij}^{(1)^2}/A_{ij}^{(2)})\ (\exp(2\ A_{ij}^{(2)}/(T\ A_{ij}^{(1)})) - 1)$$

$A_{ij}^{(1)}$, $A_{ij}^{(2)}$ are Alder's Helmholtz-energy expansion coefficients

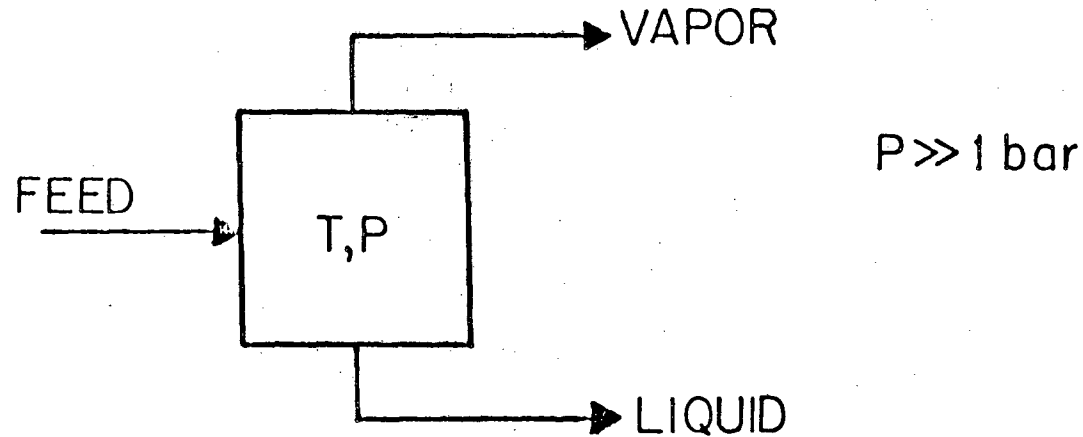for an ij-fluid at system temperature and pressure

R = gas constant

$\rho = n_T/V$

q_i = surface parameter, obtained from bond distances and bond angles

ζ = mole fraction (y for the vapor phase, x for the liquid phase)

$\tau = 0.7405$

SUPERCRITICAL FLUID EXTRACTION
FOR SEPARATION OF A LIQUID MIXTURE

$P \gg 1\,\text{bar}$

FEED CONTAINS TWO (OR MORE) MISCIBLE LIQUID
COMPONENTS PLUS A SUPERCRITICAL SOLVENT.

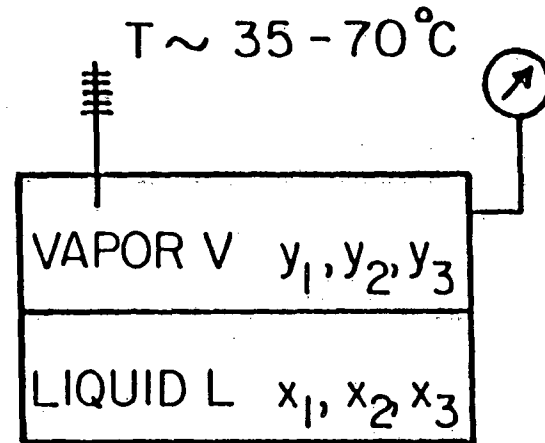THEREFORE, ORDINARY ACTIVITY-COEFFICIENT MODELS
ARE NOT USEFUL.

INDUSTRIALLY INTERESTING EXAMPLE:

WATER - ETHANOL - CARBON DIOXIDE

FIGURE 1

VAPOR-LIQUID EQUILIBRIA

FOR THE WATER (1)-ETHANOL (2)-CARBON DIOXIDE (3) SYSTEM

$T \sim 35 - 70°C$ $P \sim 50 - 150$ bar

VAPOR V y_1, y_2, y_3

LIQUID L x_1, x_2, x_3

y = MOLE FRACTION (V)

x = MOLE FRACTION (L)

AT EQUILIBRIUM

$$\phi_1^V y_1 = \phi_1^L x_1$$

$$\phi_2^V y_2 = \phi_2^L x_2$$

$$\phi_3^V y_3 = \phi_3^L x_3$$

ϕ = FUGACITY COEFFICIENT

COMPONENTS 1 AND 2 ARE SUBCRITICAL
BUT COMPONENT 3 IS SUPERCRITICAL

FUGACITY COEFFICIENT ϕ
FROM AN EQUATION OF STATE

$$RT \ln \phi_i = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \frac{RT}{V} \right] dV - RT \ln \frac{PV}{n_T RT} \qquad (1)$$

V = TOTAL VOLUME CONTAINING n_T MOLES

n_i = MOLES OF COMPONENT i

FOR EACH COMPONENT i, EQUATION (1) IS USED TWICE, ONCE FOR ϕ_i^L AND ONCE FOR ϕ_i^V.

VOLUMES V^V AND V^L ARE FOUND BY ITERATION FROM THE PRESSURE-EXPLICIT EQUATION OF STATE:

$$P = \mathcal{F} (T, V, n_i, n_j, \cdots)$$

FIGURE 3

PERTURBED HARD-BODY EQUATION OF STATE FOR MOLECULES WITH DENSITY-DEPENDENT ROTATIONS AND VIBRATIONS

$$P = P(\text{reference}) + P(\text{perturbation})$$

P(reference) IS GIVEN BY CARNAHAN-STARLING EQUATION AND PRIGOGINE'S PARAMETER c, WHERE

$$3c = \text{TOTAL NUMBER OF \underline{EXTERNAL} DEGREES OF FREEDOM (EQUIVALENT TRANSLATIONS)}$$

P(perturbation) IS GIVEN BY ALDER'S MOLECULAR-DYNAMICS CALCULATIONS FOR A SQUARE-WELL POTENTIAL.

FIGURE 4

EQUATION OF STATE FOR MIXTURES

FOR P(reference) WE USE A HYPOTHETICAL "PURE" FLUID WITH COMPOSITION-DEPENDENT SIZE PARAMETERS

$$\langle v^* \rangle = \sum_i \sum_j z_i z_j v_{ij}^*$$

z = MOLE FRACTION
  y (VAPOR)
  x (LIQUID)

$$\langle cv^* \rangle = \sum_i \sum_j z_i z_j c_{ij} v_{ij}^*$$

COMBINING RULES

$$(v_{ij}^*)^{1/3} = \frac{1}{2} (v_i^{*\,1/3} + v_j^{*\,1/3})(1 - \ell_{ij})$$

$$c_{ij} = \frac{1}{2}(c_i + c_j)$$

ℓ_{ij} IS A BINARY PARAMETER

FIGURE 5

EQUATION OF STATE FOR MIXTURES

FOR P.(perturbation) WE USE TWO-FLUID THEORY
WITH LOCAL MOLE FRACTIONS ζ_{ij} AS IN
WELL-KNOWN ACTIVITY-COEFFICIENT MODELS
(e.g. NRTL or UNIQUAC).

IN ACTIVITY-COEFFICIENT MODELS

$$\frac{x_{ij}}{x_{jj}} = \frac{x_i}{x_j} \exp\left[-\alpha \frac{(u_{ij}-u_{jj})}{RT}\right] \qquad \alpha = \text{PROPORTIONALITY FACTOR}$$

u_{ij} = FREE ENERGY OF AN ij <u>LIQUID</u> AT <u>FIXED DENSITY</u>

IN EQUATION OF STATE

$$\frac{\zeta_{ij}}{\zeta_{jj}} = \frac{\zeta_i}{\zeta_j} \exp\left[-\alpha \frac{(\eta_{ij}-\eta_{jj})}{RT}\right]$$

η_{ij} = FREE ENERGY OF AN ij <u>FLUID</u> AT <u>SYSTEM T AND P</u>

PROPERTIES OF EQUATION OF STATE
FOR MIXTURES

AT LOW DENSITIES (AS DENSITY $\rho \to 0$)

$$P \longrightarrow \rho RT$$

$$\frac{y_{ij}}{y_{jj}} \longrightarrow \frac{y_i}{y_j} \qquad \text{(RANDOM MIXING)}$$

SECOND VIRIAL COEFFICIENT

$$B_M = \sum_i \sum_j y_i y_j B_{ij}$$

AT HIGH DENSITIES (AS $\rho \to \rho^L$)

$$\frac{\zeta_{ij}}{\zeta_{jj}} \neq \frac{\zeta_i}{\zeta_j} \qquad \text{(NONRANDOMNESS) WHEN } \alpha \neq 0$$

FIGURE 7

EQUATION-OF-STATE PARAMETERS

FOR PURE COMPONENT i

$$v_i^*, \ c_i, \ T_i^*$$

$T^* = \varepsilon / ck$

k = BOLTZMANN'S CONSTANT

ε = CHARACTERISTIC POTENTIAL ENERGY

FOR BINARY ij

$$\ell_{ij} \text{ and } k_{ij}$$

$$T_{ij}^* = 2 \left(\frac{T_i^* c_i T_j^* c_j}{(c_i + c_j)^2} \right)^{1/2} (1 - k_{ij})$$

	T^*, K	v^*, cm^3/mol	c
WATER	439	10.6	1.81
ETHANOL	295	27.0	3.16
CARBON DIOXIDE	208	17.8	1.59

FIGURE 8
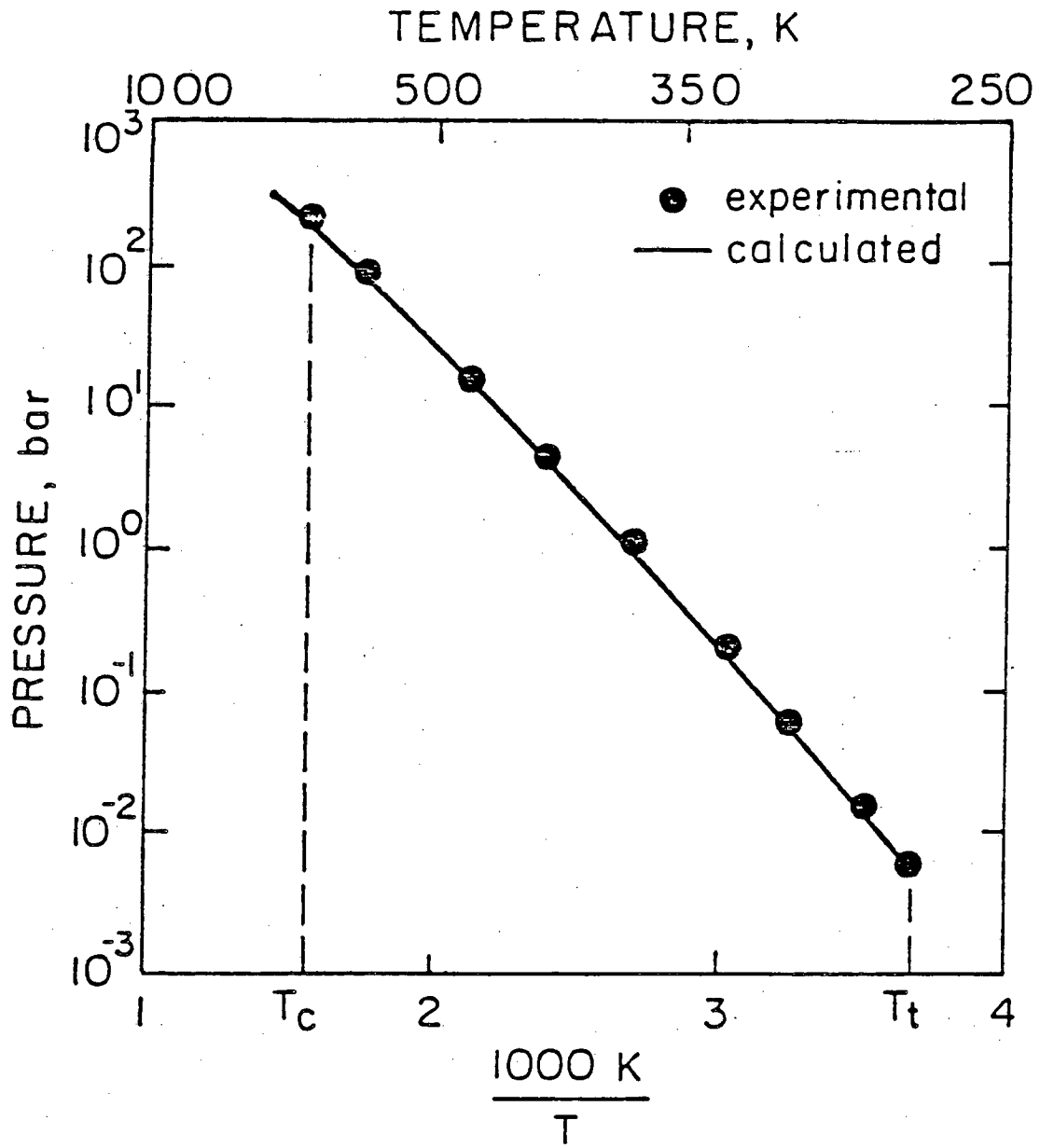
FIGURE 9

VAPOR - LIQUID EQUILIBRIA
FOR H_2O (1) / C_2H_5OH (2)
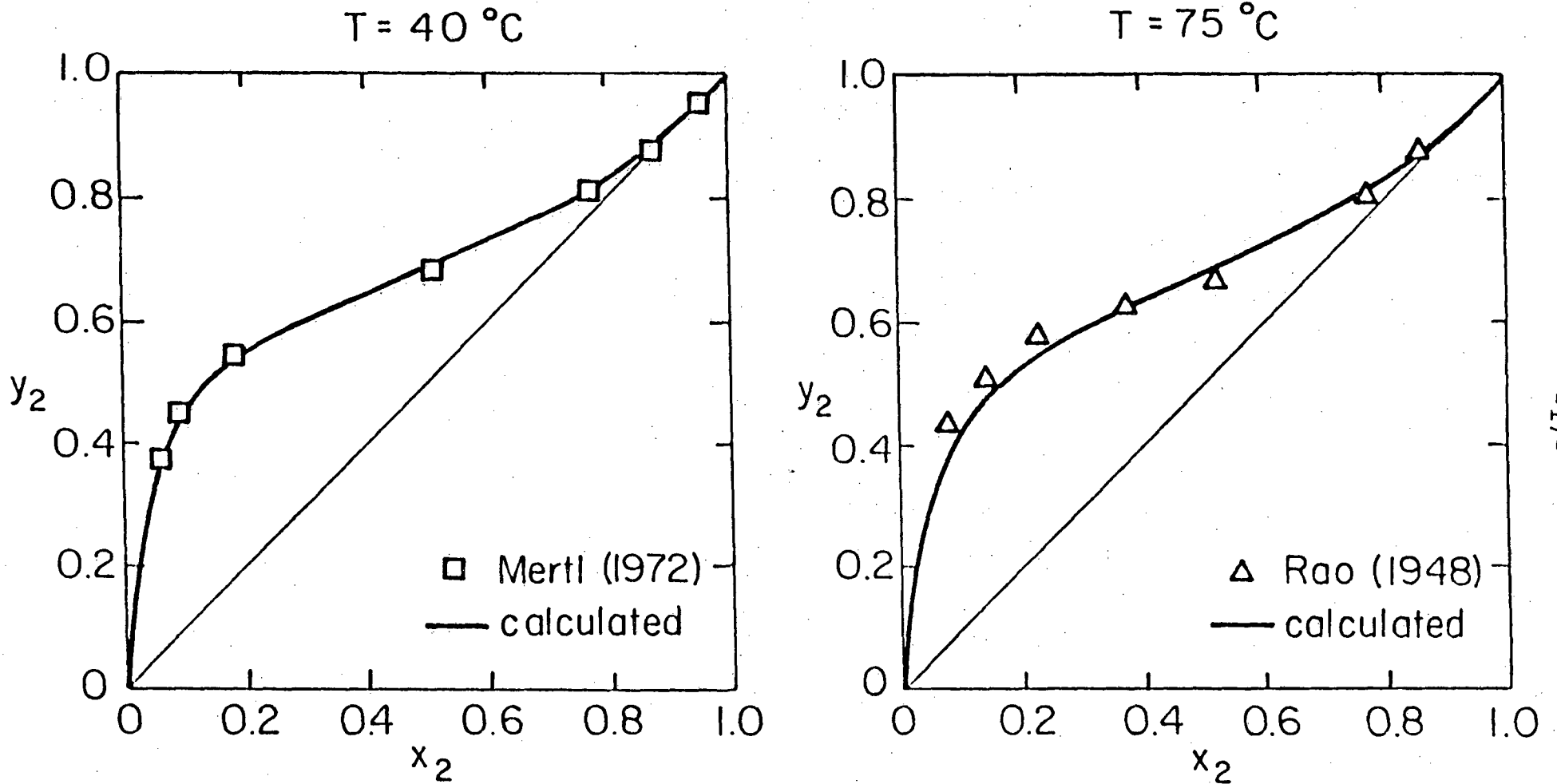
FIGURE 10

VAPOR-LIQUID EQUILIBRIA
FOR $H_2O(1)/CO_2(3)$

FIGURE 11

-18-
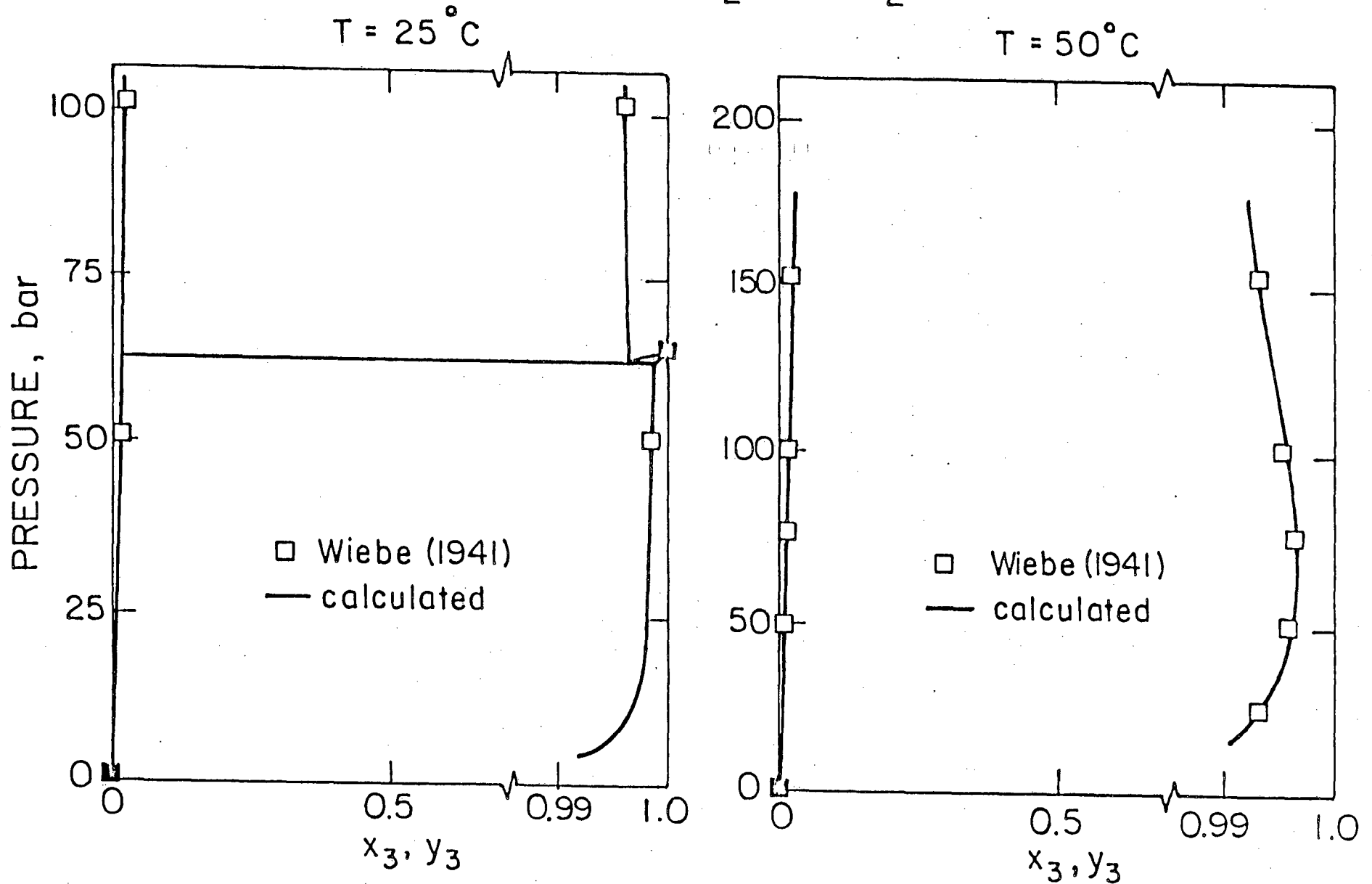
VAPOR-LIQUID EQUILIBRIA
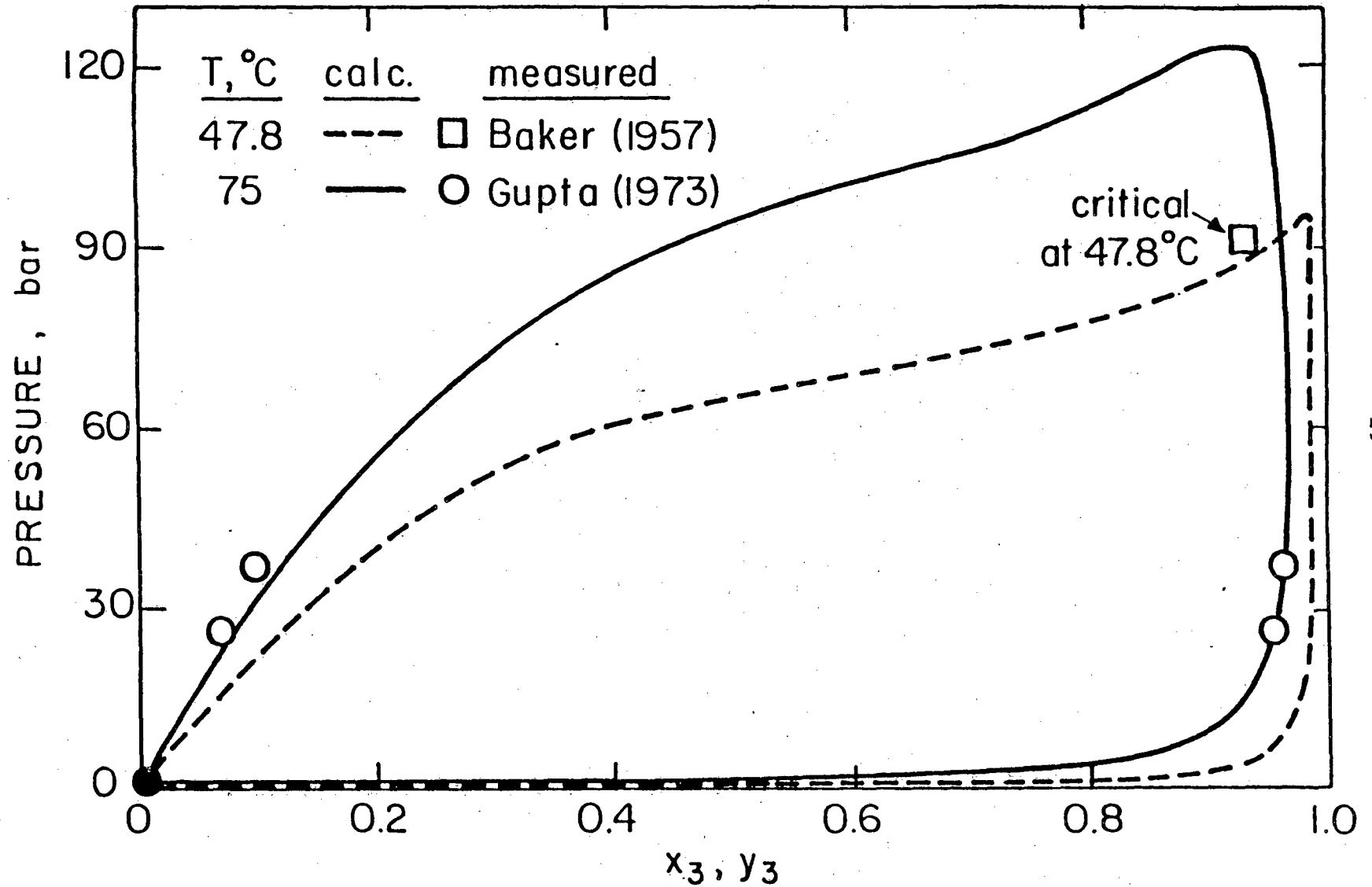FOR $C_2H_5OH(2)/CO_2(3)$

FIGURE 12

CALCULATED FLUID-FLUID EQUILIBRIA
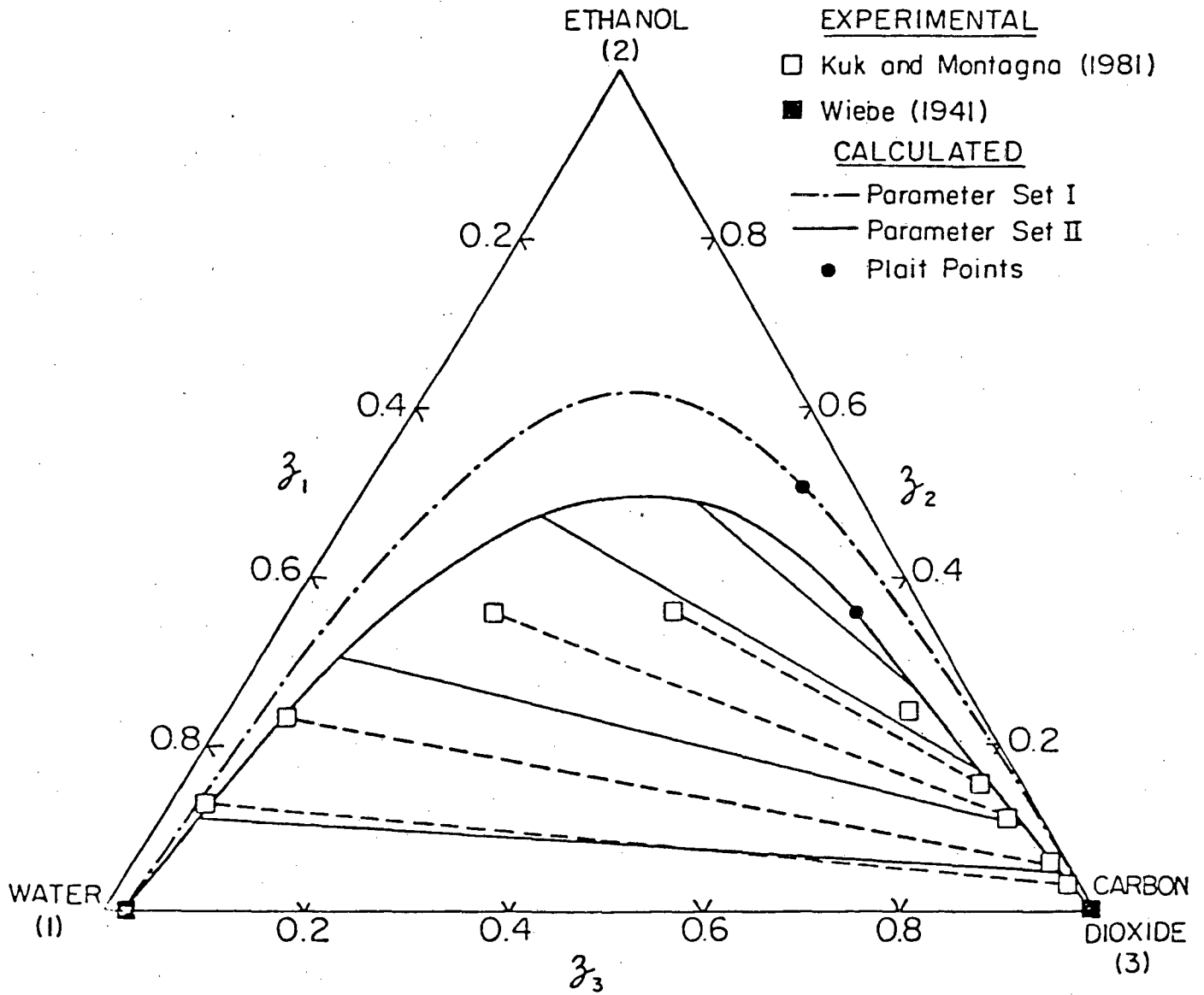FOR THE WATER-ETHANOL-CARBON DIOXIDE SYSTEM AT
40°C AND 103.4 BAR

FIGURE 13

CONCLUSIONS

1. A QUANTITATIVE MODEL HAS BEEN ESTABLISHED FOR
   PHASE EQUILIBRIA OF POLAR TERNARY FLUID MIXTURES
   CONTAINING ONE SUPERCRITICAL AND TWO SUBCRITICAL
   COMPONENTS.

2. COMPUTER PROGRAMS HAVE BEEN ESTABLISHED FOR VLE,
   LLE AND VLLE.

3. WHEN APPLIED TO WATER-ETHANOL-CARBON DIOXIDE,
   GOOD (BUT NOT PERFECT) RESULTS ARE OBTAINED.
   FOR SIGNIFICANT IMPROVEMENT, NEED
   a. SLIGHT ADJUSTMENT OF CO_2 PARAMETERS FOR
      BETTER RESULTS IN CRITICAL REGION.

   b. A FEW RELIABLE MEASUREMENTS FOR
      ETHANOL-CO_2 AT HIGH PRESSURES.

4. FOR SEPARATING WATER AND ETHANOL, EXTRACTION WITH CO_2
   a. PROBABLY DOES NOT BREAK AZEOTROPE
   b. YIELDS HIGHER ETHANOL PURITY AT
      LOWER TEMPERATURE (~20°C)
   c. REQUIRES LOWER SOLVENT FLOW AT
      HIGHER TEMPERATURE (~60°C)

FIGURE 14