COMPARISON OF CUBIC EQUATIONS OF STATE IN PREDICTING BEHAVIOR OF MIXTURES OF VARYING COMPLEXITY

by

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A

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This thesis is dedicated to my beloved parents

(Rahim and Farokh Tabatabaei Nejad)

for their unbounded support

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ABSTRACT

Accurate predictions of vapor-liquid equilibrium (VLE) and PVT data using equations of state (EOS) are important in the petroleum and chemical industries. One of the relatively simple and reliable forms of EOS is the cubic EOS form. Even though cubic EOS are considered to be reliable and simpler than non-cubic forms, the question of accuracy is still a matter of discussion.

The objective of this study involved the determination of the best EOS for consistently describing both liquid-vapor compositions and the corresponding phase densities. Other objectives were to assess whether or not more complicated EOS forms were useful in describing a progression of complexity of reservoir fluid systems.

To achieve these objectives, predictions using the various EOS were compared with corresponding experimental data. Five (SRK, PR, PT, SW, LLS), commonly used EOS of varying number of parameters were used to calculate VLE and phase densities for five chemical systems for which corresponding experimental data were available. Regressions were performed on VLE data to allow an assessment of which EOS form was optimal for a given mixture when the best values for the equation parameters used.

A comparison of the performance of the chosen cubic EOS for simple and complex mixtures before and after regression suggested that prediction of VLE composition data was improved when optimum parameters obtained by regression were used. However, the results indicated that the error associated in predicting VLE data after regression on all parameters was nearly the same for a given mixture regardless of which EOS was used. A three parameter EOS gives better prediction of liquid densities than the nominal two parameter forms. Liquid densities using the four parameter, Lawal-Lake-Silberberg form were inconsistent.

Among the five cubic EOS, the PT EOS did the best job in predicting both VLE and phase densities for the systems and conditions of this study, as predicted by Patel and Teja (1980) and Ahmed (1986).

Regression on single parameters a_i and b_i may have improved the prediction of VLE compositions more than regression on other parameters. However, an examination of density predictions using the regressed values of a_i and b_i reveals that the average error in values of liquid densities were often significantly greater than the values calculated before regression. Thus, regression on one type of data is risky if other types of data are to be described.

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NOMENCLATURE

a : Attraction parameter

b : Repulsion parameter

c : Third parameter used in PT EOS

f : Fugacity

f_w : Weight fraction

F : Objective function, used in Powell's method

i : Single carbon number index (=n,n+1,...,N) (Eqn. 5-5 to 5-9)

I : Multiple carbon number index (=1,2,3,...,N_g)

Int : Integer of the argument

M : Search direction (used in Appendix A)

Mw : Molecular weight

n : Number of moles; also first single carbon number in C_n+ fraction (Eqn. 5-4)

N : Last single carbon number in a C_n+ fraction

N_g : Number of multiple carbon groups (Pseudo-components)

NC : Number of components

NTL : Number of tielines

P : Absolute pressure

P_c : Critical pressure

P_{pc} : Pseudocritical pressure

P_r : Reduced pressure, P/P_c

P^{sat} : Saturated vapor pressure

R : Gas constant

T : Absolute temperature

T_c : Critical temperature

T_{pc} : Pseudocritical temperature

T_r : Reduced temperature, T/T_c

v : Molar volume, V/n

V : Volume

V_c : Critical volume

V_{pc} : Pseudocritical volume

x_i : Liquid mole fraction of component i

x_{exp} : Experimental liquid mole fraction

x_{cal} : Calculated liquid mole fraction

X_i : Independent variables, used in Powell's method

y_i : Vapor mole fraction of component i

y_{exp} : Experimental vapor mole fraction

y_{cal} : Calculated vapor mole fraction

z_i : over all concentration of component i (Eqn. 5-5 to 5-8)

Z : Compressibility factor

Z_c : Critical compressibility factor

α, β : Parameters used in LLS EOS

β_c : A parameter of function of ω, used in SW EOS

δ : Partial derivative

δ_{ij} : Binary interaction parameters

μ : Chemical potential

ρ_{exp} : Experimental density (liquid and/or vapor)

ρ_{cal} : Calculated density (liquid and/or vapor)

ω : Acentric factor, also third parameter in SW EOS

Ω : Parameter for LLS EOS, b/V_c

Ω_a , Ω_b , Ω_c : Experimentally evaluated parameters of EOS

1. INTRODUCTION

Accurate descriptions of thermodynamic properties are essential for design work in the petroleum and chemical industries. A knowledge of vapor-liquid equilibrium (VLE) and pressure-volume-temperature (PVT) behavior of fluids is a prerequisite for predicting petroleum reservoir performance in gas, condensate and volatile oil systems, and for predicting multi-contact miscibility in miscible oil recovery methods. Several methods of predicting thermodynamic properties are available to engineers (Abbott and Van Ness, 1972). These methods may be divided into three categories: the corresponding states principle and its extensions, methods based on equations of state (EOS), and activity coefficient methods. The corresponding states and activity coefficient methods will not be discussed in this work. The topic of this study involves the prediction of thermodynamic properties using EOS.

Generally, EOS predict VLE and densities of simple, non-polar compounds accurately, especially in the vapor phase (Tarakad et al, 1979). However, for practical description of petroleum mixtures, conventional practice involves fitting EOS parameters to experimental data prior to use in a reservoir simulator. The principle difficulties found with cubic EOS in these simulations are poor predic-

tions of liquid densities and inaccurate VLE predictions near the critical point (Teja & Patel, 1981). This study does not address the near critical problems, but concentrates on the consistency of representing both VLE and density data for systems not near the critical point using different EOS. Thus, the work of this study was an initial effort to decide which cubic EOS form is most appropriate for use in future compositional simulations of EOR processes.

Equations of state include both cubic in volume and non-cubic forms. In this study cubic forms were used because these forms offer the possibility for adequately describing all possible regions of VLE and PVT space with the economy of calculation required in large computer simulations of petroleum reservoir processes (Tarakad et al 1979).

This thesis is divided into several sections. The first section is a background section in which EOS, in general, and the development of the five EOS used in this study are described. Next a review of previous studies in which the performance of cubic EOS were compared. This is followed by a review of previous studies in which regression for obtaining EOS parameters were conducted. An objective section presents a more comprehensive statement of the

approach use to achieve objectives of this study. A methods section includes descriptions of the regression procedures used in this study and the lumping procedures used in characterizing the heavy components for the separator oil-CO_2 system. The results section includes a presentation of the errors between experimentally measured VLE and phase density data and calculated values both before and after regression on VLE data. An analysis of the results is followed by conclusions and suggestions for further work.

2. CUBIC EQUATIONS OF STATE

Cubic equations of state (EOS) are commonly used forms in calculations involving phase properties of complex mixtures found in petroleum reservoir fluids. Here, background information on the use of general EOS in phase behavior calculations and cubic EOS for reservoir fluid phase behavior is presented. The development of cubic EOS forms is then traced from the development by van der Waal's (1873) to popular forms found in recent literature and used in this study.

2.1 EOS and Phase Behavior

An equation of state (EOS) may be defined as an expression of the analytical relationship between the equilibrium state variables of pressure (P), volume (V), temperature (T), and composition (x_i, y_i; where x_i and y_i are, respectively, the liquid and vapor concentrations of component i). For any homogeneous fluid of constant composition and existing in equilibrium in a PVT system the relationship between P, V, and T can be written as:

$$V = V(T,P,x) \qquad (2\text{-}1)$$

These relationships are called PVT EOS.

The criterion for phase equilibrium for PVT systems of

uniform T and P may be concisely stated by equality of the chemical potentials (Van Ness and Abbott, 1982):

$$\mu^{\alpha}_i=\mu^{\beta}_i=\ldots=\mu^{\pi}_i \quad (i=1,2,\ldots,n) \qquad (2\text{-}2)$$

where μ^{α}_i = chemical potential of component i in phase α

This equation (2-2), in terms of fugacity, may also be written as:

$$f^{\alpha}_i=f^{\beta}_i=\ldots=f^{\pi}_i . \qquad (2\text{-}3)$$

where f^{α}_i = fugacity of component i in phase α

In this study, two phases (liquid, 1, and vapor, v) are used and equation (2-3) becomes:

$$f^{v}_i=f^{l}_i \quad (i=1,2,\ldots,n) \qquad (2\text{-}4)$$

Each f^{v}_i is a function of T, P, and n-1 independent vapor-phase mole fractions (y_i). Similarly, each f^{l}_i is a function of T, P, and n-1 independent liquid-phase mole fractions (x_i). from these constraints, VLE problems fall into one of five categories:

1. Calculate T and y_i at given P and x_i.
2. Calculate p and y_i at given T and x_i.
3. Calculate T and x_i at given P and y_i.
4. Calculate p and x_i at given T and y_i.
5. Calculate x_i and y_i at given T, P and z_i.

Numbers 1 and 2 are known as bubble-point calculations, 3 and 4 are known as dew-point calculations and 5 is called a flash calculation.

Although the details of the procedures differ for each of the VLE calculations presented above, they all begin with the same mathematical formulation (Van Ness & Abbott, 1982). Fugacities are expressed as functions of T, P, and compositions are derived from an EOS. An iterative procedure is employed to satisfy the conditions of equilibrium, i.e. Equation (2-4). For flash calculations, mass conservation must also be satisfied. Once the T, P and phase compositions are known, calculation of V or its inverse, density, is straight forward with the EOS, Equation (2-1).

EOS are considered to be either theoretical or semi-theoretical (Patel & Teja 1980). Theoretical equations are based on either kinetic or statistical mechanics models involving intermolecular forces, while the semi-theoretical equations combine theoretical concepts with correlations on a limited amount of experimental data. According to Patel and Teja (1980), the semi-theoretical EOS have been the most successful in representing properties of interest.

In this study, only cubic EOS are used (Equation (2-12)). Although cubic EOS are generally considered to be reliable, relatively simple, and computationally inexpensive (Patel & Teja, 1980), the question of accuracy is still a matter of discussion, especially when describing the VLE or PVT behavior of complex mixtures like reservoir fluids

(Patel & Teja, 1980 and Ahmed, 1986). Numerous equation forms have appeared in the literature and development of new forms is, no doubt, on-going. As with EOS in general, cubic EOS may be based on both theoretical and empirical considerations. But all cubic EOS have fundamental discrepancies at the critical point (Kossack et al, 1985) and, some investigators consider that all cubic EOS should be considered empirical forms when applied to the span of conditions associated with petroleum reservoir fluids. The parameters of cubic EOS may be adjusted to fit particular data sets. Such optimization of parameters implies that predictions using EOS may never describe the behavior of reservoir fluids for all regions and all thermodynamic properties without a significant error. Therefore, absolute conclusions about best EOS forms are difficult.

2.2 Gas Equations

For over 300 years, people have tried to describe the volumetric properties of gases. The first attempt was by Boyle, and this effort finally led to the ideal gas law, the simplest form of an equation of state (Patel & Teja 1980):

$$PV = nRT \qquad (2\text{-}5)$$

where:

P = pressure

V = volume

n = number of moles

R = gas constant

T = temperature

For real gases the ideal gas equation is often inaccurate. An improvement in the ideal gas equation was obtained by introducing an empirically determined compressibility factor, Z, which is a function of pressure and temperature. Thus, equation (2-5) becomes:

$$PV = ZnRT \qquad (2\text{-}6)$$

The compressibility factor, Z, is a measure of the departure of PVT behavior of an actual gas from that of an ideal gas where Z= 1 for the ideal gas.

2.3 Cubic EOS

The publication of van der Waals' classical equation of state (1873) was result of a systematic effort to describe the occurrence of two phases and the equilibrium properties of real gases. The van der Waals equation for a single component has been written in the following form:

$$P = \frac{RT}{(v-b)} - \frac{a}{v^2} \qquad (2\text{-}7)$$

where:

P, T, and R were defined in equation (2-5)

a,b are constants; 'a' is called the

attraction parameter (attraction forces between the molecules) and 'b' is called the repulsion parameter (related to the molecular size)

v = molar volume (V/n)

The van der Waals equation (2-7) is an analytical cubic EOS which satisfies thermodynamic stability criteria at the critical point (Reid et al. 1977), i.e:

$$(\delta P/\delta V)_{T_c} = 0 \qquad (2\text{-}8)$$

and

$$(\delta^2 P/\delta V^2)_{T_c} = 0 \qquad (2\text{-}9)$$

The constants a and b, are defined by:

$$a = \frac{27}{64}\frac{R^2 T_c^{\,2}}{P_c} \qquad (2\text{-}10)$$

$$b = \frac{1}{8}\frac{RT_c}{P_c} \qquad (2\text{-}11)$$

where:

T_c is the critical temperature

P_c is the critical pressure

Equation (2-7) may also be written as:

$$Z^3 - (B+1)Z^2 + AZ - AB = 0 \qquad (2\text{-}12)$$

where:

Z is gas compressibility factor and is defined as Pv/RT

$$A = \frac{aP}{R^2T^2} \qquad (2\text{-}13)$$

$$B = \frac{bP}{RT} \qquad (2\text{-}14)$$

Equation (2-12) is a cubic in Z (or v) and hence, the term cubic EOS has been used. For mixtures, a and b are defined by the following mixing rules:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \qquad (2\text{-}15)$$

$$b_m = \sum_i \sum_j x_i x_j b_{ij} \qquad (2\text{-}16)$$

where:

the subscript m indicates the value to be used with the mixture

x_i and x_j are the mole fractions in each phases, vapor or liquid

$$a_{ij} = (a_{ii} a_{jj})^{1/2} \qquad (2\text{-}17)$$

$$b_{ij} = (1/2)(b_{ii} + b_{jj}) \qquad (2\text{-}18)$$

The van der Waals (VDW) EOS proved to have deficiencies in predicting phase behavior or VLE near the critical region, in predicting VLE of complicated mixtures, and in predicting densities, especially liquid densities. Numerous modifications to improve the accuracy of the prediction of the results have been presented. The Redlich-Kwong (RK) EOS (Redlich & Kwong, 1949) is one of the successful modifications of van der Waal's equation. Like the VDW equation, the RK equation has two constants (a and b) which were based on theoretical and practical, or empirical considerations. Redlich and Kwong found by experiment that the volume of all gases approaches a limiting value at high pressure and they

assumed for their equation that

$$b = .26\ V_c \tag{2-19}$$

where:

V_c = critical volume

The form presented by Redlich and Kwong was:

$$P = \frac{RT}{(v-b)} - \frac{a}{T^{1/2}v(v+b)} \tag{2-20}$$

where:

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c}, \quad \Omega_a = 0.42748 \tag{2-21}$$

$$b = \Omega_b \frac{RT_c}{P_c}, \quad \Omega_b = 0.08664 \tag{2-22}$$

Equation (2-20) may also be expressed as:

$$Z^3 - Z^2 + (A-B^2-B)Z - AB = 0 \tag{2-23}$$

where B is the same as defined by VDW and:

$$A = \frac{aP}{R_2 T^{2.5}} \tag{2-24}$$

Redlich and Kwong used the same mixing rule for the attraction parameter, a_m, as VDW and for b:

$$b_m = \sum_i x_i\ b_i \tag{2-25}$$

where b_m, b_i, and x_i have been defined earlier.

The RK equation (2-20) differs from the VDW equation (2-7) in that temperature is included in the attraction term $(a/T^{1/2})$ and the mixing rules are slightly different. This equation gives satisfactory results above the critical temperature for any pressure, as long as the compounds are

not very complex (Shah & Thodos, 1965).

Even though the RK EOS was an improvement over the VDW EOS above T_c and P_c while maintaining simplicity, it does no better than the VDW equation in the near critical region. Patel (1980) found that the deficiencies of the RK equation are related to the fact that it contains only two parameters and predicts a universal critical compressibility which is much higher than the actual experimental value for almost all fluids.

Soave (1972) proposed a modified RK EOS. He believed that the RK equation gave poor prediction for VLE because the influence of temperature was not represented adequately. Therefore, he proposed that 'a' be a function of temperature and the Pitzer acentric factor, ω. The acentric factor is defined as (Van Ness & Abbot, 1982):

$$\omega = -1-\log10(P_r^{sat})_{Tr=.70} \qquad (2\text{-}26)$$

where:

$(P_r^{sat})_{Tr=0.7}$ = reduced vapor pressure (P^{sat}/P_c), evaluated at $T_r = 0.7$

P^{sat} = saturated vapor pressure

T_r = reduced temperature, T/T_c

The Soave-Redlich-Kwong (SRK) equation is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)} \qquad (2\text{-}27)$$

where:

$$a(T) = a(T_c)\ \alpha(T) \qquad (2\text{-}28)$$

$$a(T_c) = \Omega_a \frac{R^2 T_c^{\,2}}{P_c}, \quad \Omega_a = 0.42478 \qquad (2\text{-}29)$$

$$\alpha(T) = (1+m(1-T_r^{\,1/2}))^2 \qquad (2\text{-}30)$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \qquad (2\text{-}31)$$

$$b = \Omega_b \frac{RT_c}{P_c}, \quad \Omega_b = 0.08664 \qquad (2\text{-}32)$$

Equation (2-27) can be rewritten as:

$$Z^3 + Z^2 + (A-B^2-B)\ Z - AB = 0 \qquad (2\text{-}33)$$

where A and B are defined in the same manner as in the VDW EOS and the mixing rule for b_m is the same as for the RK EOS. For a_m the mixing rule is:

$$a_m = \sum_i \sum_j x_i\ x_j\ (a_i a_j)^{1/2} (1-\delta_{ij}) \qquad (2\text{-}34)$$

where:

x_i and x_j are defined the same as VDW.

δ_{ij} is an empirically defined binary interaction coefficient which must be obtained experimentally.

To demonstrate the effectiveness of the modified equation (2-25), Soave calculated the vapor pressures of a number of hydrocarbons and compared these values with experimental data. The results of these comparisons indicate a significant improvement over the original RK equation (2-20) in both the predictions of vapor pressures and in predicting phase compositions. However, Soave

observed relatively larger deviations for systems containing carbon dioxide, hydrogen sulfide and other polar compounds. The calculated liquid densities were, in general, lower than experimental values. However, for small molecules like argon, nitrogen and methane at very low temperature, predicted values of liquid densities were slightly higher than experimental values.

Peng and Robinson (1976) presented a new two-parameter equation of state. In their equation the attractive pressure term, a, of the semi-empirical van der Waals equation was modified. The Peng-Robinson (PR) equation form is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \qquad (2\text{-}35)$$

where:

$$a(T) = a(T_c)\,\alpha(T) \qquad (2\text{-}36)$$

$$a(T_c) = \Omega_a \frac{R^2 T_c^{\,2}}{P_c}, \quad \Omega_a = 0.45724 \qquad (2\text{-}37)$$

$$\alpha(T) = (1+m(1-T_r^{\,1/2}))^2 \qquad (2\text{-}38)$$

$$m = 0.37464 + 1.54226\omega - 0.2699\omega^2 \qquad (2\text{-}39)$$

$$b = \Omega_b \frac{RT_c}{P_c}, \quad \Omega_b = 0.0778 \qquad (2\text{-}40)$$

Equation (2-35) can be rewritten as:

$$Z^3 + (1+B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \qquad (1\text{-}40)$$

where A, B and the mixing rules are the same as for the SRK EOS.

The PR equation (2-35) holds the same combination of simplicity and accuracy as the SRK (2-27) equation and both equations predict vapor densities with similar accuracy. The PR EOS is superior to SRK in the representation of vapor pressures and liquid densities. In general, the PR equation gives better results than SRK, RK or VDW when predicting liquid phase properties (i.e. density, composition etc.). Exceptions occur in the predictions of very light components, such as argon, for which it gives poor prediction in the region away from the critical point (T_r<0.8) (Patel & Teja 1982).

The PR equation assumes that the critical compressibility factor, Z_c, be constant with a value of 0.3074 which may be compared with the values of Z_c for the SRK equation or 0.333. This difference in values of Z_c accounts for improved predictions for heavier components (Patel & Teja 1982). However, due to the constant Z_c, the PR EOS is limited when predicting VLE and liquid densities near the critical region. Patel and Teja (1982) believed that the applicability of PR equation could be extended to a wide range of substances if a way could be found to make the predicted critical compressibility a substance dependent parameter.

As temperatures approach the critical temperature,

Schmidt and Wenzel found that large deviations between calculated and experimentally determined values of liquid volume occurred because the experimental critical volume is not accurately reproduced. Schmidt and Wenzel (1979) presented a cubic equation of the van der Waals type in which the critical compressibility factor was taken as substance dependent. They treated the parameters 'a' and 'b' similar to that proposed by Soave (1972) and Peng-Robinson (1976), ie, 'a' is temperature dependent, while 'b' is only a function of the critical properties. The constants in parameters 'a' and 'b' are also functions of ω. The Schmidt-Wenzel (SW) equation form is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2+(1+3\omega)bv-3\omega b^2} \qquad (2\text{-}42)$$

where:

$$a(T) = a(T_c)\ \alpha(T) \qquad (2\text{-}43)$$

$$a(T_c) = \Omega_a \frac{R^2 T_c^{\,2}}{P_c} \qquad (2\text{-}44)$$

$$b = \Omega_b \frac{RT_c}{P_c} \qquad (2\text{-}45)$$

$$\Omega_a = 3(1-Z_c(1-\beta_c))^3 \qquad (2\text{-}46)$$

$$\Omega_b = \beta_c Z_c \qquad (2\text{-}47)$$

and β_c is the smallest positive root of the equation:

$$(6\omega+1)\ \beta_c^{\,3} + 3\beta_c^{\,2} + 3\beta_c - 1 = 0 \qquad (2\text{-}48)$$

$$Z_c = \frac{1}{3(1-\beta_c \omega)} \qquad (2\text{-}49)$$

$$\alpha(T) = (1+m(1-T_r^{\,1/2}))^2 \qquad (2\text{-}50)$$

For the slope, m, the authors proposed the following

expression:

$$m = m_1 \quad \text{for } \omega \leq 0.40$$

$$m = m_2 \quad \text{for } \omega \geq 0.55$$

$$m = ((\omega-0.4)/0.15)\ m_2 + ((0.55-\omega)/.15)\ m_1 \quad \text{for } 0.4 < \omega < 0.55 \qquad (2\text{-}51)$$

where:

$$m_1 = m_o + \frac{(5T_r - 3m_o - 1)^2}{70} \qquad (2\text{-}52)$$

$$m_2 = m_o + \frac{71(T_r - 0.779)^2}{100} \qquad (2\text{-}53)$$

$$m_o = 0.465 + 1.347\omega - 0.528\omega^2 \quad \text{for } \omega \leq 0.3671 \qquad (2\text{-}54)$$

$$m_o = 0.5361 - .9593\omega \quad \text{for } \omega > 0.3671 \qquad (2\text{-}55)$$

For supercritical ($T_r > 1$) compounds:

$$\alpha(T) = 1 - (0.4774 + 1.328\omega)\ \ln T_r \qquad (2\text{-}56)$$

Equation (2-42) can be rewritten as:

$$Z^3 + (UB-B-1)\ Z^2 + (WB_2 - UB_2 - UB + A)\ Z - (WB_3 + WB^2 + AB) = 0 \qquad (2\text{-}57)$$

where:

$$U = 1+3\omega \qquad (2\text{-}58)$$

$$W = -3\omega, \text{ and} \qquad (2\text{-}59)$$

A and B are the same as for the SRK EOS. The mixing rules for a_m and b_m are the same as the SRK EOS and the mixing rule for ω is given by:

$$\omega_m = \frac{\sum_i (\omega_i x_i b_i \cdot^7)}{\sum_i (x_i b_i \cdot^7)} \qquad (2\text{-}60)$$

It can be seen from equations (2-46 & 2-47), that with the SW EOS values of the Ω's are not constant and, more importantly, they are functions of the critical compressibility and acentric factors.

By comparing calculations with experimental values, Schmidt and Wenzel demonstrated that their EOS reproduces experimental data at pressures above 1 bar with an accuracy similar to that of the PR equation (liquid volume, which basically leads to be the liquid density improvement, and pressure by keeping temperature constant or change of temperature, keeping the pressure constant). However, for some inorganic gases, the PR equation produces slightly better results. At lower pressures the SW EOS yields better agreement with experiments than either the SRK or PR equations. Schmidt and Wenzel demonstrated that their equation describes, for low reduced temperatures, molar liquid volume with an error of less than two percent.

Schmidt and Wenzel (1980, 1981) indicated that an accurate representation of liquid density becomes important when the molar volume or density is used to correlate and to predict the EOS parameters of a substance for which no critical data are available. Such correlations, for other

cubic EOS have been investigated elsewhere (Hederer et al, 1976 and Brunner et al, 1977).

Although, the SW equation was made more complicated by the introduction of a substance dependent critical compressibility factor, in comparison with the SRK and PR EOS, they found no noticeable increase in calculation time, nor were convergence difficulties observed when calculating vapor pressures or VLE of mixtures.

In an effort to find a cubic equation of state suitable for representing both single phases, vapor and liquid as well as two-phase behavior (VLE), a three parameter equation of state was proposed by Patel and Teja (1980). This equation requires Tc and Pc, as well as two additional measured values (Z_c, m) to characterize each particular fluid (Patel & Teja 1982). The first parameter, Z_c, is the critical compressibility factor which is a function of the acentric factor, ω. The second parameter, m, is a function of the acentric factor similar to the m of previously presented EOS. Values of these parameters are obtained by minimizing deviations in saturated liquid densities while simultaneously satisfying the equality of fugacities along the saturation curve. Patel and Teja (1982) attribute good predictions of volumetric properties in the liquid region while maintaining accuracy in VLE calculations to the method

of evaluating ζ_c and m. In the case of non-polar fluids, Patel and Teja (1982) suggest that the two parameters required can be correlated with the acentric factor, so that, with suitable assumptions, the equation reduces to forms similar to those of SRK, PR, and SW. Thus, the PT equation retains many of the good features of those three equations and in addition, can be successfully applied to polar fluids such as water, ammonia, and alcohols. Patel and Teja also demonstrated the extension of this equation to mixtures. The Patel-Teja (PT) equation form is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+c(v-b)} \qquad (2\text{-}61)$$

Where:

$$a(T) = a(T_c)\ \alpha(T) \qquad (2\text{-}62)$$

$$a(T_c) = \Omega_a \frac{R^2 T_c^{\,2}}{P_c} \qquad (2\text{-}63)$$

$$b = \Omega_b \frac{RT_c}{P_c} \qquad (2\text{-}64)$$

$$c = \Omega_c \frac{RT_c}{P_c} \qquad (2\text{-}65)$$

$$\Omega_a = 3Z_c^{\,2} + 3(1-2Z_c)\ \Omega_b + \Omega_b^{\,2} + (1-3Z_c) \qquad (2\text{-}66)$$

As with the SW EOS, the values of Ω_a, Ω_b, and Ω_c for this equation are functions of critical compressibility and acentric factor. The values of Ω_b are defined as the smallest positive root of the equation:

$$\Omega_b^{\,3} + (2-3Z_c)\ \Omega_b^{\,2} + 3Z_c^{\,2}\Omega_b - Z_c^{\,3} = 0 \qquad (2\text{-}67)$$

while,

$$\Omega_c = 1 - 3Z_c \qquad (2\text{-}68)$$

$$\alpha(T) = (1+m(1-T_r^{1/2}))^2 \qquad (2\text{-}69)$$

$$m = 0.452413 + 1.30982\omega - 0.295937\omega^2 \qquad (2\text{-}70)$$

and

$$Z_c = 0.329032 - .076799\omega - 0.0211947\omega^2 \qquad (2\text{-}71)$$

The PT equation (2-61) can be rewritten as:

$$Z^3 + (C-1)\ Z^2 + (A-2BC-B-C-B^2)\ Z +$$

$$(BC+B^2\,C-AB) = 0 \qquad (2\text{-}72)$$

where A and B are the same as for the SRK EOS and C is defined as:

$$C = \frac{cP}{RT} \qquad (2\text{-}73)$$

The mixing Rule for c is:

$$c_m = \sum_i x_i c_i \qquad (2\text{-}74)$$

Patel and Teja (1980, 1982) demonstrated the capability of their EOS for the accurate and consistent predictions of thermodynamic properties of both pure fluids and mixtures. They stated that the most interesting feature of the new equation is its applicability to mixtures containing heavy hydrocarbons and polar substances, while, because it is cubic in volume, it is computationally easy to handle. They indicated that their new equation can reproduce with sufficient accuracy both liquid and vapor phase densities and still yield very accurate VLE predictions for composi-

tions. They have shown, by comparison, that for VLE calculations their equation is as good as SRK and PR equations for mixtures of light hydrocarbons. For systems containing heavy hydrocarbons and polar substances, they have shown their equation to be superior to the SRK and PR equations.

Lawal, Lake, and Silberberg (1985) presented a four parameter cubic equation of state which uses two more constants than either VDW, PR, or SRK EOS. They expected that the four parameter equation would predict VLE and phase densities better than the earlier two and three parameter cubic EOS. Specifically, they claimed that their equation is a better tool for VLE calculations with complex hydrocarbon systems.

The form of the Lawal-Lake-Silberberg (LLS) equation is:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v^2+\alpha bv-\beta b^2} \qquad (2\text{-}75)$$

where

$$a(T) = a(T_c)\ \gamma(T_r, \omega) \qquad (2\text{-}76)$$

$$a(T_c) = \Omega_a \frac{R^2 T_c^{\,2}}{P_c} \qquad (2\text{-}77)$$

$$b = \Omega_b \frac{RT_c}{P_c} \qquad (2\text{-}78)$$

$$\Omega_a = (1 + (\Omega-1) Z_c)^3 \qquad (2\text{-}79)$$

$$\Omega_b = \Omega Z_c \qquad (2\text{-}80)$$

$$\gamma(T_r,\omega) = (1+m(1-T_r^{1/2}))^2 \qquad (2\text{-}81)$$

$$m = 0.14443 + 1.06624\omega + 0.02756\omega^2 - 0.18074\omega^3 \qquad (2\text{-}82)$$

$$\alpha = \frac{1+(\Omega-3)Z_c}{\Omega Z_c} \qquad (2\text{-}83)$$

$$\beta = \frac{Z_c^2(\Omega-1)^3 + 2\Omega^2 Z_c + \Omega(1-3Z_c)}{\Omega^2 Z_c} \qquad (2\text{-}84)$$

where

$$\Omega = b/v_c \qquad (2\text{-}85)$$

Values of Ω were given by Lawal and co-workers for single components, or they must be obtained by fitting to single component PVT data.

The LLS equation (2-75) can be rewritten as:

$$Z^3 + (B-1)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0 \qquad (2\text{-}86)$$

where A and B are defined the same as VDW and the mixing rules for a_m and b_m are the same as for the SRK EOS. The mixing rules for α and β are:

$$\alpha_m = \sum_i x_i \alpha_i \qquad (2\text{-}87)$$

$$\beta_m = \sum_i \sum_j x_i x_j (\beta_i \beta_j)^{1/2} \qquad (2\text{-}88)$$

Lawal et al (1986 & 1985), modified the LLS EOS for calculating gas-condensate and crude oil phase equilibria without splitting the C7+ fraction into smaller pseudo-components. These modifications were made on parameters α and β and presented in their 1985 paper. They concluded

that the modified LLS EOS predicts mixture densities more reliably than either the PR or SRK EOS. They also claimed that the modified LLS EOS also predicts VLE better than either the PR or SRK EOS for both gas condensate and crude oil systems. Lawal et al noted that, for sensitive applications, the validity of EOS techniques should always be verified against experimental data and adjustments made as needed. They also pointed out that, if deviations from experimental data are significant, adjustment of binary interaction coefficients will be required. They based, their conclusions on studies for systems containing essentially paraffin hydrocarbons (except for the heavy fraction in mixtures). They believed that the existence of extended errors in results probably results from significant amounts of non-hydrocarbons. In their paper they presented equations which allow VLE calculations to be made for such a system.

In 1986, Lawal and co-workers presented a novel fugacity correction factor (FCF) technique for the C_7+ pseudo-component. They established the difference between pseudo-component fugacity dictated by the material balance equation and the equilibrium state with LLS EOS used to adjust the K-values of the C7+ fraction. They presented a robust algorithm which incorporates the FCF. This algorithm was evaluated by comparing calculated and experimental data

for three crude-oil systems and six volatile/near-critical, gas condensate, reservoir fluids. They concluded that the feasibility of the FCF technique was demonstrated for predicting VLE and volumetric properties of solvent/crude oil systems containing significant C7+ fractions without splitting the heavy fraction into pseudo-components. They claimed that FCF algorithm can be used with other VDW like equations.

2.4 Summary

Cubic EOS are commonly used to describe phase behavior in economic processes involving petroleum reservoir fluids. Over time, the complexity of the equation forms has increased as workers have attempted to more accurately and consistently describe the behavior of complicated mixtures found in reservoir fluids. Each succeeding development has usually resulted from observations on fundamental limitations of other forms, but both empirical and fundamental forms have been proposed.

3. LITERATURE REVIEW

The studies reviewed here concentrate on work which compared the accuracy of EOS and/or were involved with regressing EOS to determine optimal parameters.

3.1 Comparative Studies on EOS

Shah and Thodos (1965) compared fourteen of the most commonly used cubic and non-cubic equations of state in the subcritical, critical, and hypercritical region for argon and n-butane. The results of his study indicated that the two constant RK EOS predicts PVT behavior reasonably well for the argon and n-butane systems. For argon, the agreement between experimental and calculated values was found to be excellent; whereas, for n-butane this agreement was found to be reasonably good. He also noted that the more complex equations of Beattie and Bridgeman (1928) and Benedict, Webb and Rubin (1940) predicted values for n-butane which were comparable in accuracy to those predicted by the simpler RK EOS.

Tarakad et al (1979) compared eight cubic and non-cubic equations of state to predict gas-phase density and fugacity. The equations used were the original RK (1949), the

Redlich-Kwong-Chueh (1967), the SRK (1972), the Banner-Adler-Joffe (1970), the Virial (1977, or 1974, 1975), the Nakamura-Breedveld-Prausnitz (1976), the Redilch-Kwong-de Santis (1974), and the Redilch-Kwong-Guerreri (1973). Their objectives were as follows:

1. To evaluate the merits of EOS that have been commonly used for calculating density and fugacity in the gas phase.
2. To compare these equations with others that have appeared more recently in literature.
3. To get an idea of the magnitude of error to be expected when some common EOS are used for systems containing polar species.
4. To provide some insight as to what equation is most appropriate in a given design situation.

Tarakad and co-workers found that in the subcritical, critical, and supercritical regions the preferred equation varied depending on which region of the PVT space was considered. Further, the type of compound (non-polar, mildly-polar, or highly-polar) or the type of mixture (nonpolar-nonpolar,polar-nonpolar, polar-polar) also influenced the best choice of the EOS forms. Although, other equations were successful for describing individual regions for one type of compound, cubic forms were found to be the best for describing all regions of PVT and VLE space

for both polar and non-polar compounds and mixtures.

Ahmed (1986) compared eight cubic EOS for predicting the volumetric and phase composition equilibria of gas condensate systems. The EOS used in his study included: PR, SRK, SW, Usdin-McAuliffe, Heyen, Kubic, Adachi-Lu, and PT. He found that the SW EOS exhibits a superior predictive capability for volumetric properties of gas condensate systems. The PR equation was found to accurately represent the phase equilibrium behavior of condensate systems. Ahmed found that the SW and PT equations gave better predictions of the compressibility factor, Z, than the other equations. He also concluded that, for prediction of VLE, the PR, the PT, and the SW EOS all performed equally well.

In 1986, Trebble and Bishnoi compared the accuracy and consistency in predicting PVT behavior using the following ten cubic EOS for polar and non-polar compounds: SRK (1972), PR (1976), Fuller (1976), SW (1980), Harmens-Knapp (1980), Heyen (1981), PT and PT(G) (1981 & 1982), Kubic (1982), Adachi-Lu-Sugie (1983), Lin-Kim-Guo-Chao (1983). In the equations presented by Heyen (1981) and Fuller (1976), repulsion parameter, b, was defined to be temperature dependent. Trebble and Bishnoi found this dependence directly led to the prediction of negative heat capacities in single phase regions. They also concluded that a

temperature dependent b must obey certain limitations if thermodynamic consistency is to be maintained. They have concluded that the Adachi-Lu-Sugie (1983) and PT (1981) EOS appear to be more accurate than previous equations, while maintaining thermodynamic consistency.

Tsonopoulos and co-workers (1985) presented a study of EOS which span the time period from the development of the Redilch-Kwong equation to the present. They concluded that, because of the simplicity, reliability and the amply demonstrated flexibility of cubic EOS, they are "here to stay". They also pointed out that in a cubic EOS, the use of only two parameter equations is unnecessarily restrictive, since such equations either well fit VLE or PVT data but not both. They also concluded that if a new cubic EOS is developed, its developer should recognize that:

1. Modifying the volume dependence can improve the PVT prediction.
2. Only better mixing rules can significantly improve the VLE prediction.
3. At least three parameters are required to accurately represent vapor and liquid PVT and VLE.

Varotsis and co-workers (1986) described the develop-

ment of a phase behavior simulator which used a combination of the PR and SW EOS. First, they predicted phase composition values using the PR EOS and then, using the phase composition values generated with the PR EOS, the SW EOS was used to predict liquid densities. They concluded that the SW EOS was a great improvement over the PR EOS in the prediction of liquid volumes. They also concluded that the underestimation of these volumes is the main disadvantage of the PR EOS.

3.2 Regression Studies on EOS

Because EOS do not always provide good predictions for PVT and VLE behavior researchers in the petroleum industry are seeking simpler and more accurate methods of prediction. At the same time, it is impractical, if not impossible, to use all the compositional information which could be obtained for a particular crude oil in EOS calculations and therefore, one simplifying approach is to characterize the crude oil using a reduced number of components, while retaining enough information to produce accurate results. This method lumps fractions of the petroleum fluid together and treats each fraction as if it were a single component or a pseudo-component. Values for EOS parameters are obtained through correlations of measured physical properties of the

pseudo-components. Another approach, which can be used with one or more pseudo-components is the regression based method. With this method, values of EOS parameters for one or several pseudo-components are obtained by fitting the EOS to experimental data to find parameter values which yield the least error. Thus, the optimized EOS can be used with confidence over the range of conditions used to find the EOS parameters. One reason this method has gained popularity, is because the mathematical basis of the least square techniques has been well established (Coats and Smart, 1986).

Kossack and Hagen (1985) studied the simulation of phase behavior and slim-tube displacements using the PR and SRK EOS. Their objective was to study how well these EOS simulate phase behavior in a simple hydrocarbon system where there are no pseudo-components and where there exists published experimental results for the phase behavior and critical points. They found, based on the available data, that the set of parameters for the EOS that matched the PVT experiments did not match the slim tube displacement results and another set that matched the slim tube did not match the PVT experiments. From this work, they concluded that EOS, in the forms used at the time of their study, can not accurately simulate compositional paths of displacements in reservoirs.

In a later study Kossack and co-workers (1985) performed studies with the PR EOS using systems containing three components, six components, and twenty-two components. These studies were performed so that the critical points for the mixtures were approached either by increasing the temperature, while keeping the composition constant or by changing the composition, while keeping the temperature constant. Using regression, they were able to give a better EOS match, and thus a better simulation of slim-tube displacements. In their studies, they limited regression to values of δ_{ij}, Ω_a, and Ω_b. They pointed out that the regression on Ω_a and Ω_b directly translates into adjustments of Tc, Pc, and ω. They also concluded that the PR EOS is not able to simulate the PVT behavior near the critical point. They concluded that, in regressions on PT-x (VLE) data, the more parameters were allowed to vary, the better matched obtained. They also found that by ignoring the pure component values of Tc, Pc, and ω and regressing on these parameters leads to a better match of PT-x data.

Application of a regression-based EOS PVT program was applied by Coats and Smart (1986) to match laboratory data. The data used in their study were from six oil and three retrograde gas condensate samples including constant-composition, constant-volume, and differential expansions, surface separations, temperature-dependent saturation

pressure, and N_2 reservoir fluid behavior. One set of multiple-contact oil vaporization data was also reported. The calculations made by their PVT program include:

1. Saturation pressure and equilibrium-phase properties for a given composition and T.
2. Density and viscosity calculation for specific P, T, and composition.
3. Constant composition, constant volume, and differential expansion for specified sets of pressure level.
4. Single or multistage flash tests.
5. Phase envelope calculations for swelling tests.
6. Pseudozation (lumping) to fewer components.

Coats and Smart used The PR (1976) and Zudkevitch-Joffe-Redlich-Kwong (ZJRK, 1970) EOS to match these nine fluids and three published fluid data sets under conditions of prediction (no altering of EOS parameters), adjustment (altering one binary coefficient), and regression on Ω_a, Ω_b. They generally found good to excellent agreement between laboratory data and the regressed EOS results. They also concluded that the results for these 12 fluids and a large number of unreported studies indicate that regressed PR and ZJRK EOS gave very comparable agreement with data. They also found regression necessary for required engineering accuracy in EOS results.

Coats and Smart also concluded that for prediction of

the methane-plus fraction, regression on the Ω_a, Ω_b EOS parameters and methane-plus fraction binary interaction coefficients is frequently necessary and sufficient for good data match. Further, they found a minimal need for the extensive splitting of the C_7+ fraction to match data in several published studies. In their work, generally good agreement with data was obtained when splitting the C7+ into none to four fractions. In some cases, a portion of laboratory PVT data remained poorly described by regressed EOS results. They said such disparity can frequently be resolved by more fully exploring regression variable sets and C7+ characterization (splitting). Finally, they concluded that the remaining disparity leaves an open question regarding causes of EOS inadequacy as opposed to poor data.

3.3 Summary

Previous works suggest that cubic EOS are suitable for describing PVT and VLE (or PT-x) behavior of complex reservoir fluids (Tarakad et al, 1979). It has been noted that at least three parameters are required for adequately describing both VLE (or PT-x) and PVT data (Tsonopoulos et al, 1986). However, investigators argue that four parameters will give improved predictions (Lawal et al, 1985).

Regression has often been used to describe VLE data and some investigators feel that such uses of cubic EOS are necessary to adequately describe systems such s reservoir fluids (Kossack et al, 1985 and Coats & Smart, 1986). However, modifying EOS parameters (by regression or other considerations) to improve fits to one type of data or one region of PVT space may cause inconsistent or worse descriptions of either other thermodynamic behavior or other regions of PVT space (Tarakad et al, 1979). Coats and Smart also point out the accuracy of data must be questioned when compared to EOS predictions.

4. OBJECTIVES

The questions addressed in this study include: Which EOS forms most accurately predict VLE and density data? Are more complicated EOS forms required to accurately describe progressively complex mixtures found in petroleum reservoirs? Are the EOS consistent, i.e. do the EOS predict phase densities as well as VLE behavior accurately? Are errors associated with a particular EOS due to the equation forms or do errors result from the method of calculating EOS parameters? If an optimum set of EOS parameters can be obtained for describing VLE data, do these parameters improve phase density predictions?

To answer these questions, five, commonly used, cubic EOS of varying number of parameters were used to calculate VLE and phase density data for six chemical systems for which corresponding experimental data were available. The chemical systems consisted of components which might be found in reservoir fluids and the complexity of the systems varied from ternary mixtures containing only light components to a separator liquid combined with CO_2. In all cases, the conditions of temperature and pressure were such that two phases existed and the two-phase region was well away from any critical or plait point. In order to assess which EOS was the best for describing both VLE (or phase

compositions) and PVT (or density) data for the progression of complexity of mixtures, the average absolute relative deviation (or when it was not practical to use relative deviations, the average absolute deviations) between predicted and measured VLE and density data were calculated and compared. Regressions were then performed on the VLE data to allow an assessment of which EOS form was optimal for a given mixture when the best values for the equation parameters were used. These optimal parameters were then used to calculate the corresponding phase densities to see how thermodynamic consistency was affected by variations in the values of equation parameters.

5. METHODS

The objectives of this study involved the determination of the best EOS for describing liquid-vapor compositions and corresponding phase densities from among five EOS. Other objectives are to assess whether or not more complicated EOS forms were useful in describing a progression of complexity of reservoir fluid systems, whether or not the methods for determining EOS parameters may be improved, and whether or not the improved parameters used in the EOS provide a more thermodynamically consistent description of the behavior of the systems studied. Achieving these objectives required that predictions using the various EOS be compared with corresponding experimental data, that regressions be performed using the EOS, and for the case where the systems were so complex that determining the exact chemical compositions of the systems was impractical, that a method for characterizing the system be utilized. This section includes descriptions of the calculation procedures for prediction errors used in the comparisons and the objective functions in the regression procedure, a brief description of the regression procedures and the crude oil characterization procedure.

5.1 Calculation of Errors and Regression

The evaluation of which EOS was best in describing either VLE or phase densities required the development of a quantitative measure of how well the description fit the experimental data. It is common in such studies to use one or another form of the absolute error between calculated and experimental data. It was desirable to compare how the error varied between different chemical systems, all of which contained differing numbers of data points, and accordingly, average absolute errors or deviations (AAD) were determined. The regression procedure also uses this error as an objective function which is minimized. Early calculations revealed that tie-line slopes obtained using EOS parameters from minimizing the AAD were often worse than the slopes obtained before regression. This action was attributed to the equal weighting of the errors for both large and small values of composition. To solve the problem the average, absolute, relative error or deviation (AARD) was used. Tie-line slopes using parameters obtained by minimizing the AARD were always as good as, or improved over, those calculated before regression, with one exception; when the concentration of a component was so low in a phase that the calculation of the AARD required division of the deviations by a very small value. For that case, the AAD was used. The equations for calculating the AAD and

AARD between the experimental VLE and calculated values were:

$$AAD = \frac{\sum_{j=1}^{NTL} \sum_{i=1}^{NC} |x_{exp} - x_{cal}| + |y_{exp} - y_{cal}|_{ij}}{NC * NTL} \quad (5\text{-}1)$$

$$AARD = \frac{\sum_{j=1}^{NTL} \sum_{i=1}^{NC} \left|\frac{x_{exp} - x_{cal}}{y_{exp}}\right| + \left|\frac{y_{exp} - y_{cal}}{y_{exp}}\right|_{ij}}{NC * NTL} \quad (5\text{-}2)$$

where:

x_{exp} = experimental liquid mole fraction

x_{cal} = calculated liquid mole fraction

y_{exp} = experimental vapor mole fraction

y_{cal} = calculated vapor mole fraction

NC = number of components

NTL = number of tielines, and

i,j = the component and tieline indices, respectively.

There was never a need to calculate the AAD between calculated and experimental density data so only the AARD were used. The equation for calculating AARD between calculated and experimental density values was

$$AARD = \frac{\sum_{j=1}^{NLT} \left|\frac{\rho_{exp} - \rho_{cal}}{\rho_{exp}}\right|_j}{NTL} \quad (5\text{-}3)$$

where:

NTL and j have been defined previously

ρ_{exp} = experimental density (liquid and/or vapor), and

ρ_{cal} = calculated density (liquid and/or vapor).

The regression procedure followed Powell's method (1964). In this method, a value of a parameter, or a parameter vector, is estimated and the error between the calculated and experimental value of data is found. A change in the value of the parameter or parameter vector is made and a new value of error determined. If the new error is less than the previous error, another change in the parameter vector of the same direction and magnitude is made and the process repeated until the error is small or unchanged. If the new error is greater than the previous error, a change in the parameter vector of the same magnitude but opposite direction is made and the process repeated. When the direction of the slope of the error changes, ie a small error becomes bracketed by two larger values of error, the algorithm fits a quadratic to the values of the parameters to estimate a minimum error value of the parameter vector. The new error is again compared to the previous low value of error and the regression procedure repeated until a predetermined small magnitude of error is reached or until there is no change (within predetermined limits) in the value and direction of the parameter vector. Details of the regression algorithm

may be found in Appendix A.

5.2 Characterization of Crude Oil

The common method for characterizing the composition of a crude oil is to report the composition of individual, light components exactly and to lump the heavier (usually the C_7+) components into one or more fractions or pseudo-components. Properties of the pseudo-components are averaged and the pseudo-components are assumed to act as a single component in calculations. The number and specification of pseudo-components can affect the outcome of EOS calculations and the procedure for fractioning, or lumping, the heavy components into more than one pseudo-component is a suitable subject for study in itself. Whitson's method (1983) was chosen for this study as it is relatively simple, widely used and has provided suitable results in previous studies (Lawal et al 1985, Ahmed 1986). The number of pseudo-components using Whitson's method may be calculated as follows:

$$N_g = \text{Int}\ (\ 1. + 3.3\ \log_{10}(N-n)) \qquad (5\text{-}4)$$

where:

N_g = number of multiple carbon groups (pseudo-components)

n = first single carbon number in a C_n+ fraction

N = last single carbon number in a C_n+ fraction

Int = integer of the found number

To calculate the properties which are required to estimate EOS parameters for each pseudo-component, the following equations are given:

$$Mw_I = \sum^{I} (z_i/z_I)\ Mw_i \qquad (5\text{-}5)$$

$$P_{pcI} = \sum^{I} (z_i/z_I)\ P_{ci} \qquad (5\text{-}6)$$

$$T_{pcI} = \sum^{I} (z_i/z_I)\ T_{ci} \qquad (5\text{-}7)$$

$$\omega_I = \sum^{I} (z_i/z_I)\ \omega_i \qquad (5\text{-}8)$$

$$V_{pcI} = \sum^{I} (f_{wi}/f_{wI})\ V_{ci} \qquad (5\text{-}9)$$

where:

f_w = weight fraction

i = single carbon number index ($=n,n+1,\ldots,N$)

I = multiple carbon number index ($=1,2,3,\ldots,N_g$)

Mw = molecular weight

P_{pc} = pseudo-critical pressure

P_c = critical pressure

T_{pc} = pseudo-critical temperature

T_c = critical temperature

ω = acentric factor

V_{pc} = pseudo-critical volume

V_c = critical volume

z = mole fraction

The weight fractions are easily determined from gas

chromatograph analyses of the crude oil system (PRRC report 85-3). Values for critical properties up to C_{20} were given by Reid et al (1977). Since for the crude oil used in this study, critical properties up to C_{37} were required, and Lyderson's method (Reid et al, 1977) was used to estimate heavy component values. The method, in form of a computer program, and the correlated values are given in Appendix B.

6. RESULTS

Comparisons between phase composition and density data and the corresponding EOS predicted values for six chemical mixtures using five cubic EOS were presented. In each case, the thermodynamic conditions, i.e. the temperature, pressure and the over all compositions, were such that the mixtures exist in two phases, but well below critical points. The components in the mixtures were all components which might be found in petroleum fluids and the mixtures ranged from relatively simple, ternary mixtures of known composition, to complex, a crude oil which contained so many components that the exact composition was unknown. Because the manner in which a complex mixture, such as a crude oil, is analyzed is different from a mixture in which the exact composition is determined, the results presented here have been divided into two categories: simple and complex. However, even within the simple systems, there was a progression of complexity due to both the number and type of components. For instance, a four component system is more complex than a binary or ternary mixture and a system with three light components is less complex than a system with two light components and one heavy component, even when all components are of the same chemical family.

Likewise, with the EOS forms used, there was a progression of complexity of form and therefore, the implicit increased potential for adequately describing more complex mixtures. Each system was described using five cubic EOS, these included: PR, SRK, PT, SW, LLS. The PR and SRK are nominal two parameter EOS, while the PT and SW are three parameter forms, and the LLS is a four parameter form. Table 3.1 is a summary of the EOS used in this study and the regressed parameters corresponding to each EOS.

EOS Form	Regressed Parameters
SRK	δ_{ij}, a, b
PR	δ_{ij}, a, b
PT	δ_{ij}, a, b, c
SW	δ_{ij}, a, b, ω
LLS	δ_{ij}, a, b, α, β

Table 6.1. Summary of EOS and their parameters.

For each mixture, predictions of the phase composition and densities (when available), using both published methods for determining EOS parameters and EOS parameters obtained by regression with the phase composition data, were performed. Comparison of the predictions before regression

could provide a comparison of how well the published EOS predicts vapor liquid equilibrium (VLE) systems. However, binary interaction parameters for all EOS were not available and any conclusions from these comparisons must be limited. Where binary interaction coefficients were not available for a particular EOS, the same values used for the PR EOS were taken as an initial guess for regression. The predictions after regression on all parameters provided a comparison of how well the form of the equation predicted VLE systems when the "best" parameters were used. The prediction errors after regression on single parameters provided a basis for assessing which parameters affect EOS calculations the most. For all mixtures, phase composition data were available and the composition data were useful for evaluating comparisons between EOS for predicting phase compositions. When density data was also available, differences between predicted and experimental density data allowed the thermodynamic consistency of the EOS to be examined, i.e. whether or not a good prediction of phase composition data also provided a good prediction of density data.

Regressions were performed on single EOS parameters for each component and for all parameters on each components simultaneously. In the simplest regression procedure for the simplest mixture (3 components) with any EOS, a total of three independent component parameters were optimized. For

the most complicated system (a separator fluid represented by $CO_2-C_3-C_4$ components and five pseudo-components) and using the most complex EOS (four parameters and binary interaction parameters), 60 independent component parameters were optimized simultaneously. Thus for the entire study a total of 35 comparisons of VLE data with regressed values of EOS parameters were made and the regressions involved optimization on three to 60 parameters.

6.1 Simple Systems (Mixtures)

Five mixtures of known composition were studied. These include:

1. $CO_2-C_1-nC_4$
2. $CO_2-C_1-nC_{10}$
3. $CO_2-C_1-nC_4-nC_{10}$
4. $N_2-C_1-CO_2-C_2-nC_7$
5. $N_2-C_1-CO_2-C_2-C_3-nC_5-nC_7-nC_{10}$

The experimental data for mixtures 1 through 3 were obtained from reports by Silva and co-workers (1983) and the experimental data for mixtures 4 and 5 were published by Yarborough (1972). Yarborough's data is often used in comparative studies of EOS (Lawal et al 1981, Coats et al 1986, etc.), however, phase density data was not published for these mixtures.

Single parameter regressions were preformed using each EOS on each system and then on all parameters together. In each single parameter regression, the other parameters were held constant at the values of the published version of the EOS. Published values for δ_{ij} were only available for the PR and LLS EOS, therefore the published values of δ_{ij} used in PR were used as initial values in SRK, PT and SW EOS. In both the single parameter regressions and the regressions on all parameters together, trial values of parameters for each component were combined using the published EOS mixing rules.

Ternary Systems (Mixtures)

Figure 6.1 is a typical ternary phase-composition diagram for the ternary mixtures in this study. A ternary system is the most number of components which can be completely described in two dimensions graphically. It is possible to describe quaternary systems using a perspective drawing of the phase-composition diagram, but interpreting those diagrams is more difficult. Hence, the ternary systems were the only systems for which phase-composition diagrams were produced. Ternary composition diagrams for all ternary systems and all of the regressions on those systems are presented in a report on file in the New Mexico

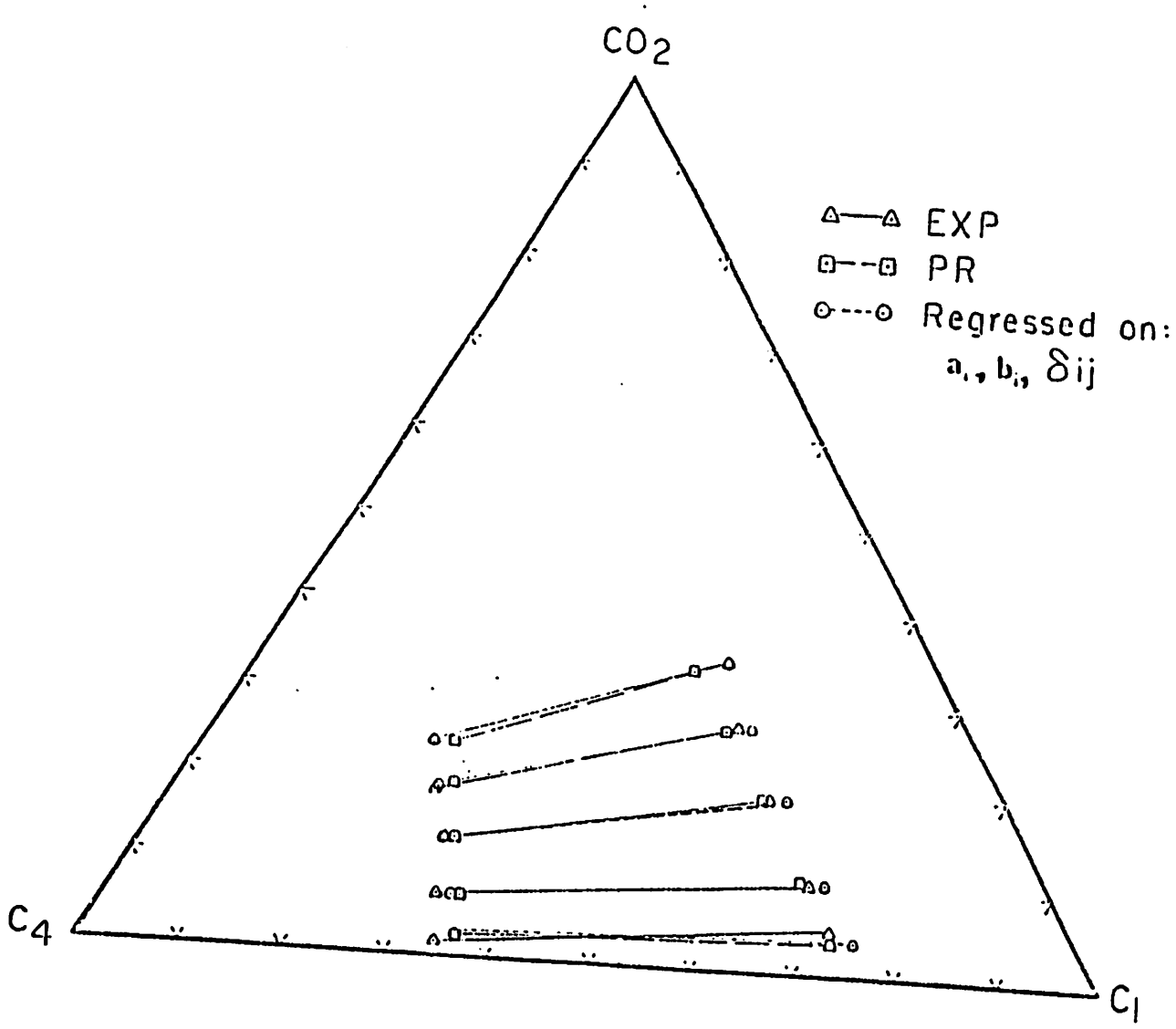

Fig. 6.1. Comparison of measured and calculated phase compositions for mixture 1, $CO_2-C_1-C_4$, at 160° F and 1250 psia.

Tech Petroleum Engineering Department (Tabaei and Bretz, 1988a). Figure 6.1 is a plot of the experimentally determined compositions of the liquid and vapor phases in equilibrium for mixture 1, CO_2-C_1-nC_4, at a temperature of 160° F and pressure of 1250 psia. Components CO_2 and nC_4 are miscible in all proportions at this temperature and pressure. In Fig. 6.1, pairs of data are connected by a line. Each pair represents an equilibrium pair and the lines are equilibrium tielines. The symbols to the right (containing more of the lighter component, C_1) are the compositions of the vapor phase. The equilibrium liquid phase compositions are located to the left and contained more of the heavier component, nC_4. From the length of the tielines, it is obvious that none of the data on Fig. 6.1 were near a critical or plait point.

Also included on Fig. 6.1 are the compositions of the equilibrium liquid and vapor phases for the systems having the same overall compositions as the corresponding experimental data pairs but predicted using the PR EOS with the parameter values before and after regression. In this case, the regression was performed on all parameters, a_i, b_i and δ_{ij}, simultaneously. As expected, the predictions using the regressed parameters generally fit the experimental data better than the PR EOS before regression. However, the prediction of the compositions of all the data pairs were

not improved by regression. The PR EOS actually predicted equilibrium phase compositions further from experimental values after regression than before for the data pair containing the least CO_2. Also, the tielines slopes predicted using the regression parameter values were more nearly the same as the experimentally obtained slopes than were the tielines slopes predicted before regression.

In fact, the tieline slopes provided the determining factor in the choice of the objective function for the regression procedure. When using the average absolute deviation (AAD), the tieline slopes of the ternary data after regression were not always better than before regression. When the objective function was changed to the average absolute relative deviation (AARD), these slopes were, in general, improved by regression.

Figure 6.2 is a typical plot of the phase densities versus mole fractions of CO_2 for mixture 1, CO_2-C_1-nC_4, the same system as in Fig. 6.1. Similar plots of the phase densities for all ternary and quaternary systems for all the regressions may be obtained upon request (Tabaei and Bretz, 1988a). The liquid densities predicted with the PR EOS before regression on the phase composition data were all less than the experimental values. After regression, the liquid densities at all compositions were greater than the

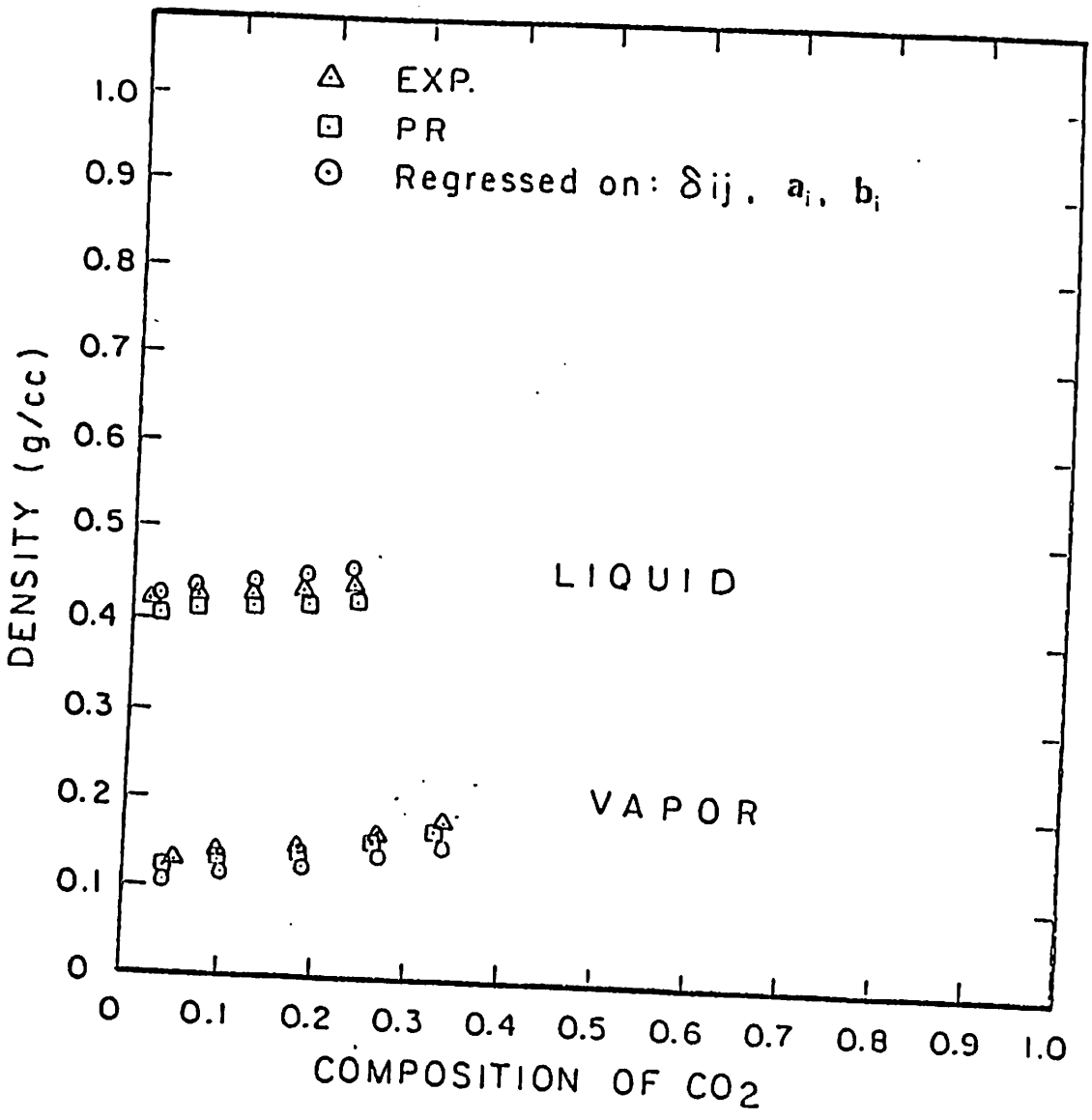

Fig. 6.2. Density vs. x_{co2} for mixture 1, CO_2-C_1-C_4.

experimental values. It is not obvious from the figure whether or not there was any improvement in predicting liquid densities due to the regression. The vapor densities predicted by the PR EOS before and after regression on all parameters were lower than experimental values and the values of vapor densities predicted after regression on the phase composition data were worse than those before regression for mixture 1.

Table 6.2 is a tabulation of the experimental and predicted composition and density data presented in Figs. 6.1 and 6.2. Similar tabulations for all systems and all regressions may be obtained upon request (Tabaei and Bretz, 1988a). Table 6.3 is a summary of AARD between the experimentally measured phase compositions and densities and the same data predicted by all five EOS before and after regression for all parameters on the phase composition data for mixtures 1 and 2. Similar tabulations of the error after regression for all mixtures (including five, eight component, and crude oil) and all regressions may be obtained upon request (Tabaei and Bretz, 1988a, 1988b, & 1988c)).

Figure 6.3 is a histogram of the equilibrium composition AARD for all five EOS before and after regression on single parameters and on all parameters together for

Table 6.2. Measured and calculated compositions and densities upon the regression of all parameters (a_i, b_i, δ_{ij}) for mixture 1, CO_2-C_1-C_4, at 160°F and 1250 psia.

EXPERIMENTAL

Tie Lines	Lower Phase				Upper Phase			
	CO_2	C_1	C_4	ρ_L (g/cc)	CO_2	C_1	C_4	ρ_V (g/cc)
1	.011	.348	.641	.4176	.047	.715	.238	.1243
2	.064	.320	.616	.4224	.095	.669	.236	.1317
3	.123	.290	.587	.4277	.183	.579	.238	.1454
4	.178	.256	.566	.4327	.265	.504	.231	.1587
5	.231	.227	.542	.4390	.337	.455	.208	.1727

RESULT FOR PENG-ROBINSON BEFORE REGRESSION

Tie Lines	Lower Phase				Upper Phase			
	CO_2	C_1	C_4	ρ_L (g/cc)	CO_2	C_1	C_4	ρ_V (g/cc)
1	.0235	.3645	.6121	.4049	.0352	.7194	.2453	.1163
2	.0645	.3401	.5954	.4091	.0956	.6596	.2448	.1256
3	.1257	.3047	.5695	.4144	.1822	.5736	.2442	.1399
4	.1845	.2719	.5436	.4185	.2609	.4952	.2438	.1544
5	.2367	.2436	.5197	.4210	.3269	.4293	.2437	.1681

AFTER REGRESSION

Tie Lines	Lower Phase				Upper Phase			
	CO_2	C_1	C_4	ρ_L (g/cc)	CO_2	C_1	C_4	ρ_V (g/cc)
1	.0237	.3637	.6126	.4260	.0360	.7424	.2215	.1067
2	.0646	.3343	.6012	.4331	.0978	.6813	.2209	.1141
3	.1246	.2933	.5821	.4425	.1870	.5932	.2198	.1254
4	.1812	.2571	.5617	.4501	.2684	.5128	.2188	.1369
5	.2310	.2270	.5420	.4558	.3371	.4550	.2079	.1478

Table 6.3. The Average Absolute Relative Deviation (AARD) results between measured and calculated compositions and densities after regression on all parameters (mixtures 1 and 2 at 160°F and 1250 psia).

	CO_2-C_1-C_4			CO_2-C_1-C_{10}		
	*Equil. Comp.	ϱ_L	ϱ_V	*Equil. Comp.	ϱ_L	ϱ_V
PR						
Before Reg.	.1623	.0334	.0584	.0957	.0667	.0328
Reg. on (δ_{ij}, a_i, b_i)	.1327	.0317	.1389	.0750	.0623	.2011
SRK						
Before Reg.	.1640	.1271	.1328	.0953	.1686	.0406
Reg. on (δ_{ij}, a_i, b_i)	.1392	.0662	.1831	.0665	.1664	.2854
PT						
Before Reg.	.1401	.0591	.0975	.1441	.0197	.0216
Reg. on ($\delta_{ij}, a_i, b_i, c_i$)	.1147	.0088	.1736	.0994	.0066	.0366
SW						
Before Reg.	.1370	.0324	.1326	.3088	.0135	.0488
Reg. on ($\delta_{ij}, a_i, b_i, \omega_i$)	.1300	.0086	.1642	.0964	.0221	.0315
LLS						
Before Reg.	.1971	.0089	.0760	.1491	.0075	.0927
Reg. on ($\delta_{ij}, a_i, b_i, \alpha_i, \beta_i$)	.1347	.0962	.0899	.1143	.0280	.1220

*Equil. Comp. = equilibrium composition

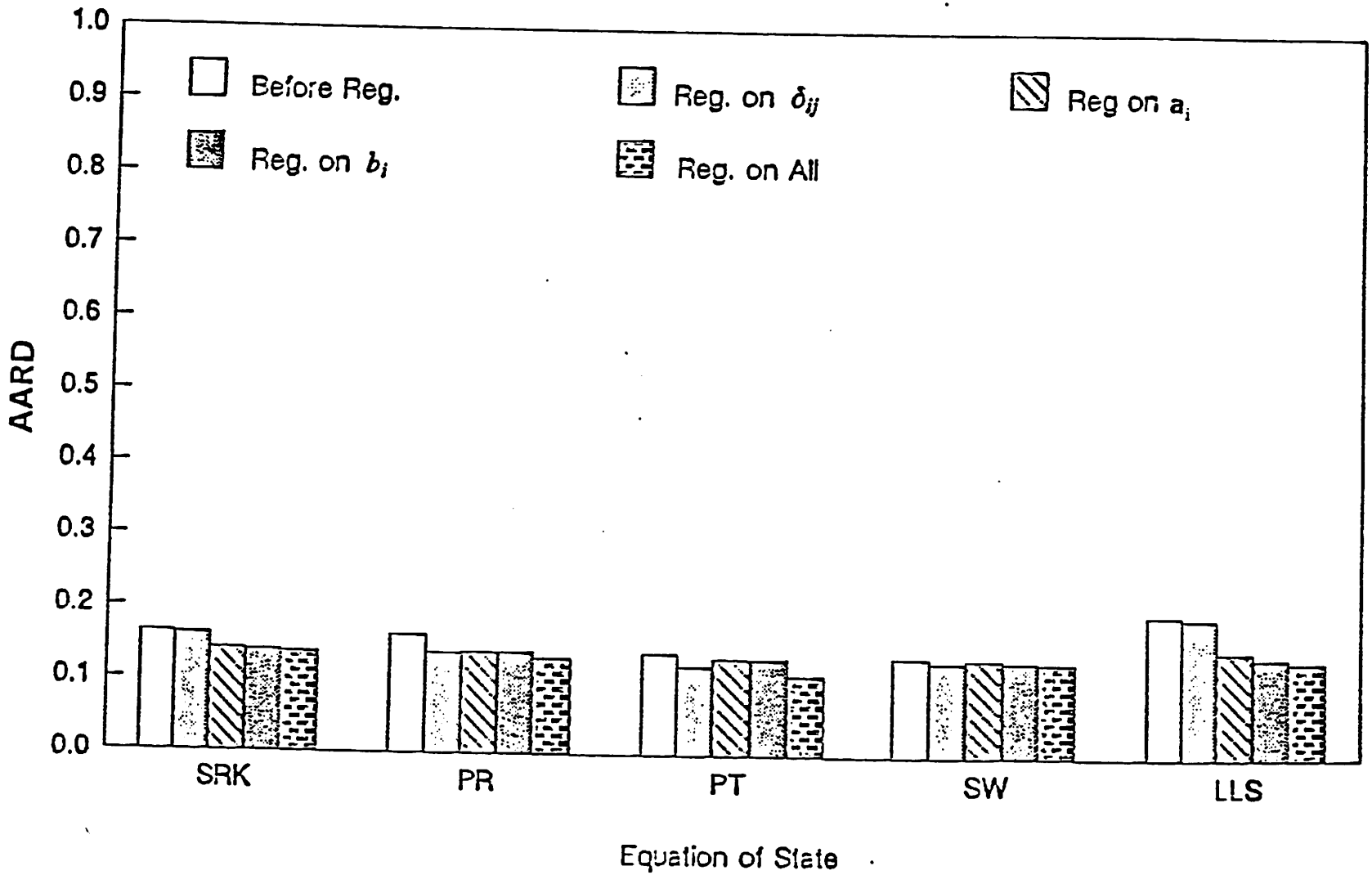

Fig. 6.3. Average Absolute Relative Deviations (AARD) between predicted and measured values of phase composition for mixture 1, CO_2-C_1-C_4 before and after regression on individual and all parameters for five cubic EOS.

mixture 1, CO_2-C_1-nC_4. From this figure, the composition errors before regression ranged from about 14 to 20 percent. The error after regression ranged between 12 and 19 percent. Even though the initial values of δ_{ij} for SRK, PT, and SW were "borrowed" from those used for PR, the initial errors for these 3 EOS were less than those from PR or LLS. There is no trend as to which single parameter regressions improved the predictions most. For instance with SRK, regression on either a_i or b_i improves the fit almost as well as regression on all parameters. For PT, the fit is most sensitive to regression on δ_{ij}. The PT EOS predicted equilibrium phase compositions marginally better (~2%) after regression on all parameters than did the other EOS. The reported results only include regressions performed on parameters δ_{ij}, a_i and b_i singly and on all parameters simultaneously. Regressions on parameters c_i for PT, ω for SW, and α and β for LLS EOS were also performed but the predictions of phase compositions after regression on these parameters never improved the prediction more than the regressions on a_i or b_i. Hence, results due to regression on parameters other than a_i, b_i or δ_{ij} were not included on the tabulations or the histogram.

Figures 6.4 and 6.5 illustrate the AARD between experimentally measured and predicted densities (liquid and vapor) before and after regression on phase composition data

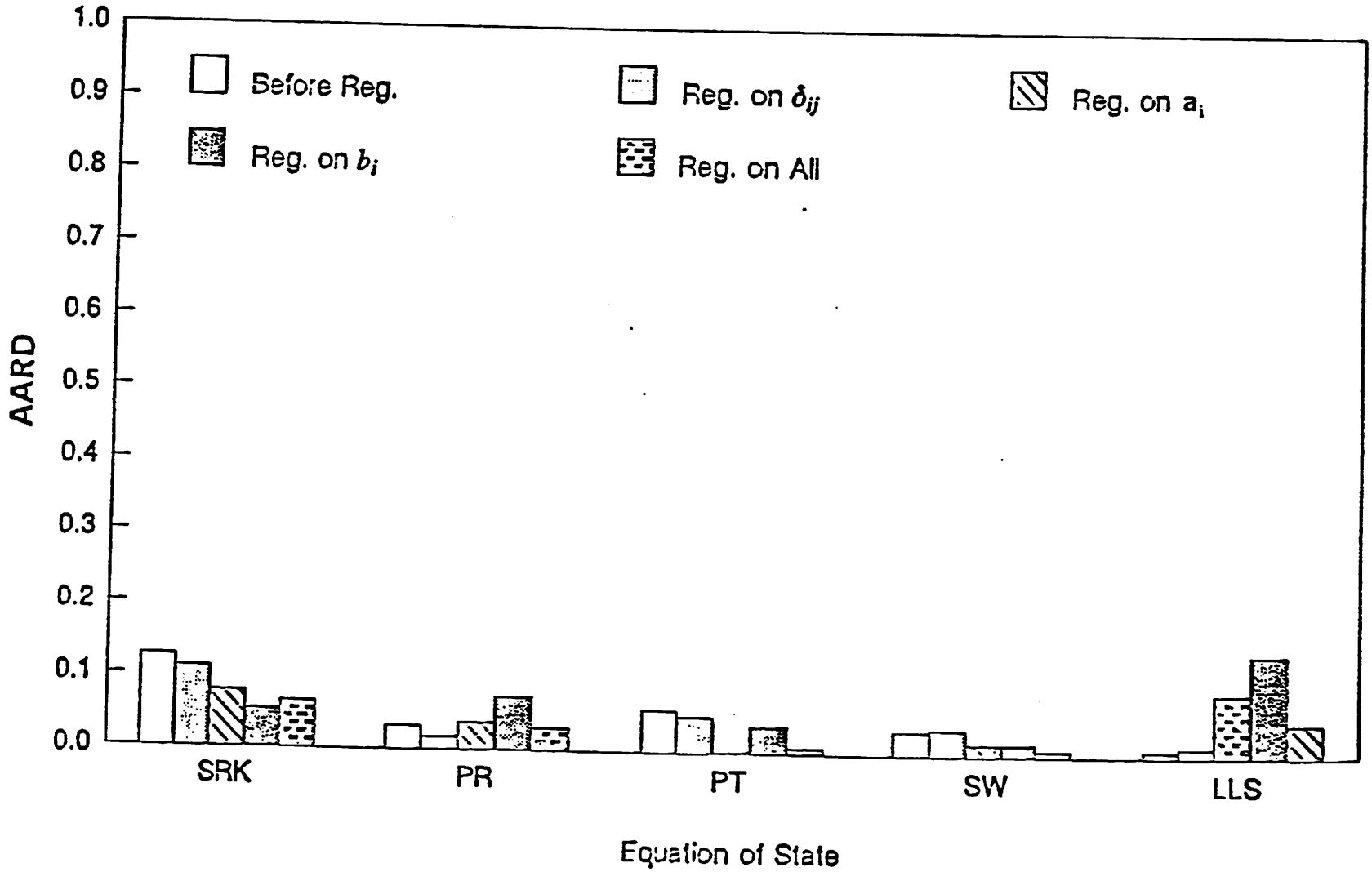

Fig. 6.4. Average Absolute Relative Deviations (AARD) between predicted and measured values of liquid density for mixture 1, CO_2-C_1-C_4 before and after regression on individual and all parameters for five cubic EOS.

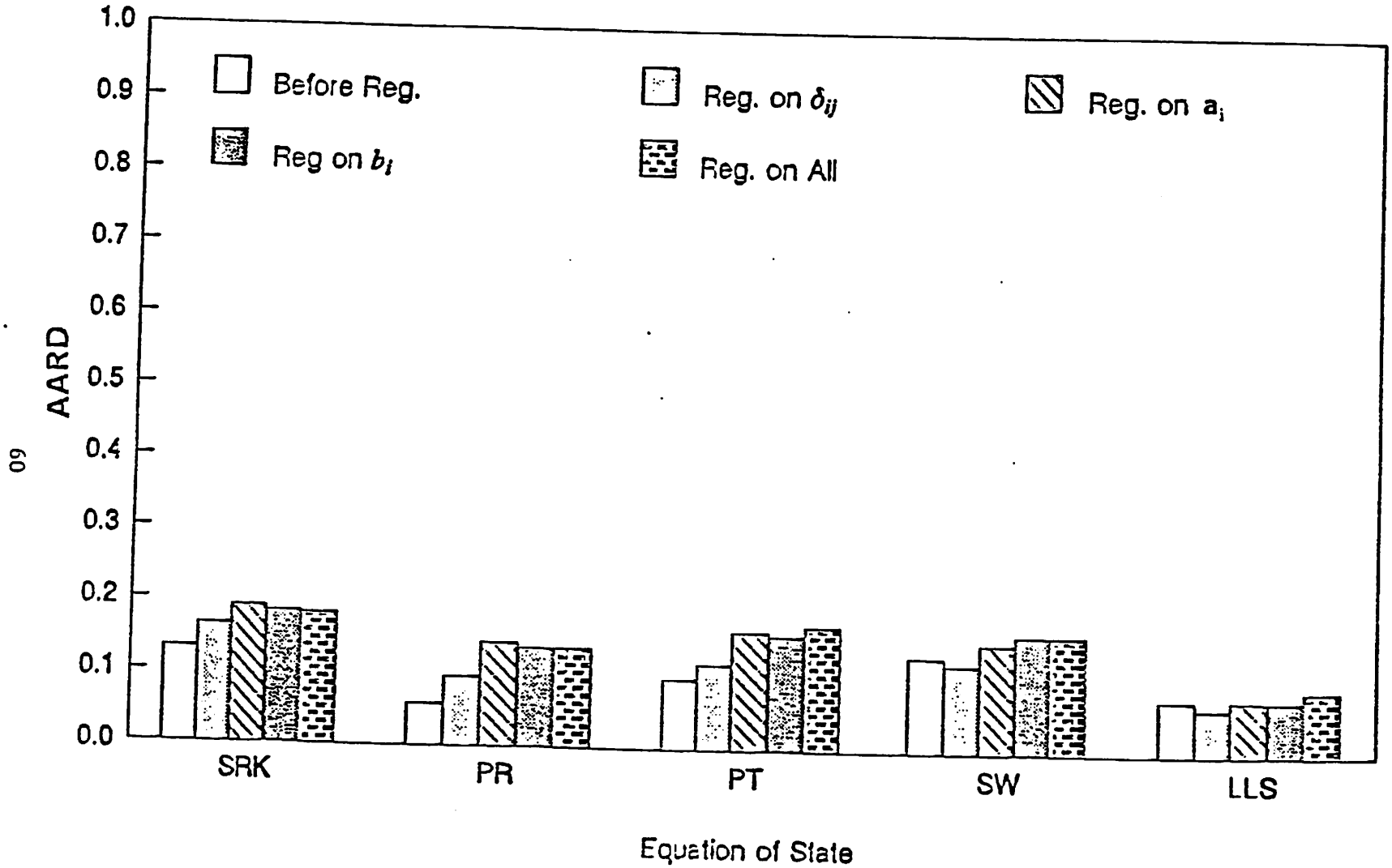

Fig. 6.5. Average Absolute Relative Deviations (AARD) between predicted and measured values of vapor density for mixture 1, CO_2-C_1-C_4 before and after regression on individual and all parameters for five cubic EOS.

for mixture 1, $CO_2-C_1-nC_4$. Figure 6.4 shows that the liquid density prediction error ranged from less than 1 percent to about 15 percent before regression. In general, the parameter values obtained by regression on equilibrium phase composition data improved the density predictions for this system. The LLS EOS was a notable exception; the initial error was quite low but greater than 10 percent using values from regression on phase composition data. The PT and SW EOS predicted liquid densities with the least error (-1%) after regression, while the LLS EOS produced the best prediction before regression (-1%). For vapor densities, Fig. 6.5, errors varied from about 5 to 13 percent before regression. Predictions using regressed parameter values uniformly gave larger errors. The PR EOS predicted vapor densities with the least error before regression (-5%) and the LLS EOS predicted the vapor densities with least error after regression (-10%). Note that the reported values of vapor densities were quite small, ranging from .12 to .173 gm/cc, and a small change produced a relatively larger error.

Figure 6.6 is a ternary, phase composition diagram for mixture 2, $CO_2-C_1-nC_{10}$. The values of concentration of nC_{10} in the vapor phase were below the resolution of the analysis technique and in calculation using this data, the nC_{10} concentration was kept constant at .0001. Until the nC_{10}

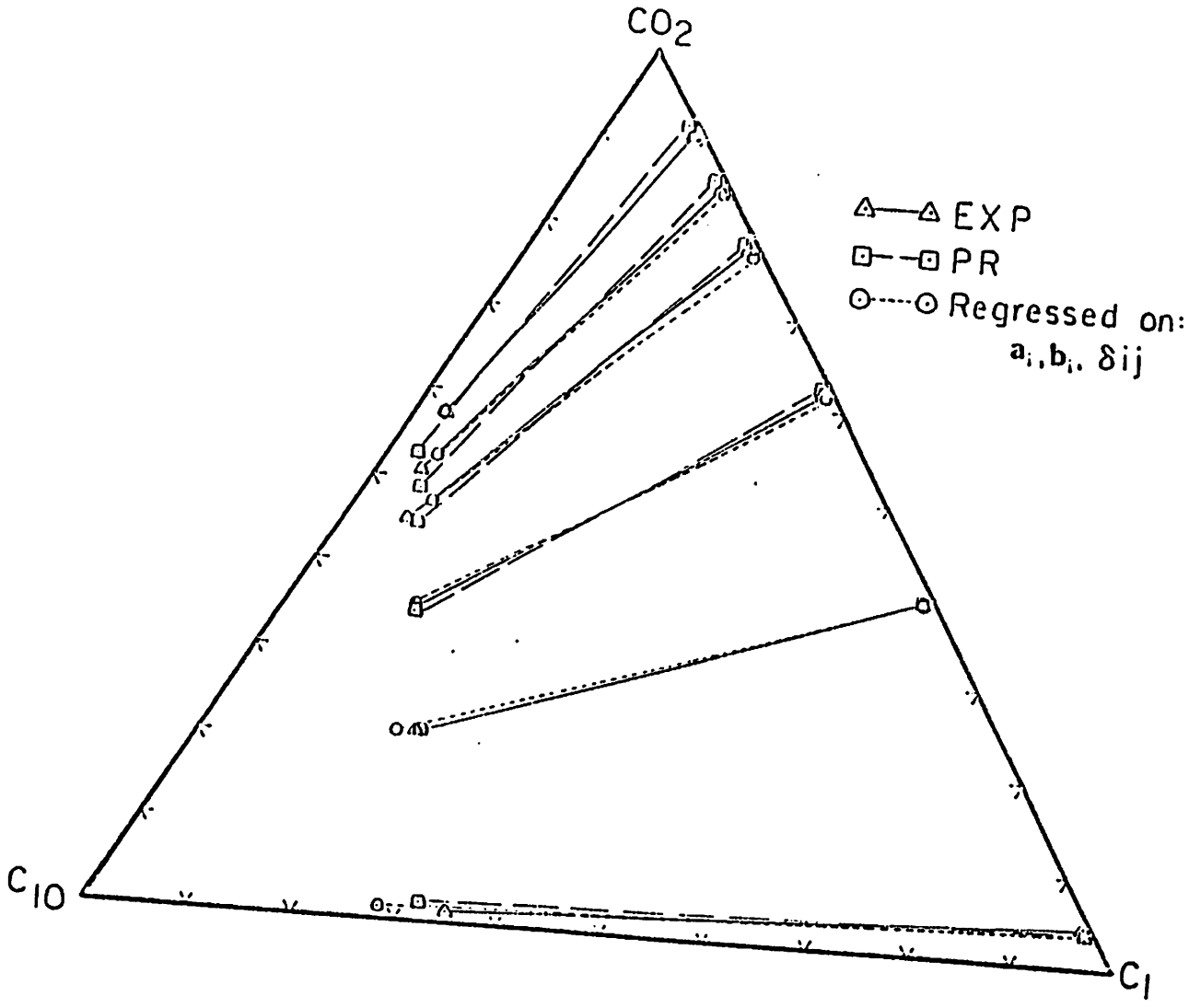

Fig. 6.6. Comparison of measured and calculated phase compositions for mixture 2, $CO_2-C_1-C_{10}$, at 160° F and 1250 psia.

composition was held constant, error between experimental and predicted compositions after regression were greater than those before regression, a development which seemed unreasonable. By fixing the composition of nC_{10} in the vapor phase, the error after regression was reduced.

Figure 6.7 is a histogram of the equilibrium composition AARD for all five EOS before and after regression on single parameters and on all parameters together for mixture 1, $CO_2-C_1-nC_{10}$. This figure shows that the errors in composition before regression ranged from slightly less than 10 to over 30 percent. The errors after regression on all parameters ranged from about 6 to 10 percent. Even though the initial values of δ_{ij} for SRK, PT and SW EOS were "borrowed" from the PR, the initial AARD for SRK EOS was slightly less than the PR and LLS. The initial error for PT was greater than that of PR by about 5 percent, while for SW EOS the error was greater by about 21 percent. As was observed for mixture 1, $CO_2-C_1-nC_4$, there was no trend of improvement associated with regression on any particular parameter. Predictions of equilibrium phase compositions were most sensitive to regression on δ_{ij} for SRK and PR, while PT was about equally sensitive to regression on δ_{ij} or b_i. Both SW and LLS were most sensitive to regression on b_i. The regression on b_i in all five EOS varies only within about 2%. The SRK EOS predicted equilibrium phase composi-

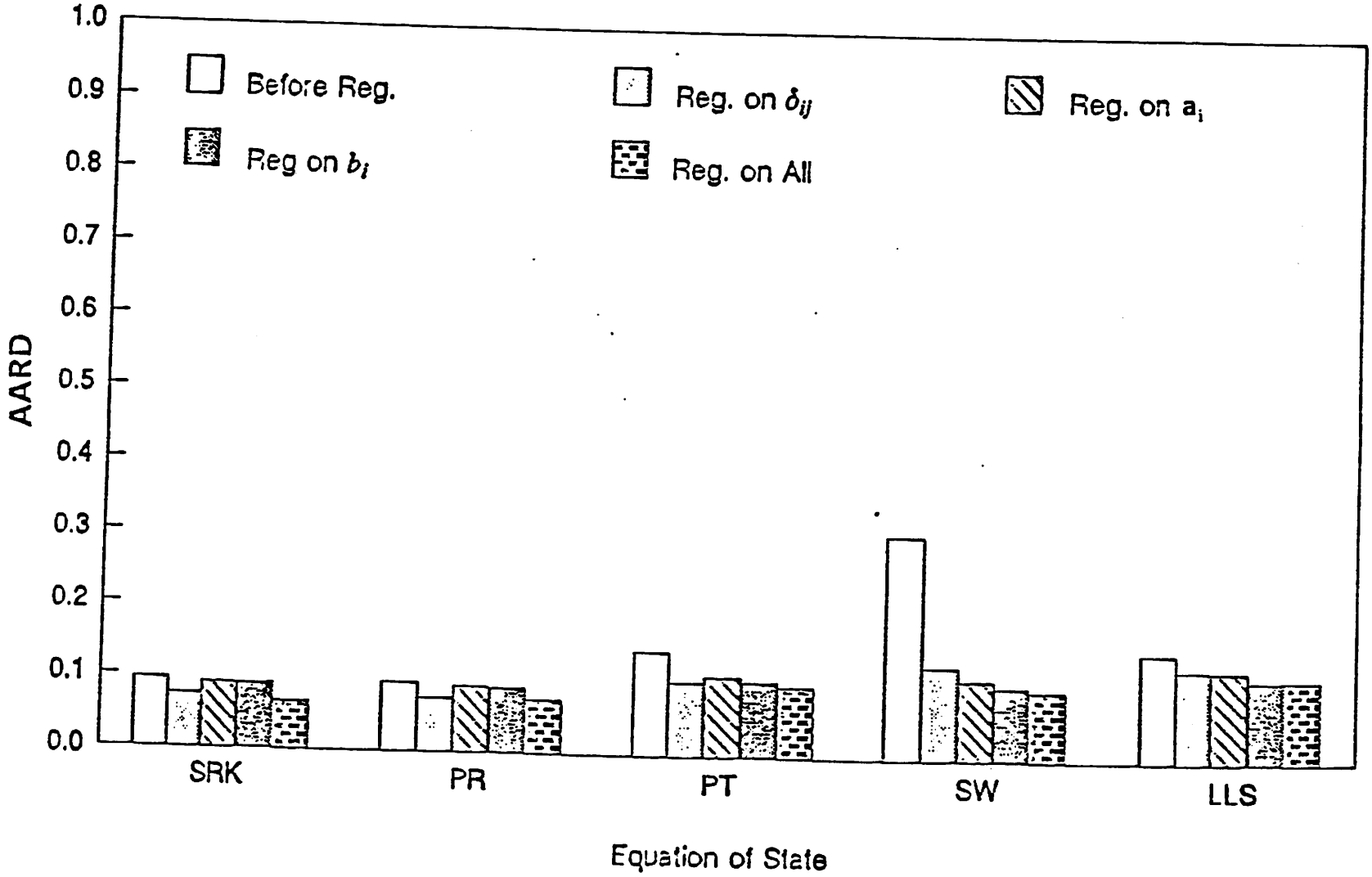

Fig. 6.7. Average Absolute Relative Deviations (AARD) between predicted and measured values of phase composition for mixture 2, CO_2-C_1-C_{10} before and after regression on individual and all parameters for five cubic EOS.

tions for mixture 2, $CO_2-C_1-nC_{10}$, marginally better than the other EOS after regression on all parameters.

Figures 6.8 and 6.9 are histograms of the relative error between predicted and experimental liquid and vapor densities for the mixture 2, $CO_2-C_1-nC_{10}$. The error in liquid density predictions, Fig. 6.8, range from less than 1 percent (PT and LLS) to over 16 percent (SRK). In general, the parameter values obtained by regression on equilibrium phase composition data improved the density predictions for this system; the LLS was a notable exception where the initial error was quite low and greater than 10 percent after regression on all parameters. The PT EOS predicted liquid densities the best (1 to 2 percent error) after regression. The error in prediction of vapor densities, Fig. 6.9, varied from about 2 to 30 percent. Predictions after regression gave larger errors in most cases. The PT EOS gave the best prediction before (-2.2 percent error) and after (-4.6 percent error) regression.

Quaternary System (Mixture)

Mixture 3, $CO_2-C_1-nC_4-nC_{10}$, was studied at the same temperature and pressure as the ternary systems (i.e. 160°F and 1250 psia) and includes all the components in the two

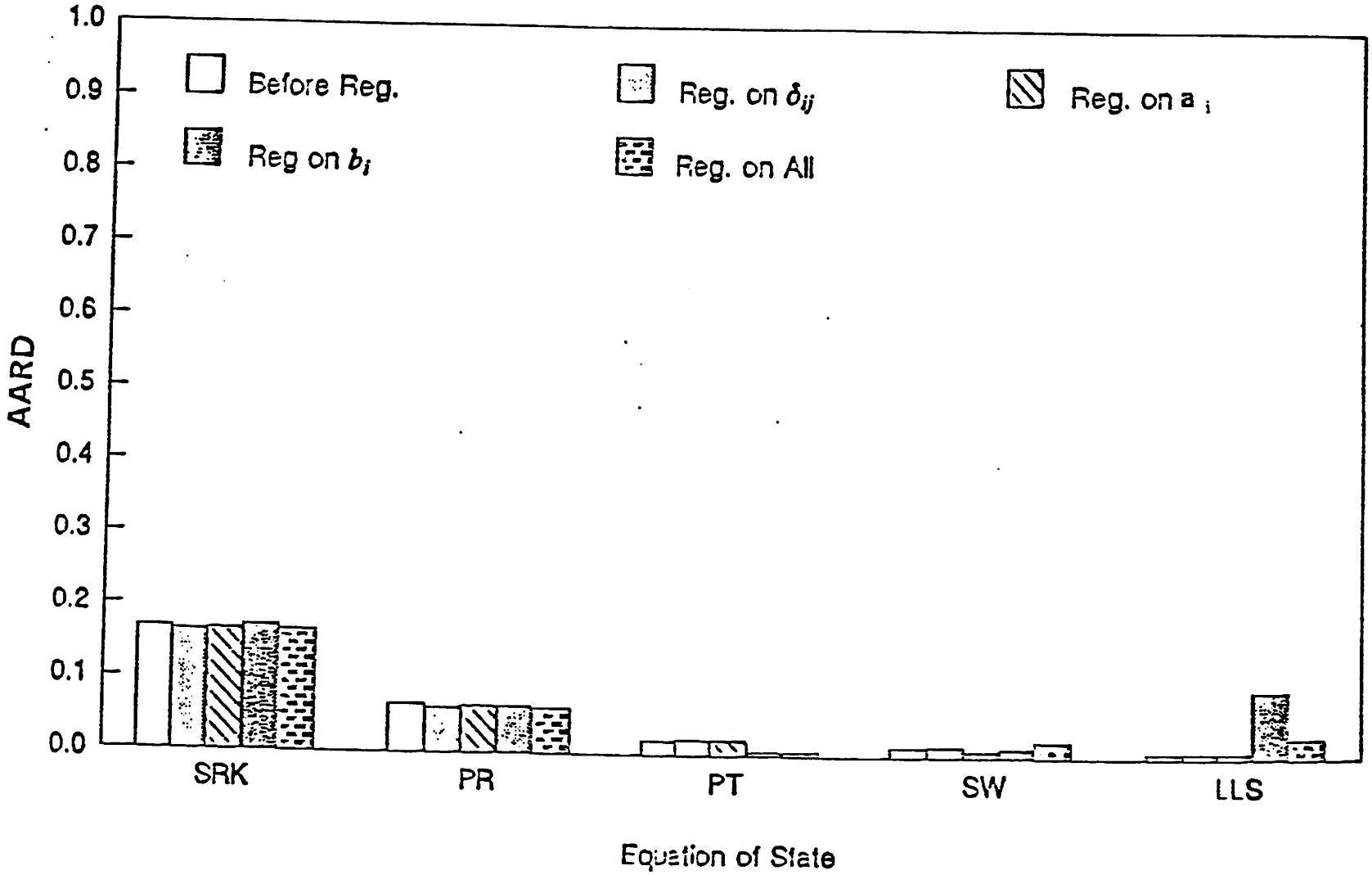

Fig. 6.8. Average Absolute Relative Deviations (AARD) between predicted and measured values of liquid density for mixture 2, CO_2–C_1–C_{10} before and after regression on individual and all parameters for five cubic EOS.

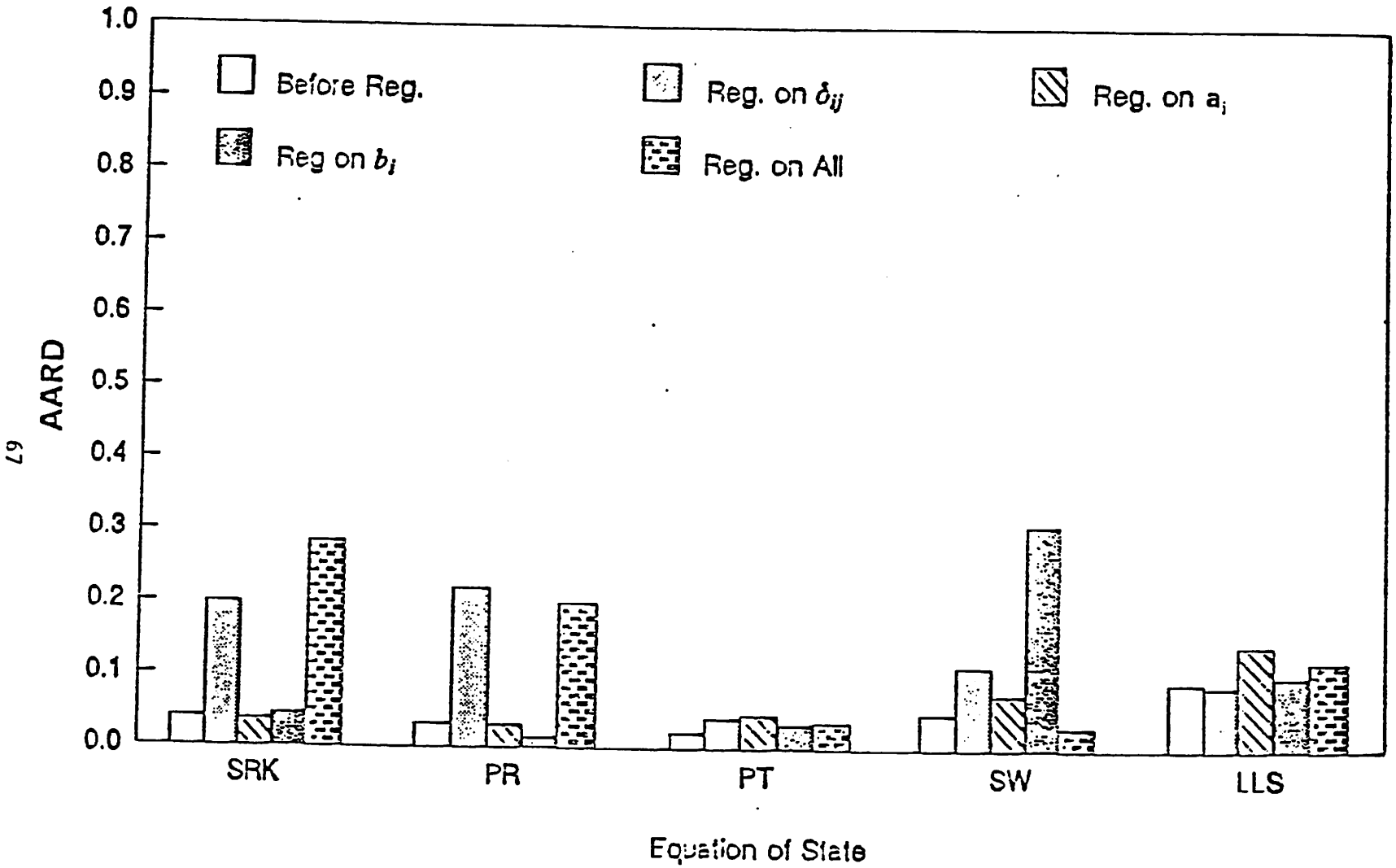

Fig. 6.9. Average Absolute Relative Deviations (AARD) between predicted and measured values of vapor density for mixture 2, CO_2-C_1-C_{10} before and after regression on individual and all parameters for five cubic EOS.

ternary systems. This system, the conditions of T and P were the same as the two ternary systems, obviously, this system was more complex due to the greater number of components.

Figure 6.10 is a histogram of the AARD between experimental and predicted equilibrium phase compositions using all five EOS before and after regression on single parameters and on all parameters simultaneously for mixture-3. This Figure shows that the errors in composition before regression ranged from 20 to over 40 percent. After regression on all parameters, the error of prediction by all EOS were about 14 percent. Even though the initial values of δ_{ij} for SRK, PT and SW EOS were "borrowed" from the PR, the initial AARD for PT EOS was less than the PR. The initial error for SRK was greater than that of PR by about 5 percent, while for SW EOS the error was greater by about 16 percent. The initial relative error between experimental and predicted phase composition was greater for the quaternary than the ternary mixtures for all equation of states, as it was expected due to more components. For all EOS, regression on the parameter b_i showed the error of prediction to be nearly the same after regression on all the parameters, i.e. the errors were reduced to around 14 percent with all five EOS.

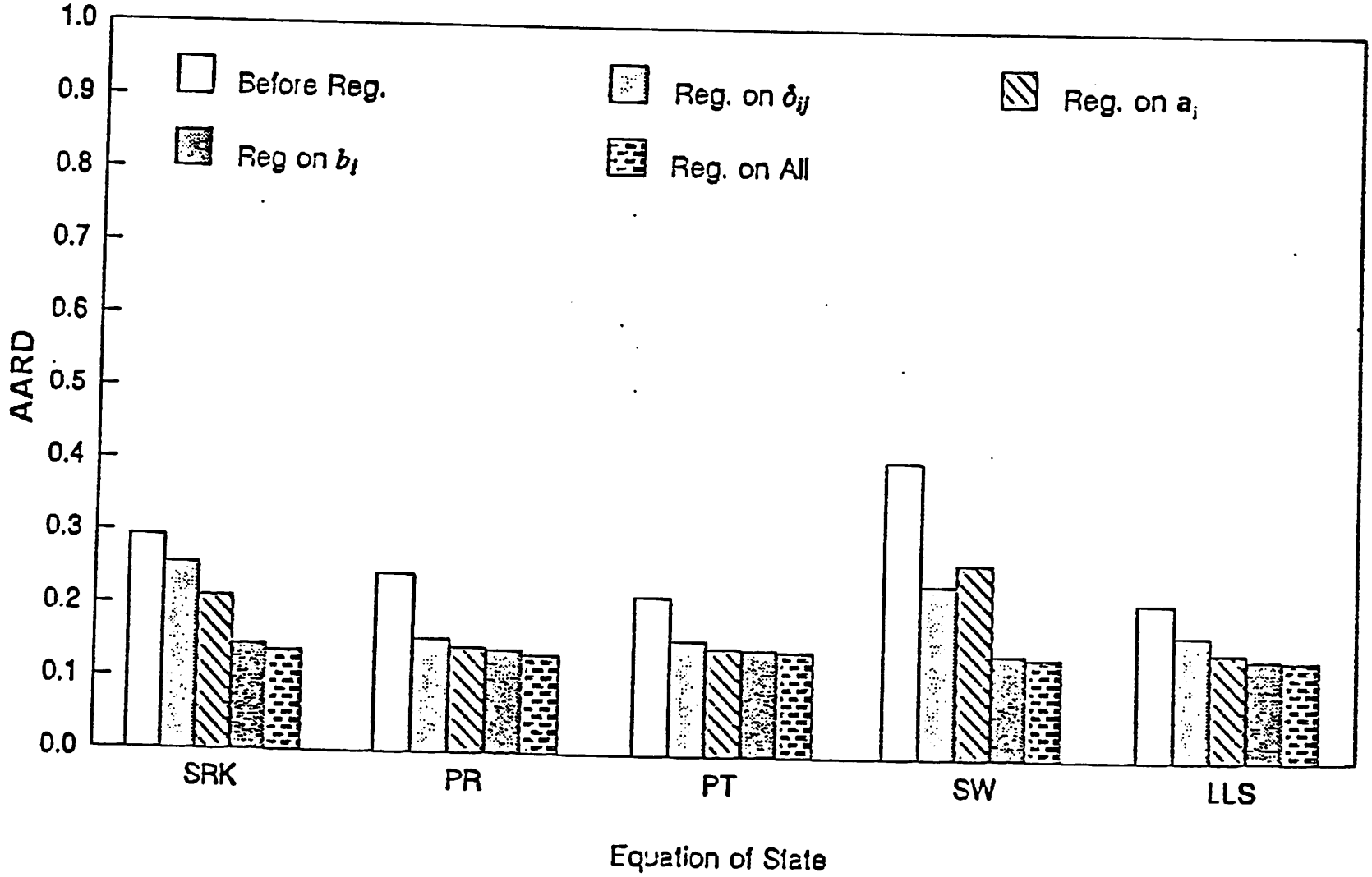

Fig. 6.10. Average Absolute Relative Deviations (AARD) between predicted and measured values of phase composition for mixture 3, CO_2-C_1-C_4-C_{10} before and after regression on individual and all parameters for five cubic EOS.

Figures 6.11 and 6.12 are histograms of the relative error between predicted and experimental liquid and vapor densities for mixture 3, $CO_2-C_1-nC_4-nC_{10}$. The error in liquid density predictions, Fig. 6.12, prior to regression on composition data, range from slightly more than one percent (SW and LLS) to about 15 percent (SRK). In general, the parameter values obtained by regression on equilibrium phase composition data did not improve the density predictions for this system; the LLS was an exception where initial error was reduced from over 2% to about 1.5 percent after regressions on all parameters. The LLS EOS predicted liquid densities the best (1 to 2% error) both before and after regression on composition data. Errors in prediction of vapor densities prior to regression on composition data, Fig. 6.9, varied from about 4.6 (LLS) to little over 16 (SRK) percent. Predictions of vapor densities after regression were improved using the EOS parameter values obtained from regression on phase composition data with an LLS error of about 4.5 percent and SRK error of about 16 percent.

Five and Eight Component Systems (Mixtures)

In this section the results for mixtures 4 and 5, $N_2-C_1-CO_2-C_2-nC_7$ and $N_2-C_1-CO_2-C_2-C_3-nC_5-nC_7-nC_{10}$ are present-

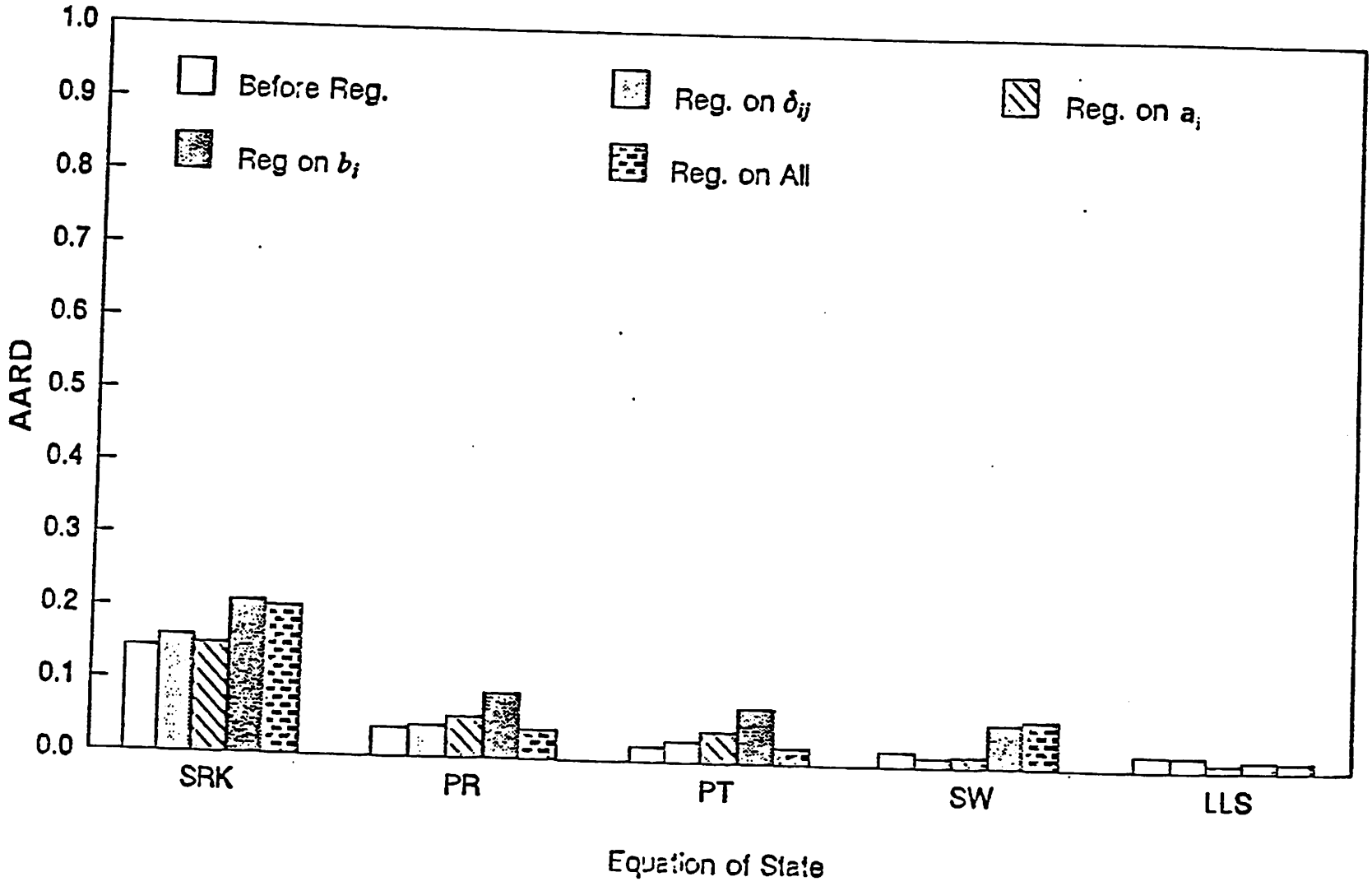

Fig. 6.11. Average Absolute Relative Deviations (AARD) between predicted and measured values of liquid density for mixture 3, CO_2-C_1-C_4-C_{10} before and after regression on individual and all parameters for five cubic EOS.

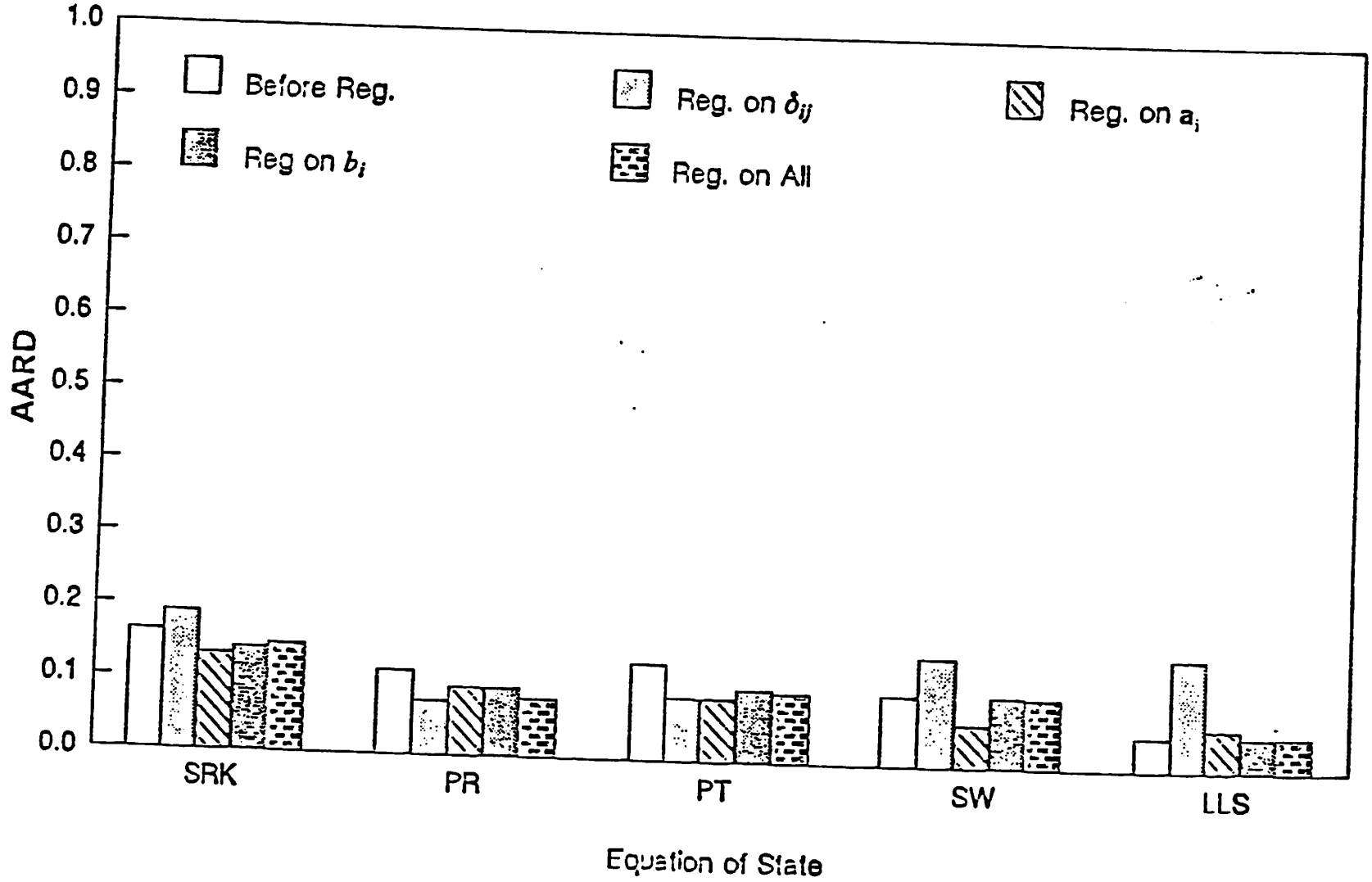

Fig. 6.12. Average Absolute Relative Deviations (AARD) between predicted and measured values of vapor density for mixture 3, CO_2-C_1-C_4-C_{10} before and after regression on individual and all parameters for five cubic EOS.

ed. Because experimental densities were not reported, no comparisons of density predictions could be made. The system temperature and pressure for these mixtures were different than the other simple systems; i.e. the 5-component system was at 1530.3 psia and 0° F and the 8-component system was at 2044 psia and 200° F. Only two tielines were reported for each of these mixtures.

Figure 6.13 is a histogram of the equilibrium composition AARD for all five EOS before and after regression on single parameters and on all parameters together for mixture-4, $N_2-C_1-CO_2-C_2-nC_7$. The errors in predicted phase compositions before regression ranged from 10 (SRK) to 49 (SW) percent. The errors after regression ranged from 2.6 to 3.2 percent. Hence, all EOS predicted phase composition equally well after regression. Even though the initial values of δ_{ij} for SRK, PT, and SW were the same as those used for PR, the initial errors for the SRK EOS was less than those from PR or LLS. There was no trend in prediction error of phase composition due to single parameter regressions. The over all concentrations of N_2 and CO_2 in these mixtures were quite small, less than 1 percent. In this mixture, the concentrations of C_1 and nC_7 were the largest in lower phase, while the concentration of C_1 was the largest in the upper phase, with experimentally measured values of over 98%.

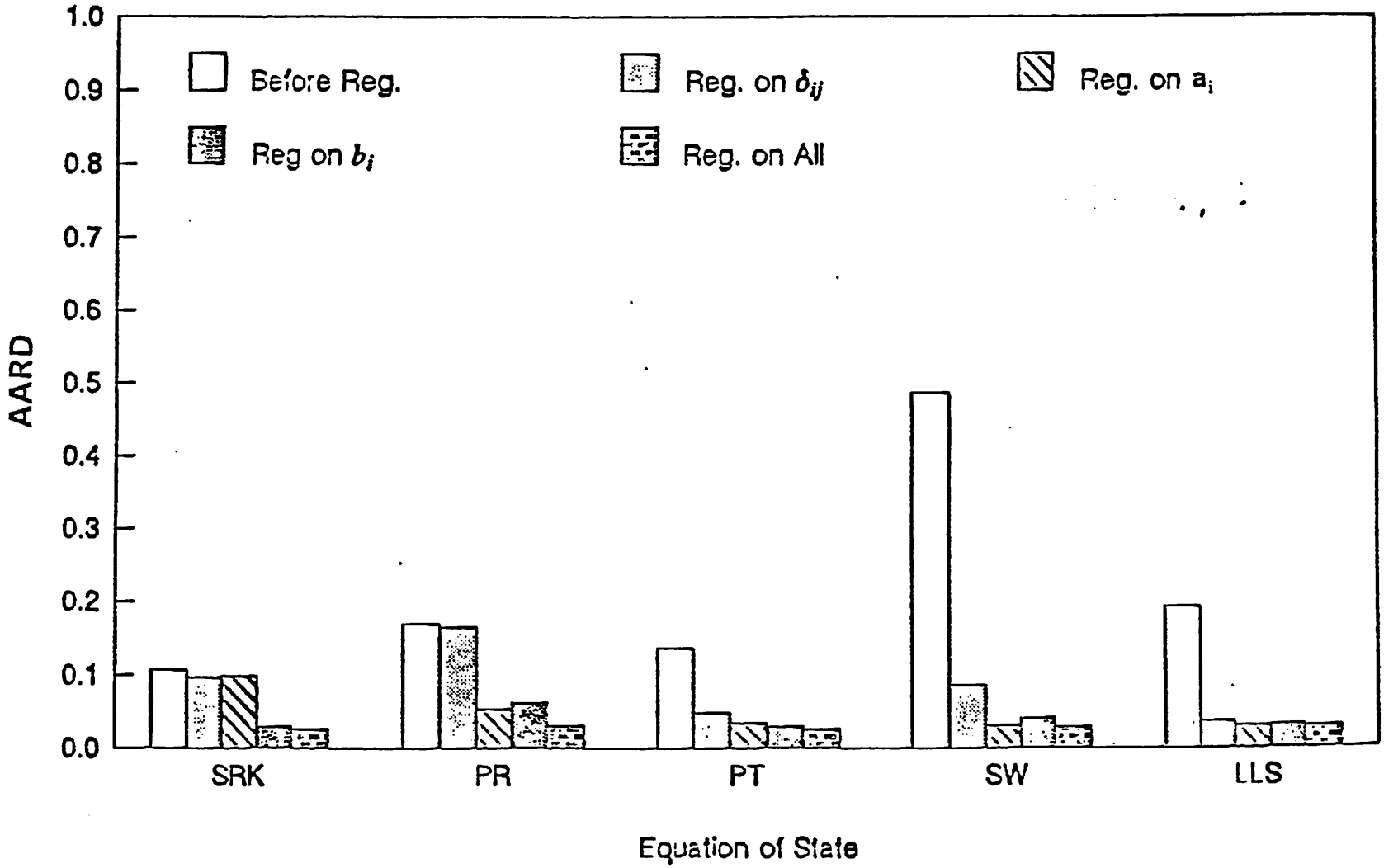

Fig. 6.13. Average Absolute Relative Deviations (AARD) between predicted and measured values of phase composition for mixture 4, $N_2-C_1-CO_2-C_2-nC_7$ before and after regression on individual and all parameters for five cubic EOS.

Figure 6.14 is a histogram of the equilibrium compositions of the AARD for all five EOS before and after regression on single parameters and on all parameters together for mixture 5, $N_2-C_1-CO_2-C_2-C_3-nC_5-nC_7-nC_{10}$. The errors before regression ranged from about 6 percent (PR) to over 35 percent (SW). The errors after regression were reduced to a range of 3-4 percent. Even though the initial values of δ_{ij} for SRK, PT, and SW were the same as those used for PR, the initial errors for the SRK and PT EOS were comparable with those from PR and were less than the error using LLS. There is no trend as to which single parameter regressions improved the predictions most. As with mixture 4, the reported values for N_2 and CO_2 in both upper and lower phases were very small.

6.2 COMPLEX SYSTEM (Mixture)

The complex system was a Maljamar separator fluid with varying concentrations of CO_2. The experimental data was obtained from a report by Silva et al (1981). This data was chosen because it met all of the requirements of this study: the data all fell within the two phase region, several tieline data were given, both liquid and vapor phase

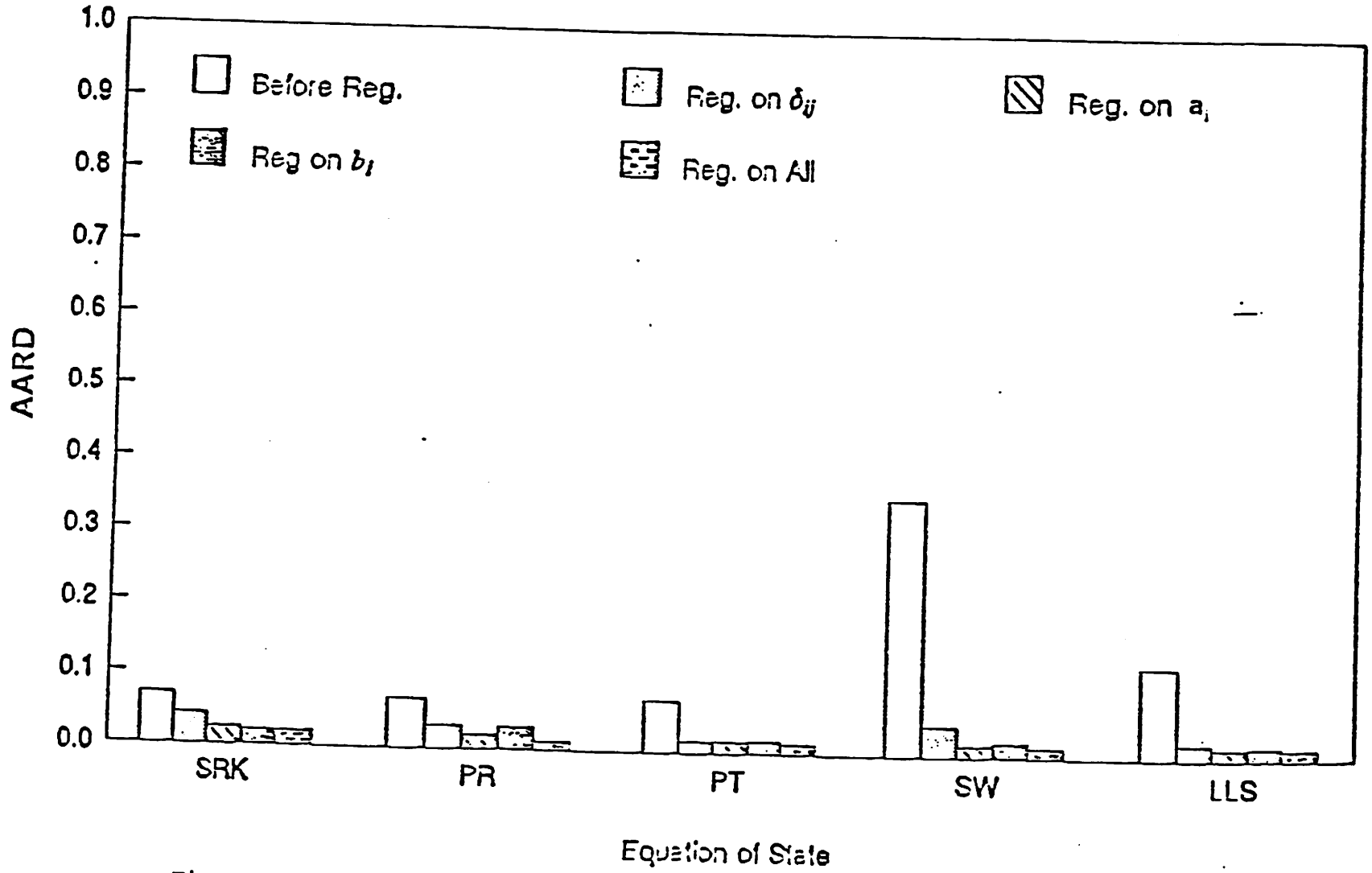

Fig. 6.14. Average Absolute Relative Deviations (AARD) between predicted and measured values of phase composition for mixture 5, N_2-C_1-CO_2-C_2-C_3-nC_5-nC_7-nC_{10} before and after regression on individual and all parameters for five cubic EOS.

densities were reported, and, of course, the system was complex and a crude oil.

As pointed out previously, measuring the exact composition of a crude oil system is impractical due to the large number of components in the system. The common procedure is to lump those components with similar values of some physical property together forming a pseudo-component. The compositional data of this study was obtained with a gas chromatograph and the lumping property used here was the elution time. Hence, the components eluted between the times of elution of two normal alkanes forms a pseudo-component. The number of pseudo-components may vary and may effect the errors of prediction using EOS. To see if the number of pseudo-components had any effect on the comparisons of the EOS performance, two common pseudo-component splitting schemes were used and the results are organized according to splitting scheme. In first scheme, representing the compositions from C_3 through C_6 and in the second scheme, representing the compositions from C_3 through C_4 were the same; the components between single carbon number increments were lumped to form three components or pseudo-components. Carbon dioxide was also represented as a separate component. The difference between the two representations is the way the C_7+ and C_5+ components were lumped. In the first case, all of the components C_7 or larger were

lumped into a single pseudo-component. In the other case, the components C_5 or larger were split into five pseudo-components using the method recommended by Whitson (1983) which was reported earlier.

In the unregressed EOS calculations which follow, the values of the binary interaction parameters (δ_{ij}) were chosen according to the method suggested by Peng and Robinson (1976a) for the PR EOS and these values were used for PR, SRK, PT, and SW EOS in this study. Using this method, binary interaction parameters had zero values for hydrocarbon pairs and non-zero values for CO_2-HC pairs. For the LLS EOS, binary interaction parameters were those given by Lawal et al (1986).

Results Using a Single C_7+ Pseudo-Component

Figure 6.15 is a histogram of the AARD between measured and predicted phase composition data for all five cubic EOS using the single C_7+ pseudo-component method. The AARD before regression ranged from 25 (PT) to 84 (SW) percent. The AARD after regression on all parameters was about 13 to 14 percent for all EOS.

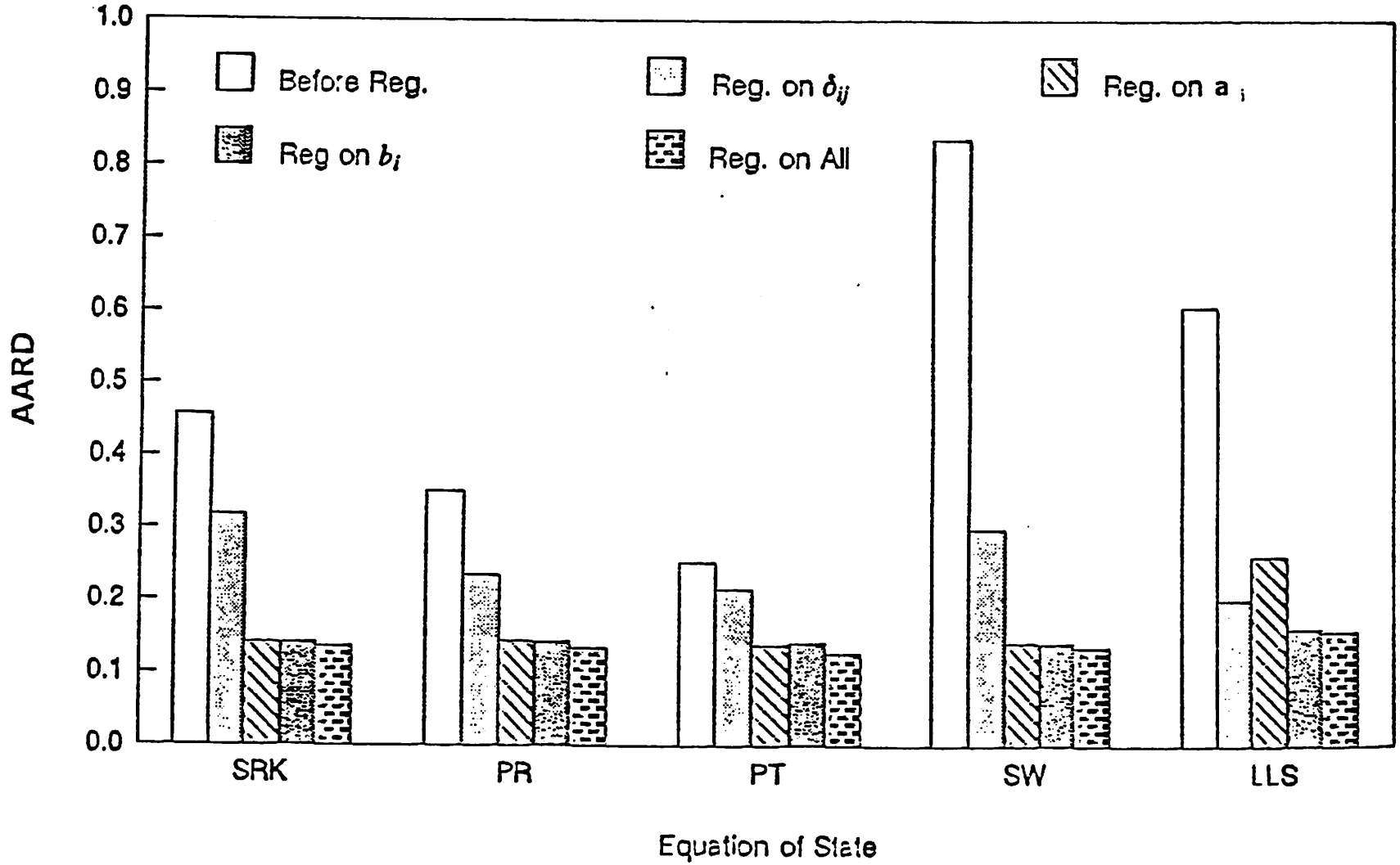

Fig. 6.15. Average Absolute Relative Deviations (AARD) between predicted and measured values of phase composition for the CO_2-Maljamar separator oil using single pseudo-component (C_7+) before and after regression on individual and all parameters for five cubic EOS.

Figures 6.16 and 6.17 are histograms of the AARD between experimentally measured and predicted liquid and vapor density data before and after regression on phase composition data. Before regression, errors in prediction of the liquid densities ranged from 9 (PT) to about 24 (SRK) percent. Liquid density predictions were worse after regression on phase composition data for all EOS except the LLS. However, the prediction using the PT EOS before regression was better than the LLS EOS after regression.

The error in predicting vapor densities varied between about one (PR and PT) to near 24 (SRK) percent before regression. Predictions using regressed parameters gave larger errors for all EOS except the SW. However, the prediction using the PT EOS before and after regression was better than the SW after regression and the differences before and after regression were only slight for the PT EOS.

Results Using Five Pseudo-Components

The number of pseudo-components and the split of components into each of the components was determined by the method suggested by Whitson (1983). The critical temperatures, critical pressures, critical compressibility factors,

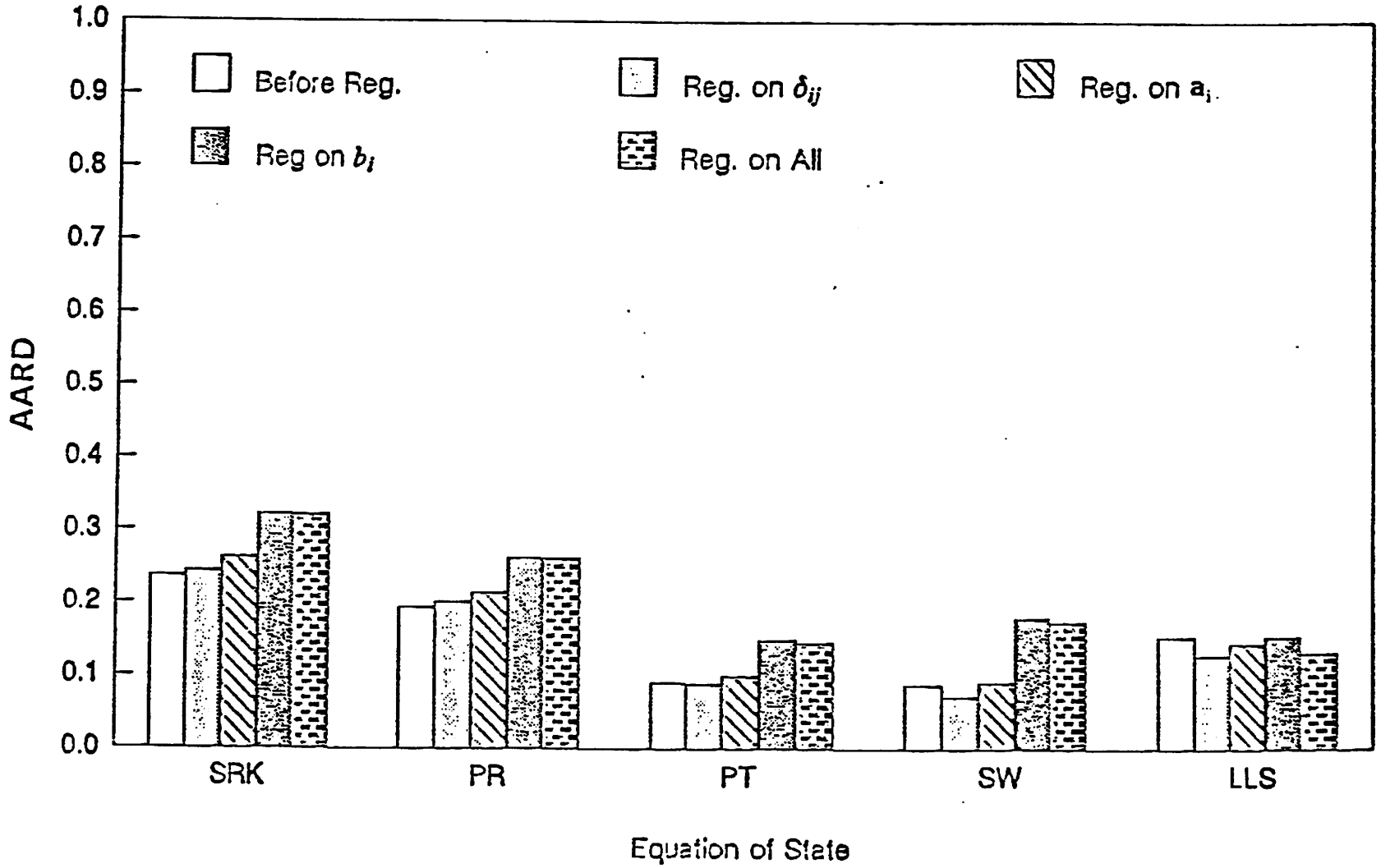

Fig. 6.16. Average Absolute Relative Deviations (AARD) between predicted and measured values of liquid density for the CO_2-Maljamar separator oil using single pseudo-component (C_7+) before and after regression on individual and all parameters for five cubic EOS.

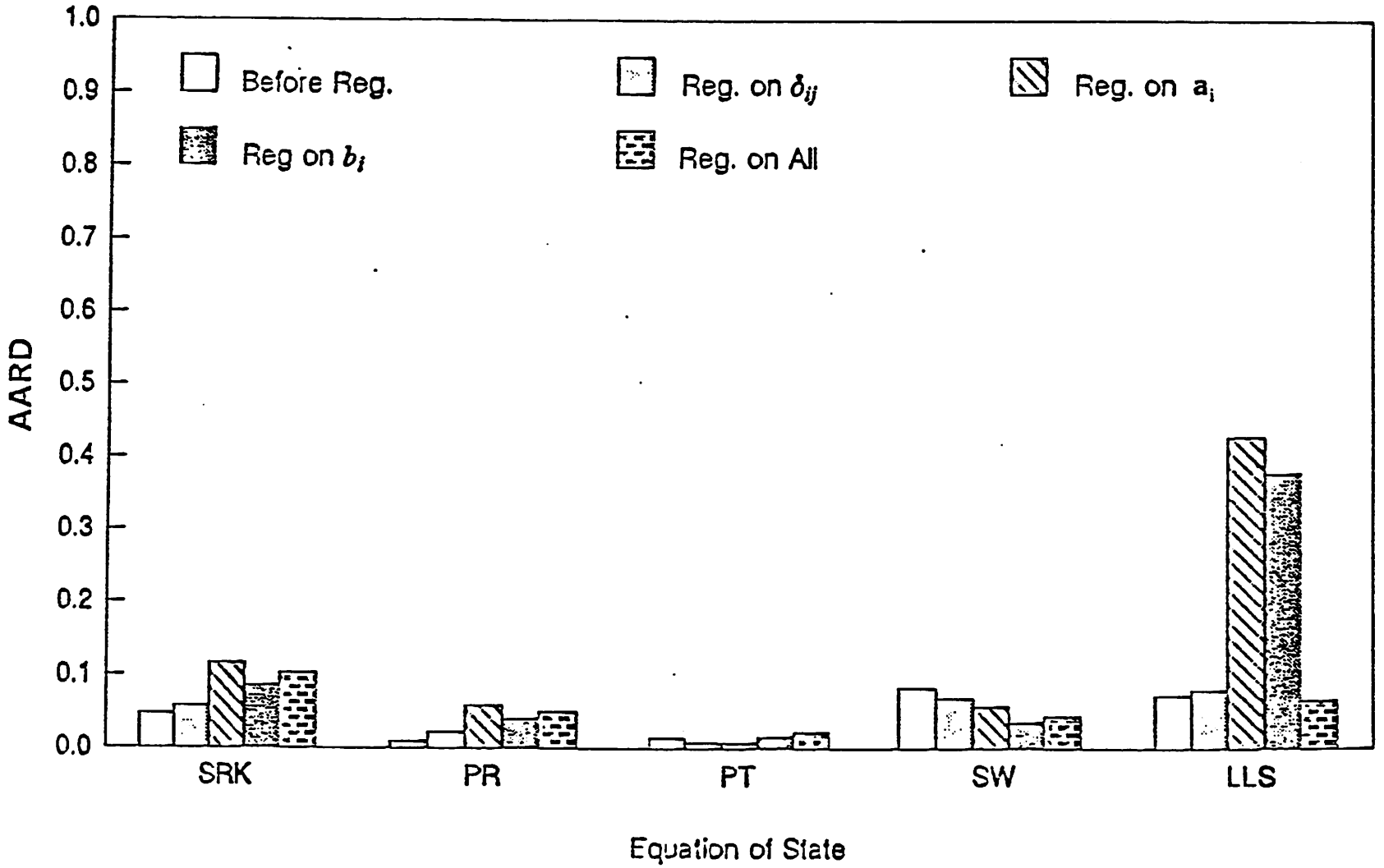

Fig. 6.17. Average Absolute Relative Deviations (AARD) between predicted and measured values of vapor density for CO_2-Maljamar separator oil using single pseudo-component (C_7+) before and after regression on individual and all parameters for five cubic EOS.

molecular weights, acentric factors, and binary interaction parameters were also calculated using Whitson's method.

By dividing the C_5+ components into five pseudo-components, the molecular make up of the heaviest pseudo-components were relatively heavy, causing concentrations of these pseudo-components in the vapor phase to be very small. Consequently, the regression objective function had to be modified because normalizing the error by dividing by the small, essentially zero, values of concentration yielded unreasonably large values for the relative error. Accordingly, the average absolute deviation, AAD, was used as the objective function in the regressions for these comparisons. Because reasonable values of the AARD could not be calculated, quantitative comparisons of the descriptions of the phase composition data using the two methods of characterizing the heavy fractions could not be drawn. However, Tables 6.4 and 6.5 contain the tabulated composition values before and after regression using the PR EOS for both characterization methods. The error before regression appeared to be larger for single C_7+ pseudo-component method than for the five pseudo-components. After regression on all parameters the error in predicting phase compositions was about the same using either characterization method. Average absolute relative deviations for the density data were, however, calculated and comparisons for predicting

Table 6.4. Measured and calculated compositions and densities upon the regression of all parameters (a_i, b_i, δ_{ij}) for single pseudo-component (C_7+) at 90°F and 800 psia.

EXPERIMENTAL

Tie Lines	Lower Phase							Upper Phase						
	CO_2	C_3	C_4	C_5	C_6	C_7+	ρ_L	CO_2	C_3	C_4	C_5	C_6	C_7+	ρ_L
1	.5631	.0055	.0169	.0236	.0212	.3696	.8480	.9909	.0020	.0032	.0023	.0016	.0001	.1509
2	.4871	.0042	.0136	.0874	.1630	.1081	.8480	.9914	.0017	.0031	.0023	.0015	.0001	.1493
3	.5575	.0041	.0143	.1121	.1259	.0777	.8500	.9920	.0015	.0029	.0022	.0014	.0001	.1487
4	.5700	.0034	.0134	.0320	.0352	.3460	.8500	.9926	.0012	.0028	.0021	.0013	.0001	.1480

RESULT FOR PENG-ROBINSON
BEFORE REGRESSION

Tie Lines	Lower Phase							Upper Phase						
	CO_2	C_3	C_4	C_5	C_6	C_7+	ρ_L	CO_2	C_3	C_4	C_5	C_6	C_7+	ρ_L
1	.6106	.0051	.0157	.0216	.0196	.3214	.7243	.9928	.0021	.0027	.0017	.0007	.00005	.1478
2	.6079	.0037	.0116	.0167	.0180	.3422	.7245	.9945	.0015	.0020	.0013	.0006	.00005	.1474
3	.6171	.0037	.0131	.0280	.0290	.3089	.7247	.9929	.0015	.0023	.0022	.0011	.00005	.1481
4	.6184	.0031	.0126	.0284	.0314	.3060	.7248	.9931	.0013	.0022	.0022	.0011	.00004	.1482

AFTER REGRESSION

Tie Lines	Lower Phase							Upper Phase						
	CO_2	C_3	C_4	C_5	C_6	C_7+	ρ_L	CO_2	C_3	C_4	C_5	C_6	C_7+	ρ_L
1	.5649	.0055	.0166	.0242	.0219	.3670	.6685	.9921	.0019	.0034	.0017	.0008	.0001	.1419
2	.5636	.0040	.0124	.0185	.0199	.3816	.6685	.9940	.0014	.0025	.0012	.0008	.0001	.1415
3	.5684	.0041	.0140	.0315	.0326	.3493	.6693	.9922	.0014	.0029	.0021	.0012	.0001	.1422
4	.5700	.0034	.0134	.0320	.0352	.3460	.6695	.9925	.0012	.0028	.0021	.0013	.0001	.1422

Table 6.5. Measured and calculated compositions and densities upon the regression of all parameters (a_i, b_i, $\hat{s}_{ij}$) for 5 pseudo-component group at 90°F and 800 psia.

EXPERIMENTAL

Tie Lines	Lower Phase									Upper Phase								
	CO_2	C_3	C_4	PS_1	PS_2	PS_3	PS_4	PS_5	ρ_L	CO_2	C_3	C_4	PS_1	PS_2	PS_3	PS_4	PS_5	ρ_V
1	.5631	.0055	.0169	.0788	.1343	.0896	.0551	.0567	.8480	.9909	.0020	.0032	.0039	.00003	.0000	.0000	.0000	.1509
2	.4871	.0042	.0136	.0874	.1630	.1081	.0671	.0696	.8480	.9914	.0017	.0031	.0037	.00003	.0000	.0000	.0000	.1493
3	.5575	.0041	.0143	.1121	.1259	.0777	.0483	.0601	.8500	.9920	.0015	.0029	.0036	.00003	.0000	.0000	.0000	.1487
4	.5700	.0034	.0134	.1117	.1205	.0733	.0453	.0623	.8500	.9926	.0012	.0028	.0034	.00003	.0000	.0000	.0000	.1480

RESULT FOR PENG-ROBINSON
BEFORE REGRESSION

Tie Lines	Lower Phase									Upper Phase								
	CO_2	C_3	C_4	PS_1	PS_2	PS_3	PS_4	PS_5	ρ_L	CO_2	C_3	C_4	PS_1	PS_2	PS_3	PS_4	PS_5	ρ_V
1	.5439	.0054	.0176	.0839	.1394	.0933	.0574	.0591	.6549	.9923	.0022	.0031	.0020	.00044	.0000	.0000	.0000	.1483
2	.5460	.0038	.0122	.1014	.1343	.0893	.0554	.0575	.6559	.9935	.0015	.0021	.0024	.00039	.0000	.0000	.0000	.1483
3	.5469	.0040	.0149	.1154	.1284	.0795	.0494	.0615	.6531	.9926	.0016	.0026	.0028	.00038	.0000	.0000	.0000	.1486
4	.5460	.0033	.0143	.1183	.1269	.0774	.0479	.0658	.6507	.9929	.0014	.0025	.0029	.00038	.0000	.0000	.0000	.1486

AFTER REGRESSION

Tie Lines	Lower Phase									Upper Phase								
	CO_2	C_3	C_4	PS_1	PS_2	PS_3	PS_4	PS_5	ρ_L	CO_2	C_3	C_4	PS_1	PS_2	PS_3	PS_4	PS_5	ρ_V
1	.5667	.0055	.0166	.0790	.1332	.0884	.0546	.0560	.6578	.9918	.0020	.0034	.0025	.00029	.0000	.0000	.0000	.1523
2	.5670	.0040	.0119	.0929	.1301	.0864	.0533	.0544	.6589	.9928	.0017	.0024	.0028	.00025	.0000	.0000	.0000	.1522
3	.5700	.0041	.0140	.1094	.1220	.0753	.0468	.0582	.6562	.9922	.0016	.0029	.0029	.00026	.0000	.0000	.0000	.1525
4	.5700	.0034	.0134	.1120	.1204	.0733	.0453	.0623	.6537	.9926	.0013	.0028	.0030	.00025	.0000	.0000	.0000	.1525

densities using the two characterizing methods could be drawn.

Figure 6.18 is a histogram of the AAD between experimentally measured and predicted phase composition data using all five cubic EOS before and after regression. The PR EOS predicted the data best before regression, while the SW EOS performed the worst by more than a factor of 10. After regression, The PT EOS fit the data best, but all of the EOS performed about the same.

Figures 6.19 and 6.20 are histograms of the AARD between experimentally measured and predicted liquid and vapor density data using all five cubic EOS before and after regression. The error in predicting liquid densities before regression ranged from about 12 (PT and SW) to 29 (LLS) percent. Liquid density predictions using the parameter values obtained by regressing on the phase composition data were slightly improved over the predictions before regression. The errors in liquid density predictions were nearly the same using either the single pseudo-component or the five pseudo-component method.

Vapor density errors ranged from about 1 (PR and PT) to over 12 percent (SW) before regression. Errors using parameter values obtained by regression on phase composition

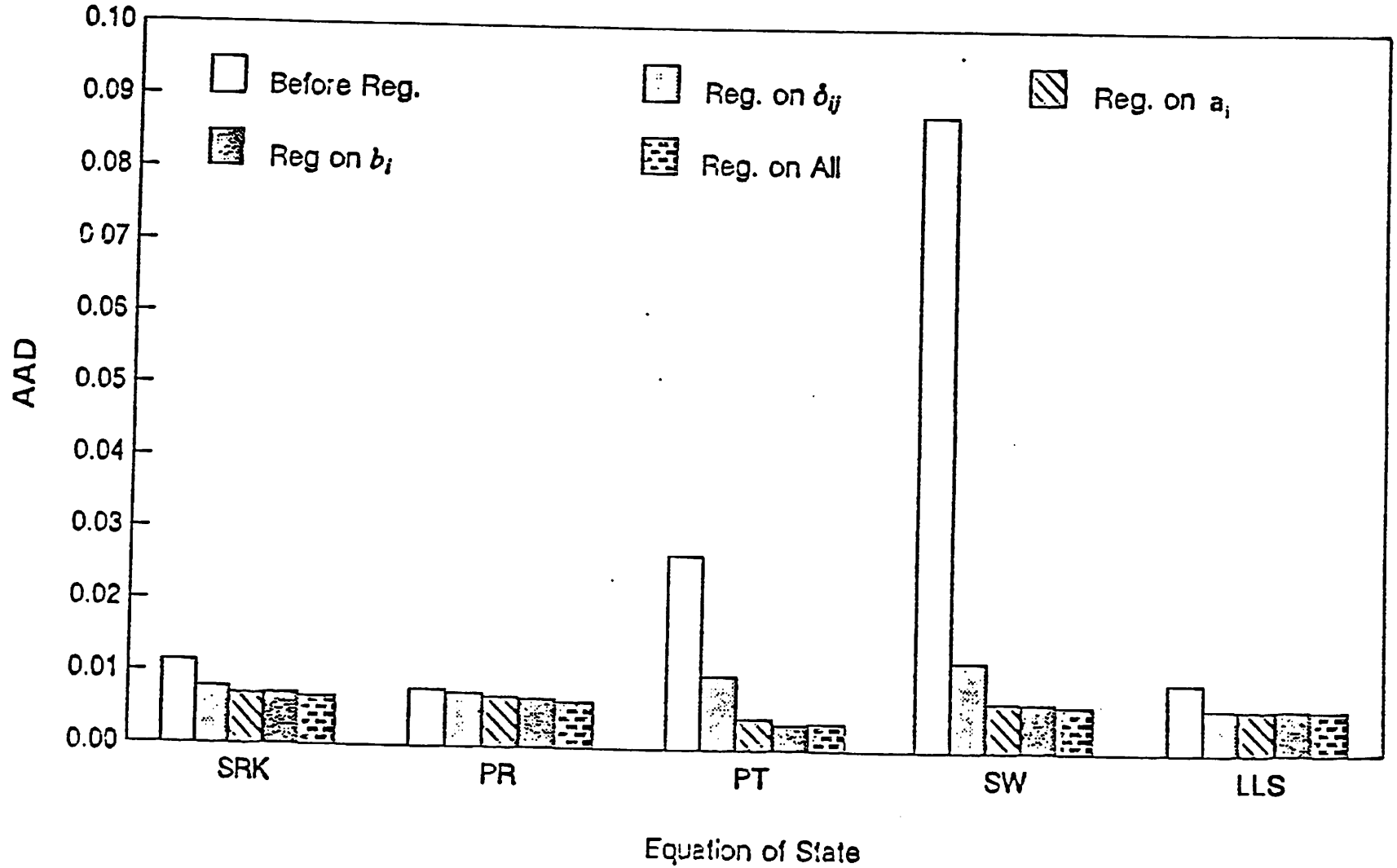

Fig. 6.18. Average Absolute Relative (AAD) between predicted and measured values of phase composition for CO_2-Maljamar separator oil using five pseudo-component before and after regression on individual and all parameters for five cubic EOS.

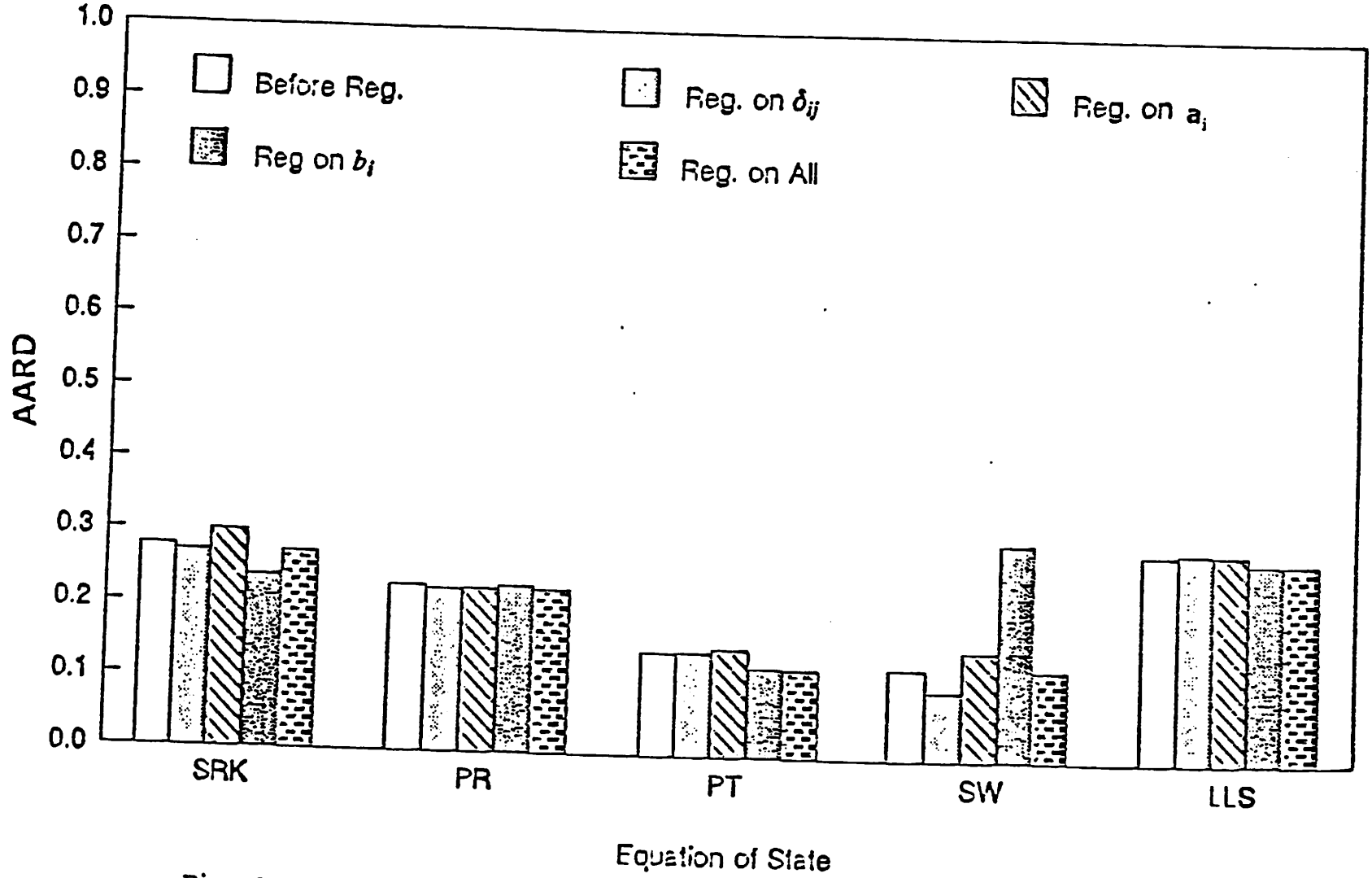

Fig. 6.19. Average Absolute Relative Deviations (AARD) between predicted and measured values of liquid density for the CO_2-Maljamar separator oil using five pseudo-component before and after regression on individual and all parameters for five cubic EOS.

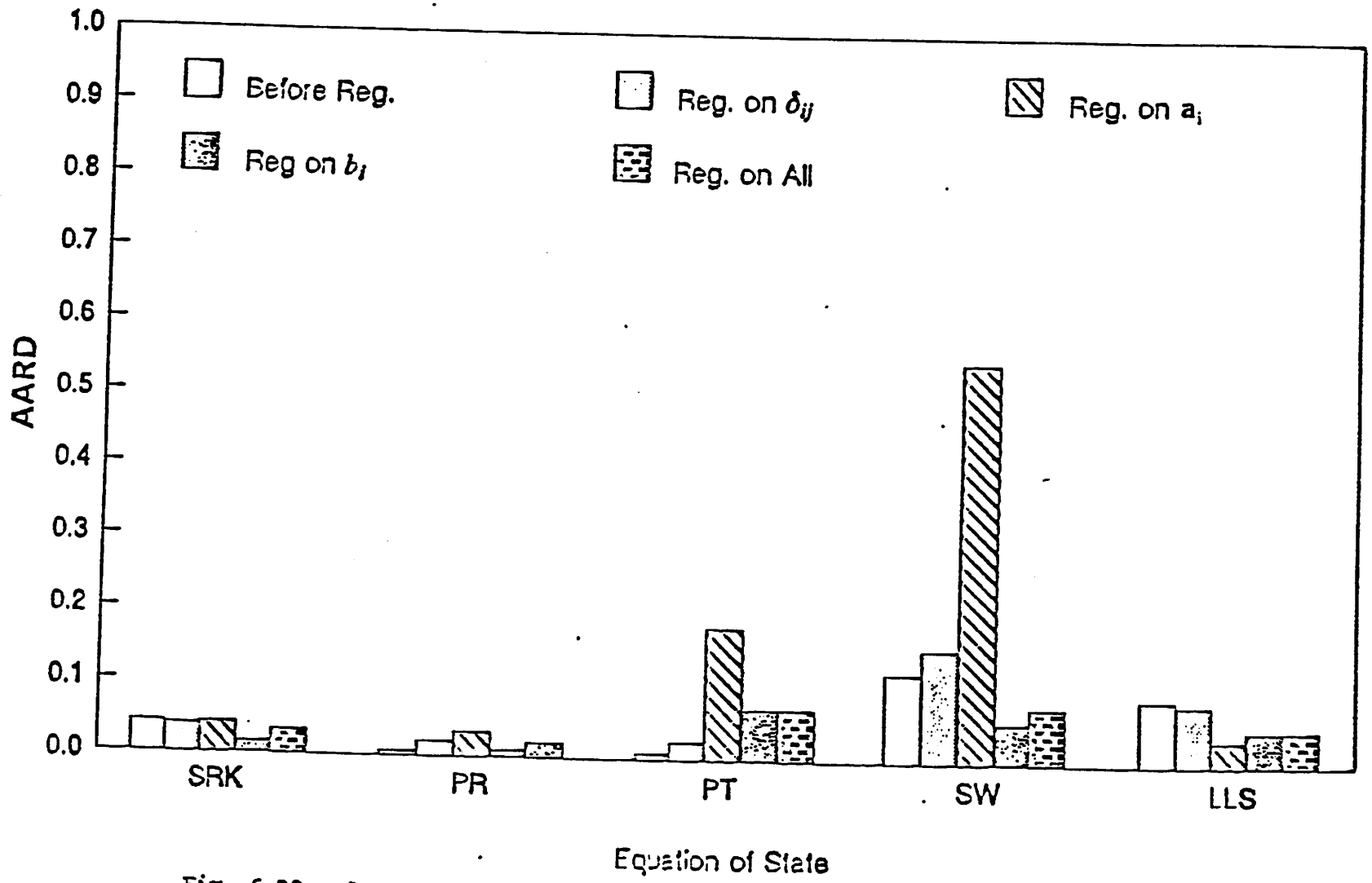

Fig. 6.20. Average Absolute Relative Deviations (AARD) between predicted and measured values of vapor density for the CO_2-Maljamar separator oil using five Pseudo-component before and after regression on individual and all parameters for five cubic EOS.

data were generally larger than errors before regression, ranging from about 2 (PR) to about 7 (SW) percent. The errors in vapor density predictions were nearly the same using either the single C_7+ pseudo-component or the five pseudo-component method.

Values of EOS parameters after regression for all mixtures and all EOS were inspected to see if any trend in the optimum values could be observed. None was discovered.

7. DISCUSSION OF RESULTS

The comparisons of this study were drawn to answer a series of questions concerning cubic EOS. These included: Which EOS give the best descriptions of progressively more complicated reservoir fluid systems? Are the descriptions measurably improved when parameters obtained by regressing on VLE data are used? If so, does using parameters obtained by regression change which EOS gives the best descriptions? Are the VLE and PVT behavior of progressively more complicated hydrocarbon systems better described with a progression of complication of the EOS form? Are the EOS which do the best job of predicting VLE data the most thermodynamically consistent by also predicting PVT behavior the best? Are errors in predicting PVT behavior associated with the EOS form or would a "better" set of parameters, determined by regressing on VLE data, provide a better, or worse, prediction of the PVT behavior? The answers to these questions, as previous investigations in this subject would suggest, cannot be answered absolutely and, as has been discussed earlier, there is usually a significant error between the values predicted by the EOS and experimentally measured data for systems other than simple gases above the critical point or at least well into the vapor region.

Reasons for the errors, especially when describing complex systems, are not well understood. The EOS forms are often based on fundamental considerations and therefore one might expect consistently low errors in VLE and PVT predictions for systems ranging from simple to complex. However, experience is that the best which can be hoped for is to predict the behavior of complex systems within acceptable limits. Predictions outside the range for which experimental data is available to verify accuracy is risky. Hence, errors are inevitable with the present forms.

The relative error between measured VLE data and predictions of that data using parameters obtained by regression was observed to be significantly less for mixtures 4 and 5 than for mixtures 1 through 3 which contained fewer components. The most probable explanation for the smaller error is that the data of mixtures 4 and 5 only contained two equilibrium tielines and the compromises in optimal fitting which occur with more data points was minimal. But other possibilities should also be considered.

First, analytical techniques for even simple chemical systems have limits of accuracy. Gas chromatography is the common method for analyzing hydrocarbon data and, if care is taken, can certainly provide composition data of sufficient accuracy for most engineering calculations. However,

obtaining sufficient and known limits of accuracy over all compositions of complex mixtures sometimes requires many calibration runs which may not be practical to be performed. Chemical analyses of reservoir fluids obtained by gas chromatography seldom include a statement about the accuracy of the data and therefore leaves room for speculation about that accuracy. Therefore, gas chromatograph data may reflect varying and unknown accuracy as the composition space varies. Errors in analysis may be reflected in the fit error when using a fundamentally correct EOS (Coats & Smart 1986). Thus an explanation of the difference in errors observed for mixtures 4 and 5 and that in mixtures 1 through 3 may reflect the quality of data from different laboratories and different analysis techniques.

A third possibility is that the magnitude of the compositions of the non-hydrocarbon constituents in mixtures 4 and 5 (CO_2 and N_2) is less than that for mixtures 1 through 3 (CO_2). It has been generally noted that cubic EOS predict behavior less well for polar compounds than for non-polar compounds (Patel & Teja, 1980, Lawal et al 1985, and Taraked et al 1979 & 1977). Even though the number of components included in the analyses of mixtures 4 and 5 is greater than the number in mixtures 1 through 3, the non-hydrocarbon constituents (CO_2 and N_2) of mixtures 4 and 5 are present in concentrations best described as impurities

and thus have less of an effect on the behavior of the mixtures and consequently, on the error of prediction.

Other errors may result because the form of the EOS is not based on correct or fundamental considerations, the method for calculating the parameters of the EOS are incorrect, or the mixing rule or rules for mixtures are incorrect. This study did not include a study of mixing rules. The comparisons of how well the EOS predict VLE and density (PVT) behavior before and after regression gives insight as to whether the error, or part of the error, is caused by the method of calculating parameters or from the EOS form. For all of the mixtures of this study, the error in predicting VLE data after regression on all parameters was nearly the same for a given mixture for all EOS. This result suggests that if the parameters were properly calculated, there would be no advantage to using a more complicated EOS form over a simpler form for predicting VLE behavior.

In contradiction, density predictions were sometimes improved but were sometimes worse when using the "best" parameters determined by regressing on VLE data. However, the differences in density predictions using the regressed parameters and the unregressed parameters were small for those EOS which predicted densities well before regression.

Liquid densities were better predicted by a three parameter EOS (PT or Sw) than the nominal two parameter forms (PR and SRK) as was also observed previously by Tsonopoulos and co-workers (1985), Varotsis and co-workers (1986), and Ahmed (1986). For the three simple mixtures for which density data was available, the LLS EOS predicted the liquid densities with the smallest relative error before regression and those predictions were excellent (1 to 3% error). However, for the complex system, errors in predicting liquid densities using the LLS EOS were greater than with PT or SW.

There was no trend as to which EOS predicted vapor densities the best. The maximum error for any EOS before regression in predicting vapor density for any of the mixtures in this study was of the order of 10% with several values of the order of 1%. Using the "best" values of EOS parameters, determined by regressing on VLE data, sometimes made the error worse than using the unregressed value. In general, if the error in predicting vapor densities before regression was low, then the error when using the "best" EOS parameters obtained by regression was also low.

As mentioned previously, when using the "best" parameters from regression on VLE data, all EOS predicted VLE data about the same. Further, for each mixture and for the EOS

which predicted VLE behavior the best, there was only a slight improvement in the prediction obtained before regression and that after regression. Hence, it cannot be expected that a major improvement in the cubic EOS predictive capability may be found by modifying the methods for calculating EOS parameters for those forms used in this study.

Because the prediction of VLE data was about the same for all of the EOS in this study when using the "best" regressed values of the EOS parameters, we must limit our comparisons and judgments concerning which EOS performs the best to predictions before regression. A confusing factor in these comparisons was the fact that the predictions using SRK, PT and SW EOS were performed using values of binary interaction parameters calculated for the PR EOS. No one EOS performed the best on both VLE and density predictions for all the mixtures of this study using parameter values before regression. When comparing the unregressed predictions of the PR and LLS EOS with those of SRK, PT, and SW after regressing on binary interaction parameters, PT predicted VLE data with the least error in every case except for the crude oil characterized with 5 pseudo-components and for mixture 2. For the crude oil characterized with 5 pseudo-components, PR predicted the VLE data with the least error, but predicted the liquid density with an average

error of about 20%, whereas PT predicted the liquid density with about a 10% error. The SRK EOS predicted the VLE data of mixture 2 with the least error, however the average error in liquid densities predicted by SRK for this mixture was also near 20%, while PT predicted those same liquid densities with an average error of about 2%. Thus the results of this study suggest that the PT EOS does the best job of predicting both VLE and phase densities for the systems and conditions of this study. This conclusion is consistent with the results of by Patel and Teja (1980), Trebble and Bishnoi (1986) and Tsonopoulos (1985).

As expected from the work by Vartosis et al (1985), the error in VLE predictions using the SW EOS were large before regression. One must remember, however, that these calculations made use of the values of the binary interaction parameters calculated for PR. Interestingly, regression on the binary interaction parameters markedly improved the predictions using SW. Errors in prediction of VLE data using the PR binary interaction parameters with the PT EOS were not as large as those observed with SW and those errors were often less than the errors observed for PR and LLS. However, there was, in some cases, a marked improvement in the predictive capacity of VLE data using PT with binary interaction parameters determined by regression. Therefore, a fruitful and productive study might be to develope

tabulated values or a correlation for binary interaction parameters for PT and/or SW.

Lawal and coworkers (1986) demonstrated that the LLS EOS was able to accurately predict VLE and density behavior of a crude oil system without regression and using only a single C_7+ pseudo-component. In the present study, the predictions using unregressed parameter values gave a nearly 60% average error in predicting VLE data for the crude oil system when only a single C_7+ pseudo-component was used. Using 5 pseudo-components, however, the error in predicting VLE data was as low as the error predicted using PR. However, the average error in predicting liquid densities was of the order of 20%. Thus, this study indicates that there is no advantage to using the four parameter LLS EOS over a three parameter form.

For each mixture and for each EOS, each single parameter was regressed against the VLE data. Observations of the results of the single parameter regressions indicated no universal trend due to regression on any particular parameter. The author did observe that in several cases, regression on the repulsion parameters, b_i, improved the VLE predictive performance of the EOS and perhaps an investigation on the method of determining that parameter was warranted. However, an examination of the density predic-

tions reveals that the average errors in the values of liquid densities predicted using the regressed b_i parameters were often significantly greater than the unregressed values. Thus, it appears that any modification of the EOS parameters should be undertaken with care so that improvement in one aspect of predictive characteristics does not cause a loss in consistency over all aspects of the uses of EOS. One must also wonder if the practice of adjusting values of critical properties, which in a way is equivalent to adjusting the values of b_i, to match VLE data might not cause larger errors in density predictions. In this study, regressing on the binary interaction parameters did not cause as large a change in the average liquid density errors as was sometimes seen when regressing on the repulsion parameters (b_i). The SW EOS, however, did produce greater average errors in vapor phase densities when regressed values of binary interaction parameters were used. Thus, the practice of adjusting binary interaction parameters to match VLE data may be less risky with some EOS than the adjustment of critical properties.

In agreement with Coats and Smart (1986) using a single pseudo-component to represent the C_7+ heavy component gave better fits to data after regression than the method which divides the C_5+ heavy fractions into five pseudo-components. Intuitively, one might expect that the more detailed

descriptions or characterization has a greater potential for accurately describing any system and, indeed, before regression that is the case. Probably, the better performance with fewer pseudo-components reflects the compromises in error which the regression algorithm makes. This result does not argue for using fewer components if the particular investigation does not utilize regression on experimental data. In fact, the results in those cases, indicate the opposite. However, if regression is to be used, then perhaps the fewest number of pseudo-components should be used, this result agrees with the observation by Coats and Smart (1986). The question not addressed in this study or by Coats and Smart is, what heavy components should be lumped into a single pseudo-component? For example, a single C_5+ pseudo-component may give better results than a C_7+ pseudo-component. Finally, consistency was not apparently affected by the method for characterizing the heavy fraction; there was no significant difference between the densities predicted using the two results.

8. CONCLUSIONS

The comparison of five EOS (SRK, PR, SW, PT, and LLS) to predict VLE and phase densities for simple and complex mixtures before and after regression lead to the following conclusions:

1. Prediction of VLE composition data has been improved when optimum parameters obtained by regression were used. However, for all of the mixtures of this study, the error in predicting VLE data after regression on all parameters was nearly the same for a given mixture regardless of which EOS was used. Thus, for describing VLE data, the form of the equation is not significant, ie. there are no advantage to using more complicated EOS.
2. In agreement with previous studies, liquid densities were better predicted by a three parameter EOS (PT or SW) than by the nominal two parameter forms. There was no clear trend to which EOS predicted vapor densities the best.
3. The LLS EOS predicted liquid densities for the three simple mixtures, with smallest relative error before regression (1 to 3%). However, for the complex system, errors in predicting liquid densities using LLS EOS were greater than those predicted with either PT or SW.

4. The results suggests that the PT EOS does the best job of predicting both the VLE and phase densities for the systems and conditions of this study, as was found previously by Patel and Teja (1980) and Ahmed (1986).
5. The improvements in prediction of VLE data after regression on single parameters varied with the data set and EOS form. Perhaps more improvement was found by regression on the repulsion parameters, b_i. However, density predictions were often made worse using the regressed values for the b_i and therefore use of those values may be risky. Regressing on the binary interaction parameters (δ_{ij}), however, did not affect density predictions to the same degree.
6. With the crude oil system, predictions before regression using more detailed heavy hydrocarbon characterization method reflected experimental VLE data more accurately than the less detailed method. After regression, however, the less detailed characterization method matched experimental data better than the more detailed method.
7. Previous claims that the LLS EOS may be used to accurately describe VLE for crude oil system using a single C_7+ pseudo-component without regression were not substantiated in this study.
8. No particular trend was observed on the EOS parameters after regression.

9. SUGGESTIONS FOR FUTURE WORK

The results of this study suggest that future work include:

1. Studies similar in nature to the work presented here to investigate the affect of mixing rules on EOS consistency and VLE prediction performance of hydrocarbon systems near critical points, and non-cubic EOS forms.
2. A comparison study should be performed to determine the optimum number of pseudo-components to use when regression is used to describe complex heavy hydrocarbon systems such as crude oils.
3. A continuation of this work in which EOS Parameters were optimized on density values and then to predict VLE data.
4. A continuation of this work in which EOS parameters are regressed on dew-point and/or bubble-point pressure and temperature is used in place of the VLE data of the present study.

REFERENCES

Abbott, M.M., "Cubic Equations of State," AIChE J., 19, No. 3, 596(1973).

Abbott, M.M. and Van Ness, H.C., "Theory and Problems of Thermodynamics," Schaum's Outline, Rensselear Polytechnic Institute (1972).

Adachi, Y. and Lu, B., "Simplest Equation of State for Vapor-Liquid Equilibrium Calculation: A Modification of van der Waals Equation," AIChE J., 30, No. 6, 991 (Nov. 1984).

Adachi Y., Lu, B., and Sugie, H., "Three-Parameter Equation of State," Fluid Phase Equilibria, 11, 29 (1983).

Ahmed, T.H., "Comparative Study of Eight Equations of State for Predicting Hydrocarbon Volumetric Phase Behavior," SPE Paper 15673, Presented at the 61st Annual Technical Conference and Exhibition, New Orleans, LA, Oct. 5-8 (1986).

Barner, H.E. and Adler, S.B., "Review and Extension of the Benedict-Webb-Rubin Equation of State," Ind. Eng. Chem. Fundam., 9, 521 (1970).

Beattie, J.A. and Bridgeman, O.C., "Equation of State for Fluids," Proc. Am. Acad. Arts. Sci., 63, 229 (1928).

Benedict, M., Webb, G.W., and Rubin, L.C., "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and their Mixtures-Fugacities and Liquid-Vapor Equilibrium," J. Chem. Phys., 8, 334 (1940).

Benedict, J.H., Webb, G.B., and Rubin, L.C., "An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures-Constants for 12 Hydrocarbons," Chem. Eng. Prog., 47, 419 (1951).

Brunner, G. and Hederer, H., "Calculation of Vapor-Liquid Equilibrium for Low Volatile Substances in Systems with Compressed Gases," 6th AIRAPT Proc., Boulder, Colorado (1977).

Chueh, P.L. and Prausnitz, J.P., "Third Virial Coefficients of Non-Polar Gases and Their Mixtures," AIChE J., 13, 896 (1967).

Coats, K.H. and Smart, G.T., "Application of Regression-Based EOS PVT Program to Laboratory Data," SPE Res. Eng., 277 (May 1986).

de Santis, R., Breedveld, G.J.F., and Prausnitz, J.M., "Thermodynamic Properties of Aqueous Gas Mixtures at Advanced Pressure," Ind. Eng. Chem. Proc. Des. Dev., 13, 374 (1974).

Fuller, G.G., "A Modified Redlich-Kwong-Soave Equation of State Capable of Presenting the Liquid State," Ind. Eng. Chem. Fundam., 15, No. 4, 254 (1976).

Guerreri, G. and Prausnitz, J.M., "Vapor-Liquid Equilibrium for the System Water-Ammonia-Molecular Nitrogen- Molecular Hydrogen-Argon-Methane," Process Technical Int., 18, No. 4, 209 (1973).

Harman, A. and Knapp, H., "Three-Parameter Cubic Equation of State for Normal Substance," Ind. Eng. Chem. Fundam., 19, 291 (1980).

Hederer, H., Peter, S., and Wenzel, H., "Calculation of Thermodynamic Properties from a Modified Redlich-Kwong Equation of State," Chem. Eng. J., II, 183 (1976).

Heyen, G., "A Cubic Equation of State with Extended Range of Application," 2nd World Congress Chem. Eng., Montreal, Oct. 4-9 (1981).

Kossack, C.A. and Hagen, S., "The Simulation of Phase Behavior and Slim-Tube Displacements with Equations of State," SPE Paper 14151, Presented at the 60th Annual Technical Conference and Exhibition, Las Vegas, NV, Sept. 22-25 (1985).

Kossack, C.A., Hagen, S., and Munkerud, P.K., "Phase Behavior Calcultations Near the Critical Point," SPE Paper 15402, Presented at the 61st Annual Technical Conference and Exhibition, New Orlean, LA, Sept. 22-25 (1985).

Kubic, W.L., Jr., "A Modification of the Martin Equation of State for Calculations of Vapor-Liquid Equilibria," Fluid Phase Equilibria, 9, 79 (1982).

Lawal, A.S., Pande, P.K., Perozzi, D.J., and Palen, W.A., "A Novel Fugacity-Correction Technique for Heptanes-Plus Pseudo Component Without Tuning Equation of State Parameters," SPE Paper 15675, Presented at the 61st Annual Technical Conference and Exhibition, New Orleans, LA, Oct. 5-8 (1986).

Lawal, A.S., Van derLaan, E.T., and Thambynayagam, R.K.M., "Four-Parameter Modification of the Lawal-Lake-Silberberg Equation of State for Calculating Gas Condensate Phase Equilibria," SPE Paper 14269, Presented at the 60th Annual Technical Conference and Exhibition, Las Vegas, NV, Sept. 22-25 (1985).

Lawal, A.S., Silberberg, I.H., "A New correlation of Vapor-Liquid Equilibrium Ratio Internally Consistent with Critical Behavior," SPE Paper 10287, Presented at the 56th Annual Fall Technical Conference and Exhibition, San Antonio, TX, Oct. 5-7 (1981).

Lee, B.I., Erbar, J.H., and Edmister, W.C., "Thermodynamic Properties at Low Temperature," Chem. Eng. Prog., 68, 83 (1972).

Lee, B.I., Erbar, J.H., and Edmister, W.C., "Prediction of Thermodynamic Properties for Low Temperature hydrocarbon Process Calculation," AIChE J., 19, 349 (1973).

Lin, H.M., Kim, H., Guo, T.M., and Chao, K.C., "Cubic Chain-of-Rotators Equation of State and VLE Calculations," Fluid Phase Equilibria, (1983).

Nakamura, R., Breedveld, G.J.F., and Prausnitz, J.M., "Thermodynamic Properties of Gas Mixtures Containing Common Polar and Non-Polar Components," Ind. Eng. Chem. Proc. Des. Dev., 15, 557 (1975).

Patel, N.C., "The Calculation of Thermodynamic Properties and Phase Equilibria Using a New Cubic Equation of State," Doctoral Dissertation, Loughborough University (1980).

Patel, N.C. and Teja, A.S., " A New Cubic Equation of State For Fluids and Fluid Mixtures," CES, 37, No. 3, 463 (1982).

Peng, D.Y. and Robinson, D.B., "A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems Using an Equation of State," AIChE, 23, 137 (1977).

Peng, D.Y. and Robinson, D.B., "A New Two-Constant Equation of State," Ind. Eng. Chem. Fundam., 15, No. 1, 59 (1976).

Peng, D.Y. and Robinson, D.B., "Two and Three Phase Equilibrium Calculation for Systems Containing Water," Can. J. Chem. Eng., 54, 595 (1976).

Peng, D.Y. and Robinson, D.B., User's Guide for GPA Peng-Robinson Program, Prepared for Gas Processors Association, Tulsa, (1976a)

Peng, D.Y., Robinson, D.B., and Bishnoi, P.R., " The Use of Soave-Redlich-Kwong Equation of State for Predicting Condensate Fluid Behavior," Ninth World Petroleum Congress, 4, 377 (1975).

Powell, M.J.D., "An Efficient Method for Finding the Minimum of a Function of Several Variables Without Calculating Derivatives," The Computer J., 7, 155 (1964).

Reid, R.C., Prausnitz, J.M., and Sherwood, T.K., The Properties of Gases and Liquids, McGraw-Hill Book Company, Third Edition (1977).

Redlich, O. and Kwong, J.N.S., "On the Thermodynamic of Solutions V. an Equation of State Fugacity of Gaseous Solutions," Chem. Rev., 44, 233 (1949).

Schmidt, G. and Wenzel, H., " A Modified van der Waals Type Equation of State," Chem. Eng. Sci., 35, 1503(1980).

Schmidt, G. and Wenzel, H., "Estimation of Critical Data by Equation of State," Cand. J. Chem. Eng., 59, 527 (1981).

Shah, K.K. and Thodos, G., "A Comparison of Equations of State," IEC, 30 (1965).

Silva, M.K., Dandge, D.K., Lein, C.L., Hutter, C.E., Heller, J.P., and Orr, F.M., Jr., "Measured Phase Compositions and Densities of Mixtures of CO_2 with a Multicomponent Synthetic Oil at 100° F and 1300 PSIA," PRRC Report # 85-23, New Mexico Recovery Research Center, Socorro, NM, (Jan. 1985).

Silva, M.K., Larsen, L.L., Lein, C.L., and Orr, F.M., Jr., "Measured Phase Compositions and Densities for CO_2-C_1-C_4-C_{10} Systems at 160° F and 1250 PSIA and Phase Compositions and Densities by Peng-Robinson EOS for Systems at 160° F and Pressure From 750 to 2250 PSIA," PRRC Report # 83-24, New Mexico Recovery Research Center, Socorro, NM, (Dec. 1983).

Silva, M.K., Lein, C.L., Pelletier, M.T., and Orr, F.M., Jr., "Phase Composition of Mixtures of CO_2 with Maljamar Separator Oil at 90° F and 800 PSIA," PRRC Report # 81-30, New Mexico Recovery Research Center, Socorro, NM, (Jul. 1981).

Soave, G., "Equilibrium Constants from a Modified Redlich-Kwong Equation of State," Chem. Eng. Sci., 27, 1197 (1972).

Tabaei, S.A.R. and Bretz, R.E., "Comparison Between Predicted and Measured Phase Compositions and Densities using Five Cubic EOS for Mixtures of $CO_2-C_1-C_4$, $CO_2-C_1-C_{10}$, and $CO_2-C_1-C_4-C_{10}$ at 160°F and 1250 PSIA," Petroleum Engineering Department Report, New Mexico Tech., Socorro, NM, (Oct. 1988a).

Tabaei, S.A.R. and Bretz, R.E., "Comparison Between Predicted and Measured Phase Compositions of Mixtures $N_2-C_1-CO_2-C_2-C_7$ at 0°F and 1530 PSIA and $N_2-C_1-CO_2-C_2-C_3-C_5-C_7-C_{10}$ at 200°F and 2044 PSIA," Petroleum Engineering Department Report, New Mexico Tech., Socorro, NM, (Oct. 1988b).

Tabaei, S.A.R. and Bretz, R.E., "Comparison Between Predicted and Measured Phase Composition and Densities for Mixtures of CO_2 with Maljamar Separator Oil Using Single (C_7+) and Five Pseudo-Components at 90°F and 800 PSIA," Petroleum Engineering Department Report, New Mexico Tech, Socorro, NM, (Oct. 1988c).

Tarakad, R.R. and Danner, R.P., "An Improved Corresponding State Method for Polar Fluids: Correlation of Second Virial Coefficients," AIChE J., 23, 685 (1977).

Tarakad, R.R., Spencer, C.F., and Adler, S.B., "A Comparison of Eight Equations of State to Predict Gas-Phase Density and Fugacity," Ind. Eng. Chem. Proc. Des. Dev., 18, No. 4, 726 (1979).

Teja, A.S. and Patel, N.C., "The Applications of Generalized Equation of State to the Correlation and Prediction of Phase Equilibria," AICHE J., 13, 39 (1981)

Trebble, M.A. and Bishnoi, P.R., "Accuracy and Consistency Comparisons of Ten Cubic Equations of State for Polar and Non-Polar Compounds," Fluid Phase Equilibria, 29, 465 (1986).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," AIChE J., 20, 263 (1974).

Tsonopoulos, C., "Second Virial Coefficients of Polar Haloalkanes," AIChE J., 21, 263 (1974).

Tsonopoulos, C. and Heidman, J.L., "From Redlich-Kwong to the Present," Fluid Phase Equilibria, 24, 1 (1985).

van der Waal, J.D., Doctoral Dissertation, Leiden, Holland (1873).

Van Ness, H.C. and Abbott, M.M., Classical Thermodynamic of Non Electrolyte Solutions With Applications to Phase Equilibrium, McGraw-Hill Book Comp. (1982).

Varotsis, N., Stewart, G., Todd, A.C., and Clancy, M., "Phase Behavior of Systems Comprising North Sea Reservoir Fluids and Injection Gases," JPT, 1221 (Nov. 1986).

Whitson, C.H., "Characterizing Hydrocarbon Plus Fractions," SPEJ AIME, 683 (Aug. 1983).

Yarborough, L.Y., "Vapor-Liquid Equilibrium Data for Multicomponent Mixtures Containing hydrocarbon and Non-Hydrocarbon Compounds," J. Chem. Eng. Data, 17, No. 2, 129 (1972).

Zudkevitch, D. and Joffe, J., "Correlation and Predictions of Vapor-Liquid Equilibria with the Redlich-Kwong Equation of State," AIChE J., 16, 112 (Jan. 1970).

APPENDIX A

Algorithm and Computer Code Regress on EOS Parameters Using Powell's Method

Figure A.1 is a flow chart of the regression algorithm. The principle steps performed by the algorithm include:

1. Enter the data; either from key board or from a data file.
2. Perform flash calculation using any of the Equations of State (EOS) and create an objective function subroutine for regressing on any parameters (binary interaction (δ_{ij}), attraction (a_i), Repulsion (b_i, c_i), etc.).
3. using Powell's method, minimize the objective function.

Powell's Method:

The procedure is based on the method of M.J.D Powell (1964). Derivatives are not required. The starting point is the calculated x_i's, y_i's in form of X_i's from the used EOS. The algorithm as follows:

1. A starting point, $\vec{X}_o^{\,o}$ is calculated. The initial search direction s, $\vec{M}_i^{(o)}$, i=1,2,...,N, are parallel to the original coordinate axes.
2. A sequence of single variable searches are made in the N initial directions, using quadratic approximation.
3. The following Points are then located:

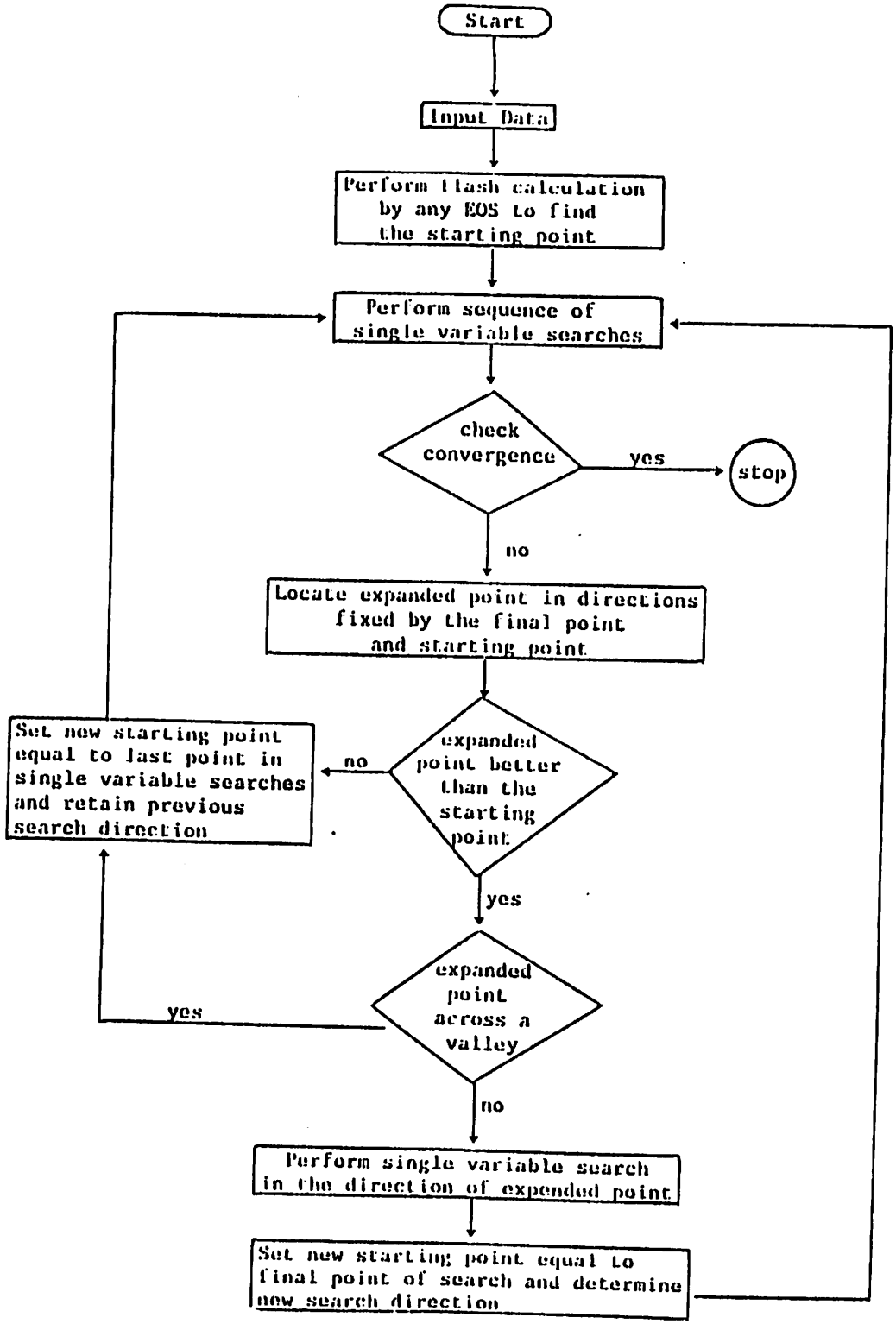

Fig. A.1. Flow chart of EOS combined with the Powell's method

$\vec{X}_n^{(k)}$ = the least point from the sequence of single variable searches

$\vec{X}_y^{(k)}$ = the point of greatest function between successive single variable searches

$\vec{X}_t^{(k)} = 2\vec{X}_N^{(k)} - \vec{X}_o^{(k)}$ = expanded point

$\vec{X}_o^{(k)}$ = starting point for iteration

where k is the stage index which is incremented for each new set of search directions.

4. A check is made to see if the value of the objective function at the expanded point, $\vec{X}_t^{(k)}$, is better than at the starting point, $\vec{X}_o^{(k)}$. If there is no improvement, the last point, $\vec{X}_N^{(k)}$, becomes the new starting point and a new sequence of single variable searches are made in the same directions as before,

$$\vec{X}_o^{(k+1)} = \vec{X}_N^{(k)} \qquad \text{(A-1)}$$

$$\vec{M}_i^{(k+1)} = \vec{M}_i^{(k)}, \quad i=1,2,\ldots,N \qquad \text{(A-2)}$$

If The objective function, $F_t^{(k)}$, at the expanded point is an improvement over the starting point function, $F_o^{(k)}$, then the following test is performed,

$$(F_o^{(k)} - 2F_N^{(k)} + F_t^{(k)})\,(F_o^{(k)} - 2F_N^{(k)} - \Delta)^2 \geq \frac{\Delta\,(F_o^{(k)} - 2F_t^{(k)})^2}{2} \qquad \text{(A-3)}$$

where $\Delta = |F_M^{(k)} - 2F_{M-1}^{(k)}|$

The test determines whether the function in this region is a valley, i.e., $F_t^{(k)}$ is an improvement but the surface is rising. It the test is satisfied the oil search directions are retained and a new sequence of single variable searches started as above. If the test is not satisfied, a single variable search is performed in the $\vec{U}^{(k)}$ direction,

$$\vec{U}^{(k)} = \vec{X}_N^{(k)} - \vec{X}_o^{(k)} \qquad \text{(A-4)}$$

until the best value, $\vec{X}_o^{(k+1)}$ is found. New search are chosen as follows:

$$\vec{M}_i^{(k+1)} = \vec{M}_i^{(k)}, \quad i=1,2,\ldots,M-1 \qquad \text{(A-5)}$$

$$\vec{M}_i^{(k+1)} = \vec{M}_{i+1}^{(k)}, \quad i=M,\ldots,N \qquad \text{(A-6)}$$

$$\vec{M}_i^{(k+1)} = \vec{U}^{(k)} \qquad \text{(A-7)}$$

A new sequence of single variable search is then started.

5. Convergence is assumed when the values for the independent variables between successive iterations are less than present limit, i.e.,

$$|X_i^{(k)} - X_i^{(k+1)}| < \epsilon, \quad i=1,2,\ldots,N \qquad \text{(A-8)}$$

APPENDIX B

Program Listing and Sample Output for Critical Properties Calculation

```
**********************************************************************
C                                                                     C
C     THIS IS THE PROGRAM TO CALCULATE THE CRITICAL PROPERTIES        C
C                                                                     C
C     LIST OF VARIABLES                                               C
C     -----------------                                               C
C     C1 THROUGH C5 : ARE THE GIVEN CONSTANTS                         C
C     TC    : CITICAL TEMPERATURE                                     C
C     PC    : CRITICAL PRESSURE                                       C
C     VC    : CRITICAL VOLUME                                         C
C     W     : ACENTRIC FACTOR                                         C
C     S     : SPECIFIC GRAVITY                                        C
C     TB    : BOILING TEMPERATURE                                     C
C     DM    : MOLECULAR WEIGHT                                        C
C     N     : GIVEN SETS OF NUMER OF VALUES FOR C1-C5                 C
C     NC    : NUMBER OF COMPONENTS                                    C
C     NI    : NUMBEER TO PRINT TO OUTPUT FILE                         C
C                                                                     C
**********************************************************************
C
      DIMENSION C1(50),C2(50),C3(50),C4(50),C5(50),TC(50)
      DIMENSION PC(50),VC(50),WTC(50),W(50),S(50),TB(50)
      DIMENSION DM(50),TETA(20,50)

      WRITE(*,*)'ENTER THE VALUE OF THE N='
      READ(*,*)N
      WRITE(*,*)'ENTER THE VALUE OF THE NC='
      READ(*,*)NC
      WRITE(*,*)'ENTER THE VALUE OF THE NI='
      READ(*,*)NI


      DO 5 I=1,N

      WRITE(*,*)'ENTER THE VALUE OF THE C1(',I,')='
      READ(*,*)C1(I)
      WRITE(*,*)'ENTER THE VALUE OF THE C2(',I,')='
      READ(*,*)C2(I)
      WRITE(*,*)'ENTER THE VALUE OF THE C3(',I,')='
      READ(*,*)C3(I)
      WRITE(*,*)'ENTER THE VALUE OF THE C4(',I,')='
      READ(*,*)C4(I)
      WRITE(*,*)'ENTER THE VALUE OF THE C5(',I,')='
      READ(*,*)C5(I)

5     CONTINUE


      WRITE(NI,*)'**********************************************
     1**********************'
      WRITE(NI,*)' '
      WRITE(NI,*)'J=; DM=; TC=(IN DEG K); PC=(IN MPA); VC=(IN CC/MOL)
```

```
     1W=; S=; TB=(IN DEG K);'
     WRITE(NI,*)' '
     WRITE(NI,*)'*************************************************
     1*********************'
     WRITE(NI,*)' '


     DO 10 J=1,NC
     DO 20 I=1,N

     CC=12.01
     HH=1.008

     DM(J)=j*CC+(2.*j+2)*HH

     TETA(I,J)=C1(I)+C2(I)*DM(J)+C3(I)*DM(J)**2+C4(I)*DM(J)**3
     1             +C5(I)/DM(J)

     TC(J)=TETA(1,J)
     PC(J)=EXP(TETA(2,J))
     VC(J)=TETA(3,J)
     WTC(J)=TETA(4,J)
     W(J)=WTC(J)/TC(J)
     S(J)=TETA(5,J)
     TB(J)=TETA(6,J)


20   CONTINUE

     WRITE(NI,3)J,DM(J),TC(J),PC(J),VC(J),W(J),S(J),TB(J)
3    format(i2,1x,7(f8.3,2x),/)


10   CONTINUE

     STOP
     END
```

```
**********************************************************************
*
J=; DM=; TC=(IN DEG K); PC=(IN MPA); VC=(IN CC/MOL);  W=; S=; TB=(IN DEG K);
**********************************************************************
```

1	16.042	190.618	6.284	99.119	0.011	0.160	111.713
2	30.068	304.568	4.996	147.347	0.090	0.423	183.756
3	44.094	372.274	4.274	201.219	0.146	0.528	232.427
4	58.120	424.493	3.753	256.744	0.198	0.589	272.953
5	72.146	468.252	3.344	313.045	0.248	0.630	308.818
6	86.172	506.166	3.011	369.831	0.297	0.660	341.321
7	100.198	539.522	2.734	426.981	0.345	0.683	371.104
8	114.224	569.097	2.499	484.444	0.393	0.702	398.558
9	128.250	595.434	2.298	542.196	0.440	0.718	423.958
10	142.276	618.961	2.124	600.233	0.487	0.731	447.519
11	156.302	640.039	1.970	658.556	0.533	0.741	469.426
12	170.328	658.993	1.834	717.173	0.578	0.750	489.846
13	184.354	676.122	1.712	776.093	0.622	0.758	508.933
14	198.380	691.711	1.601	835.330	0.665	0.764	526.832
15	212.406	706.035	1.499	894.896	0.706	0.770	543.685
16	226.432	719.361	1.405	954.806	0.744	0.774	559.631
17	240.458	731.953	1.316	1015.076	0.780	0.778	574.804
18	254.484	744.069	1.233	1075.721	0.813	0.782	589.339
19	268.510	755.964	1.153	1136.757	0.841	0.785	603.367
20	282.536	767.895	1.076	1198.201	0.866	0.788	617.021
21	296.562	780.113	1.002	1260.069	0.886	0.791	630.430
22	310.588	792.870	0.930	1322.378	0.900	0.794	643.724
23	324.614	806.416	0.860	1385.145	0.909	0.797	657.034

24	338.640	821.002	0.792	1448.386	0.911	0.801	670.489
25	352.666	836.876	0.726	1512.119	0.907	0.804	684.216
26	366.692	854.288	0.661	1576.360	0.896	0.809	698.345
27	380.718	873.486	0.598	1641.127	0.878	0.814	713.005
28	394.744	894.717	0.538	1706.437	0.852	0.820	728.323
29	408.770	918.231	0.480	1772.307	0.820	0.826	744.428
30	422.796	944.274	0.425	1838.754	0.781	0.834	761.448
31	436.822	973.093	0.373	1905.795	0.736	0.842	779.511
32	450.848	1004.937	0.324	1973.449	0.684	0.852	798.744
33	464.874	1040.052	0.279	2041.731	0.627	0.863	819.276
34	478.900	1078.685	0.237	2110.659	0.565	0.875	841.234
35	492.926	1121.083	0.200	2180.251	0.499	0.889	864.745
36	506.952	1167.494	0.166	2250.524	0.429	0.905	889.939
37	520.978	1218.163	0.137	2321.496	0.356	0.922	916.942
38	535.004	1273.338	0.111	2393.183	0.282	0.941	945.881
39	549.030	1333.264	0.089	2465.602	0.206	0.962	976.885
40	563.056	1398.189	0.070	2538.772	0.129	0.985	1010.081

*

J = hydrocarbon number
DM = molecular weight
Pc = critical pressure
Tc = critical temperature
Vc = critical volume
w = acentric factor
s = specific gravity
TB = boiling temperature

APPENDIX C

Program Listing of Regression algorithm

```
      PROGRAM PALLPOW
C
C*************************************************************************
C                                                                        C
C       THIS IS THE PROGRAM FOR POWELL METHOD WITH DIFFERENT EOS         C
C                                                                        C
C       IT HAS THREE PART:                                               C
C                                                                        C
C                                                                        C
C                       A. MAIN PROGRAM                                  C
C                       B. FUNCTION SUBROUTINE                           C
C                       C. POWELL SUBROUTINE                             C
C                                                                        C
C                ************************************                    C
C                        MAIN PROGRAM                                    C
C                                                                        C
C     THIS IS THE MAIN PROGRAM CONSIST OF THE CALLING SUBROUTINES        C
C     AND INPUTING THE DATA AND OUTPUTING THE RESULTS.                   C
C                                                                        C
C*************************************************************************
C                                                                        C
C    THE VARIABLES THAT HAVE BEEN USED IN THIS PROGRAM ARE AS            C
C    FOLLOWS:                                                            C
C    --------                                                            C
C    COMMON ; ARE ONLY RELATED WHEN IT NEEDED TO BE USED                 C
C    DIMENSION; WHEN IT NEEDED                                           C
C                                                                        C
C    PC    :  CRITICAL PRESSURE                                          C
C    TC    :  CRITICAL TEMPERATURE                                       C
C    W     :  ACENTRIC FACTOR                                            C
C    AK    :  EQUILIBRIUM CONSTANT                                       C
C    Z     :  COMPRESSIBILITY FACTOR                                     C
C    X     :  LIQUID MOLE FRACTION OF COMPONENT i                        C
C    Y     :  VAPOR MOLE FRACTION OF COMPONENT i                         C
C    AL    :  TOTAL LIQUID MOLE FRACTION                                 C
C    R     :  GAS CONSTANT                                               C
C    FL    :  FUGACITY OF LIQUID                                         C
C    FV    :  FUGACITY OF VAPOR                                          C
C    NC    :  NUMBER OF COMPONENT                                        C
C    TOL   :  TOLERANCE                                                  C
C    CNAME:  NAME OF COMPONENT                                           C
C    T     :  TEMPERATURE OF SYSTEM                                      C
C    P     :  PRESSURE OF SYSTEM                                         C
C    ITER  :  ITERATION NUMBER                                           C
C    VL    :  VOLUME OF LIQUID                                           C
C    VV    :  VOLUNE OF VAPOR                                            C
C    B     :  PRAMETER B                                                 C
C    Ac    :  PRAMETER A                                                 C
C    PR    :  REDUCED PRESSURE                                           C
C    TR    :  REDUCED TEMPERATURE                                        C
C    AMW   :  APPARENT MOLECULAR WEIGHT                                  C
C    DLJ   :  BINARY INTERACTION PARAMETERS                              C
C    XE    :  EXPERIMENTAL VALUES OF LIQUID MOLE FRACTIOM                C
```

```
C     YE    :  EXPERIMENTAL VALUES OF VAPOR MOLE FRACTION                  C
C     IEOS  :  CONTROL OF THE EQUATIONS                                    C
C     NO    :  CONTROL FOR DIFFERENT OUTPUT FILES                          C
C     NTL   :  NUMBER OF TIELINES                                          C
C     ALFA  :  PARAMETER FOR LLS EOS                                       C
C     BETA  :  PARAMETER FOR LLS EOS                                       C
C     ZC    :  CRITICAL COMPRESSILBILITY                                   C
C     NN    :  TOTAL NUMBER OF PARAMETERS T BE REGRESSED                   C
C     C     :  PARAMETERS FOR PT EOS                                       C
C     IREG  :  DUMMAY VARIABLE TO CONTROL THE REGRESSION ON ANY OR         C
C              ALL PARAMETERS                                              C
C                                                                          C
*****************************************************************************
C
```

```
C
**********************************************************************
C                                                                     C
C    THIS IS THE MAIN PROGRM CONSIST OF SOM INPUT AND CALL            C
C    SUBROUTINES                                                      C
C                                                                     C
**********************************************************************
C

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /O/ ALFA(100),BETA(100),OM(100),ZC(100)
      COMMON /G/ XXX(100)
      COMMON /N/ NN
      COMMON /P/ C(100)
      COMMON /RR/ IREG
      COMMON NI,N
      COMMON /LJ/ idd,jdd,kdd

     DOUBLE PRECISION DW(1600)
     DIMENSION NUMBER(100),E(100)

     EXTERNAL STOPFPE
     DUMMY=STOPFPE(IL)

      DATA ITMAX /50/

111     CALL INIT1
       CALL OMEGA

       WRITE(6,*)'ENTER THE VALUE OF NO='
       READ(5,*)NO

       WRITE(6,*)'ENTER THE VALUE OF THE N. IPRINT. MAXIT. ESCALE.='
        READ(5,*)N,IPRINT,MAXIT,ESCALE

     WRITE(6,*)'DO YOU WANT ALL THE E(I)S TO BE THE SAME'
     WRITE(6,*)'IF YES ENTER 1 OR NO=2'

     DO 13 I=1,N
     E(I)=.5*XXX(I)
     if(e(i) .lt. .01) e(i)=.02
     if(e(i) .gt. .02 .and. e(i) .lt. .05)e(i)=.05
     if(e(i) .gt. .05 .and. e(i) .lt. 10)e(i)=.10*xxx(i)
     if(e(i) .gt. 1000)e(i)=.01*XXX(I)
     write(6,*)' e(',i,')= ',e(i)
13   continue
```

```
      GO TO 14

 12       WRITE(6,*)'ENTER THE VALUES OF E(I)'
         READ(5,*)(E(I),I=1,N)

 14   WRITE(6,*)'THE N= ', N

      idd=0
      jdd=0
      kdd=0

      call count(idd,jdd,kdd,no)
      WRITE(NO,*)' '
      call count(idd,jdd,kdd,no)
      WRITE(NO,*)'*****************************************************'
      WRITE(NO,*)' '
      call count(idd,jdd,kdd,no)
      WRITE(NO,*)'  THIS IS THE REGRESSED S-W PROGRAM ON  '
      WRITE(NO,*)'     ALL PARAMETERS A & B & DIJ      '
      call count(idd,jdd,kdd,no)
      WRITE(NO,*)' '
      WRITE(NO,*)'*****************************************************'
      call count(idd,jdd,kdd,no)

      WRITE(NO,*)'THE P = (IN ATM)',P ,'THE  T =(IN DEG K)' ,T
      call count(idd,jdd,kdd,no)
      WRITE(NO,*)'THE NTL= ', NTL , ' THE NC =',  NC
      call count(idd,jdd,kdd,no)
      DO 1 J=1,NTL
      DO 1 I=1,NC

      WRITE(NO,*)'THE XE(',I,J,') = ',XE(I,J)
      call count(idd,jdd,kdd,no)
      WRITE(NO,*)'THE YE(',I,J,') = ',YE(I,J)
      call count(idd,jdd,kdd,no)

 1    CONTINUE

      WRITE(NO,*)'THE E(I)= ',(E(I),I=1,N)
      call count(idd,jdd,kdd,no)

      write(no,*)' '
      write(no,*)'*****************************************************'
      write(no,*)' '
      write(no,*)'THESE ARE THE EXPRIMENTAL X & Y VALUES '
      write(no,*)' '
      write(no,*)'*****************************************************'
      write(no,*)' '

      do 120 j=1,ntl
      DO 120 I=1,NC
      write(no,*) xe(i,j),'  ', ye(i,j)
```

```
120  CONTINUE

        NW=N*(N+3)
C
C     calling the subroutine BOIM to find the minimum
C

        CALL BOIM(XXX,E,N,EF,ESCALE,IPRINT,MAXIT,DW,NI,NO,NW)


        WRITE(NO,3)EF
3       FORMAT(//,'  OPTIMUM VALUE OF F=',E16.8)
      call count(idd,jdd,kdd,no)
      WRITE(6,*)'DO YOU WANT A NEW SET OF CALCULATION WITH'
      WRITE(6,*)'DIFFERENT ESCAL AND EPSILON ENTER(DDD=1:YES OR 2:NO)'
      READ(5,*)DDD
      IF(DDD .EQ. 1)GO TO  111

      STOP
         END
```

```
C
**********************************************************************
C                                                                     C
C       THIS IS THE FUNCTION SUBROUTINE, TO CALCULATE THE FUNCTION    C
C       THAT WIL BE  CREATED BY DIFFERENT EOS.                        C
C                                                                     C
**********************************************************************
C

        SUBROUTINE CALCFX(N,XXX,F)

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DLJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
       COMMON /N/ NN
       COMMON /LJ/ idd,jdd,kdd

       DIMENSION NUMBER(100),XXX(100)
       DATA ITMAX /50/


        DO 10 J=1,NTL
        DO 20 I=1,NC

        Z(I)=ZZJ(I,J)
        AK(I)=AKJ(I,J)

20      CONTINUE

      ITER=1
   50 CALL FLASH

C
C    controlling to use of right equations for calculation
C    of Fugacity
C
C    1  VAN DER WAAL'S
C    2  RK EOS
C    3  SRK EOS
C    4  PR EOS
C    5  PT EOS
C    6  SW EOS
C    7  LLS EOS
C

        GO TO(1,2,3,4,5,6,7),IEOS

1       CALL FUGAC1(X,FL,1,XXX)
```

```
      CALL FUGAC1(Y,FV,2,XXX)
      go to 1001

2      CALL FUGAC2(X,FL,1,XXX)
      CALL FUGAC2(Y,FV,2,XXX)
      go to 1001

3      CALL FUGAC3(X,FL,1,XXX)
      CALL FUGAC3(Y,FV,2,XXX)
      go to 1001

4      CALL FUGAC4(X,FL,1,XXX)
      CALL FUGAC4(Y,FV,2,XXX)
      go to 1001

5      CALL FUGAC5(X,FL,1,XXX)
      CALL FUGAC5(Y,FV,2,XXX)
      go to 1001

6      CALL FUGAC6(X,FL,1,XXX)
      CALL FUGAC6(Y,FV,2,XXX)
      go to 1001

7      CALL FUGAC7(X,FL,1,XXX)
      CALL FUGAC7(Y,FV,2,XXX)
      go to 1001

C
C    CHECKING FOR THE CONVEGENCE OF THE EOS
C
1001      DO 100 I=1,NC
         RAT=(FV(I)/FL(I))
         IF (ABS(RAT-1.) .GT. TOL) GO TO 200
  100     CONTINUE
C
C    CALLING THE PRINT TO PRINT THE OUT PUT
C
     CALL PRNT
C
C    CHEKING FOR THE CONVERGENCE OF THE REGRESSION BY USINF THE
C    OBJECTIVE FUNCTION
C    IN THIS CASE THE OBJECTIVE FUNCTION IS ABSOL;UTE RELATIVE
C    ERROR
C

        F=0.
      DO 201 I=1,NC

      F=F+(ABS(XE(I,J)-X(I))/X(I))+(ABS(YE(I,J)-Y(I))/Y(I))

201     CONTINUE
```

```
      GO TO 10
  200 DO 300 I=1,NC
     AK(I)=AK(I)*(FL(I)/FV(I))
  300 CONTINUE
      ITER=ITER+1
     do 1101 i=1,nc
     if(abs(x(i)-xe(i,j)) .gt. .10)x(i)=xe(i,j)
1101 continue

      IF (ITER .LT. ITMAX) GO TO 50

10       CONTINUE

     RETURN
        END
```

```
C
C*********************************************************************
C                                                                     C
C    THIS SUB-PROGRAM IS TO READ INPUT DATA AND TO SET THEM UP        C
C    FOR THE CALCULATIONS, ALSO SET FOR THE PARAMETERS OF             C
C    REGRESSION WHERE IT NEEDED.                                      C
C                                                                     C
C*********************************************************************
C
        SUBROUTINE INIT1

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /G/ XXX(100)
      COMMON /N/ NN
      COMMON /IJ/ idd,jdd,kdd
      COMMON /RR/ IREG

      DIMENSION NUMBER(100),E(100)
      DIMENSION ZZ(100),Z0(100),XB(100),BK(100)
      DIMENSION CA(100),CB(100),CC(100),CD(100),CE(100),CF(100),CG(100)
      DIMENSION VC(100),AMOLW(100),PARA(100)
      DIMENSION FEED(100),NUMB(100),REFER(19),COMP(100,2)
      DIMENSION ZG(100),IFD(100,100),DI4(100),A(100)
      DIMENSION SAL(100),SAV(100),GPUR(100)


        TOL=1.E-4
        R=82.0597
C
C    READING THE VALUES TRUE THE SCREEN FOR EQUATION #
C    NUMBER OF COMPONENETS
C
        WRITE(6,*)' ENTER THE IEOS AND NC = '
        READ(5,*) IEOS , NC
        NCM=NC-1
        NCP=NC+1
C
C    INPUTING THE VALUES FOR ID # OF THE COMPONENETS,
C    PRESSURE (IN PSIA) AND TEMPERATURE (IN OF)
C
        WRITE(6,*)'ENTER THE ID # FOR EACH COMPONENT='
        READ(5,*)(NUMB(I),I=1,NC)

        WRITE(6,*)' ENTER THE VALUE OF P1(PSIA) AND T1(OF)='
        READ(5,*) P1 ,T1
C
```

```
C     CONVERTING THE VALUES OF P AND T
C
         P=P1/14.696
         T=(T1+459.67)/1.8
C
C     INPUTING THE NUMBER OF TILINES TO BE USED AND WHAT
C     METHOD (EITHER TWO-PHASE OR JUST SINGLE PHASE
C     READING FOR THE INPUTING THE COMP[OSITIONS
C
         WRITE(6,*)' ENTER THE NUMBER OF TIELINE(NTL)='
         READ(5,*) NTL
      WRITE(6,*)'DO YOU WANT TO ENTER THE VAPOR AND LIQUID
      1  SEPARATE OR AS ZZ: 0 OR 1'
      READ(5,*)DZ
      IF (DZ .EQ. 0)GO TO 7
      IF (DZ .EQ. 1)GO TO 8
7          DO 10 J=1,NTL
         TOTAL(J)=0.
         DO 20 I=1,NC
C
C     INPUTING THE VALUES OF EXPERIMENTAL COMPOSITIONS
C
         WRITE(6,*)' ENTER THE XE(',I,J,') AND YE(',I,J,')= '
         READ(5,*)XE(I,J),YE(I,J)
         ZZJ(I,J)=(XE(I,J)+YE(I,J))/2.
         TOTAL(J)=TOTAL(J)+ZZJ(I,J)
         AKJ(I,J)=YE(I,J)/XE(I,J)

20       CONTINUE
10       CONTINUE

C
C     NORMALIZING THE INPUTED VALUES
C
      do 1101 j=1,ntl
      dzz=0.
      do 1102 i=1,nc
      zzj(i,j)=zzj(i,j)/total(j)
      dzz=dzz+zzj(i,j)
1102  continue
1101  continue

      GO TO 9
8     TOTAL(J)=0.
      DO 3 J=1,NTL
      DO 3 I=1,NC
      WRITE(6,*)'ENTER THE VALUE OF ZZJ(',I,J,') = ?'
      READ(5,*)ZZJ(I,J)
      TOTAL(J)=TOTAL(J)+ZZJ(I,J)
      XE(I,J)=ZZJ(I,J)/2
      YE(I,J)=XE(I,J)
3     CONTINUE
```

```
C
C     DETERMINING WHAT PARAMETERS TO BE REGRESSED ON; A, B, Dij OR ALL
C
      WRITE(6,*)'ENTER FOR WHAT PARAMETERS TO BE REGRESSED AS FOLLOWS:'
      WRITE(6,*)' IF YOU WANT TO REGRESS ON Dij; A; B; OR ALL'
      WRITE(6,*)' ENTER ;  1; 2; 3; 4'
      READ(5,*)IREG
C
C        THIS PART IS TO READ THE INPUT DATA FROM FILES THAT HAS
C        ALREADY BEEN , THIS PROPERTIES ARE DEFINED AND BEING READED
C     FROM THE FILE:
C
C     SOME CHOSEN VARIABLES ARE:
C     _____________________________
C     CO1,CO2    :  ARE TO PICK UP THE NAMES OF COMPONENTS
C     D'S        :  ARE JUST DUMMAY VAIABLES TO BE DEFINED IN ARRAY LATER
C

9     NFOUND=0
         OPEN(UNIT=20, FILE='CRIT.DAT')
200      IF(NFOUND .GE. NC)GO TO 500
         READ(20,*,END=900)NA
         READ(20,1001)CO1,CO2
1001     FORMAT(1X,2A4)
         READ(20,*)D1,D2,D3,D4,D5,D6
         READ(20,*)D7,D8,D9,D10,D11,D12,D13

         DO 300 I=1,NC
         IF(NUMB(I) .NE. NA)GO TO 300
         NFOUND=NFOUND+1
         COMP(I,1)=CO1
         COMP(I,2)=CO2
         CNAME(I,1)=COMP(I,1)
         CNAME(I,2)=COMP(I,2)
         PC(I)=D1
         TC(I)=D2
         VC(I)=D3
         W(I)=D4
         AMOLW(I)=D5
         AMW(I)=AMOLW(I)
         PARA(I)=D6
         CA(I)=D6
         CB(I)=D8
         CC(I)=D9
         CD(I)=D10
         CE(I)=D11
         CF(I)=D12
         CG(I)=D13
300      CONTINUE

         GO TO 200
```

```
500     CLOSE(UNIT=20)
      if(DZ .eq. 0.)go to 1120
C
C     CALCULATING THE K'S BY THE WILSON'S METHOD IF NECESSARY
C
      DO 6 J=1,NTL
      DO 6 I=1,NC
      AKJ(I,J)=EXP(5.3727*(1.+W(I))*(1.-TC(I)/T))*PC(I)/P
6     continue
C
C     INITIALIZING THE Dij
C

1120        DO 501 I1=1,NC-1
          DIJ(I1,I1)=0.
          DO 501 I2=I1+1,NC
          DIJ(I1,I2)=0.
          DIJ(I2,I1)=0.
501       CONTINUE

          DIJ(NC,NC)=0.

C
C     REDING THE BINARY INTERACTION PARAMETERS FROM DATA FILE
C     FOR EACH OF THE GIVEN EQUATIONS
C
          GO TO(510,520,530,540,550,560,570),IEOS

510       OPEN(UNIT=20, FILE='DVDW.DAT')
          GO TO 600
520       OPEN(UNIT=20, FILE='DRK.DAT')
          GO TO 600
530       OPEN(UNIT=20, FILE='DSRK.DAT')
          GO TO 600
540       OPEN(UNIT=20, FILE='DPR.DAT')
          GO TO 600
550       OPEN(UNIT=20, FILE='DPR.DAT')
          GO TO 600
560       OPEN(UNIT=20, FILE='DPR.DAT')
          GO TO 600
570       OPEN(UNIT=20, FILE='DLLS.DAT')
600       CONTINUE

          NFOUND=0
          DO 660 I=1,NC
          IF(NUMB(I) .EQ. 1)NFOUND=1
660       CONTINUE

700       IF(NFOUND .GE. NC)GO TO 950
          READ(20,*,END=970)NA
          NAM1=NA-1
```

```
      READ(20,*)(DI4(NBK),NBK=1,NAM1)
C
C     SETING THE Dij INTO ARRAY
C
      NN=0
      DO 800 I=1,NC
      IF(NUMB(I) .NE. NA) GO TO 800

      DO 850 I1=1,NC
      IF(I1 .EQ. I)GO TO 850
      IF(NUMB(I1) .GT. NAM1)GO TO 850
      NBK=NUMB(I1)
      DIJ(I,I1)=DI4(NBK)
      DIJ(I1,I)=DI4(NBK)

850   CONTINUE
      NFOUND=NFOUND+1
800   CONTINUE
      NN=0
      DO 101 I=2,NC
      IM1=I-1
      DO 101 J=1,IM1
      DIJ(I,I)=0.
      DIJ(J,J)=DIJ(I,I)
      DIJ(J,I)=DIJ(I,J)
C
C     MAKING THE Dij TO BE PARAMETERS IF NECESSARY
C
      IF(IREG .EQ. 1 .OR. IREG .EQ. 4) THEN
       NN=NN+1
       XXX(NN)=DIJ(I,J)
       ENDIF

101   CONTINUE

      GO TO 700
900   WRITE(6,*)'ERROR WAS FOUND BASIC DATA IN FILE CRIT.DAT.
     /           PROGRAM ABORTED'
950   CLOSE(UNIT=20)

      GO TO 990
970   WRITE(6,*)'NO BINARY INTERACTION PARAMETER WAS FOUND FOR
     /           THIS EOS SO TH DIJ=0. FOR ALL (I,J)'
990   CONTINUE

      return
      END
```

```
C
**********************************************************************
C                                                                     C
C        THIS SUBROUTINE IS TO CALCULATE THE OMEGAS FOR EVERY EOS     C
C        AND TO CONTROL ON WHAT PARAMETERS SHOULD BE REGRESSED        C
C        THE Ac, B, WILL ALSO BE CALCULATED                           C
C                                                                     C
**********************************************************************
C
        SUBROUTINE OMEGA

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /O/ ALFA(100),BETA(100),OM(100),ZC(100)
      COMMON /P/ C(100)
      COMMON /G/ XXX(100)
      COMMON /N/ NN
      COMMON /IJ/ idd,jdd,kdd
      COMMON /RR/ IREG

       DIMENSION AMO(100),A(100),RTPC(100),RTPC2(100),SI(100)
       DIMENSION BETAC(100)
       REAL OMA1(100),OMB1(100)

C
C    CALCULATIONS OF GENERAL PARAMETERS
C
        DO 11 I=1,NC

        TR(I)=T/TC(I)
        RTPC(I)=R*TC(I)/PC(I)
        RTPC2(I)=R*TC(I)*RTPC(I)

11      CONTINUE
C
C    CALCULATION OF DIFFERNET PARAMETERS FOR ALL THE EQUATIONS
C    IN THE FOLLOWING FORMS:
C    1    :  VDW EOS
C    2    :  RK  EOS
C    3    :  SRK EOS
C    4    :  PR EOS
C    5    :  PT EOS
C    6    :  SW EOS
C    7    :  LLS EOS
C
C    ALSO THE PARAMETERS BEING CONVERTED IF THEY NEEDED TO BE REGRESSED
C

        GO TO(1,2,3,4,5,6,7),IEOS
```

```
1       OMA=27./64.
        OMB=1./8.
        OMC=3./8.

        DO 20 I=1,NC
        A(I)=OMA*(RTPC2(I))
        B(I)=OMB*RTPC(I)
20      CONTINUE

        GO TO 101

2       ALPH=(4.)**(1./3.)+(2.)**(1./3.)+1.
        OMA=ALPH/9.
        OMB=1./(ALPH*3.)
        OMC=1./3.

        DO 21 I=1,NC
        A(I)=OMA*RTPC2(I)*(TC(I)**(1./2.))
        B(I)=OMB*RTPC(I)
21      CONTINUE

        GO TO 101

3       OMAC=0.42747

        DO 12 I=1,NC

        AM(I)=.480+1.574*W(I)-0.176*(W(I)**2)
        OMA=OMAC*(1.+AM(I)*(1.-(TR(I)**(1./2.))**2))
        OMB=0.08664
        A(I)=OMA*(RTPC2(I))
        B(I)=OMB*RTPC(I)
        AC(I)=OMAC*(RTPC2(I))

     IF(IREG .EQ. 2) XXX(I)=AC(I)
     IF(IREG .EQ. 3) XXX(I)=B(I)
     IF(IREG .EQ. 4) THEN

        XXX(NN+I)=AC(I)
        XXX(NN+I+NC)=B(I)
     ENDIF

12      CONTINUE

        GO TO 101

4       OMAC=0.45724
        OMB=0.0778
        OMC=0.370
        DO 13 I=1,NC
```

```
      AM(I)=0.37464+1.54226*W(I)-0.26992*(W(I)**2)
      OMA=OMAC*(1.+AM(I)*(1.-(TR(I)**(1./2.))**2))
      A(I)=OMA*(RTPC2(I))
      B(I)=OMB*RTPC(I)
      AC(I)=OMAC*(RTPC2(I))

    IF(IREG .EQ. 2) XXX(I)=AC(I)
    IF(IREG .EQ. 3) XXX(I)=B(I)
    IF(IREG .EQ. 4) THEN

      XXX(NN+I)=AC(I)
      XXX(NN+I+NC)=B(I)
    ENDIF

13     CONTINUE

       GO TO 101

5      DO 60 I=1,NC
    DOMEGB=0.
    DOMEGA=0.
    DOMEGC=0.
     SI(I)=0.329032-0.076799*W(I)+0.0211947*W(I)**2
     DC0=-SI(I)**3
     DC1=3*SI(I)**2
     DC2=(2.-3.*SI(I))
     CALL CUBE1(DC2,DC1,DC0,DOMEGB)
     DOMEGA=3.*SI(I)**2+3.*(1.-2.*SI(I))*DOMEGB+
    *          DOMEGB**2+1.-3.*SI(I)
     DOMEGC=1.-3.*SI(I)
     RTC=R*TC(I)
     RTP=RTC/PC(I)
     AC(I)=DOMEGA*RTP*RTC
     B(I)=DOMEGB*RTP
     C(I)=DOMEGC*RTP

    IF(IREG .EQ. 2) XXX(I)=AC(I)
    IF(IREG .EQ. 3) XXX(I)=B(I)
    IF(IREG .EQ. 4) THEN
    XXX(NN+I)=AC(I)
    NNN=NN+NC
    XXX(NNN+I)=B(I)
    NNNN=NNN+NC
    XXX(NNNN+I)=C(I)
    NNNNN=NNNN+NC

    ENDIF

     AM(I)=0.452413+1.30982*W(I)-0.295937*(W(I)**2)
60  CONTINUE
    WRITE(6,*)'THE NNNNN=N  = ',NNNNN
    DO 61 I=1,NNNNN
```

```
      WRITE(6,*)' THE XXX(',I,') = ' , XXX(I)
61    CONTINUE

        GO TO 101


6       DO 14 I=1,NC

      IF(TR(I) .GT. 1.)GO TO 1111
         IF(W(I) .LE. .3671)AMO(I)=0.465+1.347*W(I)-0.528*(W(I)**2)
      IF(W(I) .GT. .3671)AMO(I)=.5361+0.9593

      IF(W(I) .LE. .40)AM(I)=AMO(I)+(1./70.)*
     1                  ((5.*(T/TC(I))-3.*AMO(I)-1.)**2)
      IF(W(I) .GE. .50)AM(I)=AMO(I)+(.71)*((T/TC(I)-.779)**2)
      IF(W(I) .GT. .40 .AND. W(I) .LT. .50)AM(I)=((W(I)-.40)/.150)*
     1                 (AMO(I)+(.71)*((T/TC(I)-.779)**2))+
     1                  ((0.55-W(I))/.150)*(AMO(I)+(1./70.)*
     1                 ((5.*(T/TC(I))-3.*AMO(I)-1.)**2))

1111        BETAC(I)=0.25989-0.0217*W(I)+0.00375*(W(I)**2)

         OMC=1./(3.*(1.+BETAC(I)*W(I)))
         OMB=BETAC(I)*OMC
         OMAC=(1.-OMC*(1.-BETAC(I)))**3
      AC(I)=OMAC*(RTPC2(I))
         A(I)=OMA*(RTPC2(I))
         B(I)=OMB*RTPC(I)

      IF(IREG .EQ. 2) XXX(I)=AC(I)
      IF(IREG .EQ. 3) XXX(I)=B(I)
      IF(IREG .EQ. 4) THEN
      XXX(NN+I)=AC(I)
      NNN=NN+NC
      XXX(NNN+I)=B(I)
      NNNN=NNN+NC
      XXX(NNNN+I)=C(I)
      NNNNN=NNNN+NC

      ENDIF

14      CONTINUE

        GO TO 101

7       DO 16 I=1,NC
       RTC=R*TC(I)
       RTP=RTC/PC(I)
      OMA1(I)=((1.+(OM(I)-1.)*ZC(I))**3)
      OMB1(I)=OM(I)*ZC(I)
      ALFA(I)=(1.+(OM(I)-3.)*ZC(I))/(OM(I)*ZC(I))
      BETA(I)=((ZC(I)**2)*((OM(I)-1.)**3)+2.*(OM(I)**2)*ZC(I)+
```

```
     1          OM(I)*(1.-3.*ZC(I)))/((OM(I)**2)*ZC(I))

      AC(I)=OMA1(I)*RTP*RTC
      B(I)=OMB1(I)*RTP
      AM(I)=0.163101+0.862083*W(I)+0.227229*(W(I)**2)
     1      -0.474979*(W(I)**3)

     IF(IREG .EQ. 2) XXX(I)=AC(I)
     IF(IREG .EQ. 3) XXX(I)=B(I)
     IF(IREG .EQ. 4) THEN

     NNN=NN+I
     N3=NN+NC+I
     N4=NN+NC+NC+I
     N5=NN+NC+NC+NC+I
     XXX(NNN)=AC(I)
     XXX(N3)=B(I)
     XXX(N4)=ALFA(I)
     XXX(N5)=BETA(I)

     ENDIF

16   CONTINUE

     do 1101 i=1,n5
     write(6,*)' the xxx(',i,')= ', xxx(i)
1101 continue

       GO TO 101

101     RETURN
        END
```

```
C
C*****************************************************************
C                                                                 C
C    THIS SUBROUTINE IS FOR INITIALIZING IF NECESSARY             C
C                                                                 C
*****************************************************************
C

      SUBROUTINE INIT2

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)       COMMON
/B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /G/ XXX(100)
      COMMON /N/ NN
      COMMON /LJ/ idd,jdd,kdd

      IF (T .EQ. 0. .AND. P .EQ. 0.) STOP
C      T=5.*(T-32.)/9+273.15
C      P=P/14.696
      SUM=0.
      DO 100 I=1,NC
         SUM=SUM+Z(I)
         WRITE(NO,*) I,AK(I)
     call count(idd,jdd,kdd,no)
  100 CONTINUE
      IF (SUM .GT. 0.) GO TO 200

  200 WRITE(6,*)'DO  YOU WANT ANEW COMPOSITIO? 0-NO 1-YES'
      READ(5,*) INEW
      IF (INEW .EQ. 1) RETURN

C     1 FORMAT(' ENTER T (DEG F) AND P (PSIA): '$)
C     2 FORMAT(' ENTER COMPONENT MOLE FRACTIONS: ')
C     3 FORMAT(' COMPONENT ',I3,':'$)
C     4 FORMAT(' DO YOU WANT TO ENTER NEW COMPOSITIONS? 0-NO, 1-YES: '$)
C     5 FORMAT(' AK(',I1,')=',E10.4)
      return
       END
```

```
C
**********************************************************************
C                                                                     C
C     THIS SUBROUTINE IS TO EVALUATE THE FLASH CALCULATIONS FOR THE   C
C     USE OF ANY OF THE CHOSEN EOS.                                   C
C                                                                     C
**********************************************************************
C
      SUBROUTINE FLASH

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)

      COMMON /G/ XXX(100)
      COMMON /N/ NN
      COMMON /IJ/ idd,jdd,kdd
      DATA IFLMAX /50/
C
C     INITIALIZING FOR CALCULATION
C
      IF (AL .EQ. 0.) AL=0.5
      SUM1=0.
      SUM2=0.
      IFL=1
      DO 100 I=1,NC
     if(ak(i) .gt. 100)ak(I)=1.25
     if(ak(i) .lt. 1.e-6)ak(I)=.25
         SUM1=SUM1+AK(I)*Z(I)
         SUM2=SUM2+Z(I)/AK(I)
  100 CONTINUE

      IF (SUM1 .GT. 1. .AND. SUM2 .GT. 1.) GO TO 500
      IF (SUM1 .GT. 1.) GO TO 200
      WRITE(NO,*)'SINGLE PHASE LIQUID AT ITERATION: ',
     1           ITER,(AK(I),I=1,NC)

     X(I)=Y(I)
     GO TO 800
  200 WRITE(NO,*)'SINGLE PHASE VAPOR AT ITERATION: ',
     1           ITER,(AK(I),I=1,NC)
     Y(I)=X(I)
     GO TO 800

  500 F=0.
```

```
C
C     THIS IS NEWTON RALPHSON METHOD
C
      DFDL=0.
      DO 600 I=1,NC
         AK1=1.-AK(I)
         DFDL=DFDL-Z(I)*AK1**2/(AL*AK1+AK(I))**2
         F=F+Z(I)*AK1/(AK1*AL+AK(I))
  600 CONTINUE
      IFL=IFL+1
      IF (IFL .GT. IFLMAX) GO TO 9000
      DL=-F/DFDL
      AL=AL+DL
      IF (AL .LT. 0.) AL=1.E-6
      IF (AL .GT. 1.) AL=.999999

      IF (ABS(DL) .GT. TOL) GO TO 500
      IF (ABS(F) .GT. TOL) GO TO 500
800   DO 700 I=1,NC
         X(I)=Z(I)/(AL+AK(I)*(1.-AL))
         Y(I)=AK(I)*Z(I)/(AL+AK(I)*(1.-AL))

  700 CONTINUE
      RETURN

 9000 WRITE(NO,3)
     call count(idd,jdd,kdd,no)
      STOP

C     1 FORMAT(' SINGLE PHASE LIQUID AT ITERATION: ',I3,5X,
C     *       ' KVALUES: ',5E20.4/13X,5E20.4)
C     2 FORMAT(' SINGLE PHASE VAPOR AT ITERATION: ',I3,5X,
C     *       ' KVALUES: ',5E20.4/13X,5E20.4)
    3 FORMAT(' MAX ITERATION COUNT EXCEEDED IN FLASH.')

      END
```

```
C
**********************************************************************
C                                                                     C
C    THIS SUBROUTINE IS TO CLACULATE THE FUGACITIES BY USING          C
C    THE SRK EOS                                                      C
C                                                                     C
**********************************************************************
C
      SUBROUTINE FUGAC3(XX,F,LV,XXX)

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DLJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /N/ NN
      COMMON /IJ/ idd,jdd,kdd
      COMMON /RR/ IREG

      DIMENSION XX(100),ACLJ(100,100),ALJ(100,100),F(100),XXX(100)
      DIMENSION ACLJ0(100,100),SA(100),AMOT(100),SAB(100),TEMP(100)
C
C


      CC1=1.0+SQRT(2.0)
      CC2=2.0-CC1
      CC3=CC2-CC1
      BM=0.
C
C     CONVERTING THE PARAMETERS BACK WHEN IT HAS BEEN CHANGED
C
      DO 6 I=1,NC

      IF(IREG .EQ. 2) AC(I)=XXX(I)
      IF(IREG .EQ. 3) B(I) =XXX(I)
      IF(IREG .EQ. 4) THEN
      AC(I)=XXX(I+NN)
      B(I) = XXX(I+NC+NN)
      ENDIF

      ACLJ(I,I)=AC(I)
      ACLJ0(I,I)=AC(I)
      DLJ(I,I)=0.0
6     AMOT(I)=AM(I)/SQRT(TC(I))

      IF(NC.EQ.1) GO TO 2002

      NN=0
      DO 10 I=2,NC
      IM1=I-1
```

```
      DO 10 J=1,IM1
      DLJ(I,I)=0.

      IF(IREG .EQ. 1 .OR. IREG .EQ. 4)THEN
      NN=NN+1
      DLJ(I,J)=XXX(NN)
      ENDIF

      DLJ(J,J)=DLJ(I,I)
      DLJ(J,I)=DLJ(I,J)
      IF (DLJ(I,J) .GE. 1.0 )DLJ(I,J)=.05

      ACLJ0(I,J)=SQRT(AC(I)*AC(J))
      ACLJ(I,J) =ACLJ0(I,J)*(1.-DLJ(I,J))
      ACLJ0(J,I)=ACLJ0(I,J)

10    ACLJ(J,I)=ACLJ(I,J)
2002  DO 1 I=1,NC
      ALFSQ(I)=1.0+AM(I)*(1.0-SQRT(T/TC(I)))
1     AIJ(I,I)=ACLJ(I,I)*ALFSQ(I)*ALFSQ(I)
      IF(NC.EQ.1) GO TO 202

      DO 2 I=2,NC
      IM1=I-1
      DO 2 J=1,IM1
      AIJ(I,J)=ACLJ(I,J)*ALFSQ(I)*ALFSQ(J)
2     AIJ(J,I)=AIJ(I,J)
C
C    CALCULATING THE MIXING PARAMETERS BY USING THE MIXING RULES
C
202     AAM=0.0
        DO 3 I=1,NC
        SA(I)=0.0
        DO 4 J=1,NC
4       SA(I)=SA(I)+XX(J)*AIJ(I,J)

        AAM=AAM+XX(I)*SA(I)
3       BM=BM+B(I)*XX(I)
      AA=P*AAM/(R**2*T**2)
      BB=P*BM/(R*T)
      C0=-(AA*BB)
      C1=AA-BB**2-BB
      C2=-(1.)
C
C    CALLING THE CUBIC SUBROUTINE TO SOLVE THE EQUATION
C    WHICH IS IN CUBIC FORM AND GETTING THE COMPRESSIBILITY
C    OUT FOR CALCULATION
C
      CALL CUBE(C2,C1,C0,Z1,Z2,Z3,IEXIT)

      RTP=R*T/P
      V1=Z1*RTP
```

```
      V2=Z2*RTP
      V3=Z3*RTP
      V=V1
      IF (IEXIT .EQ. 1) GO TO 500
      IF (LV .EQ. 2) GO TO 200
C     LIQUID PHASE - V MINIMUM.
      IF (V2 .LT. V) V=V2
      IF (V3 .LT. V) V=V3
      GO TO 500
C     VAPOR PHASE - V MAXIMUM.
  200 IF (V2 .GT. V) V=V2
      IF (V3 .GT. V) V=V3
  500 IF (LV .EQ. 1) VL=V
      IF (LV .EQ. 2) VV=V
      IF (LV .EQ. 1) ZZ = (P*VL)/(R*T)
      IF (LV .EQ. 2) ZZ = (P*VV)/(R*T)
C
C    CALCULATING THE FUGACITIES
C
      ZMBB= ZZ-BB
      ALN = -ALOG(ZMBB)
      BLN=AA*ALOG((1.+BB/ZZ))/BB
      DO 33 I=1,NC
      BIOB=B(I)/BM
      SAB(I)=SA(I)*2./AAM-BIOB
      TEMP(I)=(ZZ-1.)*BIOB-BLN*SAB(I)
      FOXP=TEMP(I)+ALN
      FI=XX(I)*P*EXP(FOXP)
         IF (LV .EQ. 1) FL(I)=FI
         IF (LV .EQ. 2) FV(I)=FI
33    CONTINUE
      RETURN
      END
```

```
C
**********************************************************************
C                                                                     C
C    THIS SUBROUTINE IS TO CALCULATE THE FUGACITIES BY PR EOS         C
C                                                                     C
**********************************************************************
C
      SUBROUTINE FUGAC4(XX,F,LV,XXX)

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DLJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),total(100)
      COMMON /LJ/ idd,jdd,kdd
      COMMON /GG/ NN
      COMMON /RR/ IREG
      DIMENSION XX(100),ACLJ(100,100),ALJ(100,100),F(100),XXX(100)
      DIMENSION ACLJ0(100,100),SA(100),AMOT(100),SAB(100),TEMP(100)
C
C


      CC1=1.0+SQRT(2.0)
      CC2=2.0-CC1
      CC3=CC2-CC1
      BM=0.
      DO 6 I=1,NC

      IF(IREG .EQ. 2) AC(I)=XXX(I)
      IF(IREG .EQ. 3) B(I) =XXX(I)
      IF(IREG .EQ. 4) THEN
      AC(I)=XXX(I+NN)
      B(I) = XXX(I+NC+NN)
      ENDIF

      ACLJ(I,I)=AC(I)
      ACLJ0(I,I)=AC(I)
      DLJ(I,I)=0.0
6     AMOT(I)=AM(I)/SQRT(TC(I))
      IF(NC.EQ.1) GO TO 2002
      NN=0
      DO 10 I=2,NC
      IM1=I-1
      DO 10 J=1,IM1
      DLJ(I,I)=0.

      IF(IREG .EQ. 1 .OR. IREG .EQ. 4)THEN
      NN=NN+1
      DLJ(I,J)=XXX(NN)
      ENDIF
```

```
      DIJ(J,J)=DIJ(I,I)
      DIJ(J,I)=DIJ(I,J)
      IF (DIJ(I,J) .GE. 1.0 )DIJ(I,J)=.05
C      WRITE(NO,*)'DIJ(',I,J,') = ',DIJ(I,J)
      ACIJ0(I,J)=SQRT(AC(I)*AC(J))
      ACIJ(I,J) =ACIJ0(I,J)*(1.-DIJ(I,J))
      ACIJ0(J,I)=ACIJ0(I,J)
C      WRITE(6,*)'THE AIJC(',I,J,')IS = ',ACIJ(I,J)
10    ACIJ(J,I)=ACIJ(I,J)
2002  DO 1 I=1,NC
      ALFSQ(I)=1.0+AM(I)*(1.0-SQRT(T/TC(I)))
1     AIJ(I,I)=ACIJ(I,I)*ALFSQ(I)*ALFSQ(I)
      IF(NC.EQ.1) GO TO 202

      DO 2 I=2,NC
      IM1=I-1
      DO 2 J=1,IM1
      AIJ(I,J)=ACIJ(I,J)*ALFSQ(I)*ALFSQ(J)
2     AIJ(J,I)=AIJ(I,J)

C
C    CALCULATING THE MIXING PARAMETERS BY USING THE MIXING RULES
C

202     AAM=0.0
        DO 3 I=1,NC
        SA(I)=0.0
        DO 4 J=1,NC
4       SA(I)=SA(I)+XX(J)*AIJ(I,J)

        AAM=AAM+XX(I)*SA(I)
3       BM=BM+B(I)*XX(I)
      AA=P*AAM/(R**2*T**2)
      BB=P*BM/(R*T)
      C0=-(AA*BB-BB**2-BB**3)
      C1=AA-3*BB**2-2*BB
      C2=-(1.-BB)
C
C    CALLING THE CUBIC SOLVER TO FIND THE RIGHT Z
C
      CALL CUBE(C2,C1,C0,Z1,Z2,Z3,IEXIT)

      RTP=R*T/P
      V1=Z1*RTP
      V2=Z2*RTP
      V3=Z3*RTP
      V=V1
      IF (IEXIT .EQ. 1) GO TO 500
      IF (LV .EQ. 2) GO TO 200

C     LIQUID PHASE - V MINIMUM.
```

```
      IF (V2 .LT. V) V=V2
      IF (V3 .LT. V) V=V3
      GO TO 500

C     VAPOR PHASE - V MAXIMUM.

  200 IF (V2 .GT. V) V=V2
      IF (V3 .GT. V) V=V3

  500 IF (LV .EQ. 1) VL=V
      IF (LV .EQ. 2) VV=V

      IF (LV .EQ. 1) ZZ = (P*VL)/(R*T)
      IF (LV .EQ. 2) ZZ = (P*VV)/(R*T)

C
C     CALCULATING THE FUGACITIES
C
      ZMBB= ZZ-BB
      AIN = -ALOG(ZMBB)
      BIN=AA*ALOG((ZZ+CC2*BB)/(ZZ+CC1*BB))/BB/CC3

      DO 33 I=1,NC
      BIOB=B(I)/BM
      SAB(I)=SA(I)*2./AAM-BIOB
      TEMP(I)=(ZZ-1.)*BIOB-BIN*SAB(I)
      FOXP=TEMP(I)+AIN
      FI=XX(I)*P*EXP(FOXP)

         IF (LV .EQ. 1) FL(I)=FI
         IF (LV .EQ. 2) FV(I)=FI
33    CONTINUE

      RETURN
      END
```

```
C
**********************************************************************
C                                                                     C
C    THIS SUBROUTINE IS TO CALCULATE THE FUGACITIES BY USING          C
C    THE PT EOS                                                       C
C                                                                     C
**********************************************************************
C
      SUBROUTINE FUGAC5(XX,F,LV,XXX)

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DLJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),total(100)
      COMMON /P/ C(100)
      COMMON /H/ NN
      COMMON /LJ/ idd,jdd,kdd
      COMMON /RR/ IREG
      DIMENSION XX(100),ACLJ(100,100),ALJ(100,100),F(100),XXX(100)
      DIMENSION ACLJ0(100,100),SA(100),AMOT(100),SAB(100),TEMP(100)
C
C

      BM=0.
      CM=0.
      DO 6 I=1,NC

      IF(IREG .EQ. 2) AC(I)=XXX(I)
      IF(IREG .EQ. 3) B(I) =XXX(I)
      IF(IREG .EQ. 4) THEN
     AC(I)=XXX(NN+I)
     NNN=NN+NC
     B(I)=XXX(NNN+I)
     NNNN=NNN+NC
     C(I)=XXX(NNNN+I)
      ENDIF

      ACLJ(I,I)=AC(I)
      ACLJ0(I,I)=AC(I)
      DLJ(I,I)=0.0
6     AMOT(I)=AM(I)/SQRT(TC(I))
      IF(NC.EQ.1) GO TO 2002

      NN=0
      DO 10 I=2,NC
      IM1=I-1
      DO 10 J=1,IM1
      DLJ(I,I)=0.
```

```
      IF(IREG .EQ. 1 .OR. IREG .EQ. 4)THEN
      NN=NN+1
      DLJ(I,J)=XXX(NN)
      ENDIF

      DLJ(J,J)=DLJ(I,I)
      DLJ(J,I)=DLJ(I,J)
      IF (DLJ(I,J) .GE. 1.0 )DLJ(I,J)=.05

      ACLJ0(I,J)=SQRT(AC(I)*AC(J))
      ACLJ(I,J) =ACLJ0(I,J)*(1.-DLJ(I,J))
      ACLJ0(J,I)=ACLJ0(I,J)

10    ACLJ(J,I)=ACLJ(I,J)
2002  DO 1 I=1,NC
      ALFSQ(I)=1.0+AM(I)*(1.0-SQRT(T/TC(I)))
1     ALJ(I,I)=ACLJ(I,I)*ALFSQ(I)*ALFSQ(I)
      IF(NC.EQ.1) GO TO 202

      DO 2 I=2,NC
      IM1=I-1
      DO 2 J=1,IM1
      ALJ(I,J)=ACLJ(I,J)*ALFSQ(I)*ALFSQ(J)
2     ALJ(J,I)=ALJ(I,J)

202     AAM=0.0
        DO 3 I=1,NC
        SA(I)=0.0
        DO 4 J=1,NC

4       SA(I)=SA(I)+XX(J)*ALJ(I,J)

C
C     CALCULATING THE MIXING PARAMETERS BY USING THE MIXING RULES
C

        AAM=AAM+XX(I)*SA(I)
      CM=CM+C(I)*XX(I)
3       BM=BM+B(I)*XX(I)
      AA=P*AAM/(R**2*T**2)
      BB=P*BM/(R*T)
      CC=P*CM/(R*T)
      C0=(BB**2)*CC+BB*CC-AA*BB
      C1=-(BB**2+2.*BB*CC+BB+CC-AA)
      C2=-(1.-CC)
C
C     CALLING THE CUBIC SOLVER TO GET THE RIGHT Z
C
      CALL CUBE(C2,C1,C0,Z1,Z2,Z3,IEXIT)

      RTP=R*T/P
      V1=Z1*RTP
```

```
      V2=Z2*RTP
      V3=Z3*RTP
      V=V1
      IF (IEXIT .EQ. 1) GO TO 500
      IF (LV .EQ. 2) GO TO 200

C     LIQUID PHASE - V MINIMUM.

      IF (V2 .LT. V) V=V2
      IF (V3 .LT. V) V=V3
      GO TO 500

C     VAPOR PHASE - V MAXIMUM.

  200 IF (V2 .GT. V) V=V2
      IF (V3 .GT. V) V=V3

  500 IF (LV .EQ. 1) VL=V
      IF (LV .EQ. 2) VV=V

      IF (LV .EQ. 1) ZZ = (P*VL)/(R*T)
      IF (LV .EQ. 2) ZZ = (P*VV)/(R*T)

C
C    CALCULATING THE FUGACITIES
C
      ZMBB= ZZ-BB
      ALN = -ALOG(ZMBB)

      QQ=(V)+((BM+CM)/2.)
      DM=SQRT(BM*CM+((BM+CM)**2/4.))
      DO 33 I=1,NC

      F1=B(I)/(V-BM)
      F21=ALOG((QQ+DM)/(QQ-DM))
      F2=-(SA(I)/(DM*R*T))*F21
      F31=AAM*(B(I)+C(I))
      F32=(2.*R*T*(QQ**2-DM**2))
      F3=F31/F32
      F41=(AAM*(C(I)*(3.*BM+CM)+B(I)*(3.*CM+BM)))/(8.*R*T*(DM**3))
      F42=F21-(2.*QQ*DM)/(QQ**2-DM**2)
      F4=F41*F42
      FOXP=ALN+F1+F2+F3+F4
      FI=XX(I)*P*EXP(FOXP)

         IF (LV .EQ. 1) FL(I)=FI
         IF (LV .EQ. 2) FV(I)=FI
33    CONTINUE
      RETURN
      END
```

```
C
**********************************************************************
C                                                                     C
C    THIS SUBROUTINE IS TO CALCULATE THE FUGACITIES BY USING          C
C    THE SW EOS                                                       C
C                                                                     C
**********************************************************************
C
      SUBROUTINE FUGAC6(XX,F,LV,XXX)

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /N/ NN
      COMMON /P/ C(100)
      COMMON /LJ/ idd,jdd,kdd
      COMMON /RR/ IREG

      DIMENSION XX(100),ACIJ(100,100),AIJ(100,100),F(100),XXX(100)
      DIMENSION ACIJ0(100,100),SA(100),AMOT(100),SAB(100),TEMP(100)
      DIMENSION DZZ(100),BET(100),ALF(100),U(100)
C
C


      BM=0.
      WM=0.
      DO 6 I=1,NC

      IF(IREG .EQ. 2) AC(I)=XXX(I)
      IF(IREG .EQ. 3) B(I) =XXX(I)
      IF(IREG .EQ. 4) THEN
      AC(I)=XXX(I+NN)
      NNN=NN+NC
      B(I)=XXX(I+NNN)
      NCC=NC+NNN
      W(I)=XXX(I+NCC)
      ENDIF

      ACIJ(I,I)=AC(I)
      ACIJ0(I,I)=AC(I)
      DIJ(I,I)=0.0
6     AMOT(I)=AM(I)/SQRT(TC(I))
      IF(NC.EQ.1) GO TO 2002

      NN=0
      DO 10 I=2,NC
      IM1=I-1
      DO 10 J=1,IM1
```

```
      DIJ(I,I)=0.

      IF(IREG .EQ. 1 .OR. IREG .EQ. 4)THEN
      NN=NN+1
      DIJ(I,J)=XXX(NN)
      ENDIF

      DIJ(J,J)=DIJ(I,I)
      DIJ(J,I)=DIJ(I,J)
      IF (DIJ(I,J) .GE. 1.0 )DIJ(I,J)=.05

      ACIJ0(I,J)=SQRT(AC(I)*AC(J))
      ACIJ(I,J) =ACIJ0(I,J)*(1.-DIJ(I,J))
      ACIJ0(J,I)=ACIJ0(I,J)

10    ACIJ(J,I)=ACIJ(I,J)
2002  DO 1 I=1,NC

     IF(TR(I) .GT. 1.)GO TO 1111
      ALFSQ(I)=1.0+AM(I)*(1.0-SQRT(T/TC(I)))
1111    ALFSQ(I)=(1.-(0.4774+1.328*W(I))*(ALOG(TR(I))))**(1./2.)
1     ALJ(I,I)=ACIJ(I,I)*ALFSQ(I)*ALFSQ(I)
      IF(NC.EQ.1) GO TO 202

      DO 2 I=2,NC
      IM1=I-1
      DO 2 J=1,IM1
      ALJ(I,J)=ACIJ(I,J)*ALFSQ(I)*ALFSQ(J)
2     ALJ(J,I)=ALJ(I,J)
C
C     CALCULATIND THE MIXING PARAMETERS BY USING THE MIXING RULES
C

202     AAM=0.0
        DO 3 I=1,NC
        SA(I)=0.0
     SSA=0.0
     SSB=0.
       DO 4 J=1,NC

     SSA=SSA+W(I)*XX(I)*(B(I)**(.7))
     SSB=SSB+XX(I)*(B(I)**(.7))

4       SA(I)=SA(I)+XX(J)*ALJ(I,J)

        AAM=AAM+XX(I)*SA(I)
    WM= SSA/SSB

3       BM=BM+B(I)*XX(I)
     AA=P*AAM/(R**2*T**2)
     BB=P*BM/(R*T)
     WW=WM
```

```
      C0=(BB**3+BB**2)*(3.*WW)-AA*BB
      C1=-((1.+6.*WW)*BB**2+(1.+3.*WW)*BB-AA)
      C2=-(1.-3.*WW*BB)

C
C     CALLING THE CUBIC SOLVER TO FINDING THE RIGHT Z
C
      CALL CUBE(C2,C1,C0,Z1,Z2,Z3,IEXIT)

      RTP=R*T/P
      V1=Z1*RTP
      V2=Z2*RTP
      V3=Z3*RTP
      V=V1
      IF (IEXIT .EQ. 1) GO TO 500
      IF (LV .EQ. 2) GO TO 200

C     LIQUID PHASE - V MINIMUM.

      IF (V2 .LT. V) V=V2
      IF (V3 .LT. V) V=V3
      GO TO 500

C     VAPOR PHASE - V MAXIMUM.

  200 IF (V2 .GT. V) V=V2
      IF (V3 .GT. V) V=V3

  500 IF (LV .EQ. 1) VL=V
      IF (LV .EQ. 2) VV=V

      IF (LV .EQ. 1) ZZ = (P*VL)/(R*T)
      IF (LV .EQ. 2) ZZ = (P*VV)/(R*T)

C
C     CALCULATING THE FUGACITIES
C
     UMIX=1.+3.*WM
     SMIX=SQRT(UMIX**2+4.*UMIX-4.)
     VMIN=(ZZ*R*T)/P+(UMIX-SMIX)*BM/2.
     VPLS=(ZZ*R*T)/P+(UMIX+SMIX)*BM/2.
     BBB=SMIX*BM
      ZMBB= (ZZ*R*T/P)-BM
      AIN = ALOG(ZMBB)

      DO 33 I=1,NC

     U(I)=1.+3.*W(I)
     BET(I)=SMIX*B(I)+(DZZ(I)/(SMIX*XX(I)))*
     1          (U(I)-UMIX)*(2.*UMIX)*BM
     ALF(I)=UMIX*B(I)+(DZZ(I)/XX(I))*(U(I)-UMIX)*BM
     F1=R*T*(AIN-(B(I)/ZMBB))
```

```
      F2=(ALOG(VPLS/VMIN)/BBB)*(2.*SA(I)-(AAM/BBB)*BET(I))
      F3=(AAM/(2.*BBB))*((ALF(I)+BET(I))/VPLS-(ALF(I)-BET(I))/VMIN)
         FOXP=-(F1+F2+F3)/(R*T)
      FI=XX(I)*P*(EXP(FOXP))

          IF (LV .EQ. 1) FL(I)=FI
          IF (LV .EQ. 2) FV(I)=FI
33     CONTINUE
       RETURN
       END
```

```
C
**********************************************************************
C                                                                     C
C    THIS SUBROUTINE IS TO CALCULATE THE FUGACITIES USING THE LLS EOS C
C                                                                     C
**********************************************************************
C
      SUBROUTINE FUGAC7(XX,F,LV,XXX)

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DIJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NTL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /GG/ NN
      COMMON /O/ ALFA(100),BETA(100),OM(100),ZC(100)
      COMMON /IJ/ idd,jdd,kdd
      COMMON /RR/ IREG

      DIMENSION XX(100),ACIJ(100,100),AIJ(100,100),F(100),XXX(100)
      DIMENSION ACIJ0(100,100),SA(100),AMOT(100),SAB(100),TEMP(100)
C
C

      CC1=1.0+SQRT(2.0)
      CC2=2.0-CC1
      CC3=CC2-CC1
      BM=0.
      DO 6 I=1,NC

      IF(IREG .EQ. 2) AC(I)=XXX(I)
      IF(IREG .EQ. 3) B(I) =XXX(I)
      IF(IREG .EQ. 4) THEN
     NNN=NN+I
     N3=NN+NC+I
     N4=NN+NC+NC+I
     N5=NN+NC+NC+NC+I
     AC(I)=XXX(NNN)
     B(I)=XXX(N3)
     ALFA(I)=XXX(N4)
     BETA(I)=XXX(N5)
     ENDIF

      ACIJ(I,I)=AC(I)
      ACIJ0(I,I)=AC(I)
      DIJ(I,I)=0.0
6     AMOT(I)=AM(I)/SQRT(TC(I))
      IF(NC.EQ.1) GO TO 2002

      NN=0
```

```
      DO 10 I=2,NC
      IM1=I-1
      DO 10 J=1,IM1
      DIJ(I,I)=0.

      IF(IREG .EQ. 1 .OR. IREG .EQ. 4)THEN
      NN=NN+1
      DIJ(I,J)=XXX(NN)
      ENDIF

      DIJ(J,J)=DIJ(I,I)
      DIJ(J,I)=DIJ(I,J)
      IF (DIJ(I,J) .GE. 1.0 )DIJ(I,J)=.05
      ACIJ0(I,J)=SQRT(AC(I)*AC(J))
      ACIJ(I,J) =ACIJ0(I,J)*(1.-DIJ(I,J))
      ACIJ0(J,I)=ACIJ0(I,J)

10    ACIJ(J,I)=ACIJ(I,J)
2002  DO 1 I=1,NC
      ALFSQ(I)=1.0+AM(I)*(1.0-SQRT(T/TC(I)))
1     AIJ(I,I)=ACIJ(I,I)*ALFSQ(I)*ALFSQ(I)
      IF(NC.EQ.1) GO TO 202

      DO 2 I=2,NC
      IM1=I-1
      DO 2 J=1,IM1
      AIJ(I,J)=ACIJ(I,J)*ALFSQ(I)*ALFSQ(J)
2     AIJ(J,I)=AIJ(I,J)

C
C     CALCULATING THE MIXING PARAMETERS BY USING THE MIXING RULES
C

202   AAM=0.0
      ALFM=0.
      BETM=0.
      DO 3 I=1,NC
      SA(I)=0.0
      DO 4 J=1,NC

4     SA(I)=SA(I)+XX(J)*AIJ(I,J)
      AAM=AAM+XX(I)*SA(I)

      BETM=BETM+XX(I)*BETA(I)
      ALFM=ALFM+XX(I)*ALFA(I)

3       BM=BM+(B(I))*XX(I)
      AA=P*AAM/(R**2*T**2)
      BB=P*BM/(R*T)
      C0=-(AA*BB-BETM*(BB**2+BB**3))
      C1=AA-ALFM*BB-(BETM+ALFM)*(BB**2)
      C2=-(1.+(1.-ALFM)*BB)
```

```
C
C     CALLING THE CUBIC SOLVER TO FIND THE RIGHT Z
C

      CALL CUBE(C2,C1,C0,Z1,Z2,Z3,IEXIT)

      RTP=R*T/P
      V1=Z1*RTP
      V2=Z2*RTP
      V3=Z3*RTP
      V=V1
      IF (IEXIT .EQ. 1) GO TO 500
      IF (LV .EQ. 2) GO TO 200

C     LIQUID PHASE - V MINIMUM.

      IF (V2 .LT. V) V=V2
      IF (V3 .LT. V) V=V3
      GO TO 500

C     VAPOR PHASE - V MAXIMUM.

  200 IF (V2 .GT. V) V=V2
      IF (V3 .GT. V) V=V3

  500 IF (LV .EQ. 1) VL=V
      IF (LV .EQ. 2) VV=V

      IF (LV .EQ. 1) ZZ = (P*VL)/(R*T)
      IF (LV .EQ. 2) ZZ = (P*VV)/(R*T)

C
C     CALCULATING THE FUGACITIES
C

      Q1=AA/(BB*(ALFM**2+4.*BETM)**(1./2.))
      Q2=ZZ+(ALFM+(ALFM**2+4.*BETM)**(1./2.))*(BB/2)
      Q3=ZZ+(ALFM-(ALFM**2+4.*BETM)**(1./2.))*(BB/2)
      QQ=Q1*(ALOG(Q2/Q3))
      SS=((ZZ/(ZZ-BB))-ZZ-QQ)
      S1=((ZZ/(ZZ-BB))-ZZ-QQ)*((ALFM**2)/(ALFM**2+4.*BETM))
      S2=((BB/(ZZ-BB))-BB)*((2.*ALFM*BETM)/(ALFM**2+4.*BETM))
      S3=((ZZ/(ZZ-BB))-ZZ-QQ)*((4.*BETM)/(ALFM**2+4.*BETM))
       ZMBB= ZZ-BB
       ALN = -ALOG(ZMBB)

       DO 33 I=1,NC
       BIOB=B(I)/BM

       SAB(I)=SA(I)*2./AAM-BIOB
       TEMP(I)=(ZZ-1.)*BIOB
```

```
      F1=-SAB(I)*QQ
      F2=SS-(ALFA(I)*(S1-S2)/ALFM)
      F3=-(BETA(I)**(1./2.))*(S3+S2)/(BEIM**(1./2.))
         F4=TEMP(I)+ALN
      FOXP=F1+F2+F3+F4
       FI=XX(I)*P*EXP(FOXP)

          IF (LV .EQ. 1) FL(I)=FI
          IF (LV .EQ. 2) FV(I)=FI
33     CONTINUE

       RETURN
       END
```

```
**********************************************************************
C                                                                     C
C     THIS SUBROUTINE IS TO PRINT THE RESULTS WHEN IT IS BEEN ASKED   C
C                                                                     C
**********************************************************************
C
      SUBROUTINE PRNT

      COMMON /A/ PC(100),TC(100),W(100),AK(100),Z(100),X(100),Y(100),AL
      COMMON /C/R,FL(100),FV(100),NC,TOL,CNAME(100,2),ALFSQ(100),B(100)
      COMMON /B/ AO,BO,PR,AAM,BM,T,P,ITER,VL,VV,AMW(100),DLJ(100,100)
      COMMON /D/ AC(100),AM(100),IEOS,TR(100),NO
      COMMON /E/ NIL,ZZJ(100,100),AKJ(100,100),XE(100,100),
     1           YE(100,100),TOTAL(100)
      COMMON /G/ XXX(100)
      COMMON /IJ/ idd,jdd,kdd

      TOUT=(T-273.15)*9/5+32.
      POUT=P*14.696
      WRITE(NO,1) TOUT,POUT,ITER
      call count(idd,jdd,kdd,no)
      AVMWL=0.
      AVMWV=0.
C
C     PRINT OUT THE CALCULTAED RESULTS
C

      DO 100 I=1,NC
      WRITE(NO,2) (CNAME(I,J),J=1,2),Z(I),X(I),Y(I),FL(I),FV(I),AK(I)
     call count(idd,jdd,kdd,no)
         AVMWL=AVMWL+X(I)*AMW(I)
         AVMWV=AVMWV+Y(I)*AMW(I)
  100 CONTINUE

C
C     PRINTING THE VALUES OF DENSITIES, AND TOTAL MOLE FRACTIONS
C

      RHOL=AVMWL/VL
      RHOV=AVMWV/VV
      WRITE(NO,3)AL,VL,RHOL,VV,RHOV
     call count(idd,jdd,kdd,no)
     call count(idd,jdd,kdd,no)
     call count(idd,jdd,kdd,no)
      RETURN

    1 FORMAT(' FLASH AT ',F6.0,' DEG F   AND ',F6.0,' PSIA AT ITERATIO
     *N ',I3//1X,'COMPONENT',8X,'Z',8X,'X',8X,'Y',9X,'FL'
     *,12X,'FV',12X,'K'/)
    2 FORMAT(1X,2A5,3(4X,F5.4),3(4X,E10.4))
    3 FORMAT(/1X,'MOLE FRACTION LIQUID   : ',F6.4/1X,
     *           'LIQUID VOLUME (CC/GMOL): ',F6.1/1X,
```

```
*           'LIQUID DENSITY (G/CC)   : ',F6.4/1X,
*           'VAPOR VOLUME (CC/GMOL)  : ',F6.1/1X,
*           'VAPOR DENSITY (G/CC)    : ',F10.4/)
 END
```

```
C
**************************************************************************
C                                                                        C
C     THIS SUBROUTINE IS TO SOLVE THE CUBIC FORM OF THE COMPRESSIBILITY C
C     FOR ANY OF THE USED EQUATIONS                                      C
C                                                                        C
**************************************************************************
C
      SUBROUTINE CUBE(A1,A2,A3,X1,X2,X3,IEXIT)
      DATA PI /3.1415927/
C
      DIH=2.*PI/3.
      Q=(3.*A2-A1**2)/9.
      R=(9.*A1*A2-27.*A3-2.*A1**3)/54.
      D=Q**3+R**2

      IF(D .GE. 0) GO TO 1000
      IEXIT=3
      TH=ACOS(R/SQRT(-Q**3))
      QS=2.*SQRT(-Q)
      X1=QS*COS(TH/3.)-A1/3.
      X2=QS*COS(TH/3.+DIH)-A1/3.
      X3=QS*COS(TH/3.+2.*DIH)-A1/3.
      RETURN

1000  IF (D .EQ. 0.) GO TO 1200
      IEXIT=1
      SD=SQRT(D)
      SS=(R+SD)**(1./3.)
      RSD=R-SD
      IF (RSD .GT. 0.) GO TO 1100
      TT=-(-RSD)**(1./3.)
      GO TO 1150
1100  TT=(RSD)**(1./3.)
1150  X1=SS+TT-A1/3.
      RETURN

1200  WRITE(NO,1)
      call count(idd,jdd,kdd,no)
      STOP

    1 FORMAT(' EQUAL ROOTS DETECTED IN CUBE.')
      END
```

```
C
**********************************************************************
C                                                                     C
C     THIS SUBROUTINE IS TO SOLVE THE CUBIC FORM OF THE ANY EQUATIONS C
C     IF IT IS NOT COMPRESSIBILITY                                    C
C                                                                     C
**********************************************************************
C

      SUBROUTINE CUBE1(A1,A2,A3,DX)
      DATA PI /3.1415927/
      DTH=2.*PI/3.

      Q=(3.*A2-A1**2)/9.
      R=(9.*A1*A2-27.*A3-2.*A1**3)/54.
      D=Q**3+R**2
      IF (D .GE. 0) GO TO 1000
      TH=ACOS(R/SQRT(-Q**3))
      QS=2.*SQRT(-Q)
      X1=QS*COS(TH/3.)-A1/3.
      X2=QS*COS(TH/3.+DTH)-A1/3.
      X3=QS*COS(TH/3.+2.*DTH)-A1/3.

     IF(X1 .GT. 0  .AND. X2 .GT. 0. .AND. X3 .GT. 0.)GO TO 1001
     IF(X1 .LE. 0. .AND. X2 .LE. 0.)DX=X3
     IF(X1 .LE. 0. .AND. X3 .LE. 0.)DX=X2
     IF(X2 .LE. 0. .AND. X3 .LE. 0.)DX=X1
     GO TO 101
1001    IF(X1 .LT. X2 .AND. X1 .LT. X3)DX=X1
     IF(X2 .LT. X1 .AND. X2 .LT. X3)DX=X2
     IF(X3 .LT. X1 .AND. X3 .LT. X2)DX=X3

     GO TO 101

 1000 IF (D .EQ. 0.) GO TO 1200

      SD=SQRT(D)
      SS=(R+SD)**(1./3.)
      RSD=R-SD
      IF (RSD .GT. 0.) GO TO 1100
      TT=-(-RSD)**(1./3.)
      GO TO 1150
 1100 TT=(RSD)**(1./3.)
 1150 X1=SS+TT-A1/3.

     DX=X1

     GO TO 101

 1200 X1=(2.*(R**(1./3.))-A1/3.)
      X2=(-(R**(1./3.))-A1/3.)
```

```
      IF(X1 .GT. 0. .AND. X2 .GT. 0.)GO TO 1002
      IF(X1 .LT. 0.)DX=X2
         IF(X2 .LT. 0.)DX=X1
      GO TO 1003
1002  IF(X1 .LT. X2)DX=X1
      DX=X2
1003        WRITE(6,*)'OFF THE TWO ROOTS', DX

101       RETURN

       END
```

```
C
**********************************************************************
C                                                                     C
C    THIS IS THE SUBROUTINE WHICH SOLVES THE POWELL METHOD            C
C    IT WILL TAKE THE PARAMETERS (XXX) AND THE FINDS THE MINIMUME     C
C    THEN IT WILL BE TRANSFERED TO THE SUBROUTINE CALCULATED          C
C    FUNCTION IF THE VALUE IS WITH IN THE TOLERANCE THEN IT WILL      C
C    STOP OTHERWISE IT WILL CONTINUE UNTIL CONVERGES THEN THE         C
C    RESULTS WILL BE PRINTED FOR THE APPROPRIATE POINTS.              C
C                                                                     C
**********************************************************************
C
      SUBROUTINE BOTM(XXX,E,N,EF,ESCALE,IPRINT,MAXIT,DW,NI,NO,NW)

      REAL*8 X(100),DW(NW)
      COMMON /LJ/ idd,jdd,kdd
      DIMENSION XXX(100),E(100)

    DO 40 I=1,N
      X(I)=XXX(I)
40  CONTINUE

      WRITE(NO,001)
001   FORMAT(10X,'POWELL-BOTM OPTIMIZATION ROUTINE')
    call count(idd,jdd,kdd,no)
      WRITE(NO,002)N,MAXIT,ESCALE,(I,X(I),I=1,N),(JJ,E(JJ),JJ=1,N)

002   FORMAT(//,2X,'PARAMETERS',//,2X,'N=',I2,4X,'MAXIT=',
    1  I4,4X,'ESCALE=',F5.2,//,2X,'INITIAL GUESSES',//,6(2X,
    2  'X(',I2,')=',1E16.8),//,2X,'ACCURACY REQUIRED FOR
    3  VARIABLES',//,6(2X,'E(',I2,')=',1E16.8))
    call count(idd,jdd,kdd,no)

      DDMAG=1.0*ESCALE
      SCER=0.05/ESCALE

      JJ=N*(N+1)
      JJJ=JJ+N
      K=N+1
      NFCC=1
      IND=1
      INN=1



      DO 4 I=1,N
      DW(I)=ESCALE

      DO 4 J=1,N
      DW(K)=0.
      IF(I-J)4,3,4
```

```
3       DW(K)=ABS(E(I))
4       K=K+1

        ITERC=1
        ISGRAD=2
        CALL CALCFX(N,XXX,F)
        FKEEP=2.*ABS(F)
5       ITONE=1
        FP=F
        SUM=0.
        IXP=JJ

        DO 6 I=1,N
        IXP=IXP+1
6       DW(IXP)=XXX(I)

        IDIRN=N+1
        ILINE=1
7       DMAX=DW(ILINE)
        DACC=DMAX*SCER

        DMAG=AMIN1(DDMAG,.1*DMAX)
        DMAG=AMAX1(DMAG,20.*DACC)
        DDMAX=10.*DMAG
        GO TO (70,70,71),ITONE

70      DL=0.
        D=DMAG
        FPREV=F
        IS=5
        FA=FPREV
        DA=DL

8       DD=D-DL
        DL=D

58      K=IDIRN

        DO 9 I=1,N
        XXX(I)=XXX(I)+DD*DW(K)
9       K=K+1
        CALL CALCFX(N,XXX,F)

        NFCC=NFCC+1
        GO TO( 10,11,12,13,14,96),IS

14      IF(F-FA)15,16,24
16      IF(ABS(D)-DMAX) 17,17,18
17      D=D+D

        GO TO 8
18      WRITE(NO,019)
```

```
019     FORMAT(5X,' MAXIMUM CHANG DOES NOT ALTER FUNCTION')
      call count(idd,jdd,kdd,no)
        GO TO 20
15      FB=F
        DB=D

        GO TO 21
24      FB=FA
        DB=DA
        FA=F
        DA=D

21      GO TO (83,23),ISGARD
23      D=DB+DB-DA

        IS=1
        GO TO 8
83      D=0.5*(DA+DB-(FA-FB)/(DA-DB))

        IS=4
        IF((DA-D)*(D-DB))25,8,8
25      IS=1
        IF(ABS(D-DB)-DDMAX)8,8,26
26      D=DB+SIGN(DDMAX,DB-DA)

        IS=1
        DDMAX=DDMAX+DDMAX
        DDMAG=DDMAG+DDMAG
        IF(DDMAG .GE. 1.0E+30) DDMAG=1.0E+30
        IF (DDMAX-DMAX)8,8,27
27      DDMAX=DMAX
        GO TO 8
13      IF(F-FA)28,23,23
28      FC=FB
        DC=DB
29      FB=F
        DB=D
        GO TO 30
12      IF (F-FB)28,28,31
31      FA=F
        DA=D
        GO TO 30
11      IF(F-FB)32,10,10
32      FA=FB
        DA=DB
        GO TO 29
71      DL=1.
        DDMAX=5.
        FA=FP
        DA=-1.
        FB=FHOLD
        DB=0.
```

```
      D=1.
10    FC=F
      DC=D
30    A=(DB-DC)*(FA-FC)
            B=(DC-DA)*(FB-FC)
      IF((A+B)*(DA-DC))33,33,34
33    FA=FB
      DA=DB
      FB=FC
      DB=DC

      GO TO 26
34    D=0.5*(A*(DB+DC)+B*(DA+DC))/(A+B)
      DI=DB
      FI=FB
      IF(FB-FC)44,44,43

43    DI=DC
      FI=FC
44    GO TO (86,86,85),ITONE
85    ITONE=2
      GO TO 45
86    IF (ABS(D-DI)-DACC)41,41,93
93    IF(ABS(D-DI)-0.03*ABS(D))41,41,45
45    IF((DA-DC)*(DC-D))47,46,46
46    FA=FB
      DA=DB
      FB=FC
      DB=DC
      GO TO 25
47    IS=2

      IF((DB-D)*(D-DC))48,8,8
48    IS=3

      GO TO 8
41    F=FI

      D=DI-DL
      DD=SQRT((DC-DB)*(DC-DA)*(DA-DB)/(A+B))
      DO 49 I=1,N
      XXX(I)=XXX(I)+D*DW(IDIRN)
      DW(IDIRN)=DD*DW(IDIRN)
49    IDIRN=IDIRN+1

      DW(ILINE)=DW(ILINE)/DD
      ILINE=ILINE+1
      IF(IPRINT-1)51,50,51

50    WRITE(NO,052)ITERC,NFCC,F,(XXX(I),I=1,N)
052   FORMAT(/,' ITERATION',I5,I15,' FUNCTION VALUES',10X,'F =',
     1       E15.8/6(E16.8,2X))
```

```
      GO TO(51,53),IPRINT
51    GO TO (55,38),ITONE
55    IF(FPERV-F-SUM)94,95,95
95    SUM=FPREV-F
      JIL=ILINE
94    IF (IDIRN-JJ)7,7,84
84    GO TO (92,72),IND
92    FHOLD=F
      IS=6
      IXP=JJ
      DO 59 I=1,N
      IXP=IXP+1
59    DW(IXP)=XXX(I)-DW(IXP)
      DD=1.
      GO TO 58
96    GO TO (112,87),IND
112   IF(FP-F)37,37,91
91    D=2.*(FP+F-2.*FHOLD)/(FP-F)**2
      IF(D*(FP-FHOLD-SUM)**2-SUM)87,37,37
87    J=JIL*N+1
      IF(J-JJ)60,60,61
60    DO 62 I=J,JJ
      K=I-N
62    DW(K)=DW(I)
      DO 97 I=JIL,N
97    DW(I-1)=DW(I)
61    IDIRN=IDIRN-N
      ITONE=3
      K=IDIRN
      IXP=JJ
      AAA=0.
      DO 67 I=1,N
      IXP=IXP+1
      DW(K)=DW(IXP)
      IF(AAA-ABS(DW(K)/E(I))) 66,67,67
66    AAA=ABS(DW(K)/E(I))
67    K=K+1
      DDMAG=1.
      DW(N)=ESCALE/AAA
      ILINE=N
      GO TO 7
37    IXP=JJ
      AAA=0.
      F=FHOLD
      DO 99 I=1,N
      IXP=IXP+1
      XXX(I)=XXX(I)-DW(IXP)
      IF(AAA*ABS(E(I))-ABS(DW(IXP))) 98,99,99
98    AAA=ABS(DW(IXP)/E(I))
```

```
99      CONTINUE
        GO TO 72
38      AAA=AAA*(1.+DI)
        GO TO (72,106),IND
72      IF(IPRINT-2)53,50,50
53      GO TO (109,88),IND
109     IF(AAA-0.1)20,20,76
76      IF(F-FP)35,78,78
78      WRITE(NO,080)
080     FORMAT(5X,' ACCURACY LIMILITED BY ERROR IN F')
        call count(idd,jdd,kdd,no)
        GO TO 20
88      IND=1
35      DDMAG=0.4*SQRT(ABS(FP-F))
        IF(DDMAG .GE. 1.0E+30) DDMAG=1.0E+30
        ISGARD=1
        ITERC=ITERC+1
        IF(ITERC-MAXIT)5,5,81
81      WRITE(NO,082)MAXIT
082     FORMAT(I5,' ITERATIONS COMPLETED BY')
        call count(idd,jdd,kdd,no)
        IF(F-FKEEP)20,20,110
110     F=FKEEP
        DO 111 I=1,N
        JJJ=JJJ+1
111     XXX(I)=DW(JJJ)
        GO TO 20
106     IF(AAA-0.1) 20,20,107
20      EF=F
        WRITE(NO,*)'NUMBER OF ITERATIONS ARE= ',ITERC
        call count(idd,jdd,kdd,no)

        WRITE(NO,1111)
1111       FORMAT(//,5X,'  VALVE OF THE VARIABLES')
        call count(idd,jdd,kdd,no)
        DO 100 J=1,N
        WRITE(NO,222)J,XXX(J)
222       FORMAT(//,5X,'XXX(',I2,')=',E16.8)
        call count(idd,jdd,kdd,no)
100     CONTINUE

        WRITE(NO,333)EF
333       FORMAT(//,'  OPTIMUM VALUE OF F=',E16.8)
        call count(idd,jdd,kdd,no)

        RETURN
107     INN=1

        GO TO 35
        END
```

```
C
**********************************************************************
C                                                                     C
C    this subroutine is to control the output files                   C
C                                                                     C
**********************************************************************
C
        subroutine count(idd,jdd,kdd,no)

        idd=idd+1
        if(idd .le. 1000)go to 101

        if(idd .gt. 1000)idd=1001
        jdd=jdd+1
        if(jdd .eq. 1)no=no+1
        if(jdd .le. 1000)go to 101
        if(jdd .gt. 1000 .and. kdd .eq. 0) close(unit=no)

        if(jdd .gt. 1000)jdd=1001
        kdd=kdd+1
        if(kdd .eq. 1)no=no+1
        if(kdd .le. 1000)go to 101

        close(unit=no)

        jdd=1
        kdd=0
        no=no-1
101     continue

C
C    THESE ARE THE FILES THAT THE OUTPUT WILL BE PUT INTO
C
     IF(NO .EQ. 20) OPEN(UNIT=20,FILE='PSW0.ALL')
     IF(NO .EQ. 21) OPEN(UNIT=21,FILE='PSW1.ALL')
     IF(NO .EQ. 22) OPEN(UNIT=22,FILE='PSW2.ALL')
     IF(NO .EQ. 23) OPEN(UNIT=23,FILE='PSW3.ALL')
     IF(NO .EQ. 24) OPEN(UNIT=24,FILE='PSW4.ALL')
     IF(NO .EQ. 25) OPEN(UNIT=25,FILE='PSW5.ALL')
     IF(NO .EQ. 26) OPEN(UNIT=26,FILE='PSW6.ALL')
     IF(NO .EQ. 27) OPEN(UNIT=27,FILE='PSW7.ALL')
     IF(NO .EQ. 28) OPEN(UNIT=28,FILE='PSW8.ALL')
     IF(NO .EQ. 29) OPEN(UNIT=29,FILE='PSW9.ALL')
     IF(NO .EQ. 30) OPEN(UNIT=30,FILE='PSWD0.ALL')
     IF(NO .EQ. 31) OPEN(UNIT=31,FILE='PSWD1.ALL')
     IF(NO .EQ. 32) OPEN(UNIT=32,FILE='PSWD2.ALL')
     IF(NO .EQ. 33) OPEN(UNIT=33,FILE='PSWD3.ALL')
     IF(NO .EQ. 34) OPEN(UNIT=34,FILE='PSWD4.ALL')
     IF(NO .EQ. 35) OPEN(UNIT=35,FILE='PSWD5.ALL')
     IF(NO .EQ. 36) OPEN(UNIT=36,FILE='PSWD6.ALL')
     IF(NO .EQ. 37) OPEN(UNIT=37,FILE='PSWD7.ALL')
```

```
IF(NO .EQ. 38) OPEN(UNIT=38,FILE='PSWD8.ALL')
IF(NO .EQ. 39) OPEN(UNIT=39,FILE='PSWD9.ALL')


return
end
```

This thesis is accepted on behalf of the faculty of the Institute by the following committee:

Advisor

Date