

VAN DER WAALS MIXING RULES FOR CUBIC EQUATIONS OF STATE  
(Applications for Supercritical Fluid Extraction Modeling  
and Phase Equilibrium Calculations)

T. Y. Kwak, E. H. Benmekki and G. A. Mansoori

Department of Chemical Engineering  
University of Illinois  
BOX 4348 Chicago, Illinois 60680

Introduction

There has been extensive progress made in recent years in research towards the development of analytic statistical mechanical equations of state applicable for process design calculations (1,2). However cubic equations of state are still widely used in chemical engineering practice for calculation and prediction of properties of fluids and fluid mixtures (3). These equations of state are generally modifications of the van der Waals equation of state (4,5),

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \quad [1]$$

which was proposed by van der Waals (4) in 1873. according to van der Waals for the extension of this equation to mixtures, it is necessary to replace a and b with the following composition-dependent expressions :

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad [2]$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} \quad [3]$$

Equations [2] and [3] are called the van der Waals mixing rules. In these equations  $a_{ij}$  and  $b_{ij}$ , ( $i=j$ ) are parameters corresponding to pure component (i) while  $a_{ij}$  and  $b_{ij}$ , ( $i \neq j$ ) are called the unlike-interaction parameters. It is customary to relate the unlike-interaction parameters to the pure-component parameters by the following expression :

$$a_{ij} = (1 - k_{ij}) (a_{ii} a_{jj})^{1/2} \quad [4]$$

$$b_{ij} = (b_{ii} + b_{jj})/2 \quad [5]$$

In Eq.[4]  $k_{ij}$  is a fitting parameter which is known as the coupling parameter. With Eq.[5] replaced in Eq.[3], the expression for b will reduce to the following one-summation form:

$$b = \sum_i^n x_i b_{ii} \quad [3.1]$$

The Redlich-Kwong equation of state (6),

$$P = \frac{RT}{v - b} - \frac{a}{T^{1/2} v(v-b)} \quad [6]$$

and the Peng-Robinson equation of state (7),

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad [7]$$

$$a(T) = a(T_c) \{1 + \kappa(1 - T_r^2)\}^2 \quad [8]$$

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c \quad [8.1]$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad [9]$$

$$b = 0.0778 RT_c/P_c \quad [10]$$

are widely used for thermodynamic property calculations.

#### The Theory of the Van Der Waals Mixing Rules

Leland and Co-workers (8-10) have been able to re-derive the van der waals mixing rules with the use of statistical mechanical theory of radial distribution functions. According to these investigators for a fluid mixture with a pair intermolecular potential energy function ,

$$u_{ij}(r) = \epsilon_{ij} f(r/\sigma_{ij}) \quad [11]$$

the following mixing rules will be derived :

$$\sigma^3 = \sum_i^n \sum_j^n x_{ij} x_{ij} \sigma_{ij}^3 \quad [12]$$

$$\epsilon\sigma^3 = \sum_i^n \sum_j^n x_{ij} x_{ij} \epsilon_{ij} \sigma_{ij}^3 \quad [13]$$

In these equations,  $\epsilon_{ij}$  is the interaction energy parameter between molecule  $i$  and  $j$  while  $\sigma_{ij}$  is the intermolecular interaction distance between the two molecules. Knowing that coefficients (a) and (b) of the van der Waals equation of state are proportional to  $\epsilon$  and  $\sigma$  according to the following expressions :

$$a = 1.1250 RT_c v_c = N_0 \epsilon \sigma^3 \quad [14]$$

$$b = 0.3333 v_c = N_0 \sigma^3 \quad [15]$$

We can see that Eq.[12] and Eq.[13] are identical with Eqs.[2] and [3] respectively. Statistical mechanical arguments which are used in deriving Eq.[12] and Eq.[13] dictate the following guidelines in using the van der Waals mixing rules :

(1) The van der Waals mixing rules are for constants of an equation of state.

(2) Equation [12] is a mixing rule for the molecular volume, and Eq.[13] is a mixing rule for (molecular volume).(molecular energy). It happens that  $b$  and  $a$  of the van der Waals equation of state are proportional to (molecular volume) and (molecular volume).(molecular energy), respectively, and as a result, these mixing rules are used in the form which was proposed by van der Waals.

(3) Knowing that  $\sigma_{ij}$  (for  $i \neq j$ ), the unlike-interaction diameters, for spherical molecules is equal to

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \quad [16]$$

This will make the expression for  $b_{ij}$  for spherical molecules to be

$$b_{ij} = [ (b_{ii}^{1/3} + b_{jj}^{1/3}) / 2 ]^3 \quad [17]$$

Then for non-spherical molecules expression for  $b_{ij}$  will be

$$b_{ij} = (1 - l_{ij}) [ (b_{ii}^{1/3} + b_{jj}^{1/3}) ]^3 \quad [18]$$

With the use of these guidelines, we now derive the van der Waals mixing rules for the two representative equations of state. Similar procedure can be used for deriving the van der Waals mixing rules for other equations of state.

#### Mixing Rules for the Redlich-Kwong Equation of State

The Redlich-Kwong equation of state, Eq.[6], can be written in the following form:

$$Z = \frac{PV}{RT} = \frac{v}{v-b} - \frac{a}{RT^{1.5}(v+b)} \quad [19]$$

In this equation of state,  $b$  has the dimension of a molar volume,

$$b = 0.26v_c = N_0 \sigma$$

Then the mixing rule for  $b$  will be the same as the one for the first van der Waals mixing rules, Eq.(3). However mixing rule for  $a$  will be different from the second van der Waals mixing rule, Eq.[2]. Parameter  $a$  appearing in the Redlich-Kwong equation of state has dimension of  $R^{-1/2}$ . (molecular energy)<sup>3/2</sup> (molecular volume), that is

$$(a = 1.2828RT_c^{1.5}v_c = N_0(\epsilon/k)^{1.5}\sigma^3)$$

As a result the second van der Waals mixing rules, Eq.[13], cannot be used directly for the  $a$  parameter of the Redlich-Kwong equation of state. However, since  $(R^2ab^2)$  has the dimension of (molecular energy).(molecular volume), the second van der Waals mixing rules, Eq.[13], can be written for this term. Finally the van der Waals mixing rules for the Redlich-Kwong equation of state will be in the following form:

$$a = \left\{ \sum_i \sum_j x_i x_j a_{ij}^{2/3} b_{ij}^{1/3} \right\}^{1.5} / \left( \sum_i \sum_j x_i x_j b_{ij} \right)^{1/2} \quad [20]$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad [3]$$

These mixing rules, when joined with the Redlich-Kwong equation of state, will constitute the Redlich-Kwong equation of state for mixtures that is consistent with the statistical mechanical basis of the van der Waals mixing rules.

#### Mixing Rules for the Peng-Robinson Equation of State

In order to separate thermodynamic variables from constants of the Peng-Robinson equation of state, we will insert Eq.[8] and Eq.[9] in Eq.[7] and we will write it in the following form :

$$Z = \frac{v}{v-b} - \frac{c/RT + d - 2\sqrt{cd/RT}}{(v+b) + (b/v)(v-b)} \quad [21]$$

where  $c = a(T_c) (1 + \kappa)^2$  and  $d = a_c \kappa^2 / RT_c$

This form of the Peng-Robinson equation of state suggests that there exist three independent constants which are b, c, and d. Now, following the prescribed guidelines for the for the van der Waals mixing rules, mixing rules for b, c, and d of the Peng-Robinson equation of state will be

$$c = \sum_{i,j}^n \sum_{i,j}^n x_i x_j c_{ij} \quad [22]$$

$$b = \sum_{i,j}^n \sum_{i,j}^n x_i x_j b_{ij} \quad [23]$$

$$d = \sum_{i,j}^n \sum_{i,j}^n x_i x_j d_{ij} \quad [24]$$

with the following interaction parameters :

$$c_{ij} = (1 - k_{ij}) (c_{ii} c_{jj})^{1/2} \quad [25]$$

$$b_{ij} = (1 - l_{ij}) \{ (b_{ii}^{1/3} + b_{jj}^{1/3}) / 2 \}^3 \quad [26]$$

$$d_{ij} = (1 - m_{ij}) \{ (d_{ii}^{1/3} + d_{jj}^{1/3}) / 2 \}^3 \quad [27]$$

#### Applications for Supercritical Fluid Extraction Modeling

A serious test of mixture equations of state is shown to be their application for prediction of solubility of solutes in supercritical fluids (11). In the present report, we apply the van der Waals, the Redlich-Kwong and the Peng-Robinson equations of state for supercritical fluid extraction of solids and the effect of choosing different mixing rules on prediction of solubility of solids in supercritical fluids.

#### Thermodynamic Model

Solubility of a condensed phase,  $y_2$ , in a vapor phase at supercritical conditions (12) can be define as :

$$y_2 = (P_2^{sat}/P) (1/\phi_2) \phi_2^{sat} \text{Exp} \left\{ \int_{P_2^{sat}}^P (v_2^{solid}/RT) dP \right\} \quad [28]$$

where  $\phi_2^{sat}$  is the fugacity coefficient at pressure P. Provided we assume  $v_2^{solid}$  is independent of pressure and for small values of  $P_2^{sat}$  the above expression will be converted to the following form:

$$y_2 = (P_2^{sat}/P) (1/\phi_2) \text{Exp} \{ v_2^{solid} (P - P_2^{sat}) / RT \} \quad [29]$$

In order to calculate solubility from Eq. [29] we need to choose an expression for the fugacity coefficient. Generally for calculation of fugacity coefficient an equation of state with appropriate mixing rules is used (12) in the following expression :

$$RT \ln \phi_i = \int_V^{\infty} [ (\partial P / \partial n_i)_{T, V, n_j} - (RT/V) ] dV - RT \ln Z \quad [30]$$

#### Solubility Calculations

In Figure 1 solubility of 2,3 dimethyl naphtalene (DMN) in supercritical carbon dioxide is reported versus pressure at 308 kelvin along with predictions using the

van der Waals equation of state. According to this figure predictions by the van der Waals equation of state will improve when Eq.[3], along with combining rule in Eq.[17], is used as the mixing rule for b instead of Eq.[3.1] which is customarily used. This comparison and other similar comparisons which are reported elsewhere (11) for other solute-solvent systems establish the superiority of double-summation mixing rules, Eq.[3], for b over single summation expression, Eq.[3.1].

In Figure 2 the same experimental solubility data as in Figure 1 are compared with predictions using the Redlich-Kwong equation of state. According to this figure the corrected van der Waals mixing rules for the Redlich-Kwong equation of state, Eqs.[3] and Eq.[20], are clearly superior to the mixing rules that are customarily used, Eq.[2] and Eq.[3.1], for this equation of state. Similar observations are made for prediction of solubilities of other solids in supercritical fluids which will not be reported here.

The Peng-Robinson equation of state with its customary mixing rules, Eqs.[2] and [3.1], is widely used for prediction of solubility of heavy solutes in supercritical gases and for petroleum reservoir fluid phase equilibrium calculations (13-15). In Figure 3 the same experimental solubility data as in Figures 1 and 2 are compared with predictions using the Peng-Robinson equation of state with its original mixing rules with the corrected mixing rules. According to Figure 3 corrected van der Waals mixing rules of the Peng-Robinson equation of state apparently do not improve solubility predictions over the original mixing rules. However, variation of solubility versus pressure for the new mixing rules is more consistent with the experimental data than the old mixing rules. Also considering the fact that new mixing rules for the Peng-Robinson equation of state contain three adjustable parameters ( $k_{ij}$ ,  $l_{ij}$  and  $m_{ij}$ ) while the old mixing rules contain only one adjustable parameter ( $k_{ij}$ ), it makes the new mixing rules more attractive. To demonstrate the superiority of the new mixing rules for the Peng-Robinson equation of state we have reported here Figures 4 to 9. According to these figures when the unlike-interaction adjustable parameters of the mixing rules are fitted to the experimental data, the Peng-Robinson equation of state with the corrected van der Waals mixing rules can predict solubility of heavy solids in supercritical fluid more accurately than with the original mixing rules over different ranges of temperature and pressure and for different solutes and supercritical solvents.

#### Applications for Correlations of Vapor-Liquid Equilibria

When applied to both vapor and liquid phases, cubic equations of state can be used to generate thermodynamically consistent data, particularly equilibrium data. Good correlations of vapor-liquid equilibria depend on the equation of state used and, for multicomponent systems, on the mixing rules.

#### Thermodynamic Model

In the equilibrium state, the intensive properties - temperature, pressure and chemical potentials of each component - are constant in the overall system. Since the fugacities are function of temperature, pressure and compositions, the equilibrium condition

$$f_i^V(T, P, \{y\}) = f_i^L(T, P, \{x\}) \quad [31]$$

can be expressed by

$$y_i \phi_i^V = x_i \phi_i^L \quad [32]$$

The expression for the fugacity coefficient  $\phi_i$  depends on the equation of state that is used and is the same for the vapor and liquid phases

$$RT \ln \phi_i = \int_V^{\infty} [(\partial P / \partial n_i)_{T, V, n_j} - (RT/V)] dV - RT \ln Z \quad [33]$$

In calculations of mixture properties with the Peng-Robinson equation of state we used the following combining rules:

$$c_{ij} = (1 - k_{ij}) [c_{ii} \cdot c_{jj} / b_{ii} \cdot b_{jj}]^{1/2} b_{ij} \quad [34]$$

$$b_{ij} = (1 - l_{ij})^3 \left[ \frac{b_i^{1/3} + b_j^{1/3}}{2} \right]^3 \quad [35]$$

$$d_{ij} = (1 - m_{ij})^3 \left[ \frac{d_i^{1/3} + d_j^{1/3}}{2} \right]^3 \quad [36]$$

A three parameter search routine using a finite difference Levenberg - Marquardt algorithm was used to evaluate the interaction parameters which minimize the objective function

$$OF = \sum_{i=1}^M \left[ \frac{P(\text{exp}) - P(\text{cal})}{P(\text{exp})} \right]_i \quad [37]$$

where M is the number of experimental points considered. The average pressure deviation is expressed as

$$\Delta P/P = (OF/M)^{1/2} \quad [38]$$

#### Phase Equilibrium Calculations

Attention will be given to complex binary systems such as water-acetone. In order to apply the Peng-Robinson equation of state to such polar compounds, some modifications must be incorporated (16). These modifications concern the values of the pure-component parameters.

The relationship  $\alpha(T_r, \omega)$  for water must be changed to

$$\alpha^{1/2} = 1.008568 + 0.8215(1 - T_r^{1/2})$$

this correlation is good for  $T_r^{1/2} < 0.85$

Figures 10, 11 and 12 show both the prediction by the Peng-Robinson equation of state with classical mixing rules and one parameter,  $k_{1,2}$ , fitted to bubble point data, and the net improvement provided by the proposed mixing rules with three fitted parameters. Figure 13 shows the Peng-Robinson prediction with new mixing rules and binary interaction parameters set to zero. It should be noted that no prediction is observed by the Peng-Robinson equation of state with classical mixing rules and binary interaction parameter,  $k_{1,2}$ , equal to zero.

## Nomenclature

a, b, c, d	:equation of state parameters
f	:fugacity
k, l, m	:binary interaction parameters
n	:number of components
$N_0$	:Avogadro number
OF	:objection function to be minimized
P	:pressure
T	:temperature
u	:intermolecular potential function
v	:molar volume
x	:mole fraction
y	:mole fraction in the vapor phase
Z	:compressibility factor
$\phi$	:fugacity coefficient
$\sigma$	:intermolecular distance parameter
$\epsilon$	:interaction energy parameter
w	:acentric factor
$\kappa$	:a function of the acentric factor

### Subscripts

c	:critical property
i, j	:component identification
2	:solute

## REFERENCES

- (1). Alem, A. H. and Mansoori, G. A., *AIChE J.*, 30, 468 (1984)
- (2). Nauman, K. H., and Leland, T. W., *Fluid Phase Equilibria*, 18, 1 (1984).
- (3). Renon, H., (Ed.), "Fluid Properties and Phase Equilibrium for Chemical Process Design", *Proceedings of the 3<sup>rd</sup> international Conference*, Callaway Gardens, GA., April 10-15, *Fluid Phase Equilibria*, 13, (1983).
- (4). Van der Waals, J. D., Phd Thesis, Leiden, 1873.
- (5). Rowlinson, J. S. and Swinton, F. L., "Liquid and Liquid Mixtures", 3<sup>rd</sup> Ed. Butterworths, Wolborn, Mass. 1982
- (6). Redlich, O. and Kwong, J. N. S., *Chem. Rev.*, 44, 233 (1949)
- (7). Peng, D. Y. and Robinson, D. B., *Ind. Eng. Chem. Fund.*, 5, 59, (1976)
- (8). Leland, T. W. and Chapplear, P. S., *Ind. Eng. Chem.*, 60, 15 (1968)
- (9). Leland, T. W., Rowlinson, J. S., and Sather, G. A., *Trans. Faraday Soc.*, 64, 1447 (1968)
- (10). Leland, T. W., Rowlinson, J. S., Sather, G. A., and Watson, I. D., *Trans. Faraday Soc.*, 65, 2034 (1969)
- (11). Mansoori, G. A. and Ely, J. F., *J. Chem. Phys.*, 82, Jan. (1985)
- (12). Prausnitz, J. M., "Molecular Thermodynamics of Fluid Phase Equilibria", Prentice-Hall, Englewood Cliffs, NJ, 1969
- (13). Kurnik, R. T., Holla, S. J. and Reid, R. C., *J. Chem. Eng. Data*, 26, 47 (1981)
- (14). Katz, D. L. and Firoozabadi, A., *J. Petrol. Tech.*, Nov, 1649 (1978)
- (15). Firoozabadi, A., Hekim, Y. and Katz, D. L., *Canadian J. Chem. Eng.*, 56, 610 (1978)
- (16). Robinson, D. B., Peng, D. Y. and Chung, S. Y. K., "Development of the Peng-Robinson Equation of state and its Application to a System Containing Methanol".
- (17). Griswold, J. and Wong, S. Y., *Chem. Eng. Progr. Sympos. Series*, 48, No 3, 18 (1952)
- (18). Ohgaki, K., Katayama, T., *J. Chem. Eng. Data*, 21, 53 (1976)

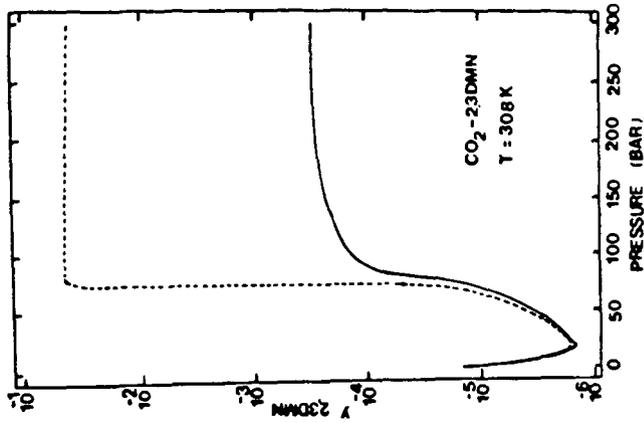


Figure 3 : Solubility of 2,3 DPN in supercritical carbon dioxide at 308 K versus pressure. The dashed lines are results of Peng-Robinson equation of state with Eqs. [2] and [3.1] as mixing rules. The solid lines are results of Peng-Robinson equation of state with Eqs. [3] and [20] as the mixing rules. Both two lines are for  $k_{ij} = 0$ .

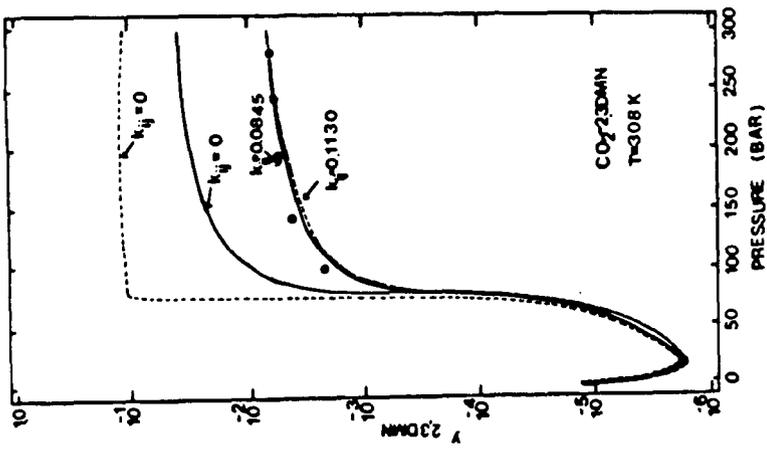


Figure 2 : Solubility of 2,3 DMM in supercritical carbon dioxide at 308 K versus pressure. The solid dots are the experimental data point used to calculate  $k_{ij}$ . The dashed lines are the results of the Redlich-Kwong equation of state with Eqs. [2] and [3.1] as the mixing rules, the solid lines are the results of the Redlich-Kwong equation of state with Eqs. [3] and [20] as the mixing rules, and the circled dot is the experimental data point used to calculate  $k_{ij}$ .

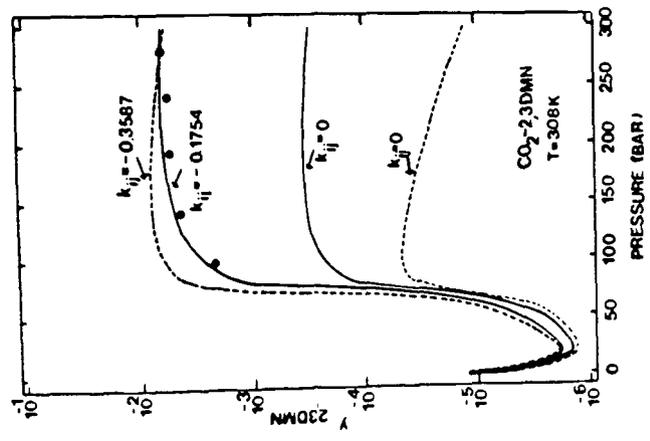


Figure 1 : Solubility of 2,3 dimethyl naphthalene (DMN) in supercritical carbon dioxide at 308 K versus pressure. The solid dots are the experimental data point used to calculate  $k_{ij}$ . The dashed lines are the results of the van der Waals equation of state with Eqs. [2] and [3] as the mixing rules. The solid lines are the results of the van der Waals equation of state with Eqs. [2] and [3] as the mixing rules, and Eqs. [4] and [17] as the combining rules. The circled dot is the experimental data point used to calculate  $k_{ij}$ .

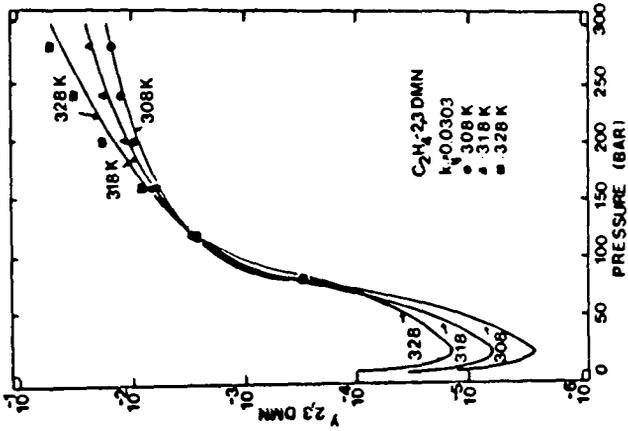


Figure 6 : solubility of 2,3 DMN in supercritical ethylene predicted by the Peng-Robinson equation of state with eqs.(2) and (3.1) as mixing rules.

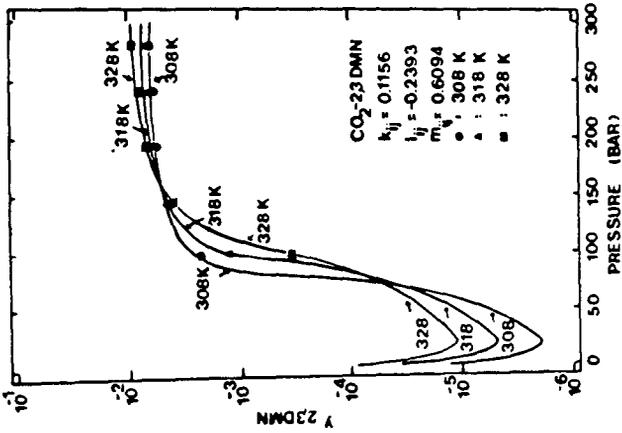


Figure 5 : Solubility of 2,3 DMN in supercritical carbon dioxide calculated by the Peng-Robinson equation of state with eqs.(2-74) as mixing rules.

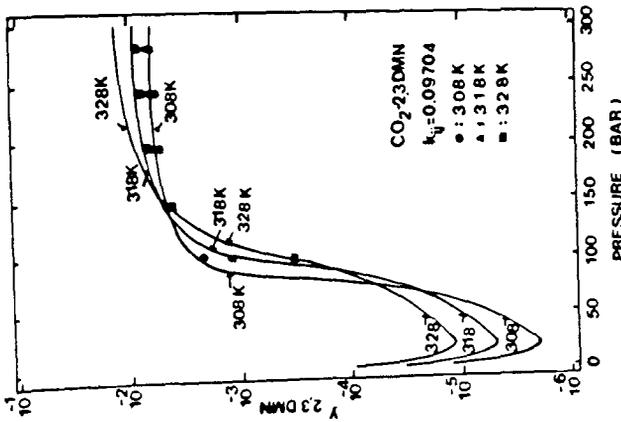


Figure 4 : Solubility of 2,3 DMN in supercritical carbon dioxide calculated by the Peng-Robinson equation of state using eqs.(2) and (3.1) as mixing rules.

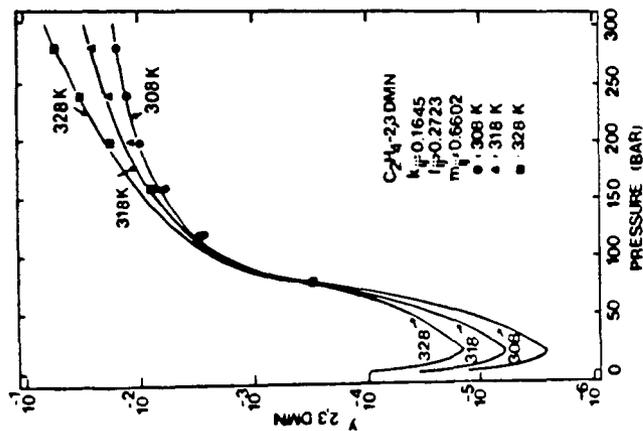


Figure 7 : solubility of 2,3 DM in supercritical ethylene predicted by the Peng-Robinson equation of state with [eq.(22-24)] as the mixing rules.

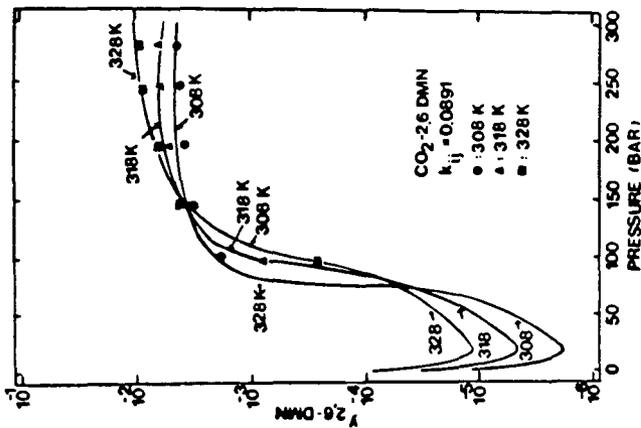


Figure 8 : solubility of 2,6 dimethyl naphthalene (DMN) in carbon dioxide calculated by the Peng-Robinson equation of state with [eq.(2)] and [3,1] as mixing rules.

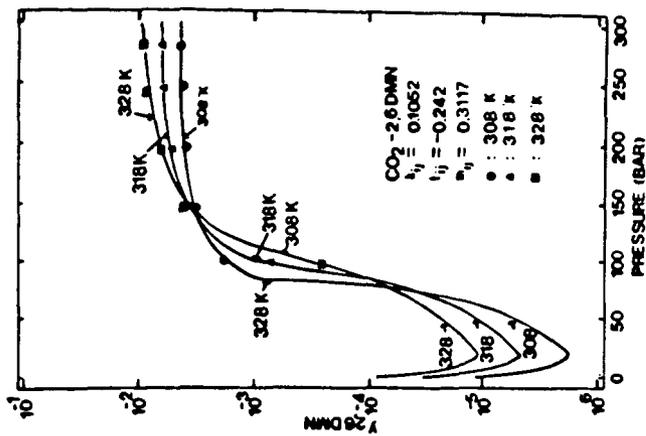


Figure 9 : Solubility of 2,6 DMN in supercritical carbon-dioxide predicted by the Peng-Robinson equation of state using [eq.(22-24)] as mixing rules.

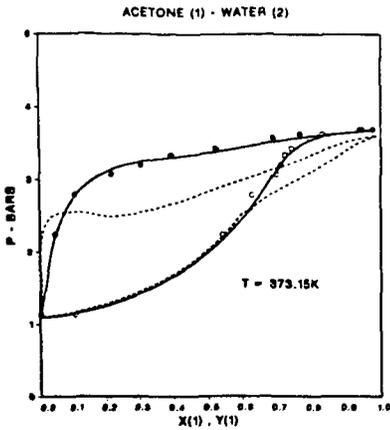


Figure 10

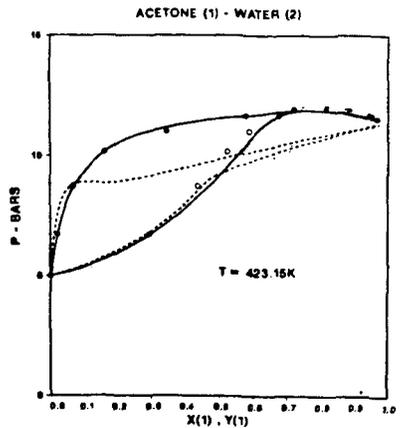


Figure 11

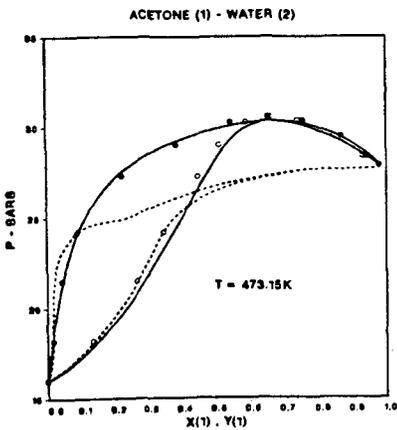


Figure 12

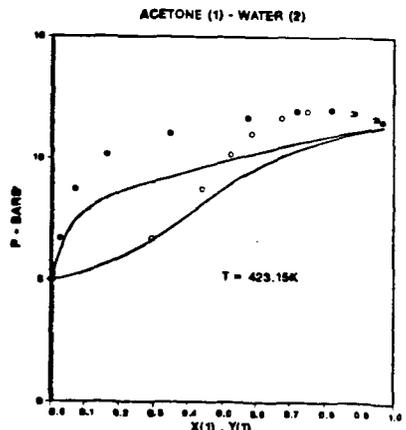


Figure 13

Figures 10, 11, 12 : Phase behavior of acetone-water systems. The solids lines are the Peng-Robinson prediction with three fitted parameters and the corrected mixing rules. The dashed lines are for Peng-Robinson prediction with one fitted parameter and the classical mixing rules. The dots and circles are experimental data (17).

Figure 13 : Acetone-water system predicted by the Peng-Robinson equation of state with the proposed mixing rules and the binary interaction parameters ( $k_{1,2}$ ,  $l_{1,2}$ ,  $m_{1,2}$ ) equal to zero.