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Statistical Mechanical Description of Supercritical Fluid Extraction and Retrograde Condensation

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The phenomena of supercritical fluid extraction (SFE) and its reverse effect, which is known as retrograde condensation (RC), have found new and important applications in industrial separation of chemical compounds and recovery and processing of natural products and fossil fuels. Full-scale industrial utilization of SFE/RC processes requires knowledge about thermodynamic and transport characteristics of the asymmetric mixtures involved and the development of predictive modeling and correlation techniques for performance of the SFE/RC system under consideration. In this report, through the application of statistical mechanical techniques, the reasons for the lack of accuracy of existing predictive approaches are described and they are improved. It is demonstrated that these techniques also allow us to study the effect of mixed supercritical solvents on the solubility of heavy solutes (solids) at different compositions of the solvents, pressures, and temperatures. Fluid phase equilibrium algorithms based on the conformal solution van der Waals mixing rules and different equations of state are presented for the prediction of solubilities of heavy liquid in supercritical gases. It is shown that the Peng–Robinson equation of state based on conformal solution theory can predict solubilites of heavy liquid in supercritical gases more accurately than the van der Waals and Redlich–Kwong equations of state.

KEY WORDS: conformal solution theory; equation of state; mixing rules; mixtures; retrograde condensation; statistical mechanics; supercritical fluid extraction.

1. INTRODUCTION

The concept of supercritical fluid extraction (SFE)/retrograde condensation (RC) is not actually new. The SFE/RC phenomenon was first recognized in

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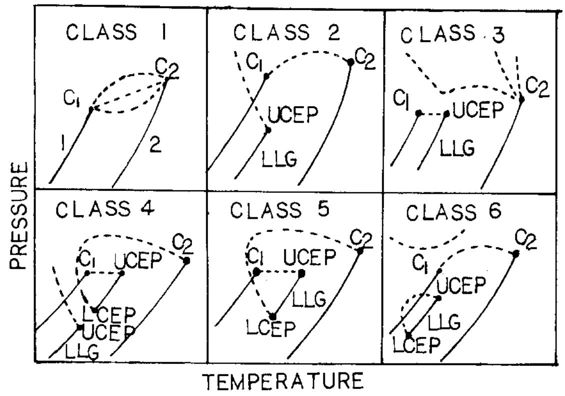
1879 by Hannay and Hogarth [3]. They discovered that solid compounds could be dissolved in supercritical fluids having densities near that of a liquid. The renewed interest in the SFE/RC process is based on the appreciable increase in solvent power of supercritical fluids at temperatures and pressures above, but not far removed from, their critical point. In recent years, an understanding of interaction of the supercritical solvent with condensed compounds (liquid or solid) has received much interest in process extraction and the development of energy-related processes [2, 17, 23].

When the supercritical fluid undergoes a sudden temperature or pressure reduction, the special properties are often lost. Probably the most important property lost at lower pressures is the solubility of some compounds in supercritical fluids. The solubility decay of most organic substances at subcritical pressures proves to be exploitable in that a substance can be extracted at supercritical conditions and precipitated by merely reducing the pressure. Thus supercritical systems combine the useful qualities of liquids and gases to produce a very versatile fluid. In order to demonstrate the phenomena of the SFE/RC process and their relationship with the phase equilibrium characteristics of mixtures, Figs. 1 and 2 are presented. In Fig. 1, six different classes of binary mixtures are distinguished from each other in *PT* diagrams by the shapes and number of their critical lines, the existence or absence of three-phase lines, and the manner in which the



C_1 : CRITICAL POINT OF PURE COMPONENT 1
C_2 : CRITICAL POINT OF PURE COMPONENT 2
LCEP : LOWER CRITICAL END POINT
LLG : LIQUID-LIQUID-GAS
UCEP : UPPER CRITICAL END POINT

Fig. 1. *PT* diagram of six different classes of binary mixtures [24, 26].

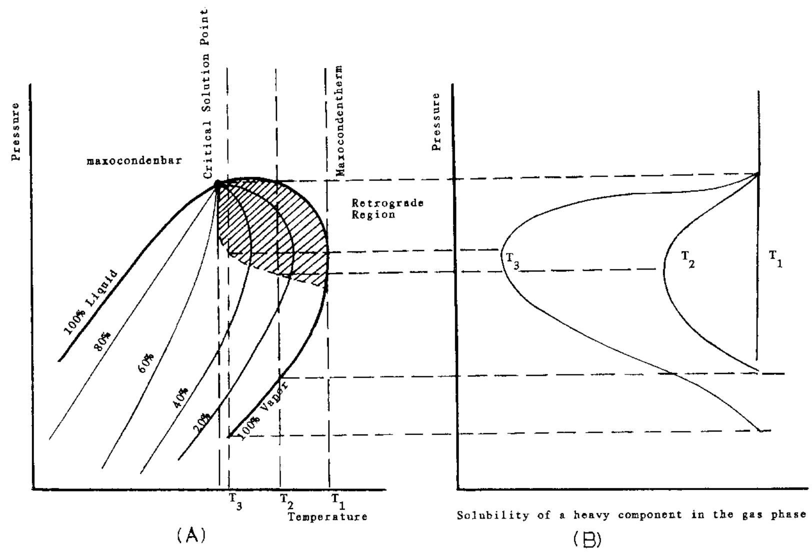


Fig. 2. *PT* and a corresponding *PY* diagram of a petroleum reservoir fluid exhibiting retrograde condensation [6, 22].

critical lines connect with the pure component critical points and three-phase lines. In Fig. 2A the *PT* diagram of a fluid mixture exhibiting retrograde condensation is presented. Figure 2B consists of the pressure versus gas phase composition of a heavy component of this fluid mixture at three different temperatures. According to these figures for a given temperature, above the critical solution temperature, with an increase in pressure, the concentration (or solubility) of heavy components in the supercritical gas will decrease. At higher pressures the solubility starts to increase rapidly and it reaches a maximum at a pressure corresponding to a region slightly above the retrograde region.

Compounds which dissolve in supercritical solvents tend to exhibit their lowest solubilities in the solvent at the lowest pressures. As the pressure rises, so does the solubility of the solute. Some solutes exhibit a crossover effect in supercritical solvents at a certain specific pressure to each solute, or crossover pressure. The crossover effect is characterized by higher solubilities of the solute at lower temperatures below the crossover pressure and higher solute solubilities at higher temperatures above the crossover pressure [30]. As the pressure continues to rise, so does the solubility of the solute; this trend ends at the solubility peak, which is the pressure at which the solute solubility in the solvent is the greatest compared to any other pressure. When the pressure is above the solubility peak pressure, the solubility of the solute decays with continued pressure increases. Such effects can be described utilizing the principles of statistical mechanics, as demonstrated later in this report.

The presence of cosolvents or entrainers can sometimes enhance the solubility of the solute as much as one or two orders of magnitude [31]. Typical cosolvents, such as ethanol, methanol, and acetone, increase the solubility of solutes containing alcohol or other polar groups due to hydrogen bonding between the solute and the cosolvent. On the other hand, cosolvents can also form solid complexes with the solute, thus reducing the solubility enhancement effect. Because some cosolvent–solute combinations form complexes which lower the solubility of the solute, each case must be individually studied to determine the optimum cosolvent. By utilizing the principles of statistical mechanics such effects are demonstrated later in this report.

Prediction of solubilities of heavy liquid hydrocarbon in compressed nitrogen and methane gases based on van der Waals mixing rules and different equations of state [van der Waals (vdW), Redlich–Kwong (RK), and Peng–Robinson (PR)] is performed later in this report. The expressions of the fugacity coefficient for the above three representative equations of state with the van der Waals mixing rules, which are based on conformal solution theory, are used here to predict solubilities of condensed compounds (liquid or solid) in compressed gases. The mixing rules which are used here were derived using the conformal solution theory of statistical mechanic.

The major requirement in the design of SFE systems is the choice of a solvent which will cause a sharp change in the solubility of the solute due to changes in pressure or temperature. Since an essentially infinite number of supercritical solvents can be formed from the currently known compounds, there is little hope of ever generating a sufficient amount of experimental data to meet present, much less future, needs. Knowledge about molecular thermodynamics of fluid mixtures consisting of molecules with large molecular size and shape differences is often required for the accurate prediction of solubilities of heavy solutes in supercritical solvents. The present report is an initial effort toward the development of predictive techniques for SFE/RC phenomena.

2. THERMODYNAMIC MODELING OF SFE/RC PHENOMENA

One can describe and model the phenomena of SFE/RC by utilizing theories of asymmetric mixtures of statistical mechanics and thermodynamics. In general, there exist two statistical mechanical ways for the development of theories of mixtures [8]. One way is through the use of rigorous statistical mechanics and the incorporation of intermolecular potential energy function in its detailed form. The second way is through the use of the conformal solution theory for the development of mixing rules and the use of equations of state of pure fluids [9]. There has been substantial progress made in the past two decades in the developments of both rigorous statistical mechanics of mixtures and conformal solution mixing rules [1, 8, 12, 14, 15, 26]. However, there is little or no information available about intermolecular interaction parameters of the kinds of asymmetric mixtures which are dealt with in the SFE/RC industries. As a result, the utility of the rigorous statistical mechanical approach for the analysis and prediction of SFE/RC phenomena is presently limited.

Conformal solutions refer to substances whose intermolecular potential energy functions, ϕ_{ij}, are related to each other and to those of a reference pure fluid, usually designated by the subscript 00.

$$\phi_{ij}=f_{ij}\phi_{00}(r/h_{ij}^{1/3}) \tag{1}$$

For substances whose intermolecular potential energy function can be represented by an equation of the form

$$\phi_{ij}=E_{ij}[(L_{ij}/r)^n-(L_{ij}/r)^m] \tag{2}$$

and for which exponents m and n are the same as for the reference substance, the conformal solution parameters f_{ij} and h_{ij} will be defined by the following relations with respect to the intermolecular potential energy parameters E_{ij} and the intermolecular length parameter L_{ij}:

$$f_{ij}=E_{ij}/E_{00}, \qquad h_{ij}=(L_{ij}/L_{00})^3 \tag{3}$$

The basic concept of the CST of mixtures is the definition of the conformal solution parameters of the mixture f_{xx} and h_{xx}, which are related to the conformal solution parameters of the components of the mixture and mixture composition according to the following equations:

$$f_{xx}=f_{xx}(f_{ij}, h_{ij}; x_i, \rho, T); \qquad h_{xx}=h_{xx}(f_{ij}, h_{ij}; x_i, \rho, T) \tag{4}$$

Equations (4) are called the conformal solution mixing rules. Functional forms of these mixing rules will be different for different theories of mixtures as demonstrated in Table I. In Table I the one-fluid and also the c-fluid conformal solution mixing rules are reported for different mixture theories [14]. In this table RMA stands for the random mixing approximation theory [13], vdW stands for the van der Waals theory of mixtures [9], HSE stands for the hard-sphere expansion theory [11], DEX stands for the density expansion theory [12], CSA stands for the conformal solution approximation theory [2], and APM stands for the

Table I. Conformal Solution Mixing Rules According to Different Theories [13]

One-fluid mixing rules

RMA

$$f_x h_x = \left[\sum_i \sum_j x_i x_j f_{ij} h_{ij}^2\right]^{3/2} \Big/ \left[\sum_i \sum_j x_i x_j f_{ij} h_{ij}^4\right]^{1/2}$$

$$h_x = \left[\sum_i \sum_j x_i x_j f_{ij} h_{ij}^4 \Big/ \sum_i \sum_j x_i x_j f_{ij} h_{ij}^2\right]^{1/2}$$

vdW

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij}$$

$$h_x = \sum_i \sum_j x_i x_j h_{ij}$$

HSE

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij}$$

$$h_x = \left[\sum_i \sum_j x_i x_j f_{ij} h_{ij}\right]^2 \Big/ \sum_i \sum_j x_i x_j f_{ij}^2 h_{ij}$$

DEX

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij} \{1 - (f_{ij}/f_{xi} - 1)[\Delta u_{xi}/kT + T\Delta C_{vxi}/\Delta u_x]\}$$

$$h_x = \sum_i \sum_j x_i x_j h_{ij}$$

Multifluid mixing rules

RMA

$$f_{xi} h_{xi} = \left[\sum_j x_j f_{ij} h_{ij}^2\right]^{3/2} \Big/ \left[\sum_j x_j f_{ij} h_{ij}^4\right]^{1/2}$$

$$h_x = \left[\sum_j x_j f_{ij} h_{ij}^4 \Big/ \sum_j x_j f_{ij} h_{ij}^2\right]^{1/2}$$

vdW

$$f_{xi} h_{xi} = \sum_j x_j f_{ij} h_{ij}$$

$$h_x = \sum_j x_j h_{ij}$$

HSE

$$f_{xi} h_{xi} = \sum_j x_j f_{ij} h_{ij}$$

$$h_x = \left[\sum_j x_j f_{ij} h_{ij}\right]^2 \Big/ \sum_j x_j f_{ij}^2 h_{ij}$$

DEX

$$f_{xi} h_{xi} = \sum_j x_j f_{ij} h_{ij} \{1 - (f_{ij}/f_{xi} - 1)[\Delta u_{xi}/kT + T\Delta C_{vxi}/\Delta u_x]\}$$

$$h_{xi} = \sum_j x_j h_{ij}$$

$$\Delta_x = \rho RT \kappa_{Tx}; \quad \kappa_T = -(1/V)(\partial V/\partial P)_T$$

average potential model theory [13]. According to Table I DEX and CSA mixing rules are density and temperature dependent, while the other mixing rules are independent of ρ and T [14]. In the analysis made earlier by other investigators it was demonstrated that the RMA and APM mixing rules are valid for a mixture consisting of components with close molecular sizes and shapes [14, 20]. The HSE mixing rules are actually for the excess properties of mixtures over the hard-sphere mixture [11]. The DEX and CSA mixing rules, which are composition-, temperature-, and density-dependent mixing rules [12–14], require special thermodynamic consistency rules in order to be applied for mixture calculations. In the present report we utilize the van der Waals mixing rules in order to calculate the solubility of solutes in supercritical mixed solvents. As demonstrated in the next section the conformal solution van der Waals mixing rules, when joined with the PR equation of state, give us an opportunity to perform the accurate calculation of the solubility of heavy solutes in supercritical solvents. In the formulation of a mixture theory we also need to know the combining rules for unlike-interaction potential parameters which are expressed by the following expressions [5]:

$$\begin{aligned} f_{ij} &= (1-k_{ij})\, h_{ij}(f_{ii} f_{jj}/h_{ii} h_{jj})^{1/2} \\ h_{ij} &= (1-l_{ij})\{(h_{ii}^{1/3}+h_{jj}^{1/3})/2\}^{3} \end{aligned} \tag{5}$$

where k_{ij} and l_{ij} are adjustable parameters.

Utilizing the conformal solution approximation (CSA) and assuming that the scaled radial distribution functions (RDFs) between every two species of a fluid mixture are all identical [9, 14], the following mixing rules will be derived:

$$\begin{aligned} f_{xx} h_{xx} &= \sum_i \sum_j x_i x_j f_{ij} h_{ij} \\ h_{xx} &= \sum_i \sum_j x_i x_j h_{ij} \end{aligned} \tag{6}$$

where h_{xx} and f_{xx} are the conformal solution parameters of a hypothetical pure fluid which can represent the mixture. Equations (6) are actually the van der Waals mixing rules, which are well known.

With the aid of the conformal solution guidelines [8, 14], one can develop mixing rules for the three representative cubic equations of state (vdW, RK, and PR). The vdW mixing rules for the different equations of state can be derived [8].

(i) The van der Waals equation of state can be written as

$$Z = Pv/RT = v/(v-b) - a/(vRT) \tag{7}$$

which was proposed by J. D. van der Waals [25] in 1873. The van der Waals mixing rules will be in the following form:

$$a = \sum_i \sum_j x_i x_j a_{ij}$$
$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{8}$$

From Eqs. (5), the following conformal solution combining rules can be derived:

$$\begin{aligned} a_{ij} &= (1 - k_{ij})\, b_{ij}(a_{ii}a_{jj}/b_{ii}b_{jj})^{1/2} \\ b_{ij} &= (1 - l_{ij})\{(b_{ii}^{1/3} + b_{jj}^{1/3})/2\}^3 \end{aligned} \tag{9}$$

(ii) The Redlich–Kwong equation of state [12] can be written as

$$Z = Pv/RT = v/(v - b) - a/RT^{3/2}(v + b) \tag{10}$$

The conformal solution van der Waals mixing rules can be derived as

$$a = \left\{\sum_i \sum_j x_i x_j a_{ij}^{2/3} b_{ij}^{1/3}\right\}^{3/2} \Bigg/ \left\{\sum_i \sum_j x_i x_j b_{ij}\right\}^{1/2}$$
$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{11}$$

The conformal solution combining rules for a_{ij} and b_{ij}will be the same as Eqs. (9).

(iii) The Peng–Robinson equation of state [18] is in the following form:

$$z = v/(v - b) - a(T)\, v/\{RT[v(v + b) + b(v - b)]\} \tag{12}$$

where

$$a(T) = a(T_c)\{1 + \kappa(1 - T_{r\frac{1}{2}})\}^2$$
$$a(T_c) = 0.45724(RT_c)^2/P_c$$
$$\kappa = 0.37464 + 1.54226\omega - 0.2699\omega^2$$
$$b = 0.0778RT_c/P_c, \qquad \omega = \text{Pitzer's acentric factor}$$

To extend the PR equation of state to mixtures, the following mixing rules are used:

$$a = \sum_i \sum_j x_i x_j a_{ij}(T); \qquad a_{ij}(T) = [a_{ii}(T)\, a_{jj}(T)]^{1/2}[1 - k_{ij}(T)]$$
$$b = \sum_i x_i b_i \tag{13}$$

In order to apply the conformal solution mixing rules for the PR equation of state, thermodynamic variables must be separated from the constants of the equation of state. Then the PR equation of state will be written as the following [8]:

$$Z = Pv/RT = v/(v-b) - \{a/RT + c - 2\sqrt{ac/RT}\}/\{(v+b) + (b/v)(v-b)\} \tag{14}$$

where

$$a = a(T_c)(1+\kappa)^2 \qquad \text{and} \qquad c = a(T_c)\kappa^2/RT_c$$
$$a_c = a(T_c) = 0.4572(RT_c)^2/P_c$$
$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$
$$b = 0.0778RT_c/P_c, \qquad \omega = \text{Pitzer's acentric factor}$$

Then the conformal solution van der Waals mixing rules can be derived as the following [8]:

$$\begin{aligned} a &= \sum_i \sum_j x_i x_j a_{ij} \\ b &= \sum_i \sum_j x_i x_j b_{ij} \\ c &= \sum_i \sum_j x_i x_j c_{ij} \end{aligned} \tag{15}$$

with the following conformal solution combining rules for a_{ij}, b_{ij}, and c_{ij}:

$$\begin{aligned} a_{ij} &= (1-k_{ij})\, b_{ij}(a_{ii}a_{jj}/b_{ii}b_{jj})^{1/2} \\ b_{ij} &= (1-l_{ij})[(b_{ii}^{1/3} + b_{jj}^{1/3})2]^3 \\ c_{ij} &= (1-m_{ij})[(c_{ii}^{1/3} + c_{jj}^{1/3})/2]^3 \end{aligned} \tag{16}$$

The above three representative cubic equations of state will be used to predict solubilities of condensed compounds in supercritical gases. To calculate the solubilities of heavy solutes in compressed gases, the fluid phase equilibrium algorithms are used. Since the chemical potentials are functions of temperature, pressure, and compositions, the equilibrium conditions

$$\mu_i^G(T, P; \{y_i)) = \mu_i^C(T, P; \{x_i\}), \qquad i = 1, 2, \ldots, n \tag{17}$$

where μ_i^G is the chemical potential of component i in the gas phase and μ_i^C is the chemical potential of component i in the condensed (liquid or solid) phase. For gas–liquid equilibrium calculations, the solubilities of the liquid condensed phase in a supercritical gas can be expressed as the following:

$$y_i = x_i \phi_i^{\mathrm{L}} / \phi_i^{\mathrm{G}} \tag{18}$$

where x_i is the composition of component i in the liquid condensed phase, ϕ_i^{L} is the fagacity coefficient of component i in the liquid condensed phase, and ϕ_i^{G} is the fugacity coefficient of component i in the gas phase. For gas–solid equilibrium calculations, the solubilities of the solid condensed phase in a supercritical gas can be expressed as the following [12]:

$$y_i = (P_i^{\mathrm{sat}}/P)(1/\phi_i)\,\phi_i^{\mathrm{sat}} \exp\left\{\int_{P^{\mathrm{sat}}}^{P} (v_i^{\mathrm{solid}}/RT)\,dP\right\} \tag{19}$$

where ϕ_i^{sat} is the fugacity coefficient of the solid condensed phase at saturation pressure P_i^{sat} of pure component i, and ϕ_i is the gas-phase fugacity coefficient at pressure P of component i in the mixture. The vapor pressure of the solid is small, and the fugacity coefficient of the pure solid at saturation pressure is almost unity. Also, one can assume that v_i^{solid} is independent of pressure. Thus Eq. (19) can be converted to the following form [12]:

$$y_i = (P_i^{\mathrm{sat}}/P)(1/\phi_i) \exp\{v_i^{\mathrm{solid}}(P - P_i^{\mathrm{sat}})/RT\} \tag{20}$$

In order to calculate the solubilities for both liquid and solid in supercritical gases, the following expressions of the fugacity coefficient are used:

$$RT \ln \phi_i = \int_v^{\infty} [(\partial P/\partial n_i)_{T,v,n_j} - (RT/V)]\,dV - RT \ln Z \tag{21}$$

For the vdW equation of state, the following expression for the fugacity coefficient can be derived:

$$\begin{aligned} \phi_i = {} & [RT/(v-b)]\,(1/p) \\ & \times \exp\left[\left(-b + 2\sum_j x_j b_{ij}\right)\Big/(v-b) - 2\left(\sum_j x_j a_{ij}\right)\Big/(vRT)\right] \end{aligned} \tag{22}$$

The expression for the fugacity coefficient of the RK equation of state can be written in the following form:

$$\begin{aligned} \ln \phi_i = {} & \ln[v/(v-b)] - \ln Z + \left(2\sum_j x_j b_{ij} - b\right)\Big/(v-b) \\ & + (a/RT^{3/2})\left(-b + 2\sum_j x_j b_{ij}\right)(1/b^2)\{\ln[(v+b)/v] - b/(v+b)\} \\ & - (1/bRT^{3/2})\left(2\sum_j x_j a_{ij}\right)\ln[(v+b)/v] \end{aligned} \tag{23}$$

The expression for the fugacity coefficient of the PR equation of state can be written in the following form:

$$\begin{aligned}\ln \phi_i = & \biggl\{\Bigl(2 \sum_j x_j b_{ij} - b\Bigr)\Big/ b\biggr\}(Z-1) - \ln(Z - B^*) \\ & - (A^*/2\sqrt{2}B^*)\biggl\{(1/\alpha^*)\biggl[\Bigl(2\sum_j x_j a_{ij}\Bigr) + 2RT\sum_j x_j c_{ij} \\ & - \sqrt{RT}\Bigl[2\sqrt{(a/c)}\sum_j x_j c_{ij} + 2\sqrt{(c/a)}\Bigl(\sum_j x_j a_{ij}\Bigr)\Bigr]\biggr] \\ & - \Bigl(2\sum_j x_j b_{ij} - b\Bigr)\biggr\} \ln[(Z + B^* + \sqrt{2}B^*)/(Z + B^* - \sqrt{2}B^*)] \qquad (24)\end{aligned}$$

where

$$\alpha^* = a + cRT - 2\sqrt{(acRT)}$$

$$A^* = \alpha^* P/(RT)^2$$

$$B^* = bP/RT$$

The above equations can be utilized in order to perform phase equilibrium calculations for the purpose of predicting the solubility of condensed solutes in supercritical gases.

3. CALCULATIONS AND RESULTS

Using the van der Waals mixing rules for the three equations of state [van der Waals (vdW), Redlich–Kwong (RK), and Peng-Robinson (PR)] based on the conformal solution theory, the solubilities of heavy liquid in compressed nitrogen and methane are reported in Tables II and III. The solubilities of heavy liquid in compressed gases are calculated by using Eq. (18). According to Tables II and III, predictions of the conformal solution PR equation of state are closer (by one order of magnitude) to the experimental data than those of the RK equation of state, while the predictions by the RK equation of state are closer to the experimental data than the predictions by the vdW equation of state. It is clear that the conformal solution PR equation of state can predict the solubilities of heavy liquid more accurately than the conformal solution vdW and RK equations of state. In Table IV, the numerical values of binary interaction parameters for the different equations of state are reported. The absolute values of vinary interaction parameters (k_{ij}, l_{ij}, and m_{ij}) calculated by the conformal

Table II. Solubilities of Heavy Liquid (*n*-Decane) in Compressed Nitrogen Gas According to the Different Equations of State

			$y_2 \times 10^3$ [a]			
System	T (K)	P (atm)	EXP	vdW	RK	PR
Nitrogen–*n*-decane	323	41.7	0.416	24.93	3.66	0.380
		51.0	0.395	22.70	3.44	0.350
		91.0	0.427	21.90	3.50	0.340
	348	31.5	1.540	48.37	9.82	1.460
		38.0	1.410	42.52	8.82	1.330
	373	87.4	2.700	46.47	13.26	2.400
		100.6	2.710	47.04	13.25	2.330
	398	70.4	6.570	67.65	24.15	5.800
		99.6	6.160	64.78	22.45	5.060

[a] EXP, experimental values; vdW, van der Waals equation of state; RK, Redlich–Kwong equation of state; PR, Peng–Robinson equation of state.

Table III. Solubilities of Heavy Liquid (*n*-Decane) in Compressed Methane Gas According to the Different Equations of State

			$y_2 \times 10^3$ [a]			
System	T (K)	P (atm)	EXP	vdW	RK	PR
Methane–*n*-decane	323	60.1	0.558	17.40	3.440	0.360
		74.1	0.628	17.51	3.700	0.380
		105.2	0.953	23.21	4.990	0.460
	348	88.2	1.710	29.08	8.300	1.110
		107.8	2.190	33.87	9.480	1.190
	373	72.5	3.570	42.37	14.81	2.740
		88.2	3.780	42.72	15.16	2.670
	398	75.4	7.010	67.53	25.81	6.090
		84.8	7.180	101.5	25.71	5.880

[a] EXP, experimental values; vdW, van der Waals equation of state; RK, Redlich–Kwong equation of state; PR, Peng–Robinson equation of state.

Table IV. The Binary Interaction Parameters for Heavy Liquid (*n*-Decane) and Compressed Gas (Nitrogen and Methane) Interaction as Calculated by the Use of Different Equations of State

System	EOS[a]	k_{12}	l_{12}	m_{12}
Nitrogen–*n*-decane	vdW	−5.3548	0.5966	
	RK	−0.3970	0.3244	
	PR	0.2832	−0.0307	0.2395
Methane–*n*-decane	vdW	−3.0356	0.5655	
	RK	−0.2940	0.1645	
	PR	0.1334	−0.0394	0.0444

[a] EOS, equation of state; vdW, van der Waals equation of state; RK, Redlich–Kwong equation of state; PR, Peng–Robinson equation of state.

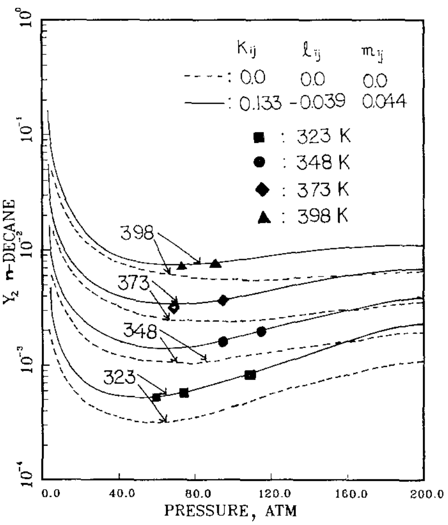


Fig. 3. Solubilities of *n*-decane in compressed methane at different temperatures vs pressures. The filled cricles are the experimental data points [29] which are used to calculate the binary interaction parameters. The solid lines are the results of the conformal solution PR equation of state with the use of the binary interaction parameters. The dashed lines are the results when the binary interation parameters are equal to zero.

solution PR equation of state are smaller than those calculated by the conformal solution vdW and RK equations of state. It should be noted that an accurate theory of mixture will produce interaction parameters which are independent of temperature. The binary interaction parameters are calculated by minimizing the following function, which is defined as follows:

$$F=\left\{\sum_{i}(\mathrm{EXP}^{i}-\mathrm{CAL}^{i})/\mathrm{CAL}^{i}\right]^{2} \qquad (25)$$

where EXP is the experimental value, and CAL is the calculated value.

In Figures 3 and 4, the solid lines are the solubilities of heavy liquid (*n*-decane) in the gas phase along with the binary interaction parameters and the dashed lines are the predictions of liquid solubilities in the gas phase when the binary interaction parameters are set equal to zero. In Figs 4 and 6, the gas solubilities (methane and nitrogen) in the liquid phase are

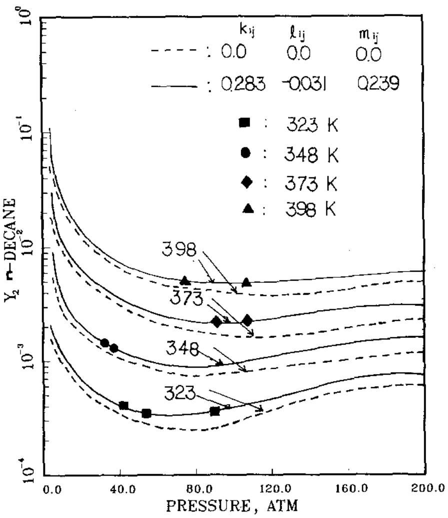


Fig. 4. Solubilities of *n*-decane in compressed nitrogen at different temperatures vs pressures. The filled circles are the experimental data points [29] which are used to calculate the binary interaction parameters. The solid lines are the results of the conformal solution PR equation of state with the use of the binary interaction parameters. The dashed lines are the results when the binary interaction parameters are equal to zero.

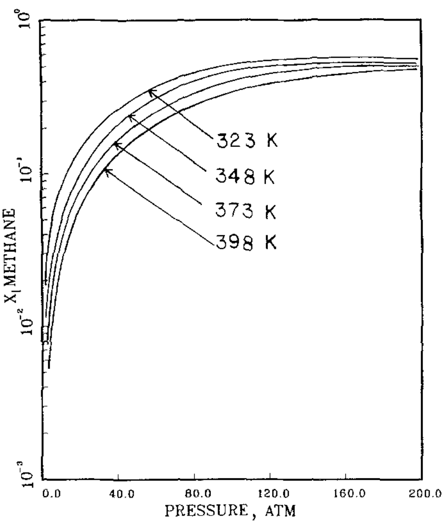


Fig. 5. The gas (methane) solubilities in the liquid phase at different temperatures vs pressures as calculated by the conformal solution Peng–Robinson equation of state with the use of the binary interaction parameters.

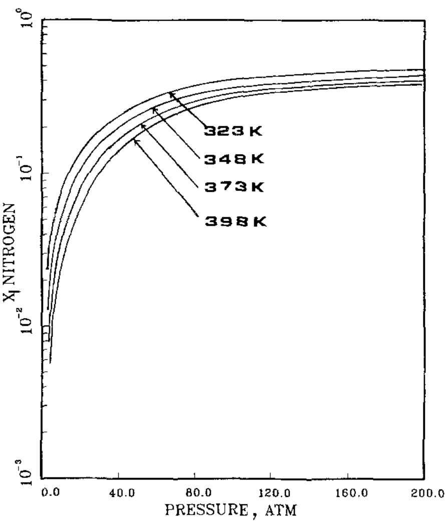


Fig. 6. The gas (nitrogen) solubilities in the liquid phase at different temperatures vs pressures as calculated by the conformal solution Peng–Robinson equation of state with the use of the binary interaction parameters.

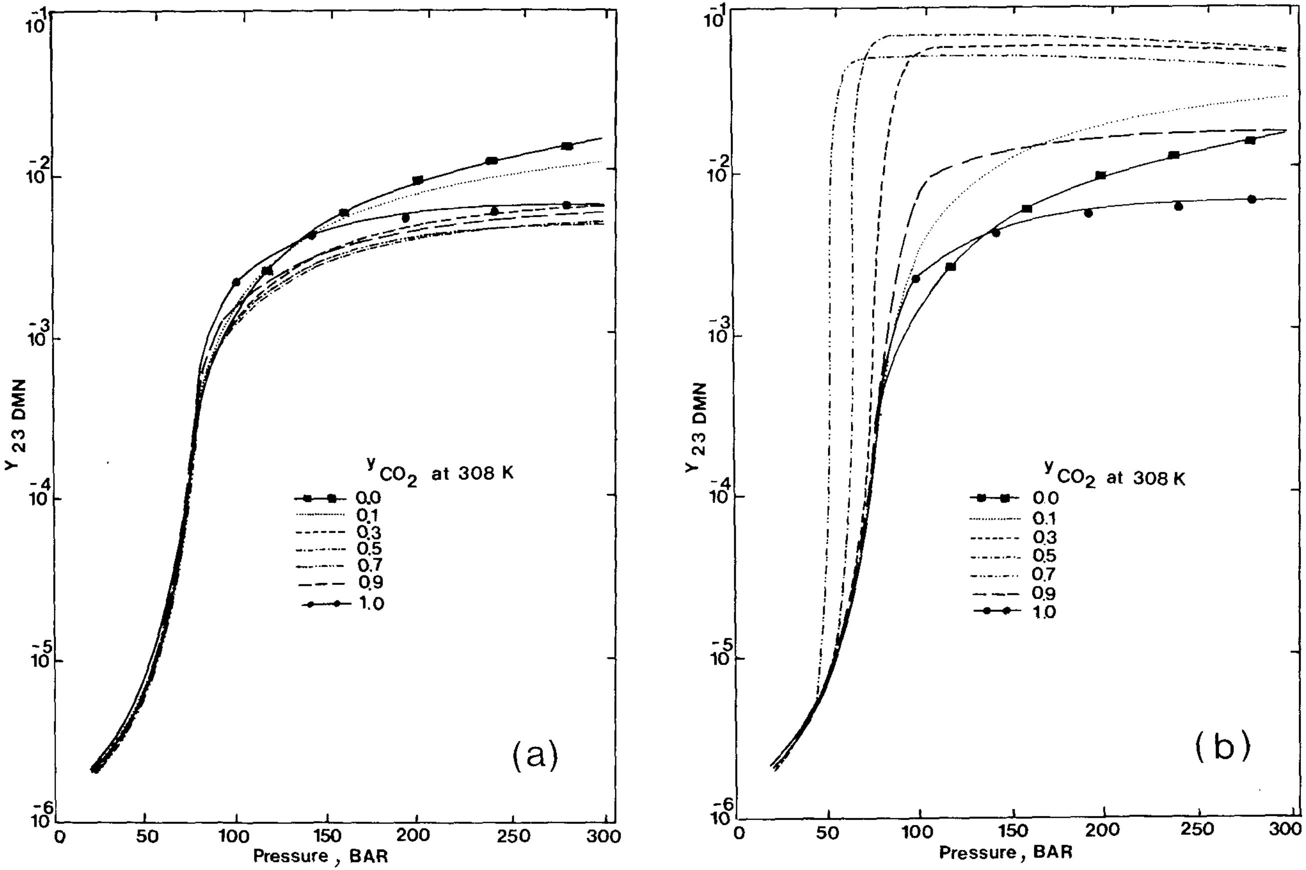


Fig. 7. Solubility of 2,3-dimethyl naphthalene in different mixtures of carbon dioxide and ethylene according to the conformal solution PR equation of state. In a it is assumed that for carbon dioxide and ethylene, $k_{12} = l_{12} = m_{12} = 0$. In b the unlike interaction parameters of carbon dioxide and ethylene are assumed to be nonzero. These parameters are calculated from $CO_2 + C_2H_4$ VLE data [16] and they are shown to be $k_{12} = 0.1829$, $l_{12} = 0.6053$, and $m_{12} = -0.2153$.

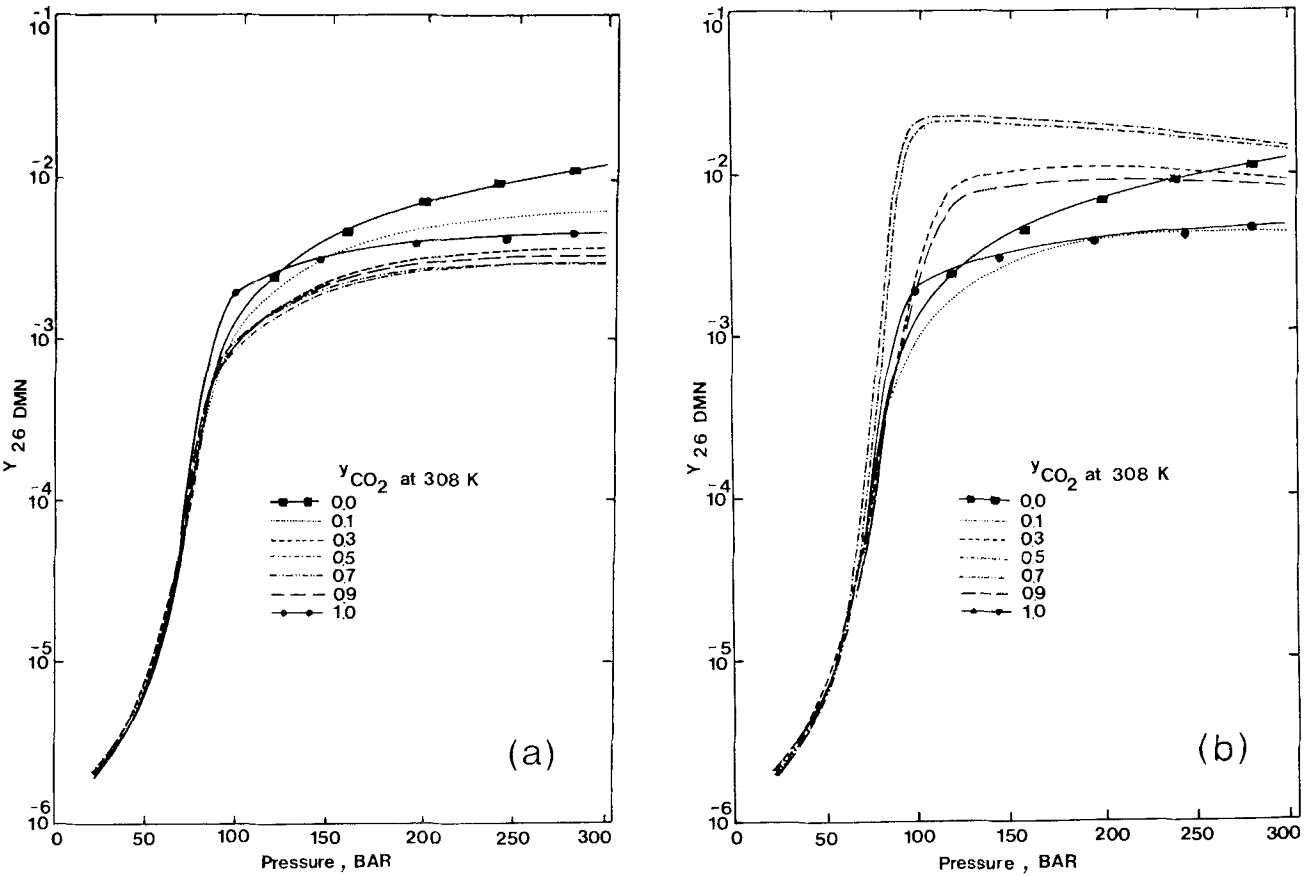


Fig. 8. Solubility of 2,6-dimethyl naphthalene in different mixtures of carbon dioxide and ethylene according to the conformal solution PR equation of state. In a it is assumed that for carbon dioxide and ethylene, $k_{12} = l_{12} = m_{12} = 0$. In b the unlike interaction parameters of carbon dioxide and ethylene are assumed to be nonzero. These parameters are calculated from $CO_2 + C_2H_4$ VLE data [16] and they are the same as those used in Fig. 7.

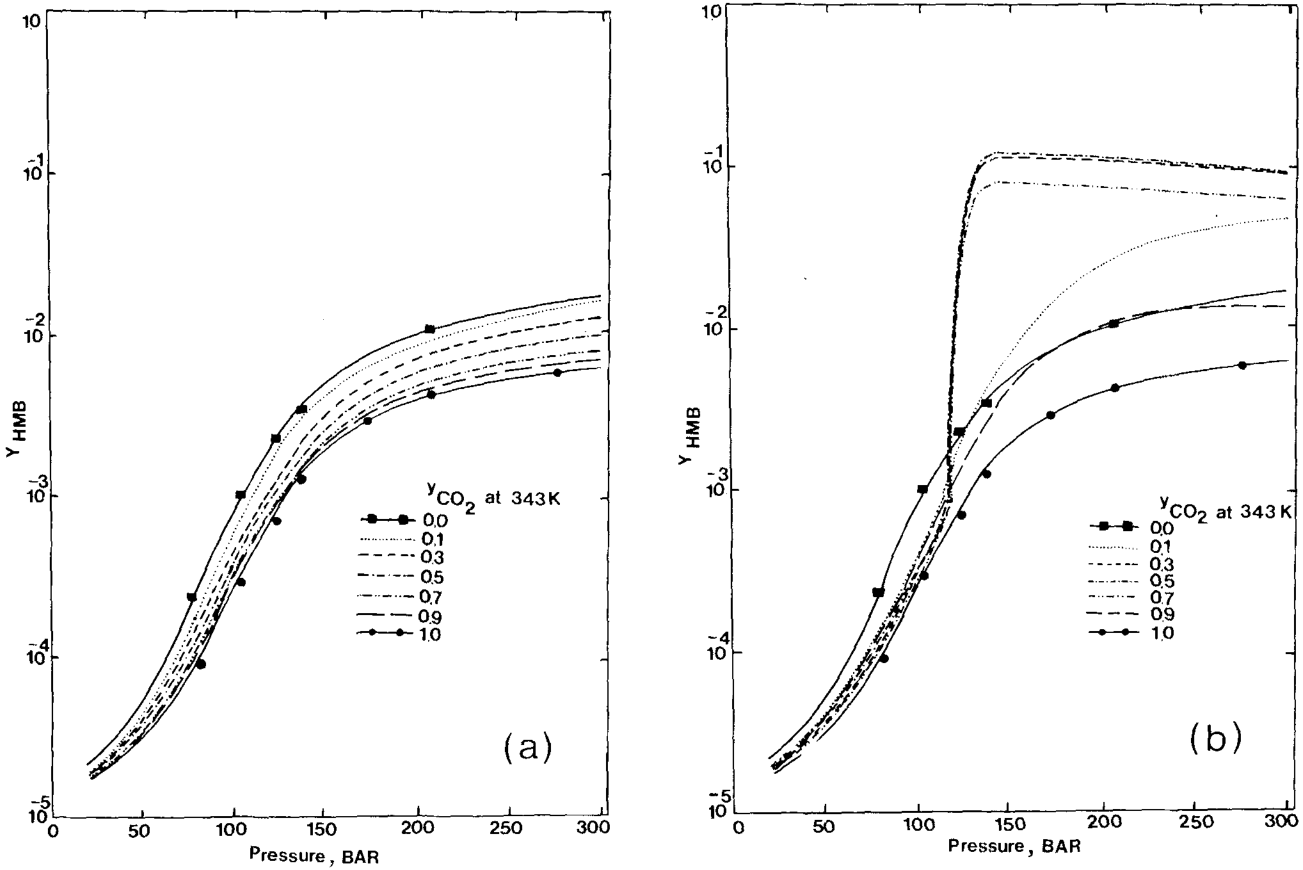


Fig. 9. Solubility of hexamethyl benzene in different mixtures of carbon dioxide and ethylene according to the conformal solution PR equation of state. In a it is assumed that for carbon dioxide and ethylene, $k_{12} = l_{12} = m_{12} = 0$. In b the unlike interaction parameters of carbon dioxide and ethylene are assumed to be nonzero. These parameters are calculated from $CO_2 + C_2H_4$ VLE data [16] and they are the same as those used in Fig. 7.

plotted for different isotherms. The gas solubilities in the liquid phase are decreased as the temperature is increased, while the liquid solubilities in the gas phase are increased as the temperature is increased.

In a previous publication [8] it was demonstrated that the conformal solution PR equation of state is capable of accurately correlating solubilities of solids in supercritical gases. It was also demonstrated that the interaction parameters appearing in the conformal solution PR equation of state are constants and insensitive to the temperature ranges for which experimental data were available. In the present report we utilize the interaction parameters reported earlier [8] in order to study the effect of mixed supercritical solvents on the solubility of solids as reported in Figs. 7–9. In these figures the mixed solvents consist of mixtures of carbon dioxide and ethylene at different compositions in contact with three different solutes. According to these figures an additional important factor to consider in order to predict the solubility of solutes in mixed solvents is the solute–solute interaction parameters.

As demonstrated here, when the solute–solute interaction parameters are ignored, solubility predictions are quite different from those when the correct solute–solute interaction parameters are used. In general, the calculations reported in Figs. 7–9 are indicative of the fact that the

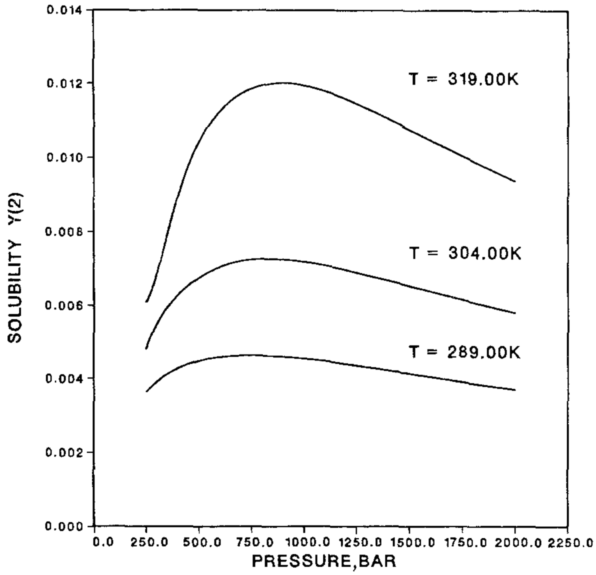


Fig. 10. Demonstration of variation of the solubility of 2,3-DMN in carbon dioxide at supercritical, critical, and subcritical temperatures of carbon dioxide according to the conformal solution PR equation of state.

solubility of a solute in mixed supercritical solvents cannot be linearly correlated with the solubilities in pure solvents and their compositions. In other words, mixed solvents could either enhance the solubility of a solute or reduce it, depending on the molecular interactive nature of the solvents and solute under consideration. This observation introduces a new challenge in the design and operation of supercritical fluid extraction and retrograde condensation systems, which is the necessity of a search for combination of mixed solvents and their composition for the optimum design and operation of such processes.

Experimental observations [30, 32, 33] on a number of solid–gas systems have exhibited a supercritical solubility decay of the solute after a certain system-specific pressure was exceeded. This same phenomenon can be observed using the conformal solution PR equation of state in predicting the behavior of model systems. As can be seen from Figs. 10–13, 2,3-DMN and 2,6-DMN exhibit solubility peaks at temperatures above and below the critical temperature of the solvent, the high-pressure solubility decay being more extreme at temperatures above the critical temperature of the solvent. In the cases where ethylene was used as the solvent,

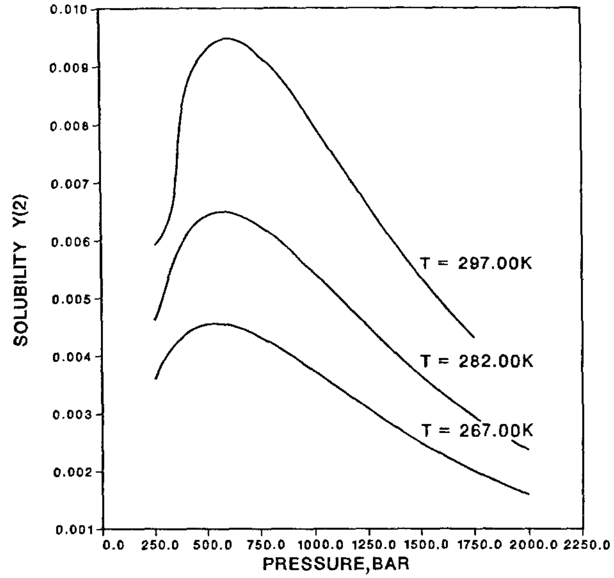


Fig. 11. Demonstration of variation of the solubility of 2,3-DMN in ethylene at supercritical, critical, and subcritical temperatures of ethylene according to the conformal solution PR equation of state. The maxima of solubilities in this case are sharper than in Fig. 10.

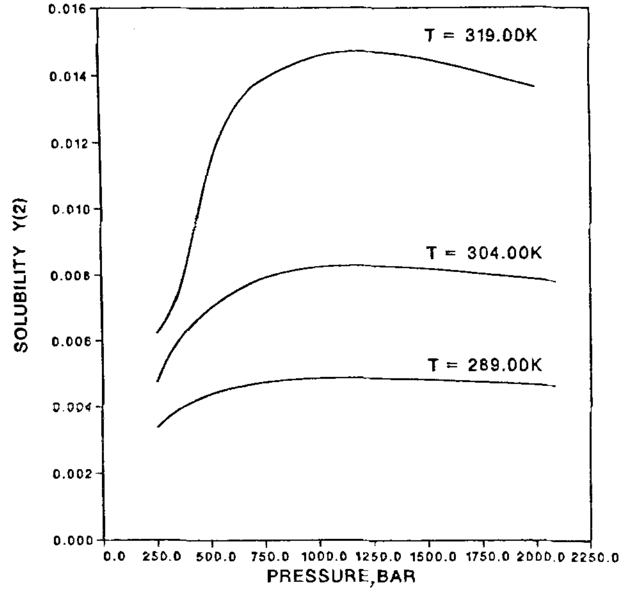


Fig. 12. Demonstration of variation of the solubility of 2,6-DMN in carbon dioxide at supercritical, critical, and subcritical temperatures of carbon dioxide according to the conformal solution PR equation of state.

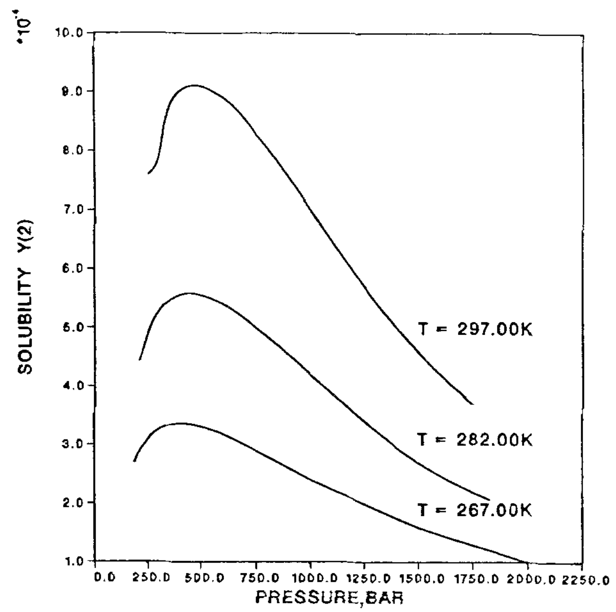


Fig. 13. Demonstration of variation of the solubility of 2,6-DMN in ethylene at supercritical, critical, and subcritical temperatures of ethylene according to the conformal solution PR equation of state. The maxima of solubilities in this case are sharper than in Fig. 12.

a more pronounced solubility peak was generated compared to the carbon dioxide solvent trials.

In the preliminary modeling and calculations reported in this paper we have demonstrated the strength of statistical mechanical approaches for a better understanding of the phenomena of SFC/RC. In addition to experimental measurements there exist a number of theoretically important questions to the answered for the full-scale industrial utilization of the phenomena of SFC/RC in separation processes. These include (i) full understanding of the molecular role of cosolvents and entrainers, (ii) prediction of properties of highly asymmetric mixtures consisting of molecules with large molecular size and shape differences, (iii) incorporation of hydrogen bonding and other association energies in the formulation and calculation of solubilities, and (iv) development of analytic approaches of statistical mechanics for extension of the ranges of prediction to extreme conditions of pressures and/or temperatures.

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REFERENCES

1. W. Byers Brown, *Proc. Roy. Soc. Lond. Ser. A* 240 (1957); *Phil. Trans. Roy. Soc. Lond. Ser. A* 250 (1957).
2. J. F. Ely and J. K. Baker, *A Review of Supercritical Fluid Extraction* (National Bureau of Standards, Boulder, Cola., 1983).
3. J. B. Hannay and J. Hogarth, *Proc. Roy. Soc. Lond.* **A29**:324 (1879).
4. K. P. Johnston, D. H. Ziger, and C. A. Eckert, *Ind. Eng. Chem. Fund.* **21**:191 (1982).
5. J. S. Rowlinson and F. L. Swinton, *Liquid and Liquid Mixtures* (Butterworths, Wolburn, Mass., 1982).
6. D. L. Katz and F. Kurata, *Ind. Eng. Chem.* **32**:817 (1940); D. L. Katz et al., *Handbook of Natural Gas Engineering* (McGraw–Hill, New York, 1959).
7. R. T. Kurnik, S. J. Holla, and R. C. Reid, *J. Chem. Eng. Data* **26**:47 (1981).
8. T. Y. Kwak and G. A. Mansoori, *Chem. Eng. Sci.* **41**:1303 (1986).
9. J. W. Leach, P. S. Chappelear, and T. W. Leland, *AIChE J.* **14**:568 (1968); *Proc. Am. Petrol. Inst. Sect. III* **46**:223 (1966); T. W. Leland, J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.* **64**:1447 (1968).
10. G. A. Mansoori and T. S. Jiang, Asphaltene Deposition and Its Role in Miscible Flood EOR Processes, Proceedings of the 3rd European Meeting on Improved Oil Recovery (Rome, Italy, 1985).

11. G. A. Mansoori and T. W. Leland, *J. Chem. Soc. Faraday Trans. II* **68**:320 (1972); J. B. Gonsolves and T. W. Leland, *AIChE J.* **24**:279 (1978).
12. G. A. Mansoori and J. F. Ely, *J. Chem. Phys.* **82**:406 (1985).
13. G. A. Mansoori and J. F. Ely, *Fluid Phase Equil.* **22**:253 (1985).
14. G. A. Mansoori, Mixing Rules for Cubic Equations of State, Symposium on Equations of State, ACS National Meeting, Miami, Fla. (April 28–May 3, 1985).
15. A. R. Massih and G. A. Mansoori, *Fluid Phase Equil.* **10**:57 (1983).
16. J. Mollerup, *J. Chem. Soc. Faraday Trans. I* **71**:2351 (1975).
17. M. E. Paulaitis et al., *Chemical Engineering at Supercritical Fluid Conditions* (Ann Arbor Sci. Publ., Ann Arbor, Mich., 1982).
18. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem . Fund.* **15**:59 (1976).
19. J. M. Prausnitz, *Molecular Thermodynamics of Fluid Phase Equilibria* (Prentice–Hall, Englewood Cliffs, N.J., 1969).
20. R. L. Scott, *J. Chem. Phys.* **25**:193 (1956).
21. R. Simon, A. Rosman, and E. Zana, *SPE J.* 20 (1978).
22. F. I. Stalkup, Miscible Diplacement, SPE Monograph, Soc. Petrol. Eng. AIME, Dallas, Tex. (June 1983).
23. K. Stephan and K. H. Schaber, *Sep. Sci. Technol.* **17**:235 (1982).
24. W. R. Streett, Phase Equilibria in Fluid and Solid Mixtures at High Pressures, Annual AIChE Meeting, New Orleans, LA (1981).
25. J. D. van der Waals, Ph.D. thesis (Leiden, 1873).
26. P. H. Van Konyenburg and R. L. Scott, *Phil. Trans. Roy. Soc. Lond.* **298**:495 (1980); R. L. Scott and P. H. Van Konyenburg, *Disc. Faraday Soc.* **49**:87 (1970).
27. D. F. Williams, *Chem . Eng. Sci.* **36**:1769 (1981).
28. API Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds, Vols. II and IV* (Thermodynamic Research Center, Tex., 1975).
29. S. G. D'Avilla, B. K. Kaul, and J. M. Prausnitz, *J. Chem. Eng. Data* **21**:4 (1976).
30. G. Brunner and S. Peter, *Separat. Sci. Technol.* **17**:199 (1982).
31. W. Fogel and J. P. Arlie, *Rev. Inst. Franc. Petrole* **39**:617 (1984).
32. A. B. Caragay, *Perfumer Flavor.* **6**(4):43 (1982).
33. D. D. Christian, J. P. Friedrich, E. B. Bagley, and G. E. Inglett, *Recent Progress in Chemistry and Technology* (Academic Press, New York, 1982).