Phase Equilibrium Study for the Separation of Solid Components Using Supercritical Carbon Dioxide

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Abstract: The equilibrium mole fraction solubility of low volatile solid components (naphthalene and phenanthrene) in supercritical pure carbon dioxide was studied at temperature range (308.15-333.15 K) and pressures up to 200 bars. In the present study a measure of the effect of temperature and pressure were considered in the extraction process using supercritical carbon dioxide. The experiments were carried out using a designed apparatus similar to that used by King *et al.*, [1]. In this apparatus, the extracted gas (carbon dioxide) was re-circulated continuously over the component to be extracted *via* a sample bomb till equilibrium is reached. The sample bomb is then isolated and its contents were analyzed.

The results of analysis showed that the solubility of naphthalene and phenanthrene expressed in mole fraction depend strongly upon the pressure (density) of the supercritical carbon above the critical density.

The obtained laboratory data are correlated with three cubic equations of state, Redlich-Kwong (RK), Soave-Redlich-Kwong (SRK), and Peng-Robinson (PR). Comparison of experimental phase equilibrium data with the results predicted by the equations of state shows good representation.

Keywords: High pressure gas-solid equilibrium, binary systems, carbon dioxide, naphthalene, phenanthrene, cubic equations of state.

INTRODUCTION

Extraction with supercritical solvent is an alternative separation process when other methods such as distillation, absorption or conventional liquid-liquid extraction are impractical or impossible. In particular, thermal processes cannot be applied in presence of thermo-labile compounds, which can generate degradation products. Further-more extraction with conventional solvent is not suitable in the field of pharmaceutical and food industries where the concentration of residual solvent and impurities in the final product must be restrictively low. In this contest supercritical fluid processes are attractive since this alternative method requires low operational temperature (around 313K) and complete solvent separation can be achieved through a simple expansion of the final product [2].

Carbon dioxide is the most commonly used as SCF, due primarily to its low critical parameters (T_c = 304.25K, P_c= 73.8 bars), low cost and non-toxicity. However, several other SCFs have been used in both commercial and development processes. Other features make carbon dioxide CO_2 the ideal solvent for supercritical fluid extraction (SFE) that it is not toxic and not inflammable, it can be obtained in large quantities with high purity and at low cost, it is easy to separate (gaseous at atmospheric pressure), and it does not damage the solutes or the matrix of the product [3].

The solvent strength of the SCF is a function of its density, and the density is a function of temperature and pressure. Hence with controlling temperature and pressure, solvent strength of the SCF can be controlled [4]. The main advantage of SCF over liquid solvents arises from this concept.

As a separation technology, SFE has considerable potential for commercial utilization. Although equipment investment costs are high, this is not the factor limiting widespread commercialization. The limitation is the lack of knowledge of the phase behavior of multicomponent mixtures near their critical points. This lack of knowledge prevents the optimal design of supercritical solvent systems, which in turn keeps the cost high [5].

Among all the wide variety of interesting studies that can emerge from this technology, all of studies focused on three main concerns to obtain a better insight into SCF:

1. The computational study of high-pressure and multiphase equilibrium and the importance of mathematical validation of the number of phases and composition.

2. The experimental and modeling of solubilities of solutes in SCF.

3. The design and optimization of supercritical fluid extraction (SFE) processes [6].

The present work will take the care of point (1) and (2) only, and will measure solubilites of naphthalene and phenanthrene as solid components in supercritical CO_2 solvent at constant temperature and different high pressures and try to correlate the experimental solubilities of solid solute with cubic equations of state using van der Waals mixing rules.

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LITERATURE REVIEW

The experimental results of naphthalene solubility in SCF's slowed until the late 1940s. But in 1948, a study of the solubility and phase behavior of naphthalene dissolved in supercritical ethylene was reported by Diepen and Scheffer [7].

Francis [8] presented an extensive, quantitative study on the solvent properties of liquid carbon dioxide with hundreds of compounds. He was primarily interested in the phase behavior of ternary systems containing liquid carbon dioxide. He collected data for 464 ternary phase diagrams and determined the solubilities of 261 compounds in near-critical liquid carbon dioxide. Although Francis studied solubility behavior (at conditions approximately 298.15K and 65.5 bar), his results are very general.

McHugh & Paulaitis [9] measured the solid solubility of naphthalene and biphenyl in supercritical carbon dioxide at various isotherms above 304K -the critical temperature of carbon dioxide- and over a range of pressures from 81.1 to 506.7 bars.

Kurink et al. [10] obtained solubility data for five different solids (including naphthalene and phenanthrene) in both supercritical carbon dioxide and supercritical ethylene by using one-pass flow system at the temperature range (308-338K) and the pressure range (80-280 bar). The data obtained correlated by using thermodynamic relationships and an equation of state.

Johnston et al. [11] presented new data for the solubility of several nonpolar hydrocarbon solids (included naphthalene and phenanthrene) in supercritical ethylene, ethane and carbon dioxide by using the same technique for Johnston and Eckert [12]. The data presented with other data reported previously have been correlated by perturbed hard-sphere equations of state that do not require the use of critical properties.

The solubility data for α-pinene, cis-verbenol and naphthalene in carbon dioxide have been measured at the temperatures from 313.15K to 328.15K and pressures from 50 bar to 120 bar by using a dynamic flow apparatus and they have been correlated using a compressed gas model with the Peng-Robinson equation of state (PR-EOS) and an empirical equations based on the dependence of the concentration of solute on the density of pure solvent by Richter and Sovova' [13].

Sauceau et al. [14] measured solubilities of naphthalene in supercritical CO_2 in the pressure range 80-300 bar along the isotherm 308.15 K, then the solubility data are correlated using the Chrastil model.

Hartono et al. [15] used six different cubic equations of state to predict the solubility of solids and they shown that the Mohsen-Nia-Moddaress-Mansoori (MMM) equation is more accurate than five of the other equations.

Unlu [16] and Baskaya [17] measured the solubility of naphthalene in supercritical CO_2 at 308 and 318 K as a calibration of the phase equilibrium analyzer system and compared their results with the literature.

Karim and Abdul Khader [18] studied the phase equilibria modeling for separation of solid mixtures by supercritical CO_2 on Excel program using PR-EOS.

Ajchariyapagorn et al. [19] presented a method to estimate the solubility of solid solutes in supercritical fluids when only the molecule structure is known. They used group contribution methods to estimate pure component properties, equations of state then used to estimate the PVT behavior of the solvent and the fugacity coefficient of solute in the solute-solvent mixture.

The solubility of triclosan, an anti-acne agent measured in supercritical carbon dioxide with a variable volume view cell at 313.15, 323.15, and 333.15 K and at pressures between 100 and 400 bars by Shin and Kim [20]. Then the data of triclosan solubility in supercritical carbon dioxide correlated using the quasi-chemical nonrandom lattice fluid equation of state.

Karim [21] studied the thermodynamic modeling of solubility of C. I. disperse orange 30 (O30) dye as a solid component in supercritical CO_2 using Peng-Robenson equation of state (PR-EOS). The sensitivity of critical properties in the calculations was also studied. He proved that the choice of the technique to calculate thermodynamic properties is very important for obtaining good results in the phase equilibrium calculations.

Karim and Mutlag [22] modeled the experimental data obtained from literatures for the separation of phenanthrene by pure supercritical CO_2 and supercritical CO_2 entrained with n-pentane as a liquid solvent by using two techniques, Peng-Robinson equation of state (PR- EOS) and Artificial Neural Networks (ANN).

THERMODYNAMIC MODELING

The calculations of solid-fluid equilibrium at high pressure are important in the modeling and design of processes that use SCFs to selectively extract solid solutes [23].

The phase behavior of solutes in SCF is an important aspect, which is often overlooked in the solubility determinations. In the presence of the solute, the vapor pressure curve for pure CO_2 is shifted ending in a critical end point. Also, solid solutes when in contact with supercritical CO_2 can exhibit complex phase behavior such as depression in melting point resulting in multiple phases. This depression in melting point can considerably influence the determination of solid solubility. In addition, density inversion may occur and lead to erroneous solubility data. This emphasizes the need for checking the phase equilibrium when the solid solubility data is measured [24,25].

The knowledge of phase behavior of solutes of interest under the SCF conditions is also essential for the development of any SCF process. Despite its importance there is very limited data on the phase behavior of solid solutes in supercritical CO_2, which is particularly true for multicomponent systems. The reasons for lack of phase behavior data can be attributed to the fact that specialized equipment is required and the experiments are generally tedious and time consuming [25].

Many models for supercritical-phase equilibrium treat the SCF phase as a dense gas and use an equation of state to calculate the fugacity of the solute in the fluid phase. The results of these models are frequently very sensitive to the interaction energies and size factors, necessitating the need

to develop improved mixing rules to estimate the mixture size and energy parameters needed in the equation of state.

Cubic equations of state are exceedingly simple, have been remarkably successful in modeling SCF-phase behavior, and are probably the most widely used in analyzing experimental data.

Cubic equations of state can take different forms from ideal gas law to more complicated forms. More complicated equations usually give more accurate results but only at the expense of being more computationally complex. For this reason it is often preferred to work with simpler EOS, which still gives satisfactory results.

In the present work, the RK, SRK, and PR-EOS were chosen to model the high-pressure phase behavior that are developed first for pure component, and then extended to mixtures through the use of mixing rules for combining the pure component parameters. For the mixture, the conventional van der Waals mixing rules were used:

$$a_m = \sum_i^n \sum_j^n y_i y_j a_{ij} \tag{1}$$

$$b_m = \sum_i^n y_i b_i \tag{2}$$

where,

$$a_{ij} = \left(a_i a_j\right)^{0.5}\left(1 - k_{ij}\right) \tag{3}$$

where a_i and b_i are calculated using the critical pressure P_c, critical temperature T_c and acentric factor ω for each component. The physical properties of the pure components used in the present work are summarized in Table (**1**). In equation (3), $\boldsymbol{k_{ij}}$ is the binary interaction parameter, which has a non-zero value.

Solid - Fluid Phase Equilibrium

Solid solubility in SCF refers to its composition in the vapor phase. The solids of interest in most SCF processes have low volatility and differ greatly from the SCF in chemical nature. In these systems the phase behavior is complex, especially if multiple solutes are present. The limiting case of a binary system consisting of single solid in a SCF offers a basis for understanding the phase behavior in multicomponent systems [25].

The most important application of the equation of state approach lies in computing solubilities of relatively nonvolatile solids in supercritical fluids. To analyze this phenomenon, it will start with the equality of the species fugacities in each phase. However, since the fluid (liquid, gas, or supercritical fluid) is not present in the solid (or it contains a neg-

ligible amount), two simplifications arise. First, the equilibrium criterion applies only to the solid solute, which it is denoted by the subscript i, and second; the solid phase fugacity of the solute is that of the pure solid. Thus a single equilibrium relation will be presented as:

$$f_i^S(T,P) = f_i^{SCF}(T,P,y_i) \tag{4}$$

where the superscript **S** and **SCF** refer to the pure solid and supercritical fluid phases, respectively, then f_i^{SCF} can be expressed as:

$$f_i^{SCF} = \phi_i^{SCF} y_i P \tag{5}$$

where (y_i) is the mole fraction of solid in the gas phase, ϕ_i^{SCF} is the gas phase fugacity coefficient, f_i^S is the fugacity of solid and it has pressure units.

For each component (i) in the fluid phase (vapor, liquid phase or supercritical state) [26]:

$$\ln\phi_i = \frac{1}{RT}\int_{v^v}^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,v,n_j} - \frac{RT}{\underline{V}}\right]d\underline{V} - \ln Z \tag{6}$$

where $\underline{V}$ is the total system volume, n_i and n_j are the number of moles of components i and j respectively.

When the cubic equation of state (RK, SRK, or PR) is introduced into Eq. (6) using mixing rules, given by Eqs. (1) and (2), the fugacity coefficient is obtained.

Because the solid phase is normally considered a pure solid (i.e. the SCF solvent does not dissolve in the solid), the fugacity f_i^S is,

$$f_i^s = P_i^{sub}(T)\phi_i^{sub}(T,P_i^{sub})\exp\left[\int_{P_i^{sub}}^{P}\left(\frac{v_i^s}{RT}\right)dP\right] \tag{7}$$

where $P_i^{sub}(T)$ is the sublimation or vapor pressure of the pure solid at the system temperature, v_i^s the molar volume of the pure solid and is independent of pressure, $\phi_i^{sub}(T, P_i^{sub})$ is the fugacity coefficient at T and P_i^{sub} to be assumed unity, and the exponential term is the Poynting factor correction for the fugacity of the pure solid. Therefore, combining Eqs. (5) and (7) for unity $\phi_i^{sub}(T, P_i^{sub})$, the mole fraction solubility of a heavy nonvolatile solid in the SCF solvent phase now becomes,

$$y_i = \frac{P_i^{sub}(T)\exp\left[\dfrac{v_i^s(P - P_i^{sub})}{RT}\right]}{\phi_i^{SCF}P} = \frac{P_i^{sub}(T)}{P}E \tag{8}$$

where,

Table 1. The Physical Properties of Components Studied [17]

Component	v^s (lit./mol)	ω	P_c (bar)	T_c (K)
Carbon dioxide	-	0.2250	73.80	304.10
Naphthalene	0.1114	0.3030	40.50	748.40
Phenanthrene	0.1820	0.4396	28.97	878.78

$$E = \frac{\exp\left[\dfrac{\upsilon_i^s(P - P_i^{sub})}{RT}\right]}{\phi_i^{SCF}} \qquad (9)$$

E is called *enhancement factor* and generally greater than unity. The most significant quantity in this factor is ϕ_i^{SCF}. Especially at low temperatures, E can exceed 10^3 or more because of ϕ_i^{SCF}.

The partial molar volume of the solid components at all pressures and temperatures is assumed equal to its molar volume at atmospheric pressure and 298K, and this will be closer to the truth [27].

The vapor pressures of solid components studied calculated by the following equation:

$$\ln(P^{sub}) = \alpha + \frac{\beta}{T} \qquad (10)$$

where P^{sub} in N/m^2, T in K, and α and β are constants and shown in Table (**2**).

Table 2. The Constants of Eq. [10, 28]

Solid Component	α	β
Naphthalene	31.5997	-8711.7396
Phenanthrene	31.8320	-10715.3350

EXPERIMENTAL

The experimental apparatus and procedures used in the present work are similar to those of King *et al.* [1] and Kassim *et al.* [29] and it is described in details by Karim [28] and are summarized briefly below.

A schematic flow diagram for the equipment is given in Fig. (**1**). The apparatus consists essentially of the following parts, 1. The equilibrium cell, 2. The vapor sampling bomb, 3. The circulation pump (driven by compressed air from a compressor) which recirculates the extracting phase through the equilibrium cell and sampling bomb, 4. The sampling unit, consisting of two glass receivers, an expansion vessel and vacuum system, 5. Mercury pump which uses to increase the pressure of the carbon dioxide gas and in pressure vessel, 6. Valves and connecting tubing.

The equilibrium cell was constructed of stainless steel and was supplied by Ruska Co. It has a volumetric capacity of the equilibrium cell was about 1000cm³ and is designed to operate at pressured up to about 300 bar and temperatures up to 200°C and is shown in Fig. (**2**). The vapor sampling bomb is the high pressure part of the sampling system; it was constructed of stainless steel and supplied by Ruska Co. The vapor sampling bomb has a capacity of 25 cm³ and is designed for a maximum working pressure of 800 bar and temperatures up to 200°C. The equilibrium cell, sampling bomb, circulation pump (produced by Haskel Eng. Supply Co. Model MCP-188-10000 psi), and a large part of the connecting pipe work are housed inside an air bath maintained at a uniform temperature to within about ± 0.1°C of the required

temperature. Air bath is an insulating box has the dimensions (120cm x 50cm x 130cm).

The air bath temperature was controlled by a thyristor controller, and heat was provided by 1KW element. Heating and air circulation within the bath were accomplished using a combined heater-extractor fan unit was installed in the above of the one of the sides of the bath. The boundaries of the air bath are shown as a broken line as in Fig. (**1**).

Two Heise pressure gauges (0 - 300 bar) in increments of 0.5 bar were connected to the recycle line immediately above the equilibrium cell and the vapor sampling bomb, as shown in Fig. (**1**).

The piping in the high pressure part of the apparatus is of stainless steel, though copper piping is used for the compressed air line leading to the circulation pump, and plastic tubing is used to connect the manometer to the expansion system.

The pumping rate of the circulation pump was controlled by regulating the compressed air supply using a regulator valve.

The expansion system is that part of the apparatus which contains the contents of the vapor sampling bomb. The greater part of the volume of the system is that of the expansion vessel though the glass receiving vessels, which were used to collect the heavy component; and the connecting tubing contribute to it. The expansion vessel is a bottle and it is placed in a wooden box for insulating and has an approximate capacity of 34.5 liter and the exact volume of the expansion system was 35.01 liter.

The solid component was inserted into the lower part of the knit-mesh cylinder and was covered with a layer of knit-mesh packing to prevent the solid particles from being carried over in the extracted stream. The knit-mesh cylinder containing the solid was inserted into the equilibrium cell and the cover was closed.

The apparatus was then evacuated to remove traces of air by using a rotary vacuum pump. The carbon dioxide may be forced in the system at point b. It is supplied from a cylinder and its pressure may be raised, if required, using the mercury injection pump (Ruska Type). The inlet valve is connected to the gas cylinder *via* a filter with a 15 micron mesh to prevent dust from the gas cylinder entering the apparatus. The valves E, F, and C were shut. Gas was then recirculated through the equilibrium cell and vapor sampling bomb for a period of at least 15 minutes. It was found that, if there was no leak in the equipment, the pressure registered by the gauge become steady by the end of the pumping period suggesting that equilibrium had been achieved (subsequent tests described verified that equilibrium was virtually complete after 10 minutes pumping [29]. The sampling bomb was then valve off and the composition of the vapor sample was determined.

The vapor sampling unit consists of an expansion vessel which is initially evacuated and the pressure in which is measured using a mercury manometer, and two glass collecting vessels. In order to determine the amounts of the extract and extractant present, the contents of the vapor sampling bomb are allowed to flow very gently into the expansion system *via* the collecting vessels. The number of moles (and hence the weight) of the light component is calculated from
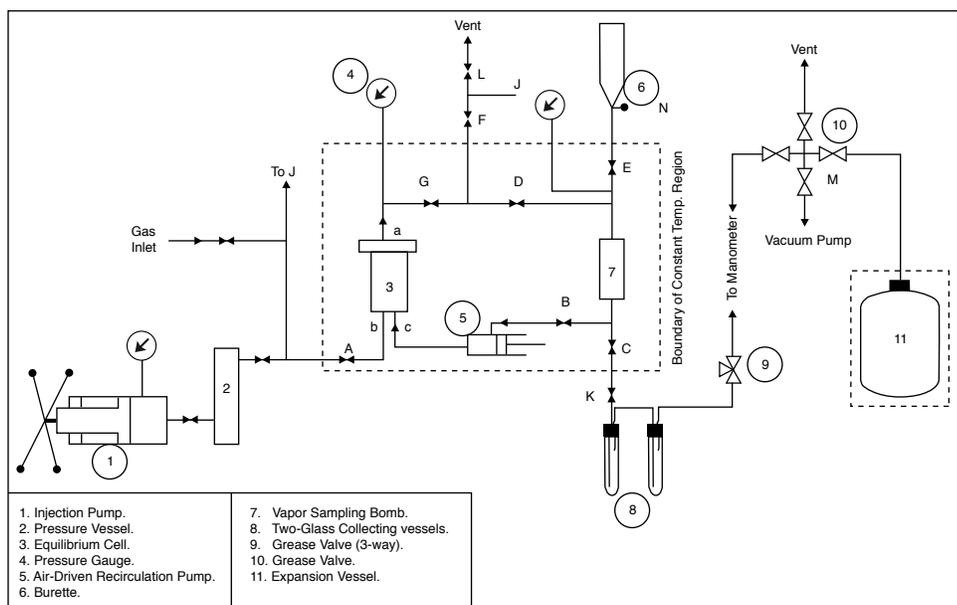
Fig. (1). Layout of equipment for equilibrium gas compositions measurements over solid phase.

the rise in pressure in the expansion system and the weight of extract is determined by transferring this to the glass collecting vessels and then weighing these. Some extract collects directly in these vessels during the expansion process. Much is however left behind in the vapor sampling bomb and lines leading from this to the collecting vessels. This is washed into the vessel using a suitable volatile liquid solvent, which is subsequently evaporated off.

RESULTS AND DISCUSSION

About 50 g of naphthalene was placed in a knit-mesh cylinder. This cylinder was placed in the equilibrium cell as shown in Fig. (**2**). The contents were contacted with recirculated compressed carbon dioxide at temperature 308.15 K and pressures up to 120 bar to insure that the apparatus would provide accurate and reliable equilibrium solubilities. The most important proof test was to compare the measured values of naphthalene solubility with those of McHugh & Paulaitis [9]. Three equilibrium vapor samples were isolated in the vapor sampling bomb. The extract was washed into the glass collecting vessels shown in Fig. (**1**) with n-pentane solvent. The n-pentane was then evaporated off in a vacuum oven at temperature 303.15 K and pressure of 20 torr. The amount of extract in each sample was determined by weighing. The equilibrium solubilities (y) are compared with McHugh & Paulaitis [9] data, the average deviation is only 4.14%. The results are shown in Table (**3**).

The mole fraction solubilities of naphthalene and phenanthrene are measured at the temperature range of (308.15-323.15 K) below the melting points of naphthalene (353.15 K) and phenanthrene (373.75 K) to keep the naphthalene and phenanthrene in solid phase and the pressures up to 200 bar as shown in Fig. (**3**) and Fig. (**4**) with those from literature. It may be seen that these results agree well with those obtained by McHugh & Paulaitis [9], Richter & Sovova [13], Unlu [16], Baskaya [17], King *et al.* [1], and Lim *et al.* [30] for the CO_2-naphthalene system and Kurink *et al.* [10], Johnston *et al.* [11] and Dobbs *et al.* [31] for the CO_2-phenanthrene system.

The 308.15 K isotherm is characteristic of solid solubility behavior at temperatures near the critical temperature of the supercritical carbon dioxide solvent. At this temperature, large changes in solubility occur for relatively small changes in pressure around the critical pressure of the carbon dioxide solvent; however, the maximum solubility at elevated pressures comparatively modest, in this case, the naphthalene mole fraction approaches 0.016 and for phenanthrene approaches 0.0014. The 313.15 K, 318.15 K and 323.15 K isotherms are exhibit essentially the same behavior, the changes in solubility with pressure near the critical point of carbon dioxide are somewhat less dramatic, but the maximum solubility at elevated pressures is greater than that at 308.15 K.
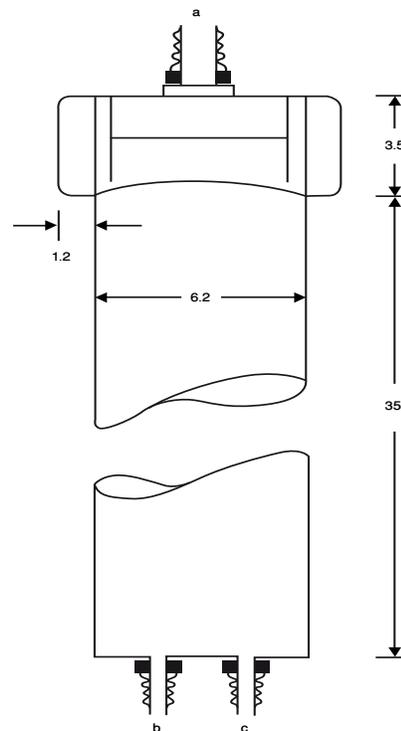
Fig. (2). High pressure cell (all dimensions in cm).

Table 3.   Comparison of Test Data with Those of McHugh & Paulaitis [9] for CO$_2$-naphthalene System at Temperature 308.15 K

Pressure (bar)	Mass of naphthalene collected (gm)	Mole fraction of naphthalene (y x 10^3)	
		Present work	McHugh & Paulaitis
90	0.5161	7.9220	8.13
100	0.6822	9.8434	9.95
120	0.8389	11.3190	12.41
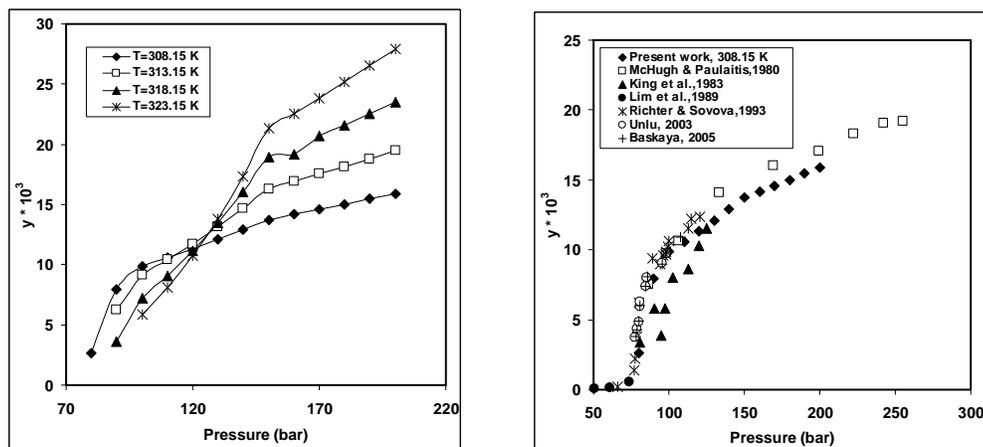
Fig. (3). The mole fraction solubility (y) of naphthalene in supercritical CO$_2$ as a function of pressure at temperatures studied.
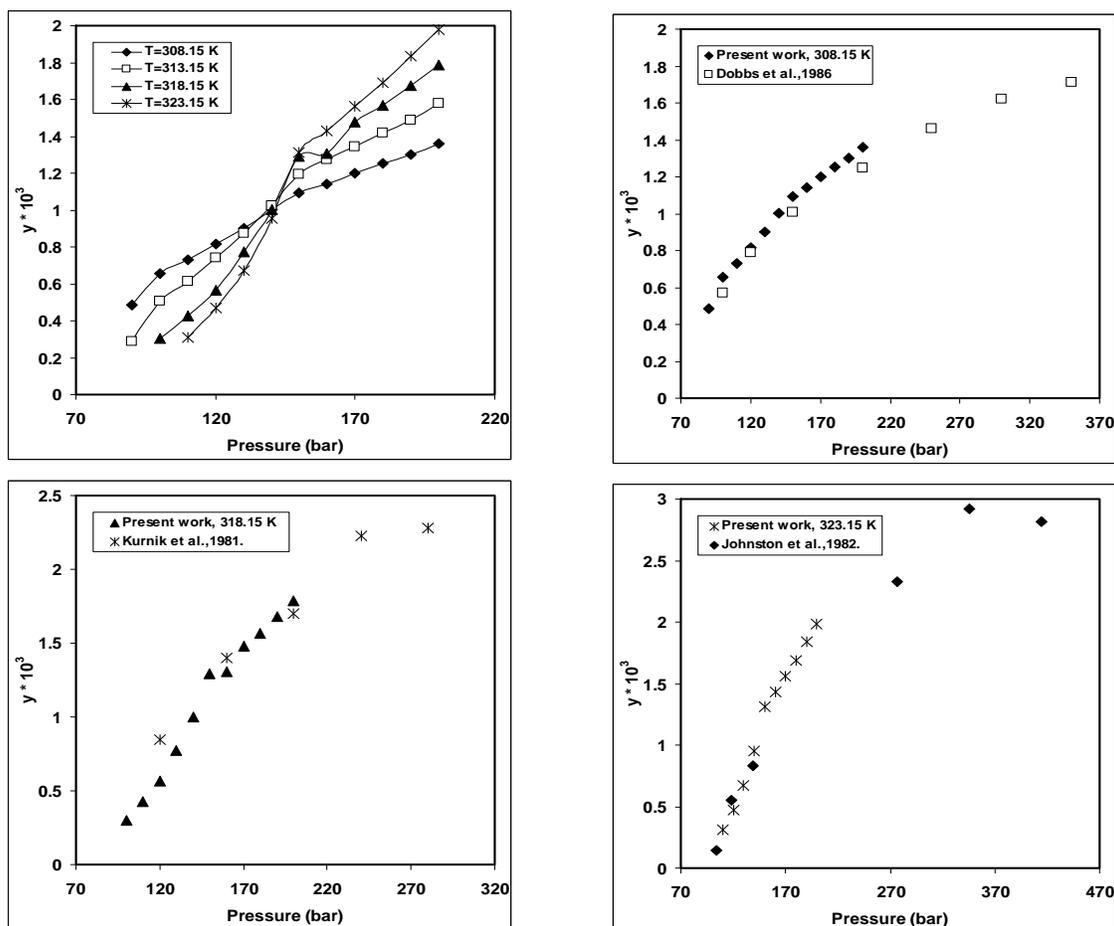
Fig. (4). The mole fraction solubility (y) of phenanthrene in supercritical CO$_2$ as a function of pressure at temperatures studied.

It is clear that the solubility of phenanthrene in super-critical carbon dioxide is less than that for naphthalene at the same conditions, because partially, the vapor pressure of naphthalene is higher than that of phenanthrene at a given temperature.

The effects of temperature and pressure on the solubility of naphthalene and phenanthrene in compressed carbon dioxide are shown in Fig. (**5**). The solubility versus temperature isobars has positive slopes in the high pressure region, and the negative slope in the low pressure regions. This is due to the two competing effects of temperature on the vapor pressure of the solute and the density of the fluid. The density is more sensitive to temperature near the critical pressure than at higher pressures. At these near-critical pressures, this density decrease with increasing temperatures dominates the effect on vapor pressure leading to negatively sloped isobars. At the higher pressure, the dominate temperature effect is on the vapor pressure giving positively sloped isobars.

When discussing the solubilities of solid components in compressed gases it is sometimes convenient to work in terms of the enhancement factor (E). This is the enhancement of the actual mole fraction solubility of the solid component (y_i) over the "ideal" value (P_2^{sub} / P). The enhance-

ment factor for naphthalene and phenanthrene contacted with carbon dioxide as a function of the density of pure carbon dioxide under the given conditions shown graphically in Fig. (**6**). The relationship between log (E) and density is linear over the range studied.

It may be seen that the enhancement factor of phenanthrene is higher than that of naphthalene under the same conditions, because of the vapor pressure of naphthalene is higher than the vapor pressure of phenanthrene at a given temperature though the actual solubilities of phenanthrene are lower than those for naphthalene.

In general, the extraction of solid components depends strongly upon the density of the extracting fluid (carbon dioxide) and only becomes appreciable when the critical density is exceeded.

A major goal of the present work is to predict the experimental data by using physical properties of the pure components with adjustable parameter. Cubic equations of state along with the mixing rules given by equations (1) and (2) are used commonly for correlating experimental data of supercritical mixtures.

Figs. (**7**) and (**8**) show reasonable agreement between present work results and the data predicted by RK-EOS,

(a) Naphthalene   **(b)** Phenanthrene
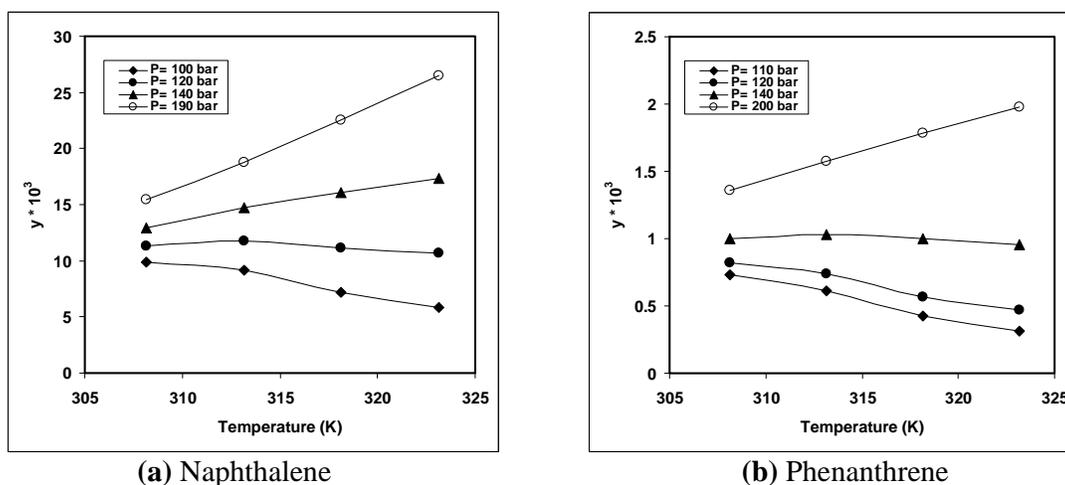
Fig. (5). Mole fraction solubility (y) of naphthalene and phenanthrene in CO_2 as a function of temperature at constant pressures.

(a) Naphthalene   **(b)** Phenanthrene
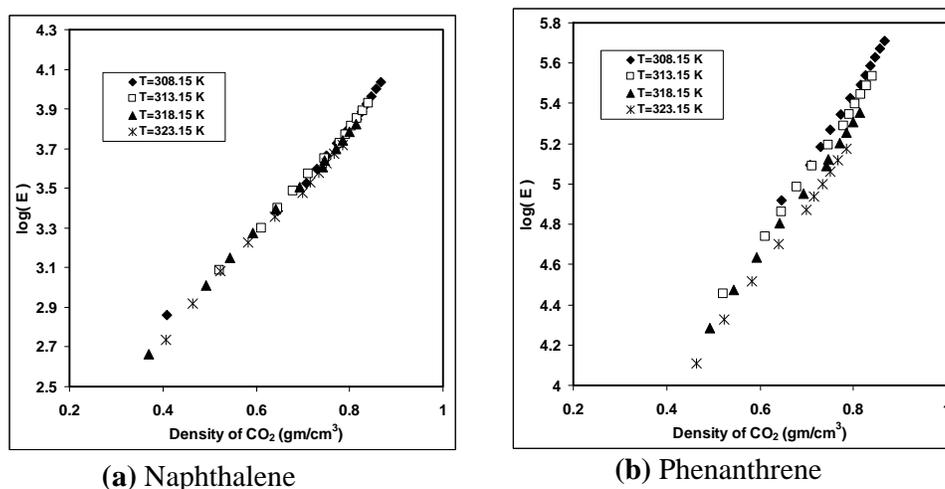
Fig. (6). The enhancement factor (E) in compressed CO_2 as a function of density of extractant.

(a) T=308.15 K

(b) T=313.15 K

(c) T=318.15 K

(d) T=323.15 K
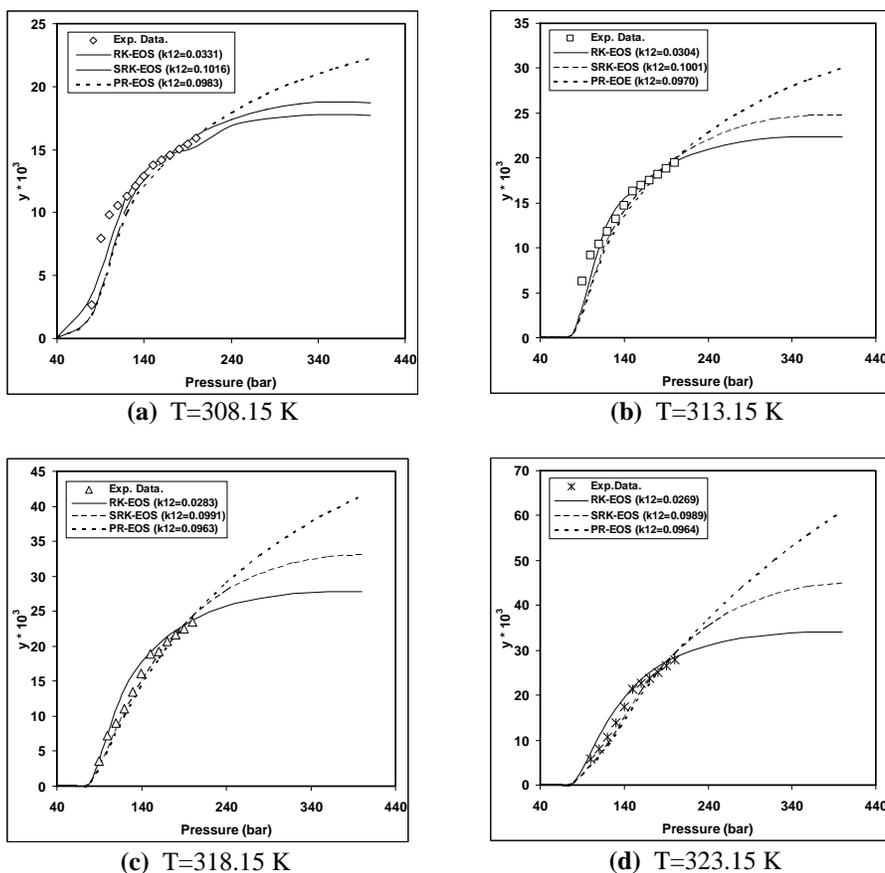
Fig. (7). The solubility of naphthalene in CO_2 curve predicted by the RK-EOS, SRK-EOS and PR- EOS at temperatures studied.

(a) T=308.15 K

(b) T=313.15 K

(c) T=318.15 K

(d) T=323.15 K
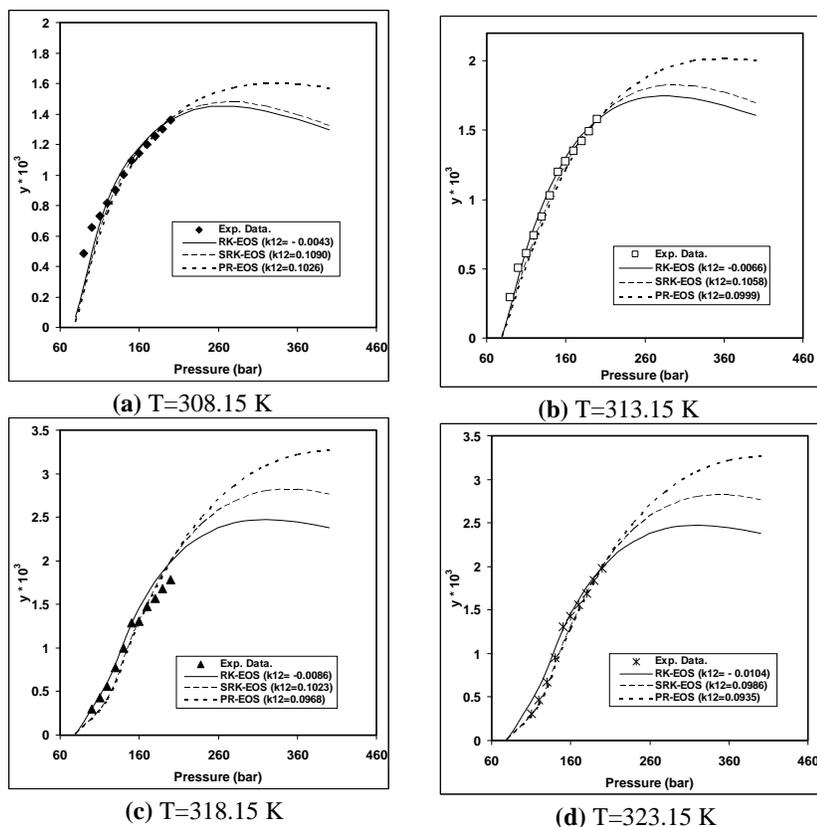
Fig. (8). The solubility of phenanthrene in CO_2 curve predicted by the RK-EOS, SRK-EOS and PR-EOS at temperatures studied.

SRK-EOS and PR-EOS. Interaction parameters k_{12}'s given in Tables (**4**) and (**5**) were used for these three equations of state. It may be seen that the interaction parameter (k_{12}) for each equation is decreased relatively with increasing the temperature, because of the solubilities are governed primarily by vapor pressure, which depends on the temperature and only secondarily by carbon dioxide-solid component interactions in the SCF phase.

The value of (k_{12}) for each temperature is determined by a series of values of (k_{12}) assumed, and the solubilities are calculated for each isotherm pressure. The accepted value of (k_{12}) is the one which yields the minimum sum of average absolute relative deviation (AARD) that is,

$$\%AARD = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{(y)_{cal.} - (y)_{exp.}}{(y)_{exp.}} \right| \qquad (11)$$

where N is the number of data points. Tables (**4**) and (**5**) show the % AARD for the equations of state used and it can be seen that the RK-EOS gives % AARD less than the other two equations of state.

CONCLUSIONS

1. As expected, the extraction of low volatility solid components depends strongly upon the density of the extracting fluid (carbon dioxide) and only becomes appreciable when the critical density is exceeded.

2. The 308.15K isotherm for the carbon dioxide-solid system is characteristic of solid solubility behavior at temperatures near the critical temperature of the carbon dioxide solvent, because large changes in solubility occur for relatively small changes in pressure around the critical pressure of the carbon dioxide at this temperature, as it was verified by other researchers [9, 10].

3. There are many options available in supercritical fluid extraction for achieving and controlling the desired selectivity, which is extremely sensitive to variations in pressure, temperature.

4. It is possible to collate vapor phase data for the carbon dioxide-solid system adequately by using the cubic equations of state.

5. The applicability of supercritical extraction is highly dependent on our ability to model and predict phase equilibrium in complex systems. Supercritical fluid systems are especially challenging because of the high compressibility and the asymmetry of the systems encountered.

6. Supercritical fluid extraction is often inappropriate for separations because easier methods are available, but when it is needed it is a very powerful tool.

ABBREVIATIONS

AARD	=	Absolute average relative deviation
EOS	=	Equation of state
PR	=	Peng-Robinson
RK	=	Redlich- Kwong
SCF	=	Supercritical Fluid
SRK	=	Soave –Redlich- Kwong

NOTATIONS

a_i, b_i	=	Parameters in equation of state of pure component
a_m, b_m	=	Parameters in equation of state of mixture
f_i^{SCF}	=	Partial molal fugacity in gas phase, bar

Table 4. The Interaction Parameters (k_{12}'s) and Average Absolute Relative Deviations (AARD) for each Equation of State of CO_2-Naphthalene System

T(K)	RK-EOS		SRK-EOS		PR-EOS	
	k_{12}	% AARD	k_{12}	% AARD	k_{12}	% AARD
308.15	0.0331	3.10	0.1016	5.75	0.0983	7.68
313.15	0.0304	2.72	0.1001	6.82	0.0970	8.56
318.15	0.0283	6.73	0.0991	9.98	0.0963	11.25
323.15	0.0269	6.45	0.0989	10.08	0.0964	11.28

Table 5. The Interaction Parameters (k_{12}'s) and Average Absolute Relative Deviations (AARD) for each Equation of State of CO_2-Phenanthrene System

T(K)	RK-EOS		SRK-EOS		PR-EOS	
	k_{12}	% AARD	k_{12}	% AARD	k_{12}	% AARD
308.15	-0.0043	5.76	0.1090	7.03	0.1026	8.67
313.15	-0.0066	7.68	0.1058	10.94	0.0999	12.81
318.15	-0.0086	9.31	0.1023	7.52	0.0968	9.19
323.15	-0.0104	11.31	0.0986	12.88	0.0935	14.12

f_i^S	=	Partial molal fugacity in solid phase, bar
k_{ij}	=	Interaction parameter in mixing rules, eq. (3)
n	=	Number of components, eq.s (1) and (2)
n	=	Total number of mole, eq. (6)
n_i	=	Number of moles of component i, mole
N	=	Number of data points
P	=	Total system pressure, bar
P_c	=	Critical pressure, bar
P^{sub}	=	Sublimation pressure, bar
R	=	Universal gas constant (0.08314 bar lit./mol K)
T	=	Absolute temperature, K
T_C	=	Absolute critical temperature, K
υ_i^S	=	Molar volume of pure solid, (lit. / mol)
$\underline{V}$	=	Total system volume, (lit.)
υ^v	=	Molar volume of vapor phase, (lit./mol)
y_{calc}	=	Calculated or predicted mole fraction solubility
y_{exp}	=	Experimental mole fraction solubility
y_i	=	Mole fraction solubility of component i
Z	=	Compressibility factor

Greek letters

α	=	Constant in eq. (10)
β	=	Constant in eq. (10)
ω	=	Acentric factor
ϕ_i	=	Partial molal fugacity coefficient of component i
ϕ_i^{SCF}	=	Partial molal fugacity coefficient of component i in gas phase, eq. (8)

Superscripts

SCF	=	Supercritical fluid
S	=	Solid
Sub	=	Sublimation

Subscripts

c	=	Critical property
m	=	Mixture
ij	=	Component indices
exp	=	Experimental measurement
calc	=	Predicted value

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