INFLUENCE OF PROPERTY ESTIMATION TECHNIQUES ON THERMODYNAMIC MODELING OF SOLUBILITY OF C. I. DISPERSE ORANGE 30 DYE IN SUPERCRITICAL CO_2

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ABSTRACT

The present work deals with the study of thermodynamic modeling of solubility of C. I. disperse orange 30 (O30) dye in supercritical CO_2 using Peng-Robenson equation of state (PR-EOS). The sensitivity of critical properties in the calculations was also studied.

The results of model showed good agreement with the experimental data of the system taken and the study proved that the choice of the technique to calculate thermodynamic properties is very important for obtaining good results in the phase equilibrium calculations.

Keywords: Phase behavior, C. I. disperses orange 30 dye, critical properties estimation techniques, CO_2, PR-EOS.

NOTATIONS

A_1, A_2, A_3, and A_4	*constants in equation (18).*
A, B	*modified adjusting parameters in equation of state of mixture.*
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}	*fugacity in fluid phase, bar.*
f_i^{S}	*fugacity in solid phase, bar.*

k_{ij}	*interaction parameter in mixing rules, equation (9).*
Mw	*molecular weight.*
n	*number of moles.*
n_c	*number of carbon atoms.*
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 m^3/ Kmol K).*
T	*absolute temperature, K.*
T_b	*normal boiling point, K.*
T_C	*absolute critical temperature, K.*
T_r	*reduced temperature (T/Tc).*
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	*quantity estimated in equation (30).*
β	*quantity estimated in equation (31).*
θ	*reduced normal boiling temperature (T_b/T_c).*
ω	*acentric factor.*
ϕ_i^{υ}	*fugacity coefficient of component i in vapor phase.*
κ	*quantity estimated in equation (4).*
ϕ_i^{SCF}	*gas phase fugacity coefficient, equation (11).*

Superscripts

SCF	*supercritical fluid.*
S	*solid.*
Sub	*sublimation.*
υ	*vapor.*

Subscripts

c	*critical property.*
m	*mixture.*
r	*reduce property.*
ij	*component indices.*

exp	*experimental measurement.*
calc	*predicted value.*

Abbreviations

AARD	*absolute average relative deviation.*
C. I.	*Color Index.*
EOS	*equation of state.*
O30	*C. I. disperses orange 30 dye.*
PR	*Peng-Robinson.*
SCF	*Supercritical Fluid.*
SRK	*Soave –Redlich- Kwong*

INTRODUCTION

The conventional wet-dyeing industry, which discharges considerable amounts of wastewater containing highly concentrated, very little biodegradable surfactants, has been continuously raising pollution problems worldwide. Supercritical fluid dyeing process is environmentally friendly because it does not require any surfactant or dispersing agent (1, 2)*. Furthermore, energy consumption may be only a half that of the conventional dyeing process as the drying step is not necessary in the supercritical fluid dyeing.*

Although there has been much research on solid solubility in supercritical fluid (SCF), the phase behavior of solids with very high molecular weights has not been fully understood yet. Some empirical equations have been used to correlate the solubility of large molecular-weight solids with pressure or density of the fluid (3)*.*

Abdul Mun'em (4) *measured the solubility of solid components in supercritical* CO_2 *at temperature range (308.15 – 323.15) K and pressure range (80 – 200) bar and the experimental data are correlated with three cubic equations of state which are Redlich-Kwonge (RK), Soave-Redlich-Kwonge (SRK) and PR. Serwan* (5) *studied the phase equiliberia modeling for separation of solid mixtures by supercritical* CO_2 *on Excel program using PR-EOS.*

Hartono et al. (6) *used six different cubic equations of state to predict the solubility of solids and they shown that the two-parameters Mohsen-Nia-Moddaress-Mansoori (MMM) equation is more accurate than five of the other equations. Beak et al.* (7) *measured and correlated the solubility of C. I. disperse orange 30 dye (O30) in* CO_2 *at temperatures between 313 and 393 K and at pressures between 110 and 330 bar.*

Phase equilibrium calculation using a thermodynamic model requires thermodynamic properties that were not found in the literature and must therefore be predicted. These properties are critical temperature, critical pressure, the acentric factor, and the parameters presented in the equation that calculated the saturation pressure of the compound. Therefore, different property estimation techniques are investigated in present work and their influence on the ability to correlate the experimental solubility data obtained from literatures (7) of C. I. disperse orange 30 dye (Fig. 1) as a solid component in supercritical CO_2 using PR-EOS.

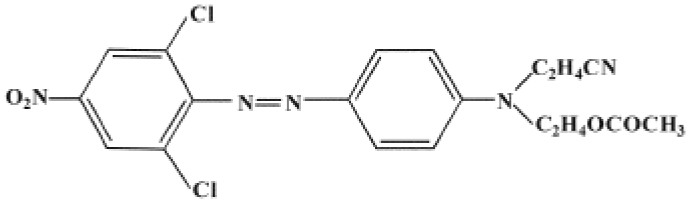

Fig. (1). The molecular structure of C. I. Disperse Orange 30 dye (7).

THERMODYNAMIC MODELING

Although solubility measurements in supercritical CO_2 are the first key step in evaluating the viability of supercritical fluid processes, thermodynamic modeling can provide feasibility analysis and reduce the number of experimental measurements required (8). On the other hand, it is important to note that rigorous thermodynamic modeling of solubilities of compounds of high molecular weight interest can be difficult due to an almost complete lack of knowledge of the physical properties necessary for pure molecule parameter used in equation of state.

The PR-EOS was chosen to model the high-pressure phase behavior with quadratic Van der Waals mixing rules and take the following form (9):

$$P = \frac{RT}{(\upsilon - b)} - \frac{a}{[\upsilon(\upsilon + b) + b(\upsilon - b)]} \qquad \dots (1)$$

where,

$$a = a(T_c)\alpha(T_r, \omega) \qquad \dots (2)$$

$$\alpha(T_r, \omega) = [1 + \kappa(1 - T_r^{0.5})]^2 \qquad \dots (3)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad \dots (4)$$

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c} \qquad \text{… (5)}$$

$$b = 0.0778\frac{RT_c}{P_c} \qquad \text{... (6)}$$

In general an equation of state is 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:

$$a_m = \sum_i^n \sum_j^n y_i y_j a_{ij} \qquad \text{…… (7)}$$

$$b_m = \sum_i^n y_i b_i \qquad \text{... (8)}$$

where,

$a_{ij} = (a_i \; a_j)^{0.5} \; (1 - k_{ij})$ *... (9)*

where a_i *and* b_i *are calculated from equations (2) and (6) using the critical pressure* P_c*, critical temperature* T_c *and acentric factor* ω *for each component. In equation (9),* k_{ij} *is the binary interaction parameter, which has a non-zero value and for an n-component mixture there are* $\frac{n(n-1)}{2}$ *possible binary interaction parameters.*

Solid - Fluid Phase Equilibrium

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 negligible 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 (10, 11)*:*

$$f_i^S(T,P) = f_i^{SCF}(T,P,y_i) \qquad \text{...(10)}$$

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

$$f_i^{SCF} = \phi_i^{SCF} y_i P \qquad \text{…(11)}$$

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) $^{(12)}$*:*

$$\ln\phi_i = \frac{1}{RT}\int_{\upsilon^v}^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,\upsilon,n_j} - \frac{RT}{\underline{V}}\right]d\underline{V} - \ln Z \qquad \text{……. (12)}$$

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 PR-EOS is introduced into Eq. (12) using mixing rules given by Eq. (7) and (8), the following closed-form expression for fugacity coefficient is obtained and used in all phases,

$$\ln\phi_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) + \frac{A}{2\sqrt{2}B}\left[\frac{b_i}{b_m} - \frac{2\sum_j y_j a_{ji}}{a_m}\right]\ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \qquad \text{…. (13)}$$

and when replacing υ in Eq.(1) in term of ZRT/P, gives the cubic equation of PR-EOS as:

$$Z^3 - (1-B)Z^2 + \left(A - 2B - 3B^2\right)Z - \left(AB - B^2 - B^3\right) = 0 \qquad \text{……(14)}$$

where Z is compressibility factor and, A and B are defined as,

$$A = \frac{a_m P}{(RT)^2} \qquad \text{…. (14a)}$$

$$B = \frac{b_m P}{RT} \qquad \text{… (14b)}$$

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

$$f_i^s = P_i^{sub}(T)\phi_i^{sub}(T, P_i^{sub})\exp\left[\int_{P_i^{sub}}^{P}\left(\frac{\upsilon_i^s}{RT}\right)dP\right] \qquad \text{…… (15)}$$

where $P_i^{sub}(T)$ is the sublimation or vapor pressure of the pure solid at the system temperature, υ_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 (11) and (15), the mole fraction solubility of a heavy nonvolatile solid in the SCF solvent phase now becomes,*

$$y_i = \frac{P_i^{sub}(T)\exp\left[\frac{\upsilon_i^s(P - P_i^{sub})}{RT}\right]}{\phi_i^{SCF} P} \qquad \text{…. (16)}$$

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 $^{(13)}$.

ESTIMATION OF PROPERTIES

To calculate the solubility and phase stability of a solute in a supercritical fluid it is necessary to have critical properties and acentric factors of all components, and molar volumes and sublimation pressures of the solid components. When some of these values are not available, as is the case here, estimation techniques must be employed. When neither critical properties nor acentric factors are available in the literature, it is desirable to have the normal boiling point (T_b) *of the compound since some estimation techniques require only* T_b *and molecular structure. Also, vaporization, sublimation and/or fusion curves and normal melting point information might be of help for the estimation of* T_b*. Some of the estimation techniques used below, where only the molecular structure and/or molecular weight are required.*

In the following subsections, different property estimation techniques used in this work will be discussed. The estimated T_c, P_c *and* ω *as parameters used in the Peng-Robinson EOS; beyond that we do not assign any physical significance to the values obtained. C. I. disperse orange 30 dye is a typical solute of high molecular mass for which critical constants are not available in the literature.*

The properties found in the literature or estimated with the methods explained below are summarized in Table (1). Note that with the objective of obtaining the best fit of the solubility behavior of C. I. disperse orange 30 dye in supercritical CO_2, *there are different sets of properties reported depending on the estimation method used.*

Boiling Point

As mentioned above, the normal boiling point of a component is one of the key properties for the estimation of other parameters or properties. Since there is no experimental boiling point available, two *methods were used to estimate boiling points: the Joback group contribution approach and by simulation with n-alkanes having the same molecular weight using the Tsonopoulos (14) method of the n-alkanes.*

The Joback group contribution approach is used to obtain an approximate estimate of T_b with the following correlation:

$$T_b = 198 + \sum \Delta_b,\ T_b[=]K \quad \text{….. (17)}$$

Here Δ_b represents group increments according to structural information. The tabulated group values are presented in Reid et al. (15).

Tsonopoulos correlated the T_b (K) of the n-alkanes with the number of carbon atoms (n_c) using a simple equation of the form,

$$\ln(A_1 - T_b) = A_2 - A_3 n_c^{A4} \quad \text{……… (18)}$$

where, A_1=1071.28, A_2=6.97569 , A_3=0.116307 , A_4=2/3

To obtain the T_b of n-alkanes as a function of molecular weight (Mw), the n_c in Eq. (18) should be replaced by the following simple expression,

$$n_c = \frac{Mw - 2.0158}{14.0268} \quad \text{…….. (19)}$$

Critical Properties

Critical properties are crucial for an accurate representation of experimental behavior. In this work, five methods were used to estimate these properties: the Fedors, Joback, Ambrose, Lydersen methods described in detail by Reid et al. (15) and Perry et al. (16) and Klincewicz method (17) group contribution approaches. The Fedors method estimates critical temperature, T_c, using group increments (ΔT) according to the molecular structure and Eq. (20). This method is particularly useful when no boiling point information is available.

$$T_c = 535\log_{10}\left(\sum \Delta T\right) \quad T_c[=]K \quad \text{……… (20)}$$

The Joback group contribution approach is useful in estimating T_c (Eq.21) as a function of T_b and group increments (ΔT) according to the molecular structure. Critical pressure, P_c, is estimated with Eq. (22) as function of the number of atoms in the molecule (n_A) and group increments (ΔP). Tabulated values used in this work were obtained from Reid et al. (15).

$$T_c = T_b\left[0.584 + 0.965\sum \Delta T - \left(\sum \Delta T\right)^2\right]^{-1}, \quad T_b, T_c[=]K \quad \text{……. (21)}$$

$$P_c = \left(0.113 + 0.0032 n_A - \sum \Delta P\right)^{-2}, \quad P_c[=]bar \qquad \text{……..} \ (22)$$

The Ambrose method is another group contribution approach to estimate the critical temperature and pressure. The method is similar to the previous one, except that the critical pressure is a function of the molecular weight, Mw, of the molecule (Eqs. 23-24).

$$T_c = T_b\left[1 + \left(1.242 + \sum \Delta T\right)^{-1}\right], \quad T_b, T_c[=]K \qquad \text{…….} \ (23)$$

$$P_c = Mw\left(0.330 + \sum \Delta P\right)^{-2}, \quad P_c[=]bar \qquad \text{……..} \ (24)$$

The Lydersen method is group contribution approach to estimate the critical temperature and pressure and is similar to Ambrose method and the relations are,

$$T_c = T_b\left[0.567 + \sum \Delta T - \left(\sum \Delta T\right)^2\right]^{-1}, \quad T_b, T_c[=]K \qquad \text{…….} \ (25)$$

$$P_c = Mw\left(0.34 + \sum \Delta P\right)^{-2}, \quad P_c[=]bar \qquad \text{……..} \ (26)$$

Klincewicz has refitted correlations for estimating the critical properties of pure components as follow,

$$T_c = 45.40 - 0.77 Mw + 1.55 T_b + \sum \Delta T, \quad T_b, T_c[=]K \qquad \text{…….} \ (27)$$

$$P_c = \left(0.335 + 0.01 Mw + \sum \Delta P\right)^{2}, \quad P_c[=]bar \qquad \text{……..} \ (28)$$

All methods mentioned above were used with the objective of finding the best fit for the experimental data.

Acentric factor

Acentric factor, ω, for molecule was estimated using the Lee-Kesler correlation Eqs. (29-31), where $\theta = T_b/T_c$ and the correlation is described in Reid et al. $^{(15)}$.

$$\omega = \frac{\alpha}{\beta} \qquad \text{……..} \ (29)$$

$$\alpha = -\ln P_c - 5.97214 + 6.09648\theta^{-1} + 1.28862\ln\theta - 0.169347\theta^{6}, \quad P_c[=]atm \qquad \text{…..} \ (30)$$

$$\beta = 15.2518 - 15.6875\theta^{-1} - 13.472\ln\theta + 0.43577\theta^{6} \qquad \text{……} \ (31)$$

Sublimation pressure

The vapor pressures of solid component (C. I. disperse orange 30 dye) studied calculated by the following equation:

$$\ln(P^{sub}) = 38.3625 - \frac{14613.55}{T} \qquad \text{……} \ (32)$$

where P^{sub} in N/m^2 , T in K and Eq. (32) is obtained by least square fittings method for the experimental values of vapor pressure at different temperatures that exist in literature ⁽⁷⁾ *and its melting point, 398.56K, and the heat of fusion, 17.08 kJ/mol, were measured by differential scanning calorimeter* ⁽⁷⁾.

Molar volume

Molar volume (υ_i^s) of the C. I. disperse orange 30 dye is found in literature and its value equal to 273 cm^3/mole ⁽⁷⁾.

k_{ij} interaction parameters

The interaction parameters between the C. I. disperse orange 30 dyes and carbon dioxide at each temperature was obtained by regression of the experimental data and the values are shown in Table (2). The objective function used was the average absolute relative deviation (%AARD), as shown in Eq. (33). Here $y_i^{\exp}$ are the experimental data y_i^{calc} are the predicted values and N is the total number of data points.

$$\%AARD = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|y_i^{\exp} - y_i^{calc}\right|}{y_i^{\exp}} \qquad \ldots\ldots\ldots (33)$$

RESULTS AND DISCUSSION

The critical properties and acentric factor of the C. I. disperse orange 30 dye were predicted using most of the group contribution methods, Joback, Lydersen, Ambrose, Klincewicz, and Fedors when using the normal boiling point (T_b) determined by Joback method (Eq. 17) and by simulation with normal alkanes having the same molecular weight (Eq. 18) to study the sensitivity of these properties in the solubility calculations.

The k_{ij} parameters was estimated from combination of the experimental solubility data for C. I. disperse orange 30 dye were collected at 313.15, 333.15, 363.15, and 393.15K and from 110 bar to 330 bar ⁽⁷⁾*. The values of k_{ij} were increased with temperature increased for all sets (see Table 2). The %AARD values are very sensitive to critical properties of the component studied and the optimum value of it when using set 7.*

A comparison between the experimental and calculated solubilities of C. I. disperse orange 30 dye in supercritical CO_2 *when using set 7 is shown in Fig.s (2-5).*

The properties obtained from the Ambrose group (set 7) gave better results than the others and linear relation obtained when regressed the values of k_{ij} *and temperatures and taken the following form when using set (7),*

$$k_{ij} = [-6.74 + 11.52T(K)] \times 10^{-4} \qquad \ldots (34)$$

with correlation coefficient and standard error are 0.9995 and 0.00753 respectively. Equation (34) can be used to obtain the value of k_{ij} *at other temperatures which is used in the calculations of the solubility of C. I. disperse orange 30 dye in supercritical* CO_2 *by using the purposed thermodynamic model with PR-EOS as shown in Fig.(6) at temperatures 305.15, 353.15, and 373.15K.*

CONCLUSIONS

The results of model showed good agreement with the experimental data of the system taken and the %AARD ranges from 8.9% to 15.8% when using set 7.

Also, the present work showed that the choice of a group contribution method and the suitable normal boiling point determination is very important to obtain good results in phase equilibrium calculations, and before equilibrium conditions are studied, the physicochemical properties must be obtained.

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Table (1)
Estimated Physical Properties for C. I. Disperse Orange 30 Dye Using Various Techniques.

SET #	T_b[K]	T_c[K]	P_c [bar]	ω	Method used to estimate			
					T_b[K]	T_c[K]	P_c [bar]	ω
1	1274.11	1560.7	13.30	1.22	Joback	Joback	Joback	Eq. 29
2	1274.11	1593	13.84	0.91	Joback	Lydersen	Lydersen	Eq. 29
3	1274.11	1537.85	24.83	2.05	Joback	Ambrose	Ambrose	Eq. 29
4	1274.11	1811.24	95.92	1.01	Joback	Klincewicz	Klincewicz	Eq. 29
5	739.37	905.67	13.30	1.22	n-alkanes	Joback	Joback	Eq. 29
6	739.37	905.3	13.83	1.26	n-alkanes	Lydersen	Lydersen	Eq. 29
7	739.37	892.42	24.83	2.05	n-alkanes	Ambrose	Ambrose	Eq. 29
8	739.37	982.4	95.92	1.65	n-alkanes	Klincewicz	Klincewicz	Eq. 29
9	739.37	945.9	13.84	0.78	n-alkanes	Fedors	Lydersen	Eq. 29

Table (2)
Binary Interaction Parameters with CO_2 and %AARD.

SET #	T=313.15K		T=333.15K		T=363.15K		T=393.15K	
	k_{ij}	%AARD	k_{ij}	%AARD	k_{ij}	%AARD	k_{ij}	%AARD
1	0.4290	9131.3	0.4539	2627.1	0.4844	952.2	0.5170	514.3
2	0.3898	7866.4	0.4168	2384.4	0.4505	887.3	0.4868	485.1
3	0.5648	174.2	0.5802	121.2	0.6055	69.8	0.6364	79.9
4	0.5361	35	0.5464	33.9	0.5833	37.2	0.6338	17.4
5	0.2426	275.1	0.2661	183.4	0.3042	104.8	0.3511	107.2
6	0.2541	226.2	0.2768	155.2	0.3145	89.3	0.3613	95.9
7	0.3640	9.4	0.3764	8.9	0.4112	15.8	0.4604	13.0
8	0.2824	46.6	0.2867	44.4	0.3405	46	0.4238	27.8
9	0.1830	285	0.1457	135.4	0.2010	78.2	0.2659	87.8

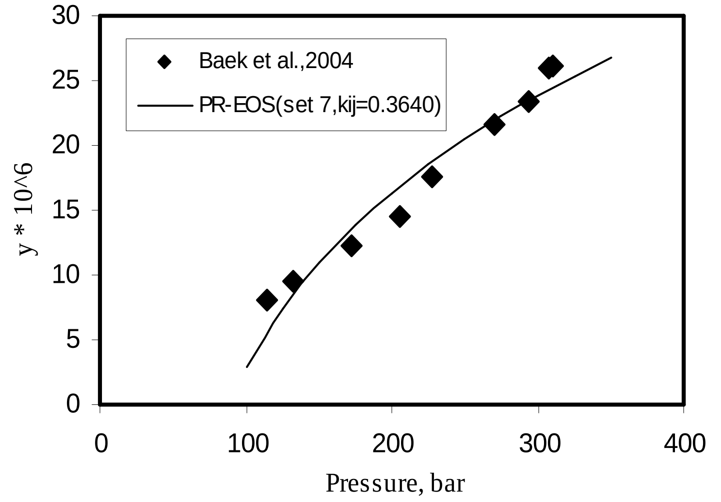

Fig.(2) . The solubility of O30 dye in supercritical carbon dioxide as a function of pressure at T=313.15K.

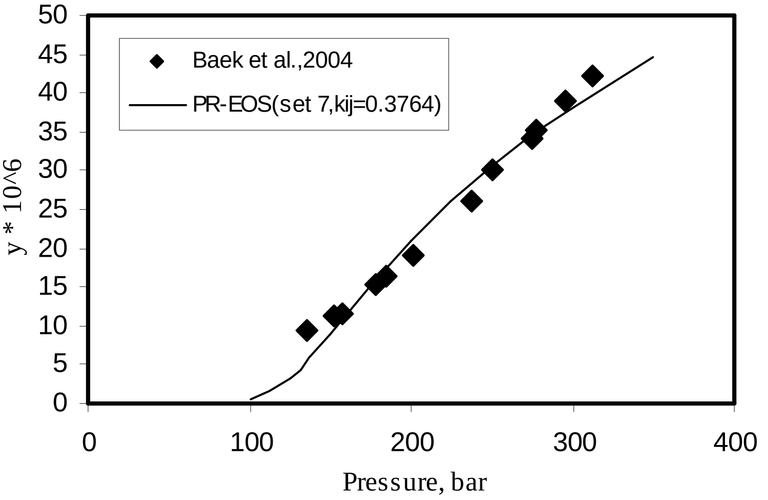

Fig.(3) . The solubility of O30 dye in supercritical carbon dioxide as a function of pressure at T=333.15K.

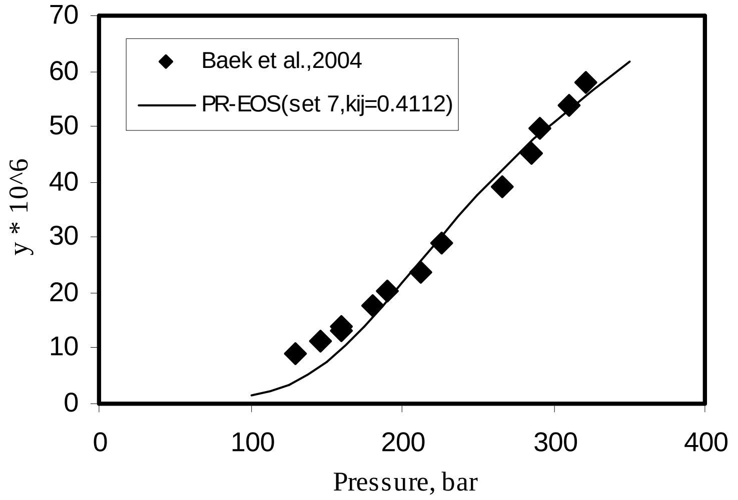

Fig.(4). The solubility of O30 dye in supercritical carbon dioxide as a function of pressure at T=363.15K.

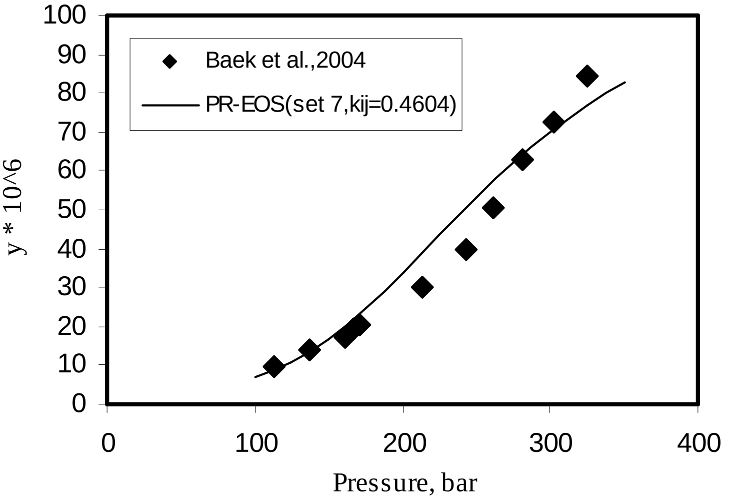

Fig.(5). The solubility of O30 dye in supercritical carbon dioxide as a function of pressure at T=393.15K.

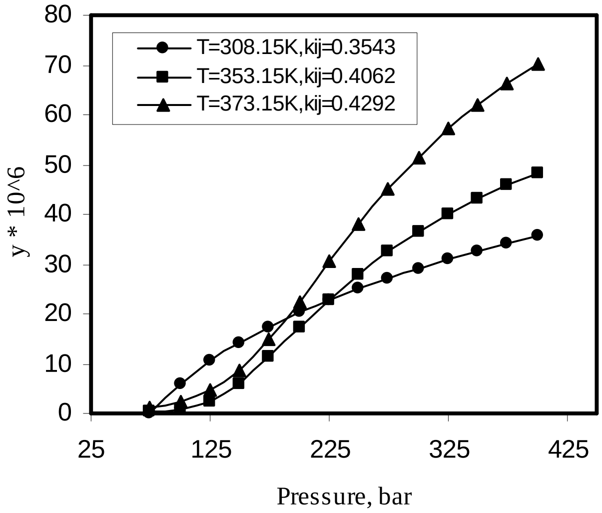

Fig.(6). The solubility of O30 dye in supercritical carbon dioxide as a function of pressure.

[illegible]

[illegible]

[illegible]

[illegible] C.I.) [illegible] (disperse orange 30 dye [illegible] (Peng-Robenson) [illegible]

[illegible]