Prediction of solubility of Chiba seed extracts in supercritical carbon dioxide by equation of state models.

B.MANOHAR* and K.Udaya Sankar
Food Engineering Department, Central Food Technological Research Institute, Mysore, India
Email: manoharb@cftri.res.in

Abstract: Solubility of Bakuchiol and Psoralen, key components of Chiba seed extracts in super critical carbon dioxide were predicted by employing well known Peng-Robinson and Soave-modified Redlich-Kwong equation of state models. Solubility (in mole fraction) of both Bakuchiol and Psoralen were in the range 10^{-6} – 10^{-4} for the pressure range 220 to 300 bar. Both the models were found to agree with the experimental solubilities of Psoralen very well. Critical properties necessary for the solubility prediction such as Critical temperature, Critical pressure, Critical volume were predicted for the key components of Chiba seeds i.e Bakuchiol and Psoralen following Group contribution methods based on Ambrose, Lyderson, Joback and Kliencewicz-Reid.

Keywords:. Bakuchiol, Peng-Robinson, Soave-modified Redlich-Kwong; equation of state.

Introduction

The Chiba seed (*Psoralea corylifolia* L) is distributed from India to southeast Asia. The seed-oil is used externally for the treatment of leucodermy, psoriasis and leprosy in Indian folk medicine [Kondo et al.,1990]. The plant, known as Bakuchi in Sanskrit, has been used in Ayurvedic medicinal system for cardiac tonic, vasodilator, alterative, pigmentor. It is also widely used in Chinese medicine to treat a variety of diseases and possesses anti-tumor, antibacterial, cytotoxic and anti-helmenthic properties [Latha et al., 2000]. Bakuchiol and Psoralen, the major components present in the seed, are of high biotechnological values and also thermally sensitive.

Determination of solubility in super critical fluid (SCF) by equation of state models:

A supercritical fluid is one of which the temperature and pressure exceed its critical temperature T_c and pressure P_c. One of the attractive features of SCF extraction technology is that it is suitable for separation of high boiling components from mixtures. The SCF technology is being used as alternate technology in food processing, pharmaceutical, cosmetic and chemical industries. In recent years, there has been enormous amount of books and research papers appearing in the scientific literature. A good introduction to fundamentals of SCF and the application of SCF to separation processes can be found [Brunner,1994]. One may refer Modeling the extraction with SCF requires the application of an equation of state. The solubility of a material is usually expressed in terms of the overall mole fraction of the solute in SCF phase. The ability of SCFs to dissolve many substances arise from highly non-ideal behaviour of SCF. The solubility of a component, as predicted by the ideal gas law, decreases asymptotically with increasing pressure because the solubility is simply the ratio of vapor pressure (P^{sat}) to the total pressure (P). Under supercritical conditions, however, the solubility is enhanced by several orders of magnitude above that predicted the ideal gas law.

Shi and Zhou, 2007 dealt a separate chapter with respect to solubility of food components in super critical processes. Various factors affecting the solubility of a component in SCF have been discussed. Interest in supercritical fluids and its related aspects has made phenomenol growth as seen from the volume of literature available [Knox, 2005]. The calculation of solubility of an organic component in SCF has included both correlative and predictive approaches. These models are summarized in empirical correlations as the Chrastil relation [Chrastil, 1982], cubic equations of state (EOS) such as Peng-Robinson [Peng and Robinson, 1976] and Redlich-Kwong [Redlich and .; Kwong, 1949]. Soave [Soave. 1972] made modification to Redlich-Kwong equation of state (RK-EOS). Later, Soave (2000) further modified and presented a simple model based on Redlich-Kwong EOS [Soave, 2000]. Modified Peng-Robinson equation of state was introduced by Schmitt and Reid [Schmitt and Reid, 1983].

Both Peng-Robinson equation of state (PR-EOS) and (RK-EOS) predict the state well in the compressed gas region. Although the equations of state mentioned above have good prediction performance, they require a lot of critical physical properties of solutes, which are not easily available and only few are available in the published literatures. Hence some empirical expressions are still widely used by researchers. For example, Saeki expressed an empirical equation based on power law and Maxwell thermodynamic relation. It has good agreement with some fluids such as neon, hydrogen, deuterium, and carbon monoxide in the supercritical state. Equations of state have a central role in supercritical fluids because they not only predict the solubility, but also give the qualitative phase behavior. Hence, more complicated theories and more multi-parameter empirical methods continue to be developed to formulate the state more accurately. Although the present model accuracy is limited by its character, they can be used to build most of the known binary phase diagrams, which are the fundamentals of supercritical fluid extraction. It must be born in mind that selecting a suitable EOS is a difficult task and no single model will work for all situations [Johnston, 1989].

The objective of the present study: a) to estimate the critical temperature, pressure and volume of key components of Chiba seed based on various group contribution methods such as Lyderson [Lyderson, 1949], Ambrose [Ambrose, 1978], Joback [Joback, 1984] and Kliencewicz-Reid [Klincewicz and Reid, 1984]. b).The prediction of solubility of key components of the Chiba seed extracts in SCF by PR-EOS and SRK-EOS and prediction of solubility of the extract considering the extract as single pseudo-component.

Methodology

EQUATION OF STATE (EOS)

Equations of state are used to describe the thermodynamic states through the relationship of state parameters such as temperature, pressure, and volume. In SFE processing, EOS describes the behavior of solute being dissolved in supercritical fluids. The solubility of a substance (component 2) in a supercritical fluid (component 1) can be obtained from fluid-solid phase equilibria. At equilibrium, the fugacities of the components in the solid and gas phases are equal, i.e.:

$$f_2^s(P,T, x_2) = f_2^v (P,T,y_2) \quad (1)$$

If the gas component 1 is assumed to be insoluble in solid phase (true in most of the cases), then

$$y_2 \varphi_2^s P = P_2^{sat} \varphi_2^{sat} \exp \int_{P2sat}^{P} ((v_2^s dP/ RT)) \quad (2)$$

$$f_2^v = P y_2 \varphi_2^v \quad (3)$$

From above equations, one can obtain:

$$y_2 = (P_2^{sat} / P) E \quad (4)$$

$$y_2 = P_2^{sat} \exp (P v_2^s / RT) / (\varphi_2^v P) \quad (5)$$

E is the enhancement factor which is the ratio of the solubility of the solute in super critical fluid to the solubility in an ideal gas. i.e $E = y_2 / y_{ideal}$

Large enhancement factors of the order of 10^5 to 10^7 are frequently observed due to small values of φ_2^v. φ_2^{sat} has a value of approximately one. V_2^s can be easily calculated from the density of component 2. Thus, to calculate E, one requires the value of φ_2^v . From well known equation of state (EOS) available such as Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK) models, φ_2^v can be calculated.

A general form of the Peng-Robinson equation is:

$$P = (RT/(V-b)) – (a / (V^2+2bV – b^2)) \quad (6)$$

The above can be written as:

$$Z^3 – (1-B) Z^2 + (A-3B^2-2B) Z - (AB-B^2-B^3) = 0 \quad (7)$$

The above equation leads to:

$$\ln \varphi_2^v = b_2 (Z-1)/b - \ln (Z-B) - [(A/2\sqrt{2}B) \{2(a_{22} y_2 + a_{12} y_1 /a) - (b_2/b)\} . \ln \{(Z+2.414 B)/(Z-2.414 B)\}] \quad (8)$$

Soave-Redlich-Kwong equation of state (SRK-EOS) is:

$$P = (RT/(V-b)) - (a / (V^2 + bV)) \quad (9)$$

Which can also be written as:

$$Z^3 - Z^2 + (A-B-B^2) Z - AB = 0 \quad (10)$$

The above equation leads to:

$$\ln \varphi_2^v = b_2 (Z-1)/b - \ln (Z-B) - [(A/B) \{2(a_{22} y_2 + a_{12} y_1 /a) - (b_2/b)\} . \ln (1 + (B/Z))] \quad (11)$$

where

$$Z = Pv / RT \quad (12)$$

$$A = aP / (R^2 T^2) \quad (13)$$

$$B = bP / RT \quad (14)$$

a = intermolecular attraction parameter;

b = covolume parameter.

When the equation is extended to mixtures, the following mixing rule is employed:

$$a = \Sigma \Sigma y_i y_j a_{ij} \quad (15)$$

$$b = \Sigma \Sigma y_i y_j b_{ij} \quad (16)$$

where a_{ij} and b_{ij} are calculated from combining rules:

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1- k_{ij}) \quad (17)$$

$$b_{ij} = (b_{ii} b_{jj})^{0.5} (1- n_{ij}) \quad (18)$$

where k_{ij} and n_{ij} are the adjustable binary interaction parameters. The adjustable parameters are determined by regressing phase equilibrium data and assumed to be independent of temperature, pressure and composition. It may be noted that these parameters can take negative values and accordingly, the software program should be allowed to adjust these values suitably. Many authors have used single binary interaction parameter k_{ij} in their works. However, a second adjustable mixture parameter n_{ij} is also used in the present study since, n_{ij} can account for the large size disparity between a heavy non-volatile solute and a light SCF solvent [Mchugh and Krukonis, 1994].

For pure components, a and b parameters are calculated from critical constants T_c, P_c and acentric factor ω depending on the type of EOS.

For, PR-EOS,

$$a_i = 0.45724 (R^2 T_c^2 / P_c) \alpha \quad (19)$$

$$\alpha = [1+ K (1-T_r^{05})]^2 \quad (20)$$

$$K = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad (21)$$

$$b_i = 0.07780 R T_c / P_c \quad (22)$$

For SRK-EOS,

$$a_i = 0.42748 (R^2 T_c^2 / P_c) \alpha \quad (23)$$

$$\alpha = [1+K (1-T_r^{05})]^2 \quad (24)$$

$$K = 0.48 + 1.57 \omega - 0.17 \omega^2 \quad (25)$$

$$b_i = 0.08664 (R T_c / P_c) \quad (26)$$

The computer program obtains the optimum k_{ij} and n_{ij} value by simple optimization technique which gives minimum average absolute relative deviation (AARD) between experimental and calculated values of solubility:

When the extract is assumed as a single pseudo-component, the T_C, P_C, ω, P^{sat} of the extract is considered to be sum of the property of the main components multiplied by mole fraction of main components. In our study, the extract is considered to be 50% Bakuchiol and 50% Psoralen and IsoPsoralen by weight.

Results and Discussion:

Table 1 gives comparative look at predicted critical properties for both Bakuchiol and Psoralen as per Ambrose, Joback, Klincewicz-Reid and Lyderson methods. It can be concluded from the Table 1 that prediction methods give almost similar results for Bakuchiol. Klincewicz-Reid simplified method, which does not require group contributions values, predicts high deviations for properties among all prediction methods compared to predictions by CHEMDRAW software. Joback method predicted very high critical pressure for Psoralen. It must be born in mind, Joback method is the only procedure for calculating normal boiling point. Predicted values for critical properties by four methods deviated 0.2% to 21.9% from CHEMDRAW prediction.

Solubility of Bakuchiol and Psoralen:

Values of experimental and predicted solubilities of Bakuchiol and Psoralen based on PR-EOS and SRK-EOS are given in Figure . The solubility (in terms of mole fraction) of both Bakuchiol and Psoralen are found in the range 10^{-06} to 10^{-04} and the solubility increases with pressure. Whereas average absolute relative deviation (AARD) for solubility of Bakuchiol is much high, AARD is much less for Psoralen.. When the extract is considered as a single pseudo component and the critical properties of pseudo-component is based on average value of critical properties of Bakuchiol and Psoralen, the predicted solubility is much better in agreement with experimental value of solubilities.

Bae et al., 1987 have also reported high values of enhancement factor up to 10^7 for several systems studied using PR and SRK equation of state. The present study also reported high enhancement factors for the Bakuchiol ($7.8x\ 10^{16}$ to $2.3x\ 10^{18}$) and Psoralen ($3.3x\ 10^3$ to $1x\ 10^4$) indicating high non-ideal behaviour of these compounds. When the extract is considered to be a single pseudo-component, the enhancement factors are in the range $1.6x\ 10^4$ to $6.6x\ 10^4$.

Conclusions

Critical properties like critical temperature, critical pressure, critical volume are predicted for Bakuchiol and Psoralen based on 4 different group contribution methods. The solubility of Bakuchiol and Psoralen at 220, 260 and 300 bar are predicted based on equation of state models Peng-Robinson and SRK. The predicted solubility agree well with experimental values of solubilities for Psoralen within 9% deviation while for Bakuchiol, the predicted solubility of Bakuchiol deviated from experimental values by about 50%. When the extract is assumed to be a single psudo-component having average properties of both Bakuchiol and Psoralen, both the PR and SRK equations of state agree better with experimental solubility values within 20% deviation.

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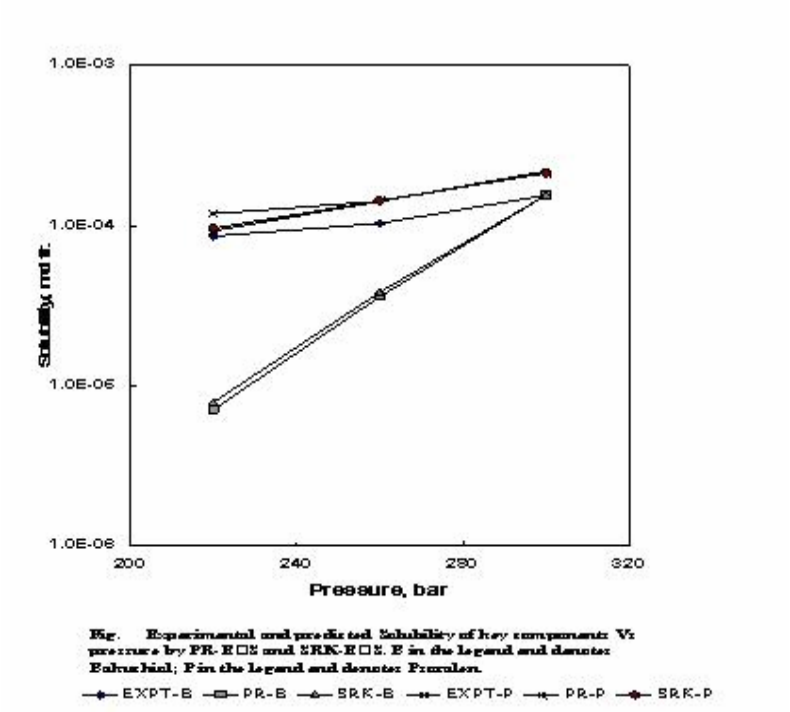

Table 1. Comparison of predicted critical properties of Bakuchiol and Psoralen.

For Bakuchiol:

Property	Ambrose	Joback	Kleincewicz-Reid[a]	Kleincewicz-Reid[b]	Lyderson	Chemdraw*
Critical temperature, K	943	947.9	991.8	1025	931.6	821.4
Critical pressure, bar	18	19.4	21.7	21.2	18	18.97
Critical volume, cc/gmole	853	832.5	884.4	618.7	804	882.5
Normal boiling point, K	--	724.9	--		--	720.4

For Psoralene:

Property	Ambrose	Joback	Kleincewicz-Reid[a]	Kleincewicz-Reid[b]	Lyderson	Chemdraw*
Critical temperature, K	850	793.7	886.9	859.3	841	881.4
Critical Pressure, bar	31	46.5	36.8	32.2	32.5	38.15
Critical volume, cc/gmole	477	485.5	504.4	304.4	469	486.5
Normal boiling point, K	--	565.4	--	--	--	594.94

*CHEMDRAW®Ultra version 8.0 (Cambridgesoft Corporation, Cambridge, USA)

Kleincewicz-Reid[a] Prediction by group contribution.

Kleincewicz-Reid[b] Prediction by simplified equation.