RESEARCH ARTICLE

SUPERCRITICAL FLUID PROCESS MODELING

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ARTICLE INFO	ABSTRACT

This paper introduces Supercritical Fluid and the factors are considered why it is used for Extraction. This describes the classification and study of various models used for predicting solubility of solid solutes in Supercritical Fluid. Correlating and Predicting of solid solubility can be done by Semi-empirical Equations and different Equations of State. Due to the various limitations of empirical equations a more exact approach is to treat the calculation of solubility in a supercritical fluid just as any other phase equilibrium calculation. Thermodynamic equilibrium is assumed to exist between the two phases, thus, they are assumed to be at the same temperature and pressure. Further, the chemical potential (or equivalently, the fugacity) of each component must be equal in each phase. Cubic Equations of State cannot be applied for associating molecules so we are approaching molecular thermodynamics which include SAFT(Statistical association Fluid Theory) and ESD(Elliott-Suresh-Donohue). For all these we need various physical parameters like Tc, Pc, ω, Ps at for some solid solute it is given in the literature but for complex solutes like pharmaceutical drugs and dyes etc. It is not given in literature so we will calculate it by various different Group Contribution Methods like Joback's , Constantino-Gani method, Ambrose-method, Lydersen Method. I had done this for various solutes. I had done calculation for pharmaceutical drugs like Flubiprofen, Ketoprofen, Naproxen, Ibuprofen and various anthraquione dyes and its derivatives

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INTRODUCTION

- Supercritical fluid it has both liquid like and gas like property.
- Like compressible fluid it fills its container and as a non-compressible fluid it has comparable densities and solvating power.
- Higher diffusivity which leads to faster mass transfer but also shorter extraction time.
- Low viscosity & Surface tension enable to penetrate the matter to be extracted.
- Solvent strength of the supercritical fluid is a function of density, which is a function of temperature and pressure.

Table 1. Comparison of different fluids[15]

Property	State		
	Gas	SCF	Liquid
Density	10^{-3}	0.3	1
Diffusivity	10^{-1}	10^{-3}	5×10^{-6}
Viscosity	10^{-4}	10^{-4}	10^{-2}

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Supercritical fluid technology is replacing older solvent technologies, pharmaceutical extractions, and creating new technologies, such as impregnation and delivery systems, because it is safe, environmentally friendly and cost effective. So. It becomes necessary to find out solubilities of solutes in Supercritical Fluid. There are semi-empirical equations used for the correlation of solubility

Charstil's Density Model (Charstil, 1982)

Chrastil's model related the solubilities of solutes directly to the density of a compressed gas solvent and avoided the complexity of equations of state.

$$S = \rho^k \exp\left(\frac{a}{T} + b\right)$$

Thermodynamic modeling (Smith et al., 1996; Sandler, 2006)

Fundamental relationship for phases at equilibrium is,

$$f_i^\alpha = f_i^\beta$$

where f_i is the fugacity of the component i in α and β phase. For solid solute (1)solubility in SCF phase (2),

$$f_1^l = f_1^{sat} = \phi_1^{sat} P^{sat}$$

$$\ln \frac{f_i}{f_i^{sat}} = \frac{1}{RT} \int_{P_i^{sat}}^{P} V_i dP$$

$$f_1^s = f_1^{sat} \exp\left(\int_{P1}^{P} \frac{V_1^s dp}{RT}\right) = \phi_1^{sat} P_1^{sat} \exp\left(\int_{P1}^{P} \frac{V_1^s dp}{RT}\right)$$

P_1^s is the vapor pressure of pure solid,

Φ_1^s is the fugacity coefficient at vapor pressure P_1^s, and V_1^s is the solid molar volume for temperature T.

Fugacity for vapor phase can be defined as:

$$\hat{f}_1^v = y_1 \hat{\phi}_1 P.$$

Combining all these equations we get

$$y_1 = \frac{P^{sat} \phi_1^{sat}}{P \hat{\phi}_1} \exp\left(\int_{P_1^s}^{P} \frac{V_1^s dP}{RT}\right) = \frac{P^{sat}}{P} F_1$$

F_1 is called enhancement factor and generally greater than unity, $\hat{\phi}_1$ is the vapor phase fugacity Coefficient for the high pressure gas mixtures. Since saturation pressure of the solid, P_1^s is generally very small, and for practical purposes, the saturated vapor is an ideal gas, Φ_1^{sat} is close to unity.

Fugacity coefficients must be computed from an equation of state, and it is crucial to calculate it correct since it is the hearth of most engineering calculations. The Classifications for calculating fugacity coefficient in this are:

1) Cubic Equations of State.
2) Molecular based Equations of State.

Cubic equations of state (Smith et al., 1996; Sandler, 2006)

Most widely used models for fugacity calculations treating the SCF solvent as a dense gas are based on cubic equations of state (CEOS), such as the Peng-Robinson (PR; Peng and Robinson, 1976) and the Soave-Redlich-Kwong (SRK; Soave, 1972) equations. These equations with different mixing and combining rules is used.

Mixing Rules and Combining Rules (Mukhopadhyay and Raghuram Rao, 1993)

The great utility of equation of state is for phase equilibrium calculations involving mixtures.

The assumption inherent in such calculation is that the same equation of state used for pure fluids can be used for mixtures if we have a satisfactory way to obtain the mixture parameters.

Cubic equations of state

We have an expression general enough, which reduces to all, equation of interest here upon assignment of appropriate parameter.

$P=[(R \times T)/(v-b)]-[(a(T)/(v+\in b)*(v+\sigma b)]$

$\in$ & σ are pure no. Same for all substances where as parameters a(T) and b are substance dependent. Temperature dependence of a(T) is specific to each E.O.S.

$a(T)=(\psi \alpha(Tr)R2Tc2)/Pc$

$b=\Omega RTc/Pc$

The usefulness of this all in respective phase equilibria to evaluate supercritical extraction process. The equations are used to generate P-T-x-y diagram over the entire range of fluid phase.

Parameter Assignments for equations of state

EOS	α(Tr)	σ	$\in$	Ω	ψ	Zc
Vdw (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$Tr^{(-1/2)}$	1	0	0.08664	0.42748	1/3
SRK (1972)	αSRK	1	0	0.0866	0.4274	1/3
PR (1976)	αPR	$1+(2)^{(1/2)}$	$1+(2)^{1/2}$	0.0777	0.45724	0.307

αSRK=$[1+(0.480+1.574\omega-0.176\omega^2)(1-Tr^{(1/2)})]^2$
αPR=$[1+(0.37464+1.54226\omega-0.26992\omega^2)(1-Tr^{(1/2)})]^2$

ALGORITHM FOR THE CALCULATION CARRIED BY DIFFERENT EQUATIONS OF STATE

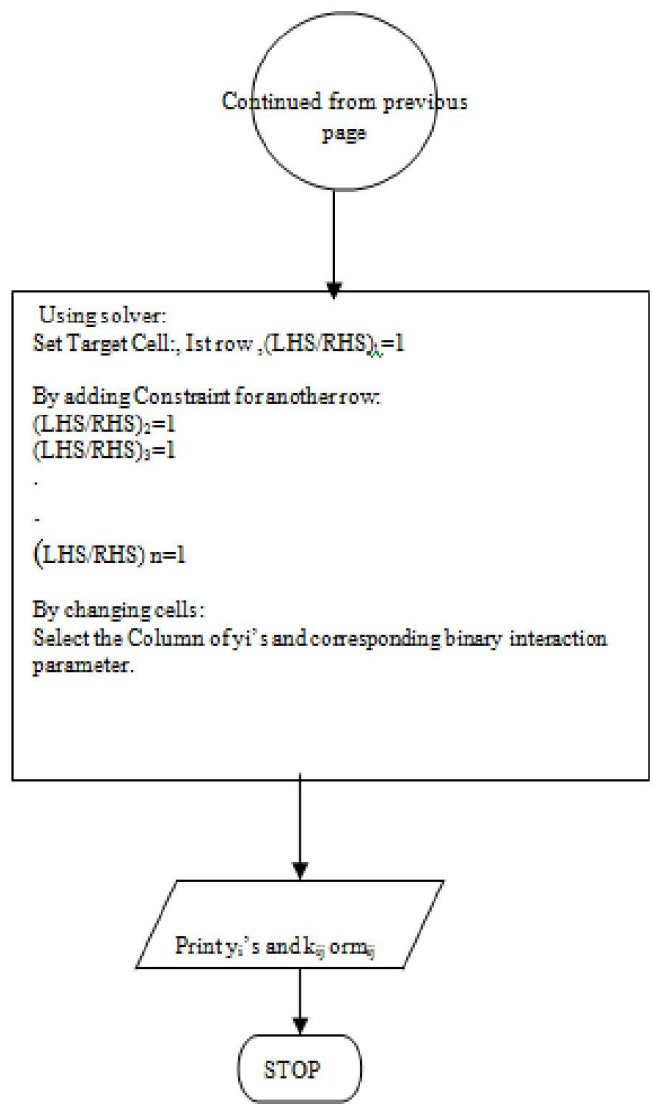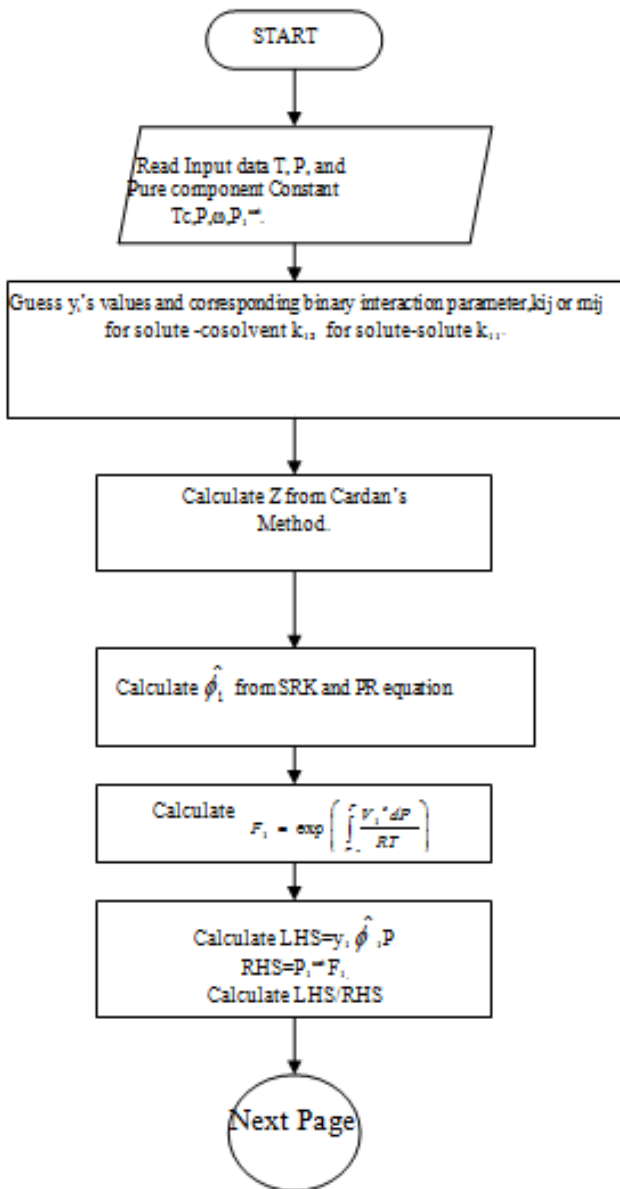FLOW CHART for different EOS of State with different mixing rule can be discussed

Programs for PR and SRK Eos with different mixing rules

Predicted results of solubility of solid solutes in supercritical co_2 by different models: (Reid et al., 2001) [23],[24]

Correlation Results of some solid solute with PR and SRK Equation of State with different mixing Rules:

Comparison of calculated binary interaction parameter and %AARD by SRK-VdWI, PR-VdWI and PR-CVD with literature data

Similarly, for different compounds calculations has been done at different temperatures using different equations and different equations of state and results compared.

START

Read Input data T, P, and Pure component Constant $T_c, P_c, \omega, P_i^{sat}$.

Guess y_i's values and corresponding binary interaction parameter, kij or mij for solute -cosolvent k_{13} for solute-solute k_{11}.

Calculate Z from Cardan's Method.

Calculate $\hat{\phi}_i$ from SRK and PR equation

Calculate $F_i = \exp\left(\int_{-}^{-} \frac{V_i \cdot dP}{RT}\right)$

Calculate LHS= $y_i \hat{\phi}_i$ P
RHS=$P_i^{sat} F_i$
Calculate LHS/RHS

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Using solver:
Set Target Cell:, Ist row ,$(LHS/RHS)_1$=1

By adding Constraint for another row:
$(LHS/RHS)_2$=1
$(LHS/RHS)_3$=1
.

.
(LHS/RHS) n=1

By changing cells:
Select the Column of y_i's and corresponding binary interaction parameter.

Print y_i's and k_{ij} or m_{ij}

STOP

Conclusion

Phase equilibria calculations have been done for solid solute and the results have been found out which is mentioned in previous chapter. The discussions related to the advantages and limitations of model have also been discussed.

From all the results giving %AARD and the study of the graph showing comparison between calculated and experimental graph we can conclude PR EOS of State with VdWI and for complex systems PR EOS with VdWII can give results approximately. So, the solubility can be predicted by using this EOS.

In the present work all the calculations are done using MICROSOFT- EXCEL®. While using Solver Prior knowledge about the range of experimental data and binary interaction parameter is necessary. So, that initial guess can have certain base and it takes less time to reach to the required results
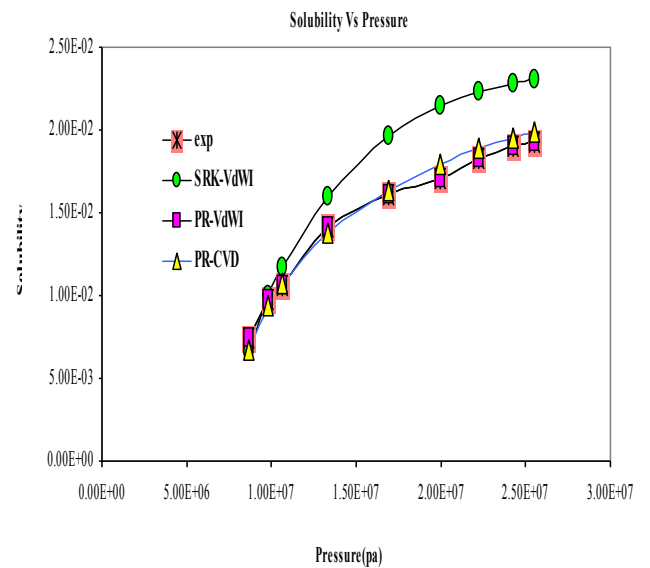
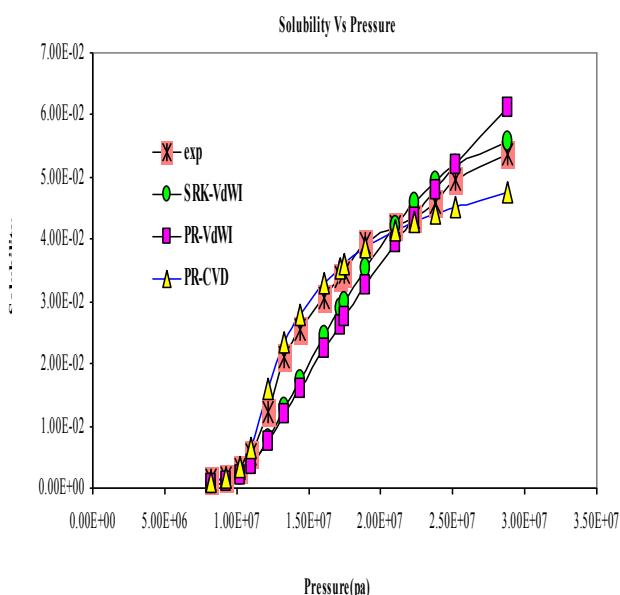**Figure 1. Comparison of solubility predictions for the Naphthalene-CO$_2$ system at 308.15 K**

Figure 2. Comparison of solubility predictions for the Naphthalene-CO_2 system at 328.15 K

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