A new three parameter thermodynamic model for the solubility of substituted phenol compounds in supercritical carbon dioxide

Sridar Ramachandran[1], Avijit Bhowal[2], Chandrasekhar Garlapati[1]*
[1]Department of Chemical Engineering, Pondicherry Engineering College, Pondicherry,India
[2]Department of Chemical Engineering, Jadavpur University, Kolkata, India
* **Corresponding author: E-mail:chandrasekar@pec.edu,**

ABSTRACT

In order to design and optimize supercritical fluid extraction (SCFE) processes, solubility of solids in supercritical fluids are very much essential as it controls the economics of the overall process. New methods for correlating and predicting high-pressure phase equilibria are needed to reduce costly and expensive experimental investigations. Therefore, in the present study, the solubility of 19 substituted phenol compounds have been correlated using the most widely employed semi-empirical models such as Chrastil, Chrastil modified by Garlapati-Madras, Kumar-Johnston and Bartle and a new three parameter thermodynamic model has been proposed. The correlation capabilities of the existing models and the proposed model were compared in terms of percentage average absolute relative deviation (%AARD). The proposed model was found to correlate better in terms of %AARD than the semi-empirical models used in this study.

Keywords: Solubility, Substituted Phenol Compounds, Semi Empirical Models, Supercritical Fluids, Average Absolute Relative Deviation

INTRODUCTION

Substituted phenol compounds are used in a variety of processes such as textile dying, pharmaceuticals, in the manufacture of pesticides, fungicides and intermediates for synthesis of a variety of specialty chemicals etc. Some of the substituted phenol compounds are highly toxic and have been listed on the United States (US) Environmental Protection Agency (EPA) priority pollutant list. Therefore, removal of these compounds should be given due importance and this requires solubility information of these compounds in supercritical fluids. Generally, there are two different approaches followed in modeling the solubility of solids in supercritical fluids. One is the equation of state (EOS) approach and the other one is the density based approach. EOS models has got its own limitations [1-15] and density based semi-empirical models has been widely employed to correlate the solubility of solids in supercritical fluids The objective of this study is to propose a new semi-empirical model to correlate the solubility of substituted phenol compounds and to compare the new model with the most commonly used existing density based models such as the Chrastil model, Chrastil modified by Garlapati and Madras [G-M], Kumar and Johnston [K-J] model and Bartle models.

REVIEW OF SOME DENSITY BASED MODELS In this section, four of the most commonly used density based semi-empirical models namely Chrastil, Chrastil modified by Garlapati and Madras, Kumar and Johnston and Bartle models are presented.

1. **Chrastil model:** It relates the solubility of the solute to the density of the supercritical solvent and temperature as follows

$$y_2 = \frac{\rho_1^{\kappa-1} \exp\left(\frac{\alpha}{T}+\beta\right)}{\left[1+\rho_1^{\kappa-1} \exp\left(\frac{\alpha}{T}+\beta\right)\right]} \quad (1)$$

2. Chrastil modified by Garlapati and Madras as follows:

$$y_2 = (\rho_1 T)^{a_1} \exp\left(a_0 + \frac{a_2}{T}\right) \quad (2)$$

where a_0, a_1 and a_2 are the model constants. The constant a_1 is the association number, a_0 is constant related to the molecular weights of the solute and the solvent and a_2 is related to the total enthalpy change

3. Kumar and Johnston model [19] According to this model, the solubility in terms of mole fraction is related to the density of the supercritical fluid (ρ_1) and temperature as follows

$$y_2 = \exp\left(b_0 + b_1\rho_1 + \frac{b_2}{T}\right) \quad (3)$$

where b_0 , b_1 and b_2 are the model constants and b_2 is related to the total enthalpy change (ΔH) as $b_2 = \frac{\Delta H}{R}$, where R is the gas constant; ΔH is equal to sum of the enthalpy of vaporization and enthalpy of salvation.

4. Bartle model: This model was based on the concept of an enhancement factor (ratio of the actual solubility to the ideal solubility) proposed by Johnston et al. According to this model the solubility of the solute and the density of the pure solvent are related as

$$y_2 = \frac{1}{P}\exp\left(c_0 + \frac{c_1}{T} + c_2\left(\rho_1 - \rho_{ref}\right)\right) \quad (4)$$

where y_2 is the solubility in mole fraction, P is the pressure, ρ_1 is density of $SCCO_2$ and ρ_{ref} is the reference $SCCO_2$ density (700 kgm^{-3}). The reason for using a value of ρ_{ref} of 700 kgm^{-3} is to make the term $\left(c_0 + \frac{c_1}{T}\right)$ much less sensitive to experimental errors in solubility data when extrapolated to zero density. c_1 is related to the enthalpy of vaporization of the solid, $\Delta_{sub}H$ by $\Delta_{sub}H = -c_1 R$ where R is universal gas constant.

5. The proposed model: The proposed model has been derived from the criterion of phase equilibrium [20]. The main assumption behind the proposed model is that the vapor pressure of the solid is negligibly smaller than the pressure of supercritical fluid system and the pressure of the system has been replaced by the density of the supercritical fluid. The model can be written as follows

$$y_2 = \frac{1}{(\rho_1 T)}\exp\left(d_0 + \frac{d_1}{T} + d_2\rho_1\right) \quad (5)$$

Where y_2 is the solubility in mole fraction, ρ_1 is density of $SCCO_2$ and d_0, d_1 and d_2 are the model constants.

METHODOLOGY

In this work, the density of $SCCO_2$ for all the models was calculated using Span and Wagner [21] equation of state (EOS) as it is specific for the estimation of density of $SCCO_2$. The parameters of the models used in this study for each compound were determined using Levenberg-Marquardt minimization algorithm which uses the following objective function:

$$OF = \sum_{i=1}^{N_i} \frac{\left|y_2^{cal} - y_2^{\exp}\right|}{y_2^{\exp}} \quad (6)$$

Where N_i is the number of experimental solubility data points y_2 represents the molar solubility of the solute in $SCCO_2$ and the superscripts cal and exp denotes the calculated and experimental values respectively.

The accuracy of the calculations was evaluated in terms of percentage average absolute relative deviation, (% AARD) and is defined as follows:

$$\frac{100}{N_i}\sum_{i=1}^{N_i} \frac{\left|y_2^{cal} - y_2^{\exp}\right|}{y_2^{\exp}} \quad (7)$$

RESULTS AND DISCUSSION

The solubilities of 19 substituted phenol compounds has been modeled using the most commonly used density based semi-empirical models such as the Chrastil , Chrastil modified by Garlapati-Madras (G-M), Kumar and Johnston (K-J) and Bartle models. The Chrastil model was based on the formation of a solvate-complex and it was modified by G-M for dimensional consistency whereas the K-J model and the Bartle model was based on the concept of an enhancement factor (the ratio of actual solubility to the ideal solubility). The major advantage of these models is that it requires only the density of the supercritical fluid and the experimental data on the solubility of the solid in $SCCO_2$. The details on the phase equilibrium data for the 19 substituted phenol compounds considered in this work is given in Table 1. A new thermodynamic model has been proposed using the criterion of phase equilibrium and it has three adjustable parameters.

The main assumption made while deriving the proposed model from the criterion of phase equilibrium is that the vapor pressure of the solid is negligibly smaller than the pressure of supercritical fluid system. Hence, all the models including the proposed model have three adjustable parameters and form the basis for comparison of the models used in this study in terms of %AARD. One of the adjustable parameters of the model is related to the total heat of reaction for Chrastil, Chrastil modified by Garlapati-Madras and K-J models and to the enthalpy of vaporization for the Bartle and the proposed model. The correlation capabilities of the models were predicted in terms of average absolute relative deviation and the average AARD of the Chrastil, Chrastil modified by G-M, K-J, Bartle and the proposed models are 15.45%, 15.37%, 11.88%, 11.42% and 10.43% respectively and are shown in Table 2. It can be seen from the average AARD that the proposed model seems to correlate better than the existing models; however Bartle's model was found to correlate better than all other models considered in this study for compound numbers 2, 4, 8, 9, 10, 11, 13, and 15.

Table.1.Details on the phase equilibrium data for the substituted phenol compounds considered in this study

S.No.	Compound	T (K)	P(MPa)	Mole fraction, $y \times 10^6$	ρ (kgmol m^{-3})	N_i
1.	3,4-Dimethylphenol	308.15	8.2-26.2	2340-9100	12.31-20.66	7
2.	2,3,5-Trimethylphenol	308	10.1-28.0	2410-4880	16.36-20.90	7
3.	2,3-Dimethylphenol	308	10.1-28.0	6180-1550	16.36-20.90	7
4.	2,4,6- Trimethylphenol	308	10.1-24.0	14700-25600	16.36-20.37	6
5.	2,4,6- Trinitrophenol	308-338	12.16-48.64	22-2650	7.44-22.76	50
6.	2,4-Dichlorophenol	309.2	8.03-20.62	20.84-108.10	8.42-19.69	8
7.	2,4-Dinitrophenol	308-348	12.16-48.54	386-14000	7.44-22.47	42
8.	2,5-Dimethylphenol	308	10.1-28.0	6400-11600	16.36-20.90	7
9.	2,5-Dinitrophenol	308-348	12.16-48.64	316-9440	7.44-22.47	45
10.	2,6-Dibromophenol	298.15-373.15	20-50	15.4-351	10.96-23.49	20
11.	2-Tert-butylphenol	353.2-393.1	6.09-20.09	600-34800	2.11-12.35	55
12.	4-(Phenylazo)phenol	308.2-333.2	9.1-25.3	1710-8570	6.74-20.53	14
13.	4-Methylphenol	353.15-423.15	2.0-20.0	506-2260	0.59-13.53	31
14.	4-Phenylphenol	308	10.1-28.0	51.4-136	16.36-20.90	7
15.	4-Tert-butylphenol	308	10.1-28.0	3090-7440	16.36-20.90	7
16.	m-Nitrophenol	308-348	12.16-48.64	132-4450	7.44-22.76	49
17.	p-Chlorophenol	309.2	8.1-23.98	5960-32890	9.04-20.24	11
18.	Pentachlorophenol	308-328	9.0-23.65	103-480	13.47-19.44	15
19.	p-Nitrophenol	308-348	12.16-48.54	98-1970	7.44-22.76	49

Table.2.AARD (%) of each model for each substituted phenol compounds

S.No.	%AARD				
	Chrastil	G-M	K-J	Bartle	Proposed Thermodynamic model
1.	1.63	2.17	2.02	8.84	2.64
2.	2.01	1.98	2.63	0.74	2.88
3.	3.2	2.16	1.96	4.48	2.00
4.	1.36	1.16	1.85	1.84	2.04
5.	11.99	11.88	10.62	13.69	11.86
6.	26.48	26.08	22.07	28.81	20.55
7.	29.27	30.21	28.01	29.93	28.71
8.	2.88	2.35	3.08	1.58	3.44
9.	14.64	14.76	13.65	14.1	14.58
10.	18.69	18	15.43	15.67	15.96
11.	34.46	34.1	16.87	11.71	15.66
12.	9.65	9.06	11.16	13.82	13.72
13.	88.72	91.3	58	18.49	24.59
14.	3.91	3.3	2.91	5.66	2.48
15.	1.98	2.39	2.9	0.69	3.02
16.	14.5	14.9	11.9	13.4	12.1
17.	15.41	15	11.94	18.39	11.01
18.	3.83	3.9	4.19	4.75	4.37
19.	8.87	7.42	4.62	10.39	6.06
Avg.	15.45	15.37	11.88	11.42	10.40

CONCLUSIONS

The solubility data for 19 substituted phenol compounds in $SCCO_2$ reported in the literature have been modeled by employing four most widely used density based semi-empirical models and a three parameter density based thermodynamic model has been

proposed using the criterion of phase equilibrium studies. The proposed model seems to correlate better than the existing models with an average AARD of 10.43%. Further, the proposed model has got a strong theoretical background as it has been derived from the phase equilibrium criterion.

REFERENCES

Bartle KD, Clifford AA, Jafar SA, Shilstone GF, J. Phys. Chem. Ref. Data 20, 1991, 713.
Chrastil J, J. Phys.Chem., 86, 1982, 3016.
Cross WJ, Akgerman A, Ind. Eng. Chem. Res., 37, 1998, 1510.
Dohrn R, Brunner G, Fluid Phase Equilibria, 106, 1995, 213.
Eckert CA, Knutson BL, Debenedetti PG, Nature, 383, 1996, 313.
Fiege H, Cresols and xylenols. In Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany 2003.
Fiege H, Voges HW, Hamamoto T, Umemura S, Iwata T, Miki H, Fujita Y, Buysch HJ, Garbe D, Paulus W, Phenol derivatives. In Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim, Germany 2003.
Foster NR, Gurdial GS, Yun JSL, Liong KK, Tilly KD, Ting SST, Singh H, Lee JH, Ind. Eng. Chem. Res., 30, 1991, 1955.
Gamse T, Steinkellner F, Marr R, Alessi P, Kikic I, Ind. Eng. Chem. Res., 39, 2000, 4888.
Garlapati C, Madras G, J. Chem. Thermodynamics, 42, 2010, 193.
Giddings JC, Myers MN, McLaren L, Keller RA, Science, 162, 1968, 67.
Huang Z, Lu WD, Kawi S, Chiew YC, J. Chem. Eng. Data, 49, 2004, 1323.
Jessop PG, Leitner W, Eds., Wiley-VCH, Weinheim, 1, 1999.
Johnston KP, Peck DG, Kim S, Ind. Eng. Chem. Res., 28, 1989, 1115.
Kumar SK, Johnston KP, J. Supercrit. Fluids, 1, 1988, 15.
Kyle GB, Chemical and Process Thermodynamics, Third Eds., Prentice Hall of India Private Limited, New Delhi, 1999, 410.
Lee MJ, Kou CF, Cheng JW, Lin Hm, Fluid Phase Equilib., 162, 1999, 211.
Maeda S, Mishima K, Matsuyama K, Baba M, Hirabaru T, Ishikawa H, Hayashi KI, J. Chem. Eng. Data, 46, 2001, 647.
McHugh MA, Krukonis VJ, Butterworth, Boston, Chapter 1, 1986.
McNally MEP, Anal. Chem., 67, 1995, 308A.
Mishima K, Matsuyama K, Ishikawa H, Hayashi KI, Maeda S, Fluid Phase Equilib., 194-197, 2002, 895.
Modell M, de Fillippi RP, Krukonis VJ, Presented at the 178th National meeting of the American Chemical Society, Miami, Fla. Sept. 14, 1978.
Mori Y, Shimizu T, Iwai Y, Arai Y, J. Chem. Eng. Data, 37, 1992, 317.
Ravipaty S, Sclafani AG, Fonslow BR, Chesney DJ, J. Chem. Eng. Data, 51, 2006, 1310.
Shamsipur M, Fat'hi MR, Yamini Y, Ghiasvand AR, J. Supercrit. Fluids, 23, 2002, 225.
Span R, Wagner W, J. Phys. Chem. Ref. Data, 25, 1996, 1509.
Sridar R, Avijit B, Chandrasekhar G, Thermochimica Acta, 561, 2013, 91-97.
Ustundag OG, Temelli F, Ind. Eng. Chem. Res., 39, 2000, 4756.
Van Leer RA, Paulaitis ME, J. Chem. Eng. Data, 25, 1980, 257.
Vitzthum O, Hubert P, German patent, 2, 357, 590, 1975.
Walther D, Maurer G, J. Chem. Eng. Data, 38, 1993, 247