Modeling the solubilities of high molecular weight n-alkanes in supercritical carbon dioxide

Sujit Kumar Jha, Giridhar Madras[*]

Department of Chemical Engineering,

Indian Institute of Science, Bangalore-560 012, India

Abstract

The Peng-Robinson equation of state with quadratic mixing rules and a single adjustable parameter was used to model the solubilities of various high molecular weight solid n-alkanes in supercritical carbon dioxide. The key conclusion of the study is that the adjustable parameter, k_{ij}, varies linearly with the number of carbon atoms in the main chain of the n-alkane. Thus, the model can be used to predict the solubilities of various high molecular weight solid n-alkanes in supercritical carbon dioxide.

Keywords: Supercritical fluids; Solubility; Model; Alkane; Equation of state

[*] Corresponding author. Tel: +91-80-2293 2321; Fax: +91-080-360 0683.
E-mail address: giridhar@chemeng.iisc.ernet.in (G. Madras)

1. Introduction

Fluids at temperature and pressure higher than their critical temperature and pressure are called supercritical fluids (ScFs). ScFs are used in the food **[1]**, pharmaceutical **[2]** and petroleum **[3]** industries related applications. A significant amount of research has been devoted to their use as alternative environmentally friendly solvents **[4]**. Whenever a solid or a liquid is contacted by a supercritical fluid, phase equilibrium exists. Thus, it becomes important to study the phase behavior involved. The experimental methods and systems investigated in high-pressure fluid phase equilibria have been reviewed **[5, 6]** and an exhaustive account on the experimental data on the solubilities of various organics in a variety of ScFs is available **[7]**. Since the experimental determination of the solubilities of various solutes in ScFs at various temperature and pressure is time consuming and expensive, modeling and prediction of the solubilities is important.

The solubility of high molecular weight n-alkanes in supercritical carbon dioxide (ScCO2) is of interest in the design of hydrocarbon processing systems **[8, 9]**. Peters et al. **[10]** postulated a relationship between the solubility of liquid i.e., relatively lower molecular weight, n-alkanes in supercritical solvents and the carbon number of the solute. The logarithm of the mole fraction of the solute was found to vary linearly with the carbon number. However, the formulation breaks down at near criticality of a solvent-n-alkane mixture. Reverchon et al. **[9]** correlated the solubility of solid n-octacosane ($C_{28}H_{58}$) and n-triacontane ($C_{30}H_{62}$) using the linear relationship between the logarithm of the solubility and the logarithm of the density of the pure solvent. Furuya and Teja **[8]**

correlated their experimental data using an extension of the theory of dilute solution proposed by Mendez-Santiago and Teja **[11]**. The Krichevskii parameters were calculated based on the solubility of heavy *n*-alkanes in supercritical carbon dioxide and the results show that the variation of the Krichevskii parameter with the carbon number of the *n*-alkane is linear **[12]**.

In this study, the Peng-Robinson equation of state (PR-EOS) with quadratic mixing rules has been used to calculate the solubilities of the solid n-alkanes in supercritical carbon dioxide. The adjustable binary interaction parameter in the model is found to vary linearly with the chain length of the n-alkanes. Based on this key observation, the binary interaction parameter and hence, the solubilities of other n-alkanes in the homologous series can be predicted.

2. Theoretical background

The solubility of a heavy nonvolatile solid in the supercritical fluid solvent phase is given by

$$y_i = \frac{p_i^{sat}\phi_i^{sat}\exp\left[\dfrac{\left(p - p_i^{sat}\right)v_{is}}{RT}\right]}{\hat{\phi}_i^{ScF}\,p} \qquad (1)$$

where p_i^{sat} is the sublimation pressure of the pure solid at the system temperature, T, p is the system pressure, v_{is} is the molar volume of the pure solid, R is the universal gas constant. The fugacity coefficient of the pure solute at its saturation pressure, ϕ_i^{sat}, is taken to be unity and the fugacity of the solute in the supercritical phase, $\hat{\phi}_i^{ScF}$, is calculated using an equation of state (EOS) in combination with a mixing rule. p_i^{sat} of

high molecular weight n-alkanes can be obtained using the correlation proposed by Pouillot et al. **[13]**. The PR-EOS **[14]** is

$$p = \frac{RT}{V-b} - \frac{a}{V^2+2Vb-b^2}$$
$$a = \frac{0.457235R^2T_c^2\gamma}{p_c}, \gamma = \left(1+(0.37464+1.54226\omega-0.26992\omega^2)\left(1-\sqrt{T/T_c}\right)\right)^2,$$
$$b = \frac{0.077796RT_c}{p_c} \qquad (2)$$

where V is the molar volume of the supercritical phase, T_c is the critical temperature, p_c is the critical pressure and ω is the accentric factor. Since the experimental values of T_c, p_c and ω are unavailable for heavy n-alkanes, these are estimated using group-contribution methods. The van der Waals quadratic mixing rules with the two parameters combining rules **[15]** are

$$a = \sum_i \sum_j y_i y_j a_{ij} \; ; \; a_{ij} = (1-k_{ij})\sqrt{a_{ii}a_{jj}}$$

$$b = \sum_i \sum_j y_i y_j b_{ij} \; ; \; b_{ij} = (1-l_{ij})\frac{\left(b_{ii}^{1/3}+b_{jj}^{1/3}\right)^3}{8} \qquad (3)$$

where indices i and j respectively refer to solute and supercritical fluid. k_{ij} and l_{ij} are two adjustable binary interaction parameters (PR2). $\hat{\phi}_i^{ScF}$ is given by

$$\ln\hat{\phi}_i^{ScF} = -\ln\left[\frac{p(V-b)}{RT}\right] + \frac{1}{b}\left(\frac{\partial nb}{\partial n_i}\right)\left(\frac{pV}{RT}-1\right) + \frac{a}{2\sqrt{2}bRT}\left[\frac{1}{a}\left(\frac{1}{n}\frac{\partial n^2 a}{\partial n_i}\right)-\frac{1}{b}\left(\frac{\partial nb}{\partial n_i}\right)\right]\ln\left[\frac{V+b\left(1-\sqrt{2}\right)}{V+b\left(1+\sqrt{2}\right)}\right] \qquad (4)$$

To reduce the number of parameters, l_{ij} is set to zero (PR1).

3. Results and discussion

Figure 1 shows the prediction of the solubility of n-octacosane in ScCO2 at 308.2 K using a one parameter model (PR1, $k_{ij} \neq 0$, $l_{ij} = 0$). The Gauss-Newton algorithm with

Levenberg-Marquardt modifications for global convergence **[17]** was used to determine the optimum value of k_{ij} that minimizes the sum of the squares of relative error in the prediction of the solubility. **Table 1** lists k_{ij} for various n-alkane-ScCO2 systems at 308.2 K, 328.2 K and 318.2 K. With the optimum value of k_{ij} for n-octacosane-ScCO2 at 308.2 K, the average absolute relative deviation (AARD) for the prediction of the solubility is 7.6%. The introduction of the second parameter (PR2, $k_{ij} \neq l_{ij} \neq 0$) results in AARD of 7.5% indicating there is no significant improvement in the prediction by introducing the second parameter. The one parameter model has been used previously **[19, 20]** for an adequate representation of the experimental solubility of organics in ScFs. Though more accurate combinations of EOS and mixing rules, such as Patel-Teja EOS with Wong-Sandler mixing rules, provide better predictions **[21]**, PR1 has been preferred because of its simplicity. The sensitivity of the parameter, k_{ij}, was investigated by increasing and decreasing the optimum value by 20%. The prediction is poor (**Figure 1**) with the AARD increasing to 91.4% and 1049 %, respectively, indicating that the value of k_{ij} is sensitive and critical for modeling the data. **Figures 2, 3** and **4** show the variation of solubilities of various n-alkanes, based on the experimental data by Reverchon et al. **[9]** and Chandler et al. **[16],** with pressure (up to 240 bar) of ScCO2 at various temperatures. The solid lines in the figures represent the prediction by PR1 with different values of the adjustable parameter, k_{ij}. These figures indicate that a single adjustable parameter is sufficient to model the experimental data of solubilities of various n-alkanes.

Figure 5 shows the variation of the adjustable parameter, k_{ij}, with the number of carbon atoms, N_c, in the main chain of the n-alkane. The variation of k_{ij} is linear and is given by $0.868 - 0.024\ N_c$, $0.946 - 0.026\ N_c$ and $1.050 - 0.029\ N_c$ at 308.2 K, 318.2 K

and 328.2 K, respectively. The weak dependence of k_{ij} on temperature is in accordance with that reported by other investigators **[12, 22]**. The linear variation of k_{ij} with the chain length can be explained in terms of the deviation of the unlike parameter, a_{ij}, from the geometric mean due to the asymmetry in the pure component parameters, a_{ii} and a_{jj}; the geometric mean increases with the molecular weight and hence the chain length of the solute **[23]**. The utility of the model is demonstrated by predicting the solubility of n-dotriacontane. The value of k_{ij} determined from the linear relationship depicted in **Figure 5** is 0.110. This value was then used to model the solubility of n-dotriacontane (**Figure 6**) and the AARD for the prediction was 10.5%. This shows that the model can be used to successfully predict the solubilities of solid n-alkanes in supercritical fluids.

4. Conclusions

The solubilities of various high molecular weight solid n-alkanes in supercritical carbon dioxide were modeled using the Peng-Robinson equation of state with quadratic mixing rules and a single adjustable parameter. Though the Peng-Robinson equation of state with quadratic mixing rules is well established for the prediction of the solubility of a solid in a supercritical fluid, the main contribution of this study is the observation that the adjustable parameter varies linearly with the number of carbon atoms in the main chain of the n-alkane. Based on the linear relationship, the adjustable parameter and hence, the solubilities of other solid n-alkanes in the homologous series can be predicted.

5. References:

1. M. Sihvonen, E. Jarvenpaa, V. Hietaniemi, R. Huopalahti, Advances in supercritical carbon dioxide technologies, Trends in Food Science & Technology 10 (1999) 217.
2. B. Subramaniam, R.A. Rajewski, K. Snavely, Pharmaceutical processing with supercritical carbon dioxide, J. Pharm. Sci. 86 (1997) 885.
3. D. E. Knowles, W. D. Felix, N. L. Porter, B. A. Jones, D. L. Knowles, Supercritical fluid chromatography applications for the petroleum industry, International Symposium on Fuels and Lubricants, New Delhi, 2000, p. 367.
4. A. S. Teja, C. A. Eckert, Commentary on supercritical fluids: research and applications, Ind. Eng. Chem. Res. 39 (2000) 4442.
5. R. Dohrn, G. Brunner, High-pressure fluid-phase equilibria: experimental methods and systems investigated (1988-1993), Fluid Phase Equilibria 106 (1995) 213.
6. M. Christov, R. Dohrn, High-pressure fluid phase equilibria experimental methods and systems investigated (1994-1999), Fluid Phase Equilibria 202 (2002) 153.
7. N. R. Foster, G. S. Gurdial, J. S. L. Yun, K. K. Liong, K. D. Tilly, S. S. T. Ting, H. Singh, J. H. Lee, Significance of the crossover pressure in solid-supercritical fluid phase equilibria, Ind. Eng. Chem. Res. 30 (1991) 1955.
8. T. Furuya, A. S. Teja, The solubility of high molecular weight n-alkanes in supercritical carbon dioxide at pressures up to 50 MPa, J. Supercrit. Fluids (2003) in press.

9. E. Reverchon, P. Russo, A. Stassi, Solubilities of solid octacosane and triacontane in supercritical carbon dioxide, J Chem. Eng. Data 38 (1993) 458.
10. C. J. Peters, J. D. S. Arons, A. H. Harvey, J. M. H. L. Sengers, On the relationship between the carbon-number of n-paraffins and their solubility in supercritical solvents, Fluid Phase Equilibria 52 (1989) 389.
11. J. Mendez-Santiago, A. S. Teja, The solubility of solids in supercritical fluids, Fluid Phase Equilibria 160 (1999) 501.
12. T. Furuya, A. S. Teja, Krichevskii parameters and the solubility of heavy n-alkanes in supercritical carbon dioxide, Ind. Eng. Chem. Res. 39 (2000) 4828.
13. F. L. L. Pouillot, K. Chandler, C. A. Eckert, Sublimation pressures of n-alkanes from $C_{20}H_{42}$ to $C_{35}H_{72}$ in the temperature range 308-348 K, Ind. Eng. Chem. Res. 35 (1996) 2408.
14. D. Y. Peng, D. B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fundam. 15 (1976) 59.
15. T. Y. Kwak, G. A. Mansoori, Van der Waals mixing rules for cubic equations of state, applications for supercritical fluid extraction modeling, Chem. Eng. Sci. 41 (1986) 1303.
16. K. Chandler, F. L. L. Pouillot, C. A. Eckert, Phase equilibria of alkanes in natural gas systems. 3. alkanes in carbon dioxide, J Chem. Eng. Data 41 (1996) 6.
17. W. H. Press, S. A. Teukolsky, W. T. Vellerling, B. P. Flannery, in: Numerical Recipes in C: Cambridge University Press, 1992, p. 683.
18. R. C. Reid, J. M. Prausnitz, B. E. Poling, in: The Properties of Gases & Liquids: McGraw-Hill Book Co., Singapore, 1988, p. 12, 23.

19. R. T. Kurnik, S. J. Holla, R. C. Reid, Solubility of solids in supercritical carbon dioxide and ethylene, J Chem. Eng. Data 26 (1981) 47.
20. E. Kosal, G. D. Holder, Solubility of anthracene and phenanthrene mixtures in supercritical carbon dioxide, J Chem. Eng. Data 32 (1987) 148.
21. S. Guha, G. Madras, Modeling of ternary solubilities of organics in supercritical carbon dioxide, Fluid Phase Equilibria, 187 (2001) 255.
22. J. J. Shim, K. P. Johnston, Phase equilibria, partial molar enthalpies, and partial molar volumes determined by supercritical fluid chromatography, J. Phy. Chem. 95 (1991) 353.
23. G. Madras, C. Kulkarni, J. Modak, Modeling the solubilities of fatty acids in supercritical carbon dioxide, Fluid Phase Equilibria 209 (2003) 207.

Table 1. Binary interaction parameter, k_{ij}, for the solubility of various n-alkanes in ScCO2.

n-Alkanes	N_c[a]	T_c[b] (K)	P_c[b] (bar)	ω[c]	k_{ij} at 308.2 K	AARD[d] (%) at 308.2 K	k_{ij} at 318.2 K	AARD[d] (%) at 318.2 K	k_{ij} at 328.2 K	AARD[d] (%) at 328.2 K
n-Tetracosane **[16]**	24	814.8	8.06	0.794	0.276	8.5				
n-Pentacosane **[16]**	25	826.7	7.64	0.759	0.264	7.8				
n-Octacosane **[16]**	28	864.1	6.55	0.609	0.212	7.6	0.216	6.2		
n-Nonacosane **[16]**	29	877.2	6.24	0.545	0.192	8.4	0.194	6.9		
n-Triacontane **[9]**	30	891.2	5.95	0.477	0.171	11.3				
n-Dotriacontane **[16]**	32	920.5	5.43	0.330	0.110[e]	10.5[e]	0.116	6.2	0.125	15.4
n-Tritriacontane **[16]**	33	939.2	5.20	0.253	0.082	10.4	0.086	7.9	0.095	16.6
n-Hexatriacontane **[16]**	36	997.4	4.58	0.074	-0.011	10.9			0.009	16.3

[a] N_c is the number of carbon atoms in the main chain of the n-alkane.

[b] Joback's method from Reid et al. **[18]**

[c] Lee-Kesler method from Reid et al. **[18]**

[d] $AARD(\%) = \frac{100}{N}\sum_{i=1}^{N}\left(\left|y^{pred} - y^{expt}\right| / y^{expt}\right)$, where N is the number of experimental data points.

[e] Predicted from the linear regression (**Figure 5**), k_{ij}=0.868-0.024N_c at 308.2 K.

Figure Captions

1. Solubility of n-octacosane in ScCO2 at 308.2 K.

■ Experimental data **[16]**, ─ PR1 prediction with different values of k_{ij}.

2. Solubility of various n-alkanes in ScCO2 at 308.2 K.

■ n-tetracosane **[16]**, □ n-pentacosane **[16]**, ▲ n-octacosane **[16]**, Δ n- nonacosane **[16]**, ● n-triacontane **[9]**, ○ n-tritriacontane **[16]**, × n-hexatriacontane **[16]**, ─ PR1 prediction.

3. Solubility of various n-alkanes in ScCO2 at 318.2 K.

■ n-octacosane **[16]**, □ n-nonacosane **[16]**, ▲ n-dotriacontane **[16]**, ○ n-tritriacontane **[16]**, ─ PR1 prediction.

4. Solubility of various n-alkanes in ScCO2 at 328.2 K.

■ n- dotriacontane **[16]**, ○ n-tritriacontane **[16]**, ▲ n- hexatriacontane **[16]**, ─ PR1 prediction.

5. Variation in the interaction parameter k_{ij} with the number of carbon atoms, $N_{c,}$ in the main chain of n-alkane.

■ k_{ij} at 308.2 K, ○ k_{ij} at 318.2 K, ▲ k_{ij} at 328.2 K. The solid, dashed and dotted lines represent linear regressed lines at 308.2 K, 318.2 K and 328.2 K, respectively.

6. Solubility of n-dotriacontane in ScCO2 at 308.2 K.

■ Experimental data **[16]**, ─ Prediction by the proposed model

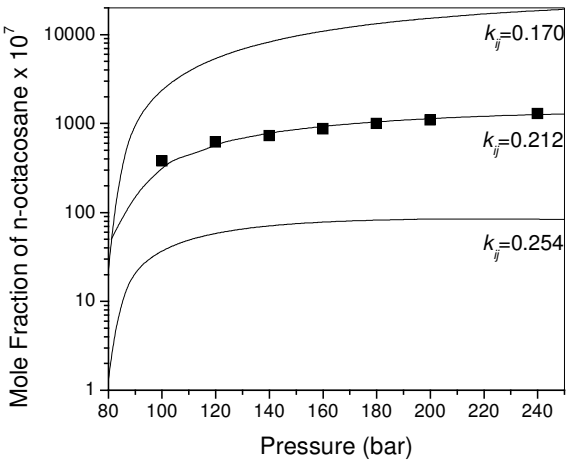
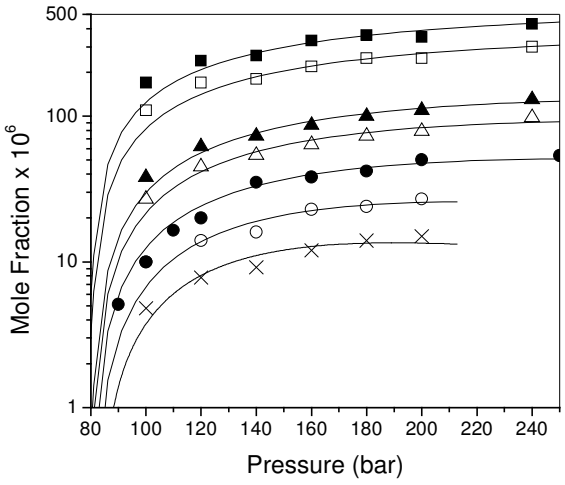

Mole Fraction of n-octacosane x 10^7
10000
1000
100
10
1
80
100
120
140
160
180
200
220
240
Pressure (bar)
k_ij=0.170
k_ij=0.212
k_ij=0.254

Figure 1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10
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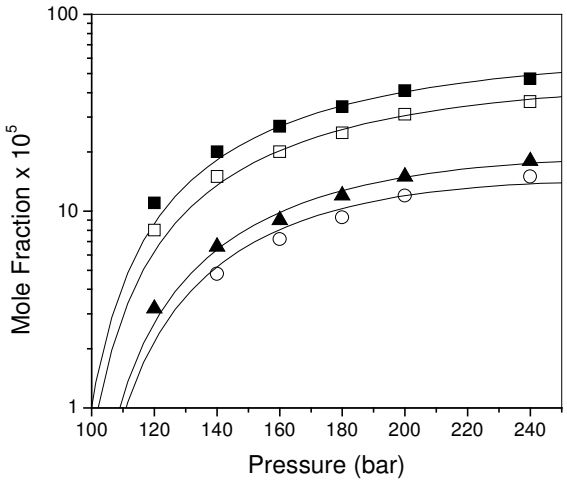
Mole Fraction x 10^6
80
100
120
140
160
180
200
220
240
Pressure (bar)

Figure 2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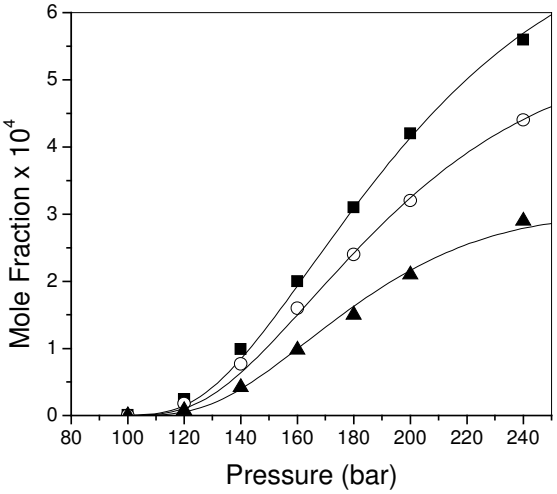
10
1
Mole Fraction x 10^5
100
120
140
160
180
200
220
240
Pressure (bar)

Figure 3


Mole Fraction x 10^4
Pressure (bar)
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1
2
3
4
5
6
80
100
120
140
160
180
200
220
240

Figure 4

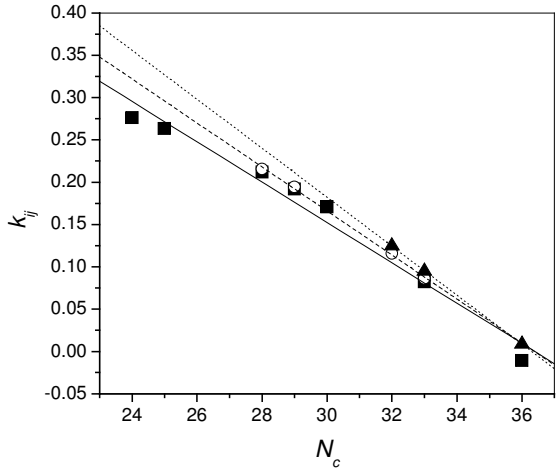
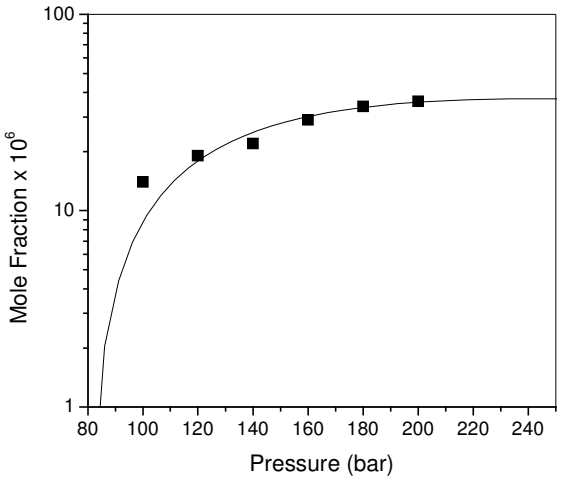


Figure 5


100
10
1
Mole Fraction x 10^6
80
100
120
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160
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200
220
240
Pressure (bar)

Figure 6