Solubility Prediction of High Molecular Weight 
n-Paraffins in Supercritical Carbon Dioxide

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ABSTRACT: Solubility of high molecular weight n-paraffins in supercritical carbon dioxide has been a matter of interest to many researchers. However, not sufficient solubility experimental data are available although the methods by which the experimental data are obtained have many varieties. Utilizing cubic equations of state is an effective method for solubility prediction of n-paraffins in supercritical fluids. In this work, five cubic equations of state (EOS) are employed to predict the solubility of six high molecular weight n-paraffins: n-tetracosane, n-pentacosane, n-hexacosane, n-heptacosane, n-octacosane and n-nonacosane, in supercritical carbon dioxide. The EOSs used are van der Waals, Redlich-Kwong and MohsenNia-Modarress-Mansoori (MMM) as two-parameter EOSs and Soave and Peng-Robinson as three-parameter EOSs. The results show that the two-parameter MMM EOS is more accurate in solubility prediction than the other EOSs.

KEY WORDS: Equation of state, Supercritical CO₂, Solubility, High molecular weight hydrocarbons.

INTRODUCTION
In recent years, the attention of many investigators is drawn to extraction by supercritical fluids (SCF) [1]. The advantages of this method of extraction in comparison with the others make the SCF the most efficient technique in various Industries; such as petroleum, nutritional and pharmaceutical. The unique feature of the supercritical state is that the solvating power strongly depends on the fluid density and can be adjusted, without changing chemical composition, by controlling the pressure and temperature. The SFE technique opens up a wide range of possibilities for selective extraction, purification and, precipitation processes [2]. In comparison with conventional solvents which are liquids, a supercritical fluid has high diffusivity and low viscosity, thus allowing rapid extraction and phase separation. Another attractive feature of supercritical solvents is the fact that their isothermal compressibility is several orders of magnitude greater than that of liquids while their density is the same as liquids [3]. The other significant advantage of supercritical fluid extraction is that the solvent can be
easily separated from the accompanying solute, thereby significantly reducing the contamination of valuable compounds with a residual solvent [4].

Another considerable aspect about SFE is the possibility of solvent selection. Some of the solvents used in this technique are ethane, ethylene, nitrous oxide, and carbon dioxide. Carbon dioxide is a promising solvent for supercritical fluid (SCF) extraction as it is nontoxic, inert, inexpensive, and available in abundance at high purity. In addition, the low critical temperature of carbon dioxide makes it attractive for the extraction of thermally sensitive products [5]. Compressed CO$_2$ has a high degree of solvency for many non-volatile components [4] and this virtue is very important for extraction of n-C$_{24}$ and n-C$_{25}$ as non-volatile n-paraffins. CO$_2$ can be easily recaptured and recycled after use as well [6].

High molecular weight n-paraffins are used as model compounds in petroleum industry applications like the Fischer-Tropsch synthesis [7,8]. Moreover, C$_{25}$-C$_{35}$ n-paraffins represent the main coextracted compounds (called cuticular waxes) in carbon dioxide SFE from vegetable matrices like herbs, flowers and roots [8].

**EQUATIONS OF STATE AND THEIR FUGACITY COEFFICIENTS**

Cubic equations of state are still widely used in chemical engineering practice for calculation and prediction of properties of fluids and fluid mixtures [9].

Cubic equations can be classified into two categories [10]:

i) Equations with two constant parameters fitted to the properties of the critical point which include equations such as van der Walls [11], Redlich-Kwong [12] and MMM [13] equations.

ii) Equations with three or more constant parameters and also equations with two or more temperature-dependent parameters which include Peng-Robinson [14], Soave [15], M$_{i}$ [16] and their modifications. In this report, we utilize vdW, RK and MMM equations among two-parameter equations and Soave and PR among three-parameter equations to calculate the solubility of high molecular weight n-paraffins in supercritical carbon dioxide.

The MMM equation of state is in the following form [13]:

$$P = \frac{RT(v + 1.3191b)}{v(v - b)} - \frac{a}{T^{0.5}v(v + b)}$$  \hspace{1cm} (1)

The mixing rules, parameters and fugacity coefficient of MMM equation of state are presented in Appendix.

The basic relation of equilibrium between two phases $\alpha$ and $\beta$ is given by equality of fugacities for the component $i$ in the two phases:

$$f_i^\alpha = f_i^\beta$$  \hspace{1cm} (2)

One of the key equations for calculating the fugacity coefficients is [17]:

$$\ln(\varphi_i) = \frac{1}{RT} \int_v^\infty \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln(z)$$  \hspace{1cm} (3)

where $z$ is the compressibility factor of the mixture and $\varphi_i$, the fugacity coefficient is defined as:

$$\varphi_i = \frac{f_i}{y_i P}$$  \hspace{1cm} (4)

The solubility, $y$, of a solute, $i$, in a supercritical fluid can be calculated using the following equation:

$$y_i = \left( \frac{P_i^{sat}}{P} \right) \left( \frac{\varphi_i}{\varphi_i^S} \right) \exp\left( \int_{P_i^{sat}}^P \frac{v_i^S}{RT} dP \right)$$  \hspace{1cm} (5)

where $P_i^{sat}$ is the saturation pressure of pure solid, $\varphi_i$ is the fugacity coefficient at pressure $P$, $\varphi_i^S$ is the fugacity coefficient at saturation pressure and $v_i^S$ is the solid molar volume, all at temperature $T$.

Since the saturation pressure of the solute, $P_i^{sat}$, is usually very small, the fugacity coefficient of this phase can be assumed as: $\varphi_i^S \approx 1$.

To compare the results of our calculations with the experimental data, we should have recourse to the reported solubility data in the literature. The solubility data of n-C$_{24}$, n-C$_{25}$, n-C$_{26}$, n-C$_{27}$ and n-C$_{29}$ are from Furuya and Teja [18] and the solubility data of n-C$_{28}$ is from Yau and Tsai [4].

**RESULTS AND DISCUSSION**

The solubility of n-paraffins (n-tetracosane, n-pentacosane, n-hexacosane, n-heptacosane, n-octacosane and n-nonacosane) in supercritical CO$_2$ are calculated by vdW, RK, Soave, PR and MMM EOSs for $k_{ij} = 0$ and plotted in Figs. 1 to 6 versus reduced pressure. In all cases, the solubility prediction by MMM EOS is more accurate.
Fig. 1: Solubility of n-tetracosane in supercritical carbon dioxide at 310K ($k_i = 0$). (●): T. Furuya, A.S. Teja (2004) data [18].

Fig. 2: Solubility of n-pentacosane in supercritical carbon dioxide at 313K ($k_i = 0$). (●): T. Furuya, A.S. Teja (2004) data [18].

Fig. 3: Solubility of n-hexacosane in supercritical carbon dioxide at 313K ($k_i = 0$). (●): T. Furuya, A.S. Teja (2004) data [18].

Fig. 4: Solubility of n-heptacosane in supercritical carbon dioxide at 313K ($k_i = 0$). (●): T. Furuya, A.S. Teja (2004) data [18].

Fig. 5: Solubility of n-octacosane in supercritical carbon dioxide at 308.2, 318.2 and 328.2 K. In each three curves, temperature increases from down to up ($k_i = 0$). Experimental points from Yau and Tsai (1993) [4].

Fig. 6: Solubility of n-nonacosane in supercritical carbon dioxide at 313K ($k_i = 0$). (●): T. Furuya, A.S. Teja (2004) data [18].
For $k_{ij}$ as an adjustable parameter in calculating the solubility of n-paraffins in supercritical CO$_2$ by an EOS, obviously more accurate results can be obtained. This parameter can be evaluated by fitting the experimental solubility data to the results of five EOSs. The fitting procedure has been carried out by minimizing the average absolute deviation (AAD) according to the following equation:

$$
AAD = \frac{1}{N} \sum_{j=1}^{N} \left| \frac{y_{j}^{\text{calc}} - y_{j}^{\text{exp}}}{y_{j}^{\text{exp}}} \right|
$$

where $N$ is the number of data points.

The results of these calculations are tabulated in table 1 for all five EOSs. The solubility curves for n-pentacosane, n-heptacosane and n-nonacosane with $k_{ij} \neq 0$ are plotted versus reduced pressure in Figs. 7 to 9. These figures provide a qualitative scale to compare the calculated solubility by the five EOSs.

CONCLUSIONS

The solubility of n-tetracosane, n-pentacosane, n-hexacosane, n-heptacosane, n-octacosane and n-nonacosane at different temperatures in supercritical carbon dioxide has been calculated by five cubic equations of state; vdW, RK, Soave, PR and MMM. The calculations were done in two cases; $k_{ij} = 0$ and $k_{ij}$ as an adjustable parameter to obtain the best fit with the experimental data.

1- $k_{ij} = 0$: Referring to Figs. 1 to 6, the MMM equation of state gives the most accurate results compared with the other four EOSs. The effect of temperature variation on solubility of n-octacosane in supercritical CO$_2$ is shown in Fig. 5 which indicates that MMM EOS is in close agreement with experimental data while the other equations have large deviations.

2- $k_{ij} \neq 0$: Referring to table 1, the MMM EOS has the smallest overall average absolute deviation (overall AAD). It means that this equation predicts the solubility of n-C$_{24}$ to n-C$_{29}$ in supercritical CO$_2$ more accurately compared with the other EOSs.

The calculations indicated that MMM EOS in both cases ($k_{ij} = 0$ and $k_{ij} \neq 0$) can predict the solubility of normal paraffins more accurately than the other EOSs. It is worth noting that the equations vdW, RK and MMM are two-parameter but Soave and PR are three-parameter equations.
Table 1: Interaction parameters and average absolute deviations of five cubic equations of state correlating the solubility of six heavy hydrocarbons in supercritical CO₂

<table>
<thead>
<tr>
<th>Equation System*</th>
<th>vdW</th>
<th>RK</th>
<th>MMM</th>
<th>Soave</th>
<th>PR</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-tricosane (T=310K)</td>
<td>k_{12}</td>
<td>4.9421×10^{-4}</td>
<td>-0.2113</td>
<td>4.2698×10^{-4}</td>
<td>0.0470</td>
</tr>
<tr>
<td>n-hexacosane (T=313K)</td>
<td>k_{12}</td>
<td>4.6110×10^{-4}</td>
<td>-0.2303</td>
<td>3.9395×10^{-4}</td>
<td>0.0407</td>
</tr>
<tr>
<td>n-hexacosane (T=313K)</td>
<td>k_{12}</td>
<td>2.0545×10^{-4}</td>
<td>-0.2189</td>
<td>1.7911×10^{-4}</td>
<td>0.0429</td>
</tr>
<tr>
<td>n-heptacosane (T=313K)</td>
<td>k_{12}</td>
<td>1.5748×10^{-4}</td>
<td>-0.2232</td>
<td>1.3150×10^{-3}</td>
<td>0.0427</td>
</tr>
<tr>
<td>n-octacosane (T=308.2K)</td>
<td>k_{12}</td>
<td>3.7154×10^{-4}</td>
<td>-0.2922</td>
<td>3.1086×10^{-4}</td>
<td>-0.0161</td>
</tr>
<tr>
<td>n-octacosane (T=318.2K)</td>
<td>k_{12}</td>
<td>3.5270×10^{-4}</td>
<td>-0.3052</td>
<td>2.8593×10^{-4}</td>
<td>-0.0335</td>
</tr>
<tr>
<td>n-octacosane (T=328.2K)</td>
<td>k_{12}</td>
<td>3.3587×10^{-4}</td>
<td>-0.2416</td>
<td>2.6018×10^{-3}</td>
<td>0.0240</td>
</tr>
<tr>
<td>n-nonacosane (T=313K)</td>
<td>k_{12}</td>
<td>3.3587×10^{-4}</td>
<td>-0.2416</td>
<td>2.6018×10^{-3}</td>
<td>0.0240</td>
</tr>
</tbody>
</table>

Overall AAD: 3.2020×10^{-4}, 2.5963×10^{-4}, 1.5803×10^{-4}, 2.5634×10^{-4}, 2.3848×10^{-4}

* The solubility data of n-C_{24}, n-C_{25}, n-C_{26}, n-C_{27} and n-C_{29} are from Furuya and Teja (2004) [18] and the solubility data of n-octacosane is from Yau and Tsai (1993) [4].

APPENDIX

Mixing Rules:

\[
a = \sum_i \sum_j y_i y_j a_{ij}
\]

\[
b = \left(\frac{1}{4} \right) \left( \sum_i \sum_j y_i y_j b_{ij} + \sum_i y_i b_{ii} \right)
\]

Parameters:

\[
a_{ii} = \frac{0.48748R^2 T_c^{2.5}}{P_{ci}}
\]

\[
b_{ii} = \frac{0.664662RT_c}{P_{ci}}
\]

\[
a_{ij} = (1-k_{ij}) \sqrt{a_{ii} a_{jj}}
\]

Fugacity coefficient:

\[
\varphi \approx \exp \left( 2.3191 \ln \left( \frac{v}{v-b} \right) + \frac{2\sum_j y_j a_{ij}}{RT^1 b} \ln \left( \frac{v}{v+b} \right) + \left( a \left( 3 \sum_j y_j b_{ij} - \sum_i \sum_j y_i y_j b_{ij} \right) + b_{ii} \right) \frac{4RT^{1.5} b^2}{4bRT^{1.5} (v+b)} - \ln(z) \right)
\]

Received: 27th December 2005; Accepted: 7th August 2006

REFERENCES


