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Equation of State-Mixing Rule Combinations Based Assessment of Solid-Fluid Equilibria Modelling at High Pressure for Various Systems

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The calculations of solid-fluid equilibrium at high pressure are important for the modelling and the design of processes that use supercritical carbon dioxide to extract solid solutes. However, the main difficulty is the choice of the most appropriate combination of an equation of state (EOS) and a mixing rule (MR).
Consequently, this work is concerned with the modelling of the solubility of four solid compounds, namely Phenanthrene (PH), Anthracene (AN), Pentachlorophenol (PCP) and Hexachlorobenzene (HCB), in supercritical carbon dioxide.
For each compound the three EOS, namely Peng Robinson (PR), Soave (S) and Redlich Kwong and Soave (RKS) were considered in combinations with van der Waals and Wong-Sandler mixing rules.
For PH and AN, the operating conditions were a temperature of 313K and a pressure range of 87.5-200 bars. The best results for AN and PH were given by the Soave-VDW and the PR-VDW models, respectively.
For PCP and HCB the solubility modeling was performed at 308 K and at pressure ranging from 72 to 200 bars, and the PR-WS and Soave-VW combinations seemed to be the most adequate, respectively.

1. Introduction

Supercritical fluids have an interesting combination of liquid like density and solvency and gas like viscosity, diffusivity compressibility, etc. This has stimulated the development of the supercritical fluid technology which mainly takes advantages of these important and useful properties shown by gases, once compressed up to their critical points and then used as solvents. This is very useful for a great number of industrial sensitive applications like in food, pharmaceutical, waste treatment, polymers and monomers processing and biochemical industries, using instead of traditional organic solvents like *n*-hexane, environmentally safe solvents like supercritical CO_2 which is non flammable, non toxic, chemically inert, odourless, etc.
The design and development of SF processes depend on the ability to model and predict accurately the solid-supercritical fluid equilibria (SFE). However, many of the existing simple predictive models are not sufficiently accurate and are subject to serious errors when used for calculations near critical points. An additional complication is that many of the solute molecules of interest are large and polar, while the solvent molecules such

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as carbon dioxide tend to be small and of low polarity. This makes the thermodynamics less amenable to the usual modeling methods.
Consequently, this work is concerned with the modeling of the solubility of certain important compounds, namely Phenanthrene (PH), Anthracene (AN), Pentachlorophenol (PCP) and Hexachlorobenzene (HCB), in supercritical carbon dioxide, where the thermodynamic behaviour of these highly asymmetric systems are described by different proposed models which, generally, involve a combination of an equation of state (EOS) along with a mixing rule (MR). However, the choice of the most appropriate combination is not an easy task, as confirmed by Haselow et al (1986) where it was reported that no reliable predictions of SFE can be obtained by means of the cubic EOS along with the usual van der Waals mixing rules and that the choice of the most appropriate mixing rule can be more important than the EOS itself.
This study is carried out in this perspective, to assess the capabilities of different combinations EOS-MR for the prediction of solubility data for the above cited systems, taken at the same temperatures adopted in the corresponding experimental works reported in the literature (Guha and Madras, 2001).

2. Thermodynamic modeling

By means of the isofugacity criteria in the two phases and neglecting any pressure influence on its volume, the solubility of a pure organic solute in the supercritical carbon dioxide is expressed as follows:

$$P_i^s \exp\left(\int_{P^s}^{P} \frac{V_i^s}{RT} dp\right) = y_i^{sf} \varphi_i^{sf} P \tag{1}$$

where P and P_i^s are the prevailing pressure and sublimation vapour pressure of the solute at a given temperature T, respectively, φ_i^{sf} is the fugacity coefficient of pure solute in the supercritical phase, V_i^s is the solute molar volume at its vapour pressure, y_i^{sf} is the solute solubility in the supercritical carbon dioxide, T is the prevailing temperature and R is the universal gas constant.
Usual two parameters equations of state can be expressed by the following general equation (Reid et al, 1978):

$$P = \frac{RT}{V-b} + \frac{a}{u^2 + ubV + wb^2} \tag{2}$$

The three well known equations of state, i.e. those of Peng-Robinson, Soave and Redlich Kwong and Soave, are obtained with u and w taking integer values as shown in Table 1. The parameters a and b are calculated in terms of critical properties as also shown in Table 1.

Table 1: Parameters of the used equations of state

$$P = \frac{RT}{V-b} + \frac{a}{u^2 + ubV + wb^2}$$

EOS	u	w	b	a
Peng Robinson (PR)	2	-1	$\frac{0.0788RT_c}{p_c}$	$\frac{0.45724R^2T_c^2}{p_c}(1+fw(1-T_r^{1/2}))^2$ $fw = 0.37464 + 1.542274w - 0.2699w^2$
Soave	1	0	$\frac{0.08644RT_c}{P_c}$	$\frac{0.42748R^2T_c^2}{p_c}(1+fw(1-T_r^{1/2}))^2$ $fw = 0.48 + 1.574w - 0.176w^2$
Redlich Kwong and Soave (RKS)	1	0	$\frac{0.08644RT_c}{p_c}$	$\frac{0.42748R^2T_c^{2.5}}{p_cT^{1/2}}(1+fw(1-T_r^{1/2}))^2$ $fw = 0.48 + 1.574w - 0.176w^2$

Two mixing rules were tested in the present work and are described as follows:

- The van der Waals MR: the mixing parameters are expressed as follows:

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{m} y_i y_j a_{ij} \quad (3a); \qquad b_m = \sum_{i=1}^{n}\sum_{j=1}^{m} y_i y_j b_{ij} \quad (3b)$$

$$a_{ij} = \sqrt{a_i a_j}\left(1-k_{ij}\right) \quad (3c); \qquad b_{ij} = \frac{\left(b_i + b_j\right)\left(1-l_{ij}\right)}{2} \quad (3d)$$

The Wong-Sandler MR: despite the fact that it is complicated compared to the standard ones such as that of van der Waals, it has been considered in many applications. Its parameters are expressed as follows:

$$a_m = \frac{RTQ_{ws}D_{ws}}{1-D_{ws}} = RTD_{ws}b_m \quad (5a) \qquad b_m = \frac{Q_{ws}}{1-D_{ws}} \quad (5b)$$

$$Q_{ws} = \sum_{i=1}^{n}\sum_{j=1}^{m} y_i y_j \left(\frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}\left(1-k_{ij}\right)\right) \quad (5c) \qquad D_{ws} = \frac{A_\infty^E}{CRT} + \sum_{i=1}^{n}\frac{y_i a_{ij}}{RTb_i} \quad (5d)$$

$$C = \left(\ln\sqrt{2}-1\right)/\sqrt{2} \quad (5e) \qquad A_\infty^E = \sum_{i=1}^{n} y_i \ln y_i^\infty \quad (5f)$$

where γ_i^∞ is the activity coefficient of component i at infinite dilution and k_{ij} is an interaction parameter. The fugacity coefficient can be expressed in a general manner as:

$$\ln\varphi_i = \frac{b_i}{b}(Z-1) - \ln\left(Z-b^*\right) + \frac{a^*}{b^*\sqrt{u^3-4w}}\left(\frac{b_i}{b} - \delta_i\right)\ln\frac{2Z+b^*\left(u+\sqrt{u^2-4w}\right)}{2Z+b^*\left(u-\sqrt{u^2-4w}\right)} \quad (6a)$$

$$\frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum_{j=1}^{n} y_i T_{ci} P_{cj}} \quad (6b); \qquad \delta_i = \frac{2a_i^{1/2}}{a}\sum x_j a_j^{1/2}\left(1-k_{ij}\right) \quad (6c)$$

$$a^* = \frac{aP}{(RT)^2} \quad (6d); \qquad b^* = \frac{bP}{(RT)} \quad (6e)$$

The numerical values of the different parameters for the four systems are shown in the following Table 2:

Table 2: Parameters of the equations of state

System	k_{ij}	$\ln \gamma_i^{\infty}$	l_{ij}
PH-CO_2	0.37	-60.12	-
AN-CO_2	0.57	-31. 97	-
PCP-CO_2	0.39	-44.40	0
HCB-CO_2	0.57	-35.74	0

3. Results and discussion

The obtained results concerning the binary solubilities of AN, PH, PCP and HCB in supercritical carbon dioxide are compared with experimental data reported in the literature (Guha and Madras, 2001), as shown in the following figures 1 & 2.

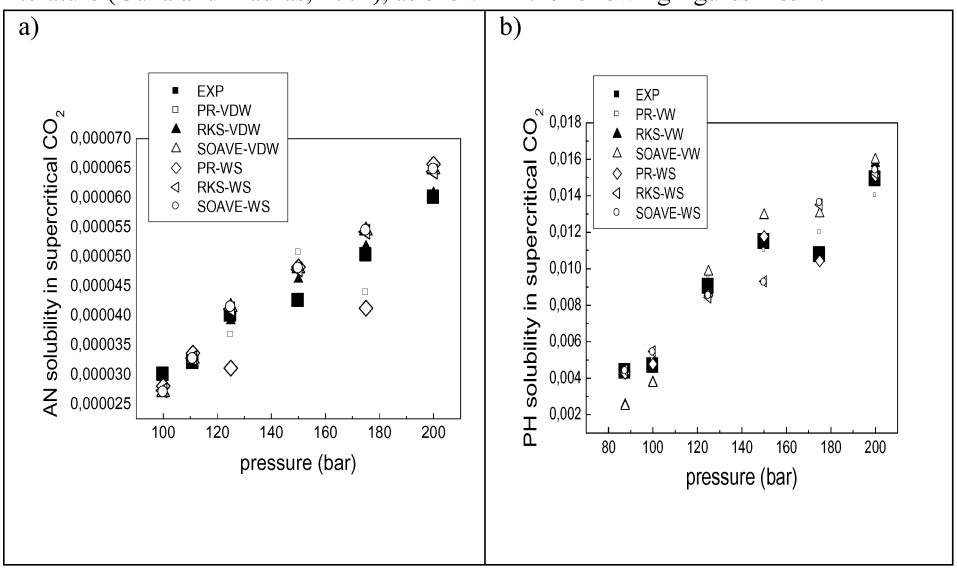

Figure1: prediction of the binary Solubilities of AN and PH at 313.1 K in supercritical carbon dioxide by three different models .Experimental data was taken from (Guha and Madras, 2001).

The obtained solubility of PH in supercritical carbon dioxide has been found to be higher than that of AN. This can be explained by the differences in the intermolecular

interactions which are relatively weak for the case of AN for which the results indicate that the Soave-VDW model is more accurate compared to the other five models whereas for PH the PR-VDW gave the best results, as shown in Table 2 where the calculated absolute average relative deviation (AARD) values were used to assess the different models. From Figure 1, it can be seen that all six models correlate reasonably well the solubility of AN and PH in the supercritical fluid, although some deviations from experimental solubility data are shown, independently of the pressure value.
The results of the solubilities of PCP and HCB in supercritical CO_2 are shown as follows:

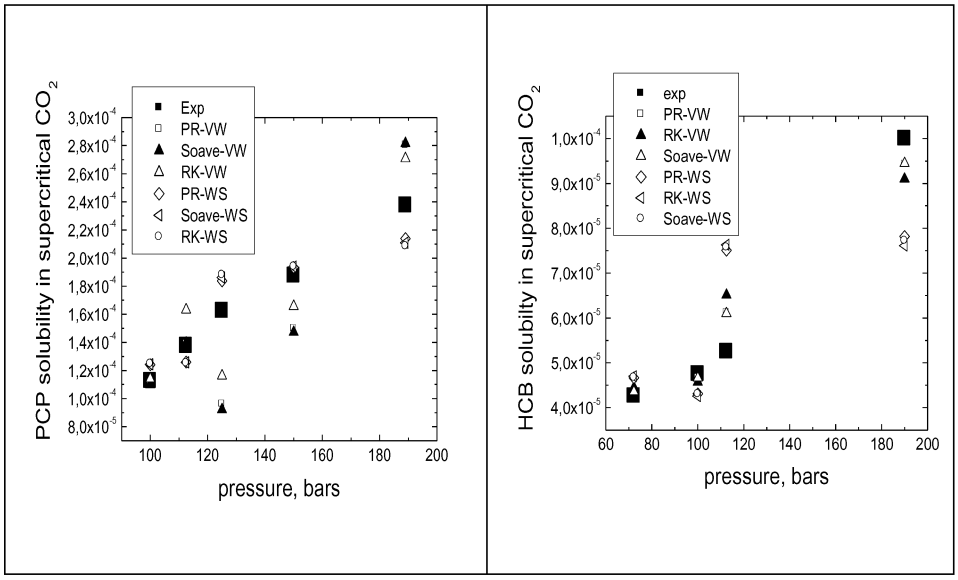

Figure 2: prediction of PCP and HCB solubilities at 308.15 K in supercritical carbon dioxide by six different models. Experimental data was taken from (Guha and Madras, 2001)

The six models are assessed according to the AARD as shown in Table 2 where Soave-VDW and PR-WS provide the best combinations, for HCB-CO_2 and for PCP-CO_2, respectively. It is important to note that the two compounds have the same molecular weight but one is non polar and the other polar with very different boiling points.

Table 2: AARD for the 6 thermodynamic models

$$AARD = \frac{1}{N}\sum_{i=1}^{i=n}\left|\frac{(y_{i,\exp} - yi,_{calc})}{y_{i,\exp}}\right|$$

System	PR-VDW	RKS-VDW	Soave-VDW	PR-WS	RKS-WS	Soave-
AN-CO_2	0.0866	0.0387	**0.0339**	0.1245	0.0696	0.0742
PH-CO_2	**0.06279**	0.19563	0.18916	0.083655	0.0776	0.1084
PCP-CO_2	0.279	0.11288	0.1741	**0.089**	0.11288	0.0996
HCB-	0.070	0.1031	**0.064**	0.20887	0.1031	0.22375

4. Conclusion

Therefore, one can see how important and difficult to make the choice of the best combination EOS-MR for a given system where much effort to improve the solubility prediction is necessary in the supercritical conditions. Also, great effort remains to be made to ultimately relate the nature or the chemical structure of the involved compounds to the choice of the best EOS-MR combination.

5. Notation

a, b	parameters in Eqns.
u, w	constant
k, l	binary interaction parameters
P	Pressure (bars)
V	volume (m^3)
R	universal gas Constant (J mol^{-1} K^{-1})
T	temperature (K)
y	solute solubility
Z	compressibility factor

Greek letters

φ	fugacity coefficient
γ	activity coefficient

Subscripts

i, j	components
ws	Wong-Sandler
m	mixture
m, n	number of components

Superscripts

c	critical
s	saturation
∞	infinite

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