SOLID-GAS EQUILIBRIUM IN SYSTEMS CONTAINING AROMATIC COMPOUNDS AND SUPERCRITICAL CARBON DIOXIDE

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A cubic equation of state, GEOS, with quadratic mixing rules and two adjustable parameters was used to correlate solid – gas equilibrium data in 13 systems containing aromatic compounds + supercritical carbon dioxide. The results are in good agreement with the experimental data for temperatures between 308 K and 373 K and pressures up to 450 bar. The adjustable parameters k_{ij} and l_{ij} u-.sed in the mixing rules vary linearly with the temperature or remain constant for the investigated systems. Based on this observation, the binary interaction parameters and hence, the solubility of the studied solid aromatic compounds in supercritical carbon dioxide can be predicted.

INTRODUCTION

The supercritical fluid extraction method has been studied extensively by many researchers lately because it allows the easy separation of extracts from solvent with minimal environmental pollution. In practical applications, it has been widely applied to the food, pharmaceutical, petroleum, petrochemical, textile, and environmental industries. In processes, it has been used for close-boiling-point and azeotropic mixture separation, crystallization, extraction of solid and liquid solutes, and isomerization reactions.

A supercritical fluid (SCF), a fluid above its critical pressure and temperature, shows densities comparable to those of liquid solvents. This is the main reason for the solubility of high molecular weight substances in SCFs. Carbon dioxide is used extensively as a SCF because it is inexpensive, easily available, non-toxic and has a low critical temperature.

Supercritical extraction processes are especially advantageous compared to distillation processes when thermally unstable compounds with low vapor pressures have to be separated. The processes can be optimized only if the dependence between solubility and both pressure and temperature can be described accurately. Since the experimental determination of the solubility of various solid solutes in SCFs at different temperatures and pressures is time consuming and expensive, modeling and prediction of solid–gas equilibrium is important. For this purpose, thermodynamic models based on equations of state (EOS) are usually taken into account together with the properties of the solid compounds.[1-3]

In our previous works, we have studied the solid – gas equilibrium in high molecular weight n-paraffins + supercritical carbon dioxide systems and also the solid – gas equilibrium in several solid aromatic compounds + three supercritical solvents (ethane, fluoroform and trichloromonofluoromethane).[4,5]

In this study, a cubic equation of state, GEOS,[6,7] with quadratic mixing rules and two adjustable parameters was used to correlate the solubility data of various solid aromatic compounds in supercritical carbon dioxide. The binary interaction parameters were adjusted to reproduce the experimental solubility data of binary systems. The adjustable parameters k_{ij} and l_{ij} used in the mixing

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rules vary linearly with the temperature or remain constant for the investigated systems. Based on this observation, the binary interaction parameters and hence, the solubility of the studied solid aromatic compounds in supercritical carbon dioxide can be predicted.

SOLID – GAS EQUILIBRIUM AND THE GEOS EQUATION OF STATE

The solubility of the heavy solid in the supercritical fluid is given by:[4]

$$Y_2 = \frac{P_2^{0S}(T)\varphi_2^{0S}(T,P_2^{0S})\exp\left[\dfrac{V_2^{0S}(P-P_2^{0S})}{RT}\right]}{\varphi_2^{G}(T,P,Y_2)\,P} \quad (1)$$

The fugacity coefficient of the pure solid at its saturation pressure, $\varphi_2^{0S}(T,P_2^{0S})$ is taken to be unity and the fugacity coefficient of the solid in the gas phase, $\varphi_2^{G}(T,P,Y_2)$, is calculated using an equation of state.

In this study, the general cubic equation of state, GEOS, was used:[7]

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2+c} \quad (2)$$

The four parameters a, b, c, d for a pure component are expressed by:[8]

$$a(T) = a_c\,\beta(T_r); \quad a_c = \Omega_a\frac{R^2T_c^2}{P_c};$$

$$b = \Omega_b\frac{RT_c}{P_c}; \quad (3)$$

$$c = \Omega_c\frac{R^2T_c^2}{P_c^2}; \quad d = \Omega_d\frac{RT_c}{P_c};$$

The temperature function used is:

$$\beta(T_r) = T_r^{-m} \quad (4)$$

with the reduced temperature $T_r = T/T_c$.

The expressions of the parameters Ω_a, Ω_b, Ω_c, Ω_d are:

$$\Omega_a = (1-B)^3; \quad \Omega_b = Z_c - B;$$

$$\Omega_c = (1-B)^2(B-0.25); \quad (5)$$

$$\Omega_d = Z_c - 0.5(1-B)$$

$$B = \frac{1+m}{\alpha_c+m} \quad \alpha_c - \text{Riedel's criterion} \quad (6)$$

As observed, the a, b, c, d coefficients of the cubic GEOS equation are finally function of critical data (T_c P_c and V_c), m and α_c parameters.

As pointed out previously,[7] the GEOS equation is a general forms for all the cubic equations of state with two, three and four parameters. This is the meaning of the statement "general cubic equation of state" used for GEOS.

In this work, the coefficients a, b, c, d of GEOS can be obtained for mixtures using the classical van der Waals mixing rules:

$$a = \sum_i\sum_j X_iX_ja_{ij}; \quad b = \sum_i\sum_j X_iX_jb_{ij}$$

$$(7)$$

$$c = \sum_i\sum_j X_iX_jc_{ij}; \quad d = \sum_i X_id_i$$

$$a_{ij} = (a_ia_j)^{1/2}(1-k_{ij}) \quad b_{ij} = \frac{b_i+b_j}{2}(1-l_{ij})$$

$$(8)$$

$$c_{ij} = \pm(c_ic_j)^{1/2}$$

(with ''+'' for c_i, $c_j > 0$ and ''−'' for c_i, $c_j < 0$).

The binary interaction parameter k_{ij} in the combining rule of the attractive parameter a is adjusted to the experimental data. The correlation can be improved significantly when the parameter l_{ij} in the combining rule for parameter b is adjusted additionally. The temperature dependence of the binary parameters is strongly determined by the quality of the experimental data used.

RESULTS AND DISCUSSION

The thirteen aromatic solutes (as listed in Table 1) studied are either simple cyclic or polycyclic hydrocarbons or functional derivatives of these compounds.

The GEOS parameters m and α_c for CO_2 and for all aromatic compounds were obtained by matching points on the saturation curve together with the corresponding liquid density.[8]

Critical data[9] for carbon dioxide and for all aromatic solutes together with the values of GEOS parameters (m and α_c) are presented in Table 1. The saturation pressure of aromatic compounds,

$P_2^{0S}(T)$, was calculated based on the $\ln P = \dfrac{a}{T} + b$ correlation, with a and b obtained

from sublimation pressure values at different temperatures.[9]

Table 1

Molar weight, critical data and GEOS parameters for CO_2 and aromatic solids[*]

Compound	M [g/mol]	T_c [K]	P_c [bar]	V_c [dm³/mol]	m	α_c
Carbon dioxide	44.009	304.2	73.83	0.094	0.3146	7.0520
Phenol	94.113	694.3	61.30	0.229	7.6829	0.7402
p-Quinone	108.097	683.0	59.60	0.291	8.8146	0.7774
p-Hydroquinone	110.112	823.0	74.50	0.300	9.3043	0.6334
Salicylic acid	138.123	739.0	51.80	0.326	10.0395	0.8412
1,4–Naphthoquinone	158.150	877.5	40.67	0.438	9.0886	0.5384
1-Naphthol	144.170	818.4	44.32	0.355	9.2771	0.3332
2-Naphthol	144.170	814.8	44.32	0.355	9.2302	0.3330
2,6 di-Me-Naphthalene	156.227	777.0	31.70	0.520	8.2296	0.4689
2,7 di-Me-Naphthalene	156.227	775.0	32.30	0.600	7.1773	0.7209
Acenaphthene	154.211	803.2	31.00	0.553	7.5909	0.5398
2-Aminofluorene	181.240	890.0	33.80	0.550	8.6407	0.5151
9,10–Anthraquinone	208.216	900.0	31.50	0.580	9.3645	0.6675
Chrysene	228.293	979.0	23.90	0.749	9.6154	0.5407

[*]All the compounds presented in this work are aromatic, except for p-Quinone

The binary interaction parameters were adjusted to reproduce the experimental solubility data of binary systems. The parameter (k_{ij} and l_{ij}) values used are shown in Table 2. As can be seen from Table 2, two binary interaction parameters (depending of temperature) were generally necessary to correlate the experimental data for the investigated systems. In some cases, the k_{ij} and l_{ij} parameters were constant. Brackets were used to indicate the temperature intervals within the two parameters were either constant or varied linearly with temperature. For the CO_2 + Salicylic acid and CO_2 + Anthraquinone systems, very good results were obtained using only one binary interaction parameter for the combining rules: l_{ij} in the first case and k_{ij} in the second one.

Table 2

Interaction parameters for CO_2 + aromatic compound systems.

Solid aromatic compound	Temp [K]	k_{12}	l_{12}	AADY %
p-Quinone	308; 318	0.09; 0.05	0; -0.06	12.72
p-Hydroquinone	308; 318	0.13; 0.11	-0.08; -0.13	21.76
Salicylic acid	313; 328	0	-0.24; -0.19	9.41
1, 4-Naphthoquinone	[318 – 343]	0.09	-0.04	12.43
1-Naphthol	[308 – 328]	-0.005 T + 1.74	-0.0085 T + 2.790	24.11
2-Naphthol	[308 – 343]	-0.08	-0.0007 T + 0.113	11.67
2,6 di-Me-Naphthalene	[308 – 328]	0.015	-0.1	15.42
2,7 di-Me-Naphthalene	[308 – 328]	0.165; 0.155	0.035	16.76
Acenaphthene	[308 – 348]	0.15	0.04	9.01
2-Aminofluorene	[318 – 343]	-0.0009 T + 0.384	0.07	12.71
9, 10-Anthraquinone	308; 318	0.102; 0.092	0	10.63
Chrysene	313; 373	0.17; 0.16	0.16; 0.15	6.38

For all investigated systems, comparisons of the calculation results with experimental data[10-21] were made. In table 2 are reported the average relative deviations of solubility (Y_2) on the available temperature range of the data:

$$\text{AADY \%} = \frac{\sum_{i=1}^{N} \left| (Y_i^{eos} - Y_i^{exp}) / Y_i^{exp} \right| \cdot 100}{N} \qquad (9)$$

with N – number of data points. The AADY % values are reasonable for a solid – gas equilibrium. Deviations higher than 20 % are obtained for p—Hydroquinone and 1-Naphthol.

Some results are presented in the figures below. Figs. 1-2 show the variation of solubilities (Y_2) of the aromatic compounds with pressure (up to 450 bar) in supercritical carbon dioxide, at different temperatures.
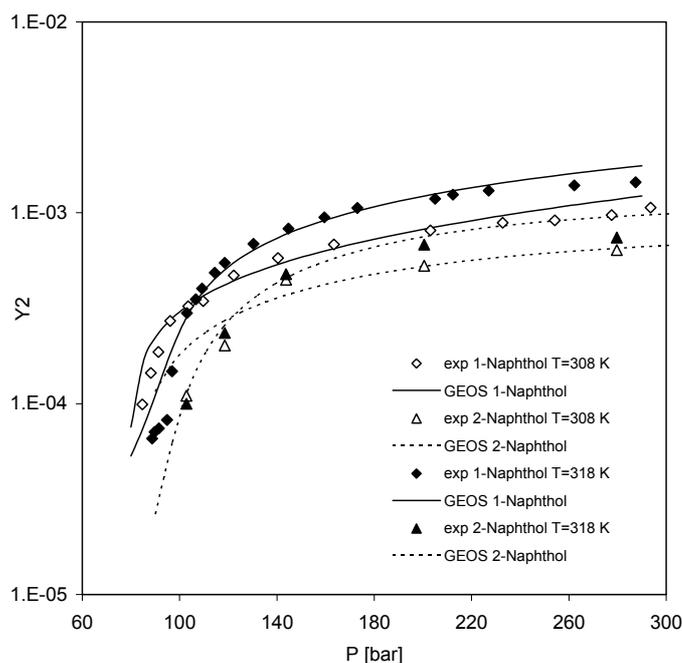

Fig. 1 – Solubility of 1-Naphthol and 2-Naphthol in SC CO_2 at T=308 K and T=318 K.
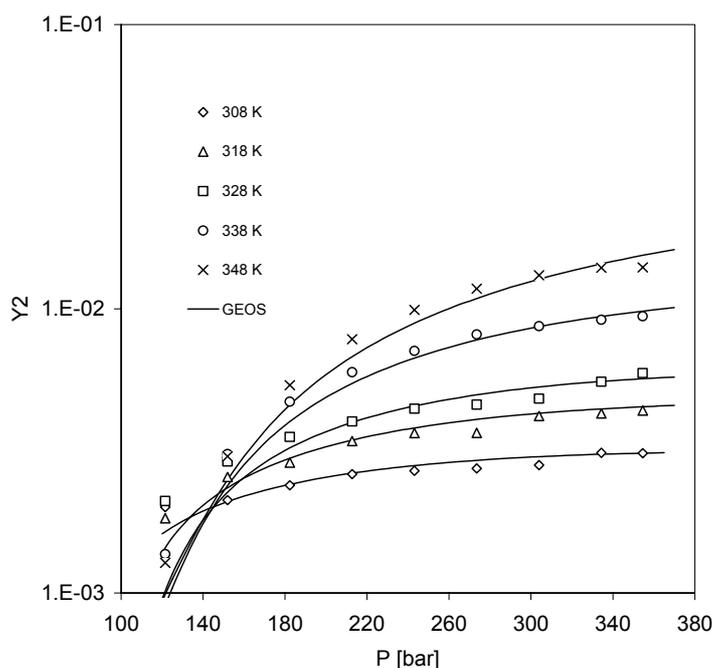

Fig. 2 – Solubility of Acenaphtene in SC CO_2.

The points in the figures represent experimental data, while the solid lines represent the solubility curves calculated with GEOS, using the values for the adjustable parameters k_{ij} and l_{ij} presented in Table 2.

As can be seen from the figures the GEOS equations, with quadratic mixing rules and two adjustable parameters, performs good for the studied aromatic compounds + CO_2 systems.

Figure 3 illustrates the significant difference in solubility between compounds, spanning nearly four orders of magnitude at the same temperature value. The diagram shows the dependence of solubility on pressure, at 318 K, for 5 compounds: 9,10–Anhraquinone, 2-Aminofluorene, p-Quinone, Acenaphthene and 1-Naphthol (the most soluble being p-Quinone and the least soluble 9,10–Anhraquinone). The results provided by GEOS are in good agreement with the experimental data.
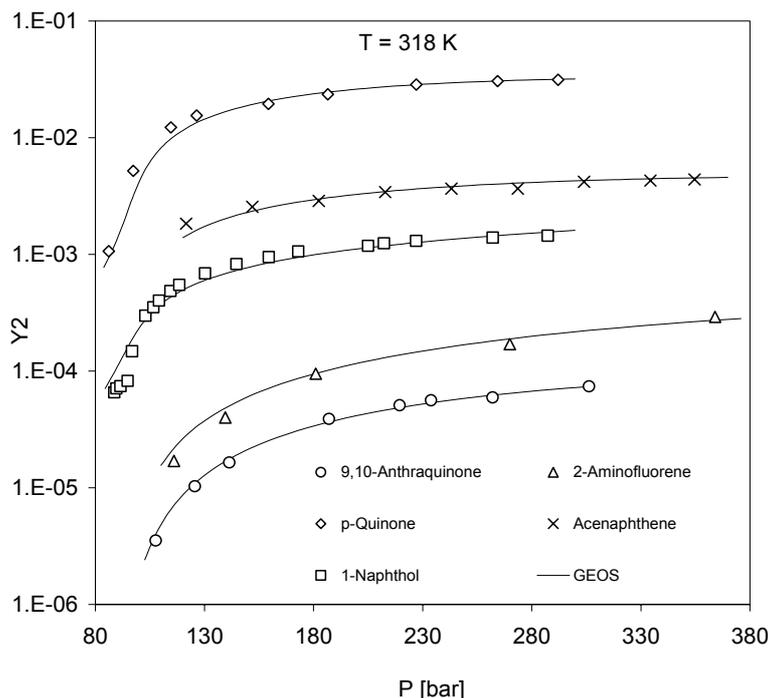

Fig. 3 – Solubility of some aromatic compounds in SC CO_2 at 318 K.

If experimental solubility data were available at three or more temperatures, linear correlations with temperature for the binary interaction parameters k_{ij} and l_{ij} were obtained. The linear correlations

$$k_{ij} / l_{ij} = m \, T + n$$

are given in Table 2. Based on these correlations solubility predictions were made at intermediate temperature values. In some cases, the values of the k_{ij} and l_{ij} parameters were constant.

The utility of the correlating equations for the binary interaction parameters is demonstrated by predicting the solubility of 1,4-Naphthoquinone, 2-Naphthol and 2-Aminofluorene in supercritical carbon dioxide at 328 K. Figure 4 shows the results obtained for these three aromatic compounds. As can be seen, the predictions are in good agreement with the experimental data.

CONCLUSIONS

The solubility of several solid aromatic compounds in supercritical carbon dioxide was modeled using the GEOS equation of state with quadratic mixing rules and two adjustable parameters. The calculated solubility curves are in good agreement with the experimental data for temperatures between 308 K and 363 K and pressures up to 450 bar, for all the investigated systems. The average absolute errors (on all temperatures) are generally lower than 20%.

The adjustable parameters k_{ij} and l_{ij} depend linearly on temperature or are constant over the given temperature range for most of the systems, meaning that their values and hence, the solubility of these aromatic compounds in the supercritical carbon dioxide, can be predicted at any temperature within that range.
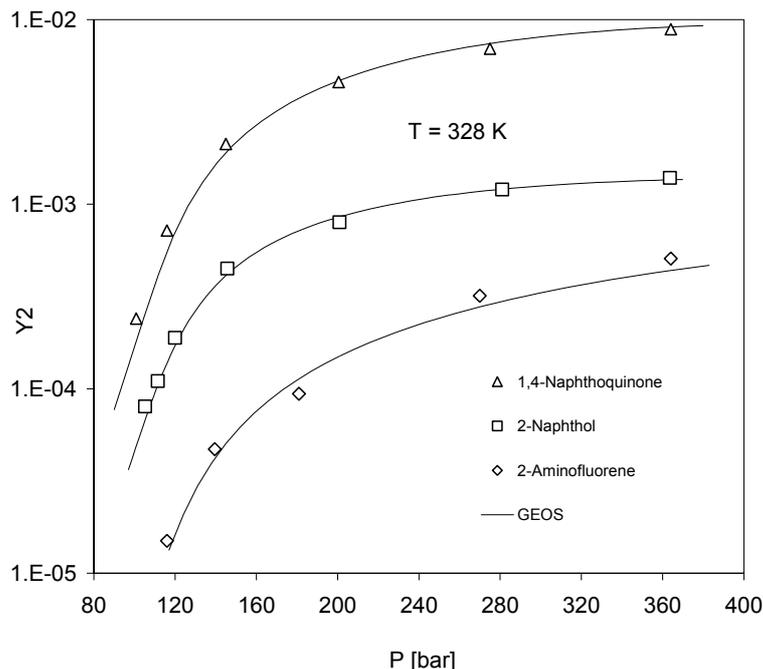
Fig. 4 – Predicted solubility of 1,4-Naphthoquinone, 2-Naphthol and 2-Aminofluorene in SC CO$_2$ at 328 K.

List of symbols

a, b, c, d	parameters of GEOS
AAD	- average absolute deviation
B	- dimensionless parameter of GEOS, defined by eq. (9)
f	- fugacity
m	- parameter of GEOS temperature function
M	- molar mass
P, P^S	- pressure, saturation pressure
R	- universal gas constant
T	- temperature
V, V^S	- molar volume, solid molar volume
Y$_2$	- solubility (mole fraction) of solid in supercritical solvents
Z	- compresibility factor
	Greeks
α_c	- Riedel's criterium (parameter of GEOS)
β	- reduced temperature function in GEOS
$\Omega_a, \Omega_b, \Omega_c, \Omega_d$	- parameters of GEOS
φ	- fugacity coefficient

Subscripts

c	- critical property
r	- reduced property

Superscripts

G	gaseous phase
L	liquid phase
V	vapor phase
S	solid phase
0	pure solid properties

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