Modelling the Solubility of Solid Aromatic Compounds in Supercritical Fluids

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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 25 systems containing aromatic compounds and 3 supercritical fluids (ethane, fluoroform and trichloromonofluoromethane). The results are in good agreement with the experimental data for temperatures between 308 K and 343 K and pressures up to 360 bar. The adjustable parameters k_{ij} and l_{ij} used 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 the supercritical fluids can be predicted.

Keywords: equation of state, solid-gas equilibrium, supercritical fluid

A supercritical fluid (SCF), in certain temperature and pressure ranges, shows densities comparable to those of liquid solvents. This is the main reason for the solubility of high molecular substances in SCFs. Supercritical extraction processes using carbon dioxide or other solvents are especially advantageous compared to distillation processes, in food and pharmaceutical industries, when thermolabile compounds with low vapor pressures have to be separated. The optimization of the processes can be performed only if the dependence of the solubility both on pressure and temperature can be accurately described. For this purpose, thermodynamic models based on cubic equations of state (EOS) are usually considered together with the solid compound properties in the correlation of experimental data.

The solubility of aromatic compounds in supercritical carbon dioxide or other solvents is of interest in practical applications especially in petrochemical and environmental industries. Unfortunately, the number of reliable experimental data for such systems is limited. Moreover, the reliable measurement of the solubility of solids in a SCF over a wide concentration range (mole fractions between 10^{-7} and 10^{-1} in the gas phase) at high pressures requires sophisticated experimental techniques. Because it is not possible to measure all of the required solubilities for various high molecular compounds in different SCFs, equations of state are applied to describe the behaviour of the phase equilibrium for such systems.

For the correlation of the experimental data, cubic EOSs with classical quadratic mixing rules for the attractive parameter *a* and the covolume parameter *b* are often used [1-3]. An equation of state based on the perturbation theory of liquid state was also used to model the solubility of solids in supercritical carbon dioxide [4].

In our previous works [5, 6], we presented studies based on a cubic equation of state [7, 8], GEOS, to describe the solid-gas equilibrium in systems containing aromatic compounds and supercritical carbon dioxide and also in systems containing high molecular weight n-paraffins and supercritical carbon dioxide.

In this study, the same cubic equation of state, GEOS, with quadratic mixing rules and two adjustable parameters, was used to correlate solid – gas equilibrium data in 25 systems containing aromatic compounds and 3 supercritical fluids (ethane, fluoroform and trichloromonofluoromethane). The binary interaction parameters were adjusted to reproduce the experimental solubility data ($P - Y_2$) of binary systems. The adjustable parameters k_{ij} and l_{ij} used 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 the supercritical fluids can be predicted.

Solid – Gas Equilibriun

If the high - molecular compound is in the liquid state (L), the phase equilibrium can be calculated starting from the fugacity condition:

$$f_i^L = f_i^V \tag{1}$$

If the high – molecular substance (component 2) is in the solid state (S), only the fugacity condition for the solid component:

$$f_2^S(T,P) = f_2^G(T,P,Y_2) \tag{1a}$$

has to be taken into account because the solubility of the supercritical gas (component 1) in the solid phase can be neglected. The fugacity of pure solid is expressed by its vapor pressure, the fugacity coefficient and the Poynting factor:

$$f_2^S(T,P) = P_2^{0S}(T)\varphi_2^{0S}(T,P_2^{0S})\exp\left[\frac{V_2^{0S}(P-P_2^{0S})}{RT}\right] \tag{2}$$

with constant volume V_2^{0S}.

The fugacity of solid in the gas phase is given by the equation:

$$f_2^G(T,P,Y_2) = \varphi_2^G(T,P,Y_2)Y_2P \tag{3}$$

Finally, the solubility of the heavy solid in the supercritical fluid is given by:

$$Y_2 = \frac{P_2^{0S}(T)\varphi_2^{0S}(T,P_2^{0S})\exp\left[\frac{V_2^{0S}(P-P_2^{0S})}{RT}\right]}{\varphi_2^G(T,P,Y_2)\,P} \tag{4}$$

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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.

The geos equation on state

The general cubic equation of state (GEOS) has the form:

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V - d)^2 + c} \tag{5}$$

The four parameters *a*, *b*, *c*, *d* for a pure component [7, 8] are expressed by:

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

$$c = \Omega_c \frac{R^2T_c^2}{P_c^2}; \quad d = \Omega_d \frac{RT_c}{P_c}; \tag{6}$$

The temperature function used is:

$$\beta(T_r) = T_r^{-m} \tag{7}$$

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

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

$$\Omega_a = (1 - B)^3; \quad \Omega_b = Z_c - B; \quad \Omega_c = (1 - B)^2(B - 0.25);$$

$$\Omega_d = Z_c - 0.5(1 - B) \tag{8}$$

$$B = \frac{1 + m}{\alpha_c + m} \qquad \alpha_c \text{ – Riedel's criterion} \tag{9}$$

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.

The above equations (6-9) are obtained by setting four critical conditions in reduced variables:

$$P_r = 1; \quad T_r = 1; \quad V_r = 1 \tag{10a}$$

$$\left(\frac{\partial P_r}{\partial V_r}\right)_{T_r} = 0; \quad V_r = 1; \quad T_r = 1 \tag{10b}$$

$$\left(\frac{\partial^2 P_r}{\partial V_r^2}\right)_{T_r} = 0; \quad V_r = 1; \quad T_r = 1 \tag{10c}$$

$$\alpha_c = \left(\frac{\partial P_r}{\partial T_r}\right)_{V_r}; \quad V_r = 1; \quad T_r = 1 \tag{10d}$$

As pointed out previously [8], the cubic GEOS equation is a general form 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.

For example, to obtain the parameters of the Soave-Redlich-Kwong (SRK) equation of state from the equations (6-9) we set the following restrictions: $\Omega_c = -(\Omega_b/2)^2$ and $\Omega_d = -\Omega_b/2$. It follows:

$$\Omega_c = (1 - B)^2(B - 0.25) = -(Z_c - B)^2/4; \tag{11}$$

$$\Omega_d = Z_c - 0.5(1 - B) = -(Z_c - B)/2 \tag{12}$$

It results Z_c (SRK) = 1/3, and the relation for B(SRK):

$$B = 0.25 - \frac{1}{36}\left(\frac{1 - 3B}{1 - B}\right)^2 \tag{13}$$

Solving iteratively this equation gives *B*(SRK)= 0.2467, and correspondingly: Ω_a(SRK)=(1 - B)^3 = 0.42748 and Ω_b(SRK)=Z_c - B = 0.08664.

For Peng-Robinson (PR) equation of state we set the restrictions: $\Omega_c = -2(\Omega_b)^2$ and $\Omega_d = -\Omega_b$. It results:

$$B = 0.25 - \frac{1}{8}\left(\frac{1 - 3B}{1 - B}\right)^2; \quad Z_c = \frac{1 + B}{4} \tag{14}$$

giving *B*(PR) = 0.2296 and Z_c(PR) = 0.3074.

In this work, the coefficients *a*, *b*, *c*, *d* were obtained for mixtures using the classical van der Waals mixing rules:

$$a = \sum_i \sum_j X_i X_j a_{ij}; \qquad b = \sum_i \sum_j X_i X_j b_{ij}$$

$$c = \sum_i \sum_j X_i X_j c_{ij}; \qquad d = \sum_i X_i d_i \tag{15}$$

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \quad b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \tag{16}$$

$c_{ij} = \pm(c_i c_j)^{1/2}$ (with "+" for $c_i, c_j > 0$ and "–" for $c_i, c_j < 0$).

The binary interaction parameters k_{ij} and l_{ij} in the combining rules are adjusted to the experimental data. Generally, these parameters are temperature dependent and their quality strongly depends on the quality of the experimental data used.

Results and discussions

The GEOS equation of state, with quadratic mixing rules and two adjustable parameters was used to calculate the solubilities of twenty fight systems containing ten solid aromatic solutes in three supercritical solvents. The ten aromatic solutes (table 1) are either simple cyclic or polycyclic hydrocarbons or functional derivatives of one. The critical data for the three supercritical solvents (ethane, fluoroform and monochlorotrifluoromethane) and for the ten aromatic compounds together with the values of GEOS parameters (*m* and α_c) are also presented in Table 1. The critical data for the solvents and for all aromatic solutes were taken from the DIPPR project [9] and the GEOS parameters *m* and α_c were obtained by matching points on the saturation curve together with the corresponding liquid density [8].

The binary interaction parameters k_{ij} and l_{ij} in the quadratic mixing rules (eq. 16) were adjusted to the experimental data for all investigated systems. The values of these parameters are shown in tables 2, 3 and 4, generally as a function of temperature. In some cases, the k_{ij} and l_{ij} parameters were kept constant. Brackets were used to indicate the temperature intervals within the two parameters were either constant or varied linearly with temperature. For some systems, a correlation of the k_{ij} and l_{ij} parameters with temperature was not possible.

Compound	M [g/mol]	T_c [K]	P_c [bar]	V_c [dm^3/mol]	m	α_c
Ethane	30.07	305.4	48.80	0.148	0.2596	6.3774
Fluoroform	70.014	299.01	48.16	0.132	0.3473	7.4626
Monochloro-trifluoromethane	104.46	302.0	38.70	0.180	0.3217	6.7696
Benzoic acid	122.123	751	44.70	0.344	0.60279	9.3043
Naphthalene	128.174	748.4	40.50	0.407	0.30203	7.4917
1,4–Naphthoquinone	158.150	877.5	40.67	0.438	9.0886	0.5384
2-Naphthol	144.170	814.8	44.32	0.355	9.2302	0.3330
Biphenyl	154.211	773	33.80	0.497	0.40287	7.9656
Anthracene	178.233	873	29.00	0.554	0.48567	9.1993
Phenanthrene	178.233	869	29.00	0.554	0.47072	8.947
Acridine	179.221	905	36.40	0.543	0.44002	7.9863
2-Aminofluorene	181.240	890	33.80	0.550	0.501	8.6407
Pyrene	202.255	936	26.10	0.660	0.50742	8.9702

Table 1
MOLAR WEIGHT, CRITICAL DATA AND GEOS PARAMETERS FOR THE SUPERCRITICAL SOLVENTS AND THE AROMATIC SOLIDS

The saturation pressure of aromatic compounds (eq. 4), $P_2^{0s}(T)$, was calculated based on the $P = \frac{a}{T} + b$ correlation, with a and b obtained from sublimation pressure values at different temperatures [9].

The solid – gas equilibrium results obtained by the GEOS equation were compared with experimental data from literature for all the investigated systems. In tables 2 – 4 are presented the calculation results in terms of average absolute relative deviations of solubility (Y_2):

$$\text{AADY }\% = \frac{\sum_{i=1}^{N} \left| (Y_i^{eos} - Y_i^{\exp}) / Y_i^{\exp} \right| \cdot 100}{N} \qquad (17)$$

Solid aromatic compound	Temp [K]	k_{12}	l_{12}	AADY %
Benzoic acid	[308 – 343]	0	0.0014 T - 0.4899	13.47
Naphthalene	[308 – 328]	0.02	-0.02	15.54
1, 4-Naphthoquinone	[308 – 343]	-0.0005 T + 0.3007	0	12.92
2-Naphthol	308 ; 318 ; 328 ; 343	-0.03 ; -0.04 ; -0.05 ; -0.05	-0.05 ; -0.05 ; -0.08 ; -0.08	17.04
Biphenyl	308 ; 318	0.02 ; 0.02	-0.02 ; -0.015	16.59
Anthracene	313 ; 323 ; 333	0.055 ; 0.055 ; 0.05	0.095 ; 0.095 ; 0.09	6.16
Phenanthrene	313; 318; 323; 328; 333	0.01 ; 0.02 ; 0.01 ; 0.02 ; 0.015	0	6.08
Acridine	[308 – 343]	-0.0012 T + 0.4	-0.09	22.44
2-Aminofluorene	[318 – 343]	-0.0004 T + 0.1672	0	22.24
Pyrene	333	0.05	0	8.85

Table 2
INTERACTION PARAMETERS FOR SYSTEMS CONTAINING C_2H_6 + AROMATIC COMPOUNDS AND AVERAGE ABSOLUTE DEVIATIONS OF SOLUBILITY OF AROMATIC COMPOUNDS IN SC C_2H_6

Solid aromatic compound	Temp [K]	k_{12}	l_{12}	AADY %
Benzoic acid	[318 – 328]	0	-0.13	16.85
Naphthalene	[308 – 328]	0.08	-0.03	16.71
1, 4-Naphthoquinone	[318 – 328]	0.07	-0.07	32.69
2-Naphthol	328 ; 343	-0.06	-0.1 ; -0.09	12.87
Anthracene	[328 – 343]	0.09	0	23.78
Phenanthrene	[318 – 328]	0.06	-0.06	6.06
Acridine	318 ; 328	0.04 ; 0.035	-0.1	25.08
2-Aminofluorene	328 ; 343	0	-0.08 ; -0.06	22.24

Table 3
INTERACTION PARAMETERS FOR SYSTEMS CONTAINING CHF_3 + AROMATIC COMPOUNDS AND AVERAGE ABSOLUTE DEVIATIONS OF SOLUBILITY OF AROMATIC COMPOUNDS IN SC CHF_3

The most AADY % values are reasonable for a solid – gas equilibrium. Deviations higher than 20% are obtained for the solubilities of acridine and 2-aminofluorene in ethane and in fluoroform, and for 1, 4-naphthoquinone and anthracene in fluoroform.

For some of the systems, notably C_2H_6 + Benzoic acid, C_2H_6 + 1, 4-Naphthoquinone and C_2H_6 + Phentanthrene, 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 others.

Table 4

INTERACTION PARAMETERS FOR SYSTEMS CONTAINING $CCIF_3$ + AROMATIC COMPOUNDS AND AVERAGE ABSOLUTE DEVIATIONS OF SOLUBILITY OF AROMATIC COMPOUNDS IN SC $CCLF_3$

Solid aromatic compound	**Temp [K]**	k_{12}	l_{12}	AADY %
Benzoic acid	[318 – 328]	0.025	-0.07	8.57
Naphthalene	[308 – 328]	0.07	-0.03	10.53
1, 4-Naphthoquinone	[318 – 328]	0.17	0	19.37
2-Naphthol	328 ; 343	0.03	-0.03 ; -0.01	10.02
Phenanthrene	318 ; 328	0.07	-0.03; -0.04	8.21
Acridine	318 ; 328	0.06 ; 0.05	-0.1	18.27
2-Aminofluorene	328 ; 343	0.08 ; 0.04	0	7.01

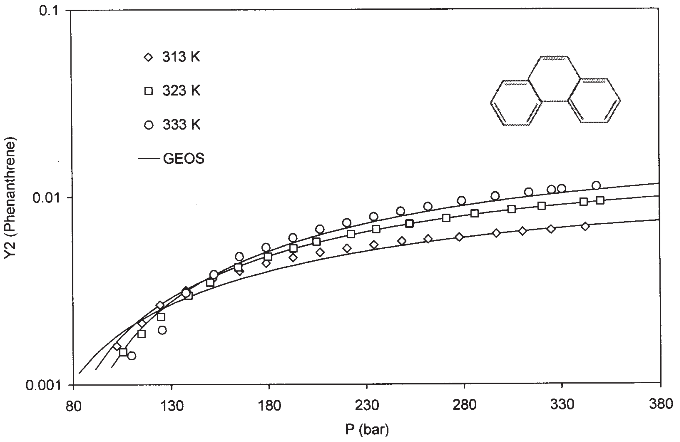

Fig. 1. Solubility of Phenanthrene in SC C_2H_6

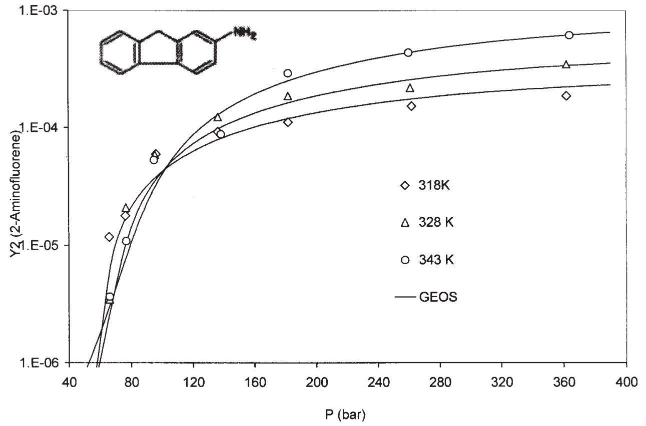

Fig. 3. Solubility of 2-Aminofluorene in SC C_2H_6

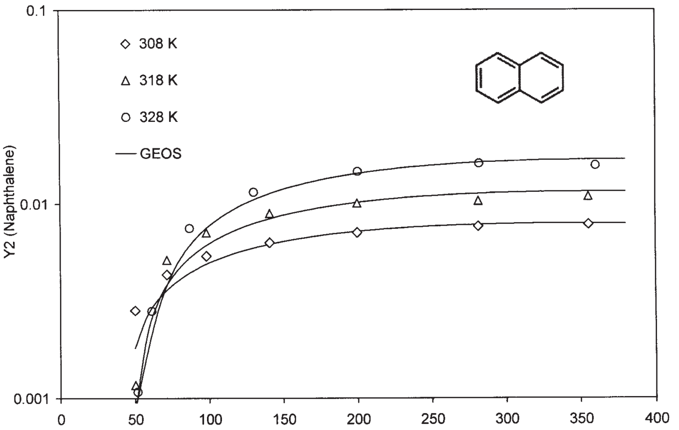

Fig. 2. Solubility of Naphthalene in SC $CCIF_3$

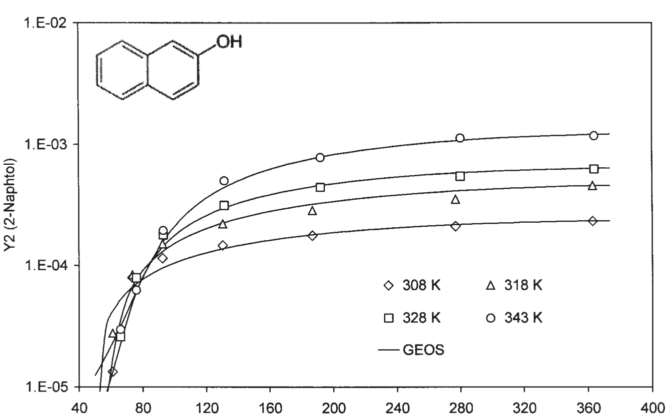

Fig. 4. Solubility of 2-Naphthol in SC C_2H_6

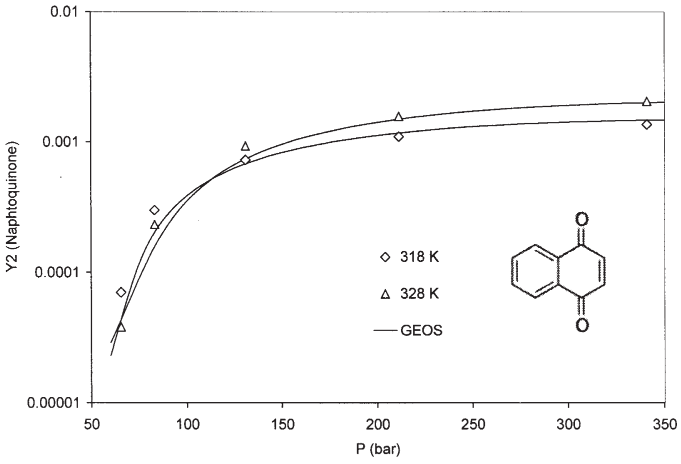

Fig. 5. Solubility of 1,4 - Naphthoquinone in SC CHF_3

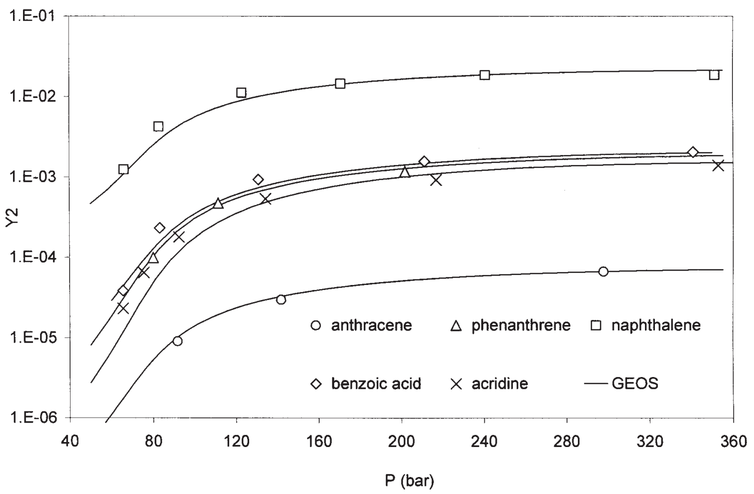

Fig. 6. Solubility of some aromatic compounds in SC CHF_3 at 328 K

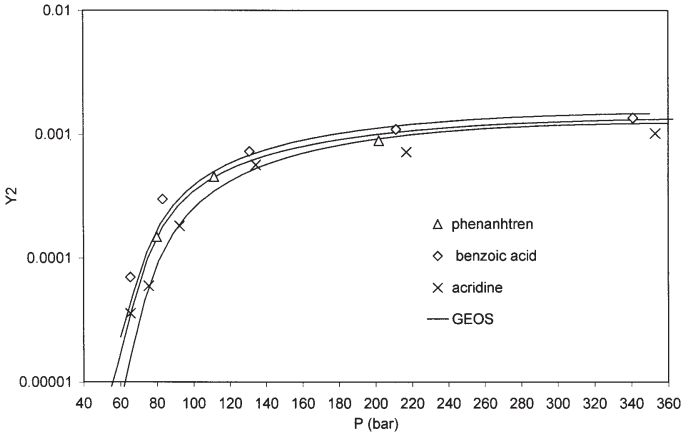

Fig. 7. Predicted solubility of Acridine, Benzoic acid and Phenanthrene in SC CHF_3 at 318 K

Some of the results are presented in the figures below. Figures 1-5 show correlations of the solubility (Y_2) of the aromatic compounds with pressure, in one of the three supercritical solvents, at different temperatures. The points in the figures represent experimental data [10, 11], 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 tables 2-4. These figures indicate that GEOS, with quadratic mixing rules and two adjustable parameters, performs good correlations for the studied aromatic compounds + SCF systems. The Y_2 scales of all the charts are logarithmic.

Figure 6 illustrates the significant difference in solubility between compounds, spanning nearly four orders of magnitude at the same value of temperature. The chart presents the variation of solubility with pressure, at 328 K, for acridine, anthracene, benzoic acid, naphthalene and phenanthrene, in supercritical fluoroform. The most soluble is naphthalene and the least soluble is anthracene. The results provided by GEOS are in good agreement with the experimental data.

As mentioned above, if experimental solubility data was available at three or more temperature values, linear correlations with temperature for the binary interaction parameters k_{ij} and l_{ij} were obtained and solubility predictions were performed for intermediate temperature values. The utility of the correlating equations for the binary interaction parameters is demonstrated by predicting the solubility of Acridine, Benzoic acid and Phenanthrene in supercritical fluoroform, at 318 K. Figure 7 shows the results obtained for these three aromatic compounds, l_{ij} and k_{ij} being either constant or obtained using linear correlations with temperature. As can be seen, the predictions are in good agreement with the experimental data.

Conclusions

The solubility of several solid aromatic compounds in supercritical solvents was modeled using the GEOS equation of state with quadratic mixing rules and two adjustable parameters. The calculated solubility curves fit well the experimental data points for temperatures between 308 K and 343 K, and pressures up to 360 bar, for all the investigated systems, the average (on all temperatures) absolute errors being generally lower than 20%.

The adjustable parameters k_{ij} and l_{ij} vary linearly with 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 solvents, can be predicted at any temperature within that range.

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 - Riedel's criterium (parameter of GEOS)
β - reduced temperature function in GEOS
Ω_a, Ω_b, Ω_c, Ω_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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