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HIGH PRESSURE PHASE EQUILIBRIUM BEHAVIOUR OF NAPHTHALENE IN SUPERCRITICAL CO₂ EXPERIMENTAL RESULTS AND CALCULATION WITH THE PENG-ROBINSON EQUATION OF STATE

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Phase equilibrium calculations involving a pure solid component are presented. The fluid phases are modelled using the Peng-Robinson's equation of state (EoS) using two different mixing rules for the covolume of mixing: the classical linear mixing rule and the van der Waals or quadratic mixing rule with a binary interaction parameter.

The pure solid chemical potential used in the model does not require the value of the sublimation pressure - it is based on the measurements made with a differential scanning calorimeter of the melting point of the solid. This model has been used for estimating the solubility of naphthalene in carbon dioxide (CO₂).

Experimental results have been obtained with an original apparatus, based on an open-circuit analytical method. These high accuracy measurements of the solubility of naphthalene in CO₂ up to the supercritical region have been compared with the predicted values.

The binary interaction parameters have been optimised using a parametric identification method. With these parameters a phase diagram of the binary mixture naphthalene - CO₂ is calculated.

INTRODUCTION

The calculation of phase and chemical equilibria is of fundamental importance for chemical process design and simulation. For particle generation processes involving fluids under supercritical conditions such as RESS or SAS processes [1], this calculation is of prime necessity:

- In the RESS (Rapid Expansion of a Supercritical Solution) processes a solid component, the substrate, has to be dissolved in a single phase mixtures of fluids, the pressure and the temperature being beyond critical coordinates. This new single phase saturated mixture is subjected to a sudden drop in pressure through a nozzle resulting in sudden supersaturated conditions leading to the precipitation of the solid.
- In the SAS (Supercritical Anti-Solvent) process the solid component is dissolved in a solvent, which is miscible with CO₂ under supercritical conditions. The saturation of this solvent with the CO₂ decreases drastically and suddenly the solubility of the solute and leads to its re-crystallisation.

In these two kinds of processes the knowledge of the thermodynamical behaviour of the solid solubility must be known for process design. Furthermore, phase equilibrium calculation could also help to avoid problems such as liquid immiscibility, which could occur in SAS process.

Our concern has been to develop an approach to calculate multiphase and multicomponent equilibria involving pure solid phases under supercritical conditions. The main objective is to

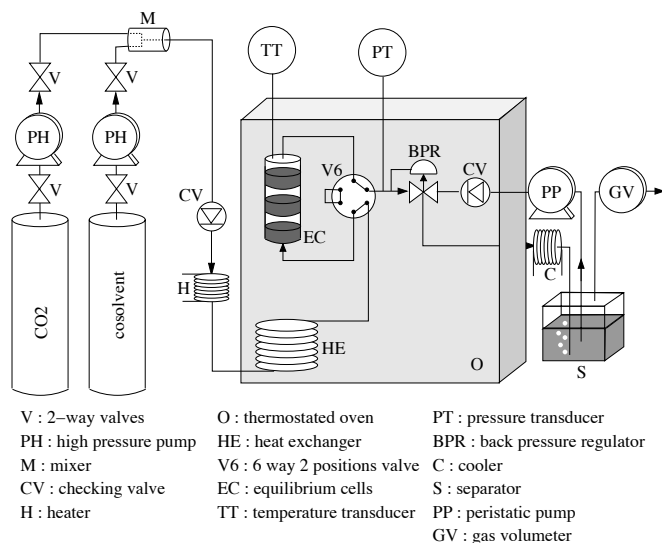


Figure 1: Flow diagram of the apparatus

$T=308.15\text{ K}$		$T=318.15\text{ K}$	
$P\text{ (MPa)}$	y_2	$P\text{ (MPa)}$	y_2
8.05	0.0044	8.49	0.0011
13.43	0.0138	9.83	0.0060
13.52	0.0139	14.65	0.0206
14.85	0.0146	15.06	0.0208
15.05	0.0147	19.77	0.0237
20.03	0.0161	24.98	0.0258
20.08	0.0163	29.70	0.0278
24.82	0.0169		
29.76	0.0174		
29.92	0.0175		

Table 1: Naphthalene solubility in CO_2

apply this method to complex organic compound such as new pharmaceutical molecules [2] or complex mixture of bio-molecules. The equipment for the solid solubility measurements in supercritical phases has been validated with a testing molecule - the naphthalene - in CO_2 and since corresponding data are very abundant in the literature, this mixture has been chosen to be a test for the model.

EXPERIMENTAL SECTION

Equilibrium solubility data were obtained by using an apparatus described in detail by Sauceau *et al.* [3]. It is based on an analytical open-circuit method where the solvent flows continuously through the solid compound and the composition of the supercritical phase is obtained by analyses. The flow diagram is shown in figure 1. Measurements of high accuracy have been obtained and for the naphthalene- CO_2 mixture the results are presented in table 1. This apparatus has been used with cosolvents and on an active substance of pharmaceutical interest [4,5].

THE EQUATION OF STATE

The results of calculation from an EoS have been compared with experimental results in order to validate the choice of a model and a mixing rule, and then optimise some parameters such as binary interaction parameters. The fluid phases properties are modelled with the Peng Robinson (PR) EoS [6] using two different mixing rules for the covolume of mixing: the classical linear mixing rule and the van der Waals mixing rule with a binary interaction parameter. On this basis phase diagrams have been calculated.

THE MODEL FOR PURE SOLID PHASE

Only pure solid phases are taken into account in the model. A limitation of the model concerns the critical temperature and pressure of which values are supposed to be known to calculate the fugacity coefficients with the PR model when a solute is present in the fluid phases. These properties can not normally be measured directly when working with organic molecules such as pharmaceutical or bio-molecules, since most of these substances usually decompose at conditions well below their critical temperature. Predictive group contribution methods [7,8,9] offer a way round this difficulty. Parametric identification on the basis of

specific experiments on the pure compound is an alternate way to estimate critical properties and the acentric factor. In the case of the naphthalene, these values are so widely used that they will be considered as fixed parameters in the model. For the naphthalene-CO₂, the influence of these values has been studied in by several predictive methods using the PR-EoS [10].

The first proposed formulation for the fugacity coefficient of the pure solid is based on the hypothesis that the EoS can be extrapolated in an undercooled liquid domain. The equality of chemical potentials when following a virtual transformation from the solid state to the melting point of the compound and then to the undercooled liquid state, gives:

$$\ln\varphi_{i,S}^{(\text{pure})}(P,T) = \ln\varphi_{i,L}^{(\text{pure})}(P,T) - \left(1 - \frac{T_i^{(\text{fus})}}{T}\right) \frac{\Delta h_i^{(\text{fus})}(P^{(\text{std})})}{RT_i^{(\text{fus})}} - \int_{P^{(\text{std})}}^P \frac{\Delta v_{i,L-S}(u,T)}{RT} du - \frac{1}{RT} \int_{T_i^{(\text{fus})}}^T \left(1 - \frac{T}{u}\right) \Delta c_{P_i}(P^{(\text{std})}, u) du \quad (1)$$

where:

$$\Delta v_{i,L-S}(P,T) = v_{i,L}^{(\text{pure})}(P,T) - v_{i,S}^{(\text{pure})}(P,T) \quad (2)$$

As shown in equations (1), another limitation to the proposed model leads to the following properties: the difference between solid and liquid heat capacity at various temperatures, the melting temperature, the heat of fusion and the difference between liquid and solid volume at various pressures and temperatures. A first approximation could be done for the third term in equation (1) by considering that the volume's difference is independent in pressure:

$$\int_{P^{(\text{std})}}^P \frac{\Delta v_{i,L-S}(u,T)}{RT} du \approx \frac{P - P^{(\text{std})}}{RT} \Delta v_{i,L-S}(T) \quad (3)$$

The heat capacities, the melting temperature and the heat of fusion can all been obtained by differential scanning calorimetry experiments. For the measurement of the liquid and solid volumes pycnometry experiments have to be done if a significant value for this difference of volume has to be taken into account.

Another formulation is possible:

$$\mu_{i,S}(P,T) = h_{i,S}(P_0, T_0) - Ts_{i,S}(P_0, T_0) + \int_{P_0}^P v_{i,S}(u, T) du + \int_{T_0}^T \left(1 - \frac{T}{u}\right) c_{P_i,S}(P_0, u) du \quad (4)$$

Several choices are possible for (P_0, T_0) , depending on the experimental data available. If the solid heat capacity, the melting temperature and the heat of fusion at the standard pressure are known, then the pure solid fugacity coefficient of component i could be written as:

$$\ln\varphi_{i,S}(P,T) = \ln\varphi_{i,L}^{(\text{fus})} - \ln\frac{P}{P^{(\text{std})}} + \left(1 - \frac{T_i^{(\text{fus})}}{T}\right) \left(\frac{\Delta h_i^{(\text{fus})}(P^{(\text{std})})}{RT_i^{(\text{fus})}} + T_i^{(\text{fus})} \left(\frac{\partial \ln\varphi_{i,L}^{(\text{fus})}}{\partial T} \right)_P \right) + \frac{1}{RT} \int_{T_i^{(\text{fus})}}^T \left(1 - \frac{T}{u}\right) \left(c_{P_i,S}(P^{(\text{std})}, u) - c_{P_i}^{(\text{std})}(u) \right) du + \int_{P^{(\text{std})}}^P \frac{v_{i,S}(u, T)}{RT} du \quad (5)$$

where:

$$\varphi_{i,L}^{(\text{fus})} = \varphi_{i,L}^{(\text{pure})}(P^{(\text{std})}, T_i^{(\text{fus})}) \quad (6)$$

$$\left(\frac{\partial \ln\varphi_{i,L}^{(\text{fus})}}{\partial T} \right)_P = \left(\frac{\partial \ln\varphi_{i,L}^{(\text{pure})}}{\partial T} \right)_P (P^{(\text{std})}, T_i^{(\text{fus})}) \quad (7)$$

In the equation (5) the same approximation as used previously in (3) is possible. In the case of the naphthalene, equation (5) has been used in the model. The correlation for standard heat capacity and the correlation in temperature for the molar volume of the solid are those proposed by the Design Institute for Physical Properties (DIPPR)[®]. In order to test all the expressions of the model the phase diagram of pure CO₂ has been calculated as shown in figure 2, and compared with other equivalent diagrams.

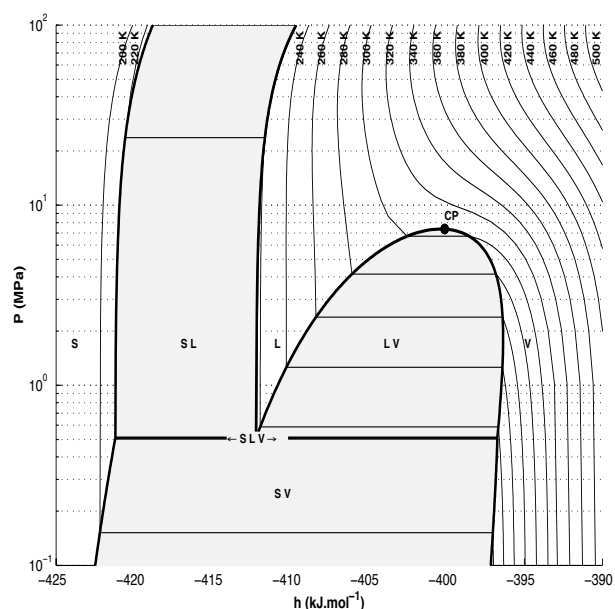


Figure 2: Phase diagram for CO₂

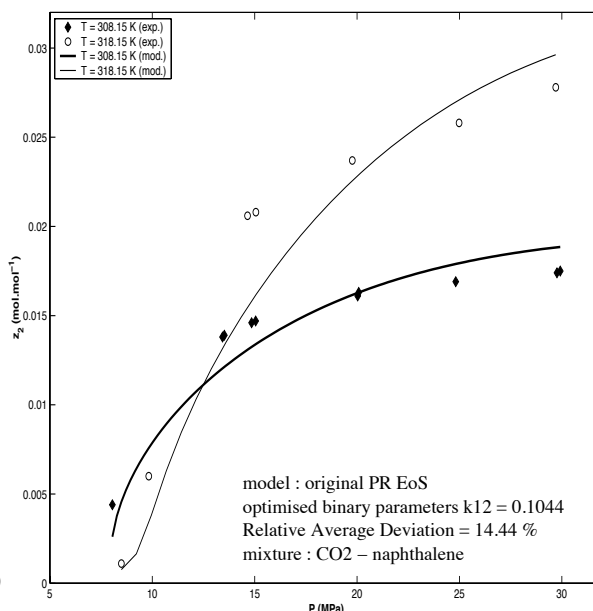


Figure 3: Comparison PR EoS-experimental

PHASE EQUILIBRIUM CALCULATION

The procedure for the calculation of multiphase equilibrium is based on the work of Michelsen [11]. This method offers the advantage of allowing flash calculation without knowing the phase distribution *a priori*. This problem could be a major difficulty – for example with a binary mixture presenting a liquid immiscibility, 19 possible cases are to be considered since two solid phases could be present: v, L, VL, VS₂, LS₂, VLS₂, VS₁S₂, LS₁S₂, VLS₁S₂, L₁L₂S₂, VL₁L₂S₂, L₁L₂S₁S₂, L₁L₂, VL₁L₂, VS₁, LS₁, VLS₁, L₁L₂S₁ and VL₁L₂S₁. Heuristic rules could help to avoid so numerous cases. For the mixture studied here, assuming there is no liquid immiscibility and assuming that if solid CO₂ (S₁) is present then solid naphthalene (S₂) is also present, the number of cases decreases to 9 (the first 9 distributions in the previous list).

Local optimisation methods do not guarantee that an equilibrium solution minimising the free energy will be always obtained. A global approach, as presented by Harding *et al.* [12], provides this guarantee when using cubic EoS for systems with fluid phases. When taking into account solid phases the calculation is more complex since distributions are numerous and since phases may vanish or appear during the iterative calculations of the minimisation of the free energy. The formulation proposed by Michelsen [11], which avoids this problem, was adopted.

Since the objective is also the determination of the phase diagram of a mixture, a continuation method is used to calculate envelopes of each region. Stability analysis by means of tangent plane distance minimisation must be applied to reveal boundary connections or to reveal attractions to the trivial solution.

Along a boundary the chosen iterative method is the globally convergent method of Powell proposed in the NAG[®] library.

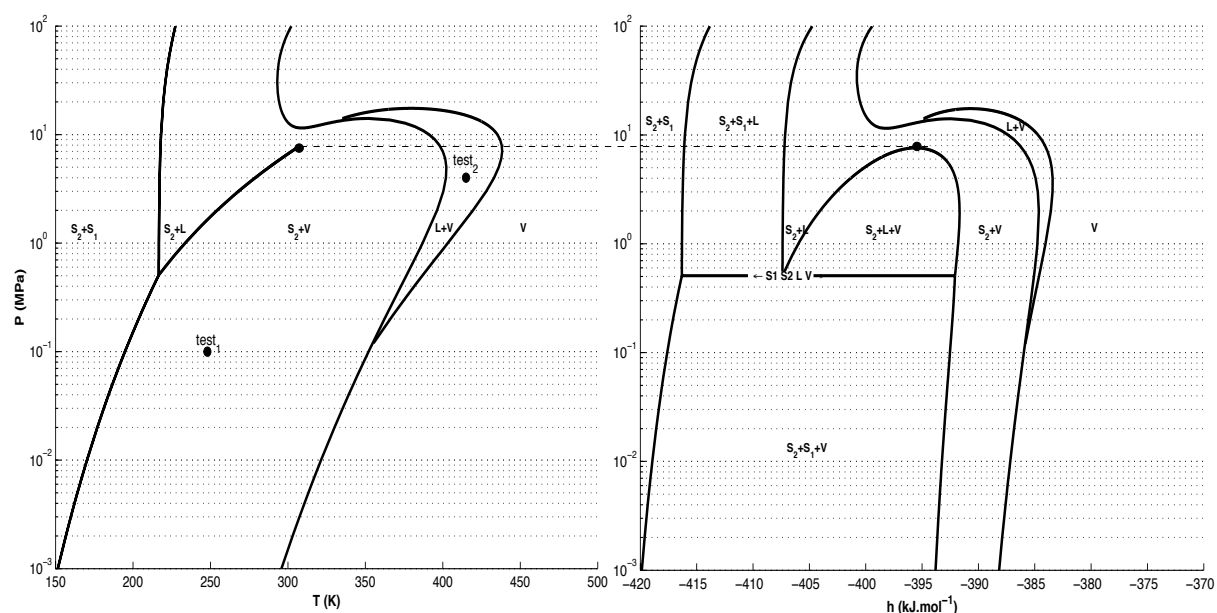


Figure 4 and 5: Phase diagram for CO₂-naphthalene (molar mixture composition 99%-1%)

RESULT AND DISCUSSION

This approach has been applied to the CO₂-naphthalene mixture. In the figure 3 the comparative results of calculations and experimental measurements of the table 1 are presented. Parametric identification has been used to fit binary parameters of each two proposed mixing rules. No significant difference appears with this mixture since the second binary parameters of the van der Waals mixing rule is found to be nearly null. In the figure 3 the classical mixing rule has been used with an optimised value of 0.1044 for the binary parameter k_{12} . When optimisation is done separately for each isotherm, a dependence on temperature appears as recommended by Clifford [13] leading to values slightly different from those proposed by Bartle *et al.* [14].

Phase diagram are presented in figures 4 and 5 and correspond to a section where the global molar composition of naphthalene is 0.01. Stability tests have been done inside each region where free energy for several distributions has been compared. As examples the values of the local minima for the two points test₁ and test₂ shown in figure 4 are:

	test ₁		test ₂	
distributions	VL	VS ₂	VL	V
$g^{(res)}$ (J.mol ⁻¹)	-267.9	-325.6	-327.9	-263.5
minimum	local	global	global	local

The approach provides an easy calculation of the boundaries of phase diagram with stability analysis of phase distributions. However two difficulties remain.

The first difficulty concerns the resultant values of fugacity of solid in regions too far from reliable limits of correlations such as heat capacity or solid molar volume. When extrapolated too far, the fugacity coefficient presented in (5) could take irrelevant values that

lead to false solutions. For the presented mixture heuristic rules was applied preventing this phenomenon by limiting the number of possible distributions. However this technique cannot be applied with new molecules of unknown behaviour.

The second difficulty concerns the complex mixtures and molecules to be studied and for which original PR EoS is inapplicable. Predictive methods based on group contributions will be the next step of this study.

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LIST OF SYMBOLS

Subscripts:

i	component i of the mixture
S	solid phase
L	liquid phase

v	molar volume
c_p	molar heat capacity
φ	fugacity coefficient
μ	molar chemical potential

Superscripts:

(std)	reference to standard state
(pure)	reference to a pure phase
(fus)	reference to the fusion