DEVELOPMENT OF A PROGRAM FOR THERMODYNAMIC CORRELATION OF SUPERCRITICAL FLUID-SOLID PHASE EQUILIBRIUM DATA

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ABSTRACT

The design and development of processes involving supercritical fluids depend on how easy the phase equilibrium can be accurately modelled and predicted. In the work described herein, the supercritical fluid-solid equilibrium has been considered. Modelling the fluid-solid equilibrium is associated with a number of drawbacks, even when it is possible to obtain the experimental solubility data for the solute in the supercritical fluid. In most cases it is necessary to introduce additional adjustment parameters into the model. In this model, three cubic equations of state have been used. The developed program, realized in Visual Basic® language, is based on the fitting of two parameters – the binary interaction parameter (K_{12}) and the solid sublimation pressure (P_2^{Sat}). This program can be used for any fluid-solid equilibrium even when both parameters are known or supposed. The model has been applied to palmitic acid-carbon dioxide system because the sublimation pressures of this fatty acid are known and the results obtained have been compared with them. The saturation pressure values obtained show that the thermodynamic model applied to fluid-solid equilibrium calculations is useful to predict the behaviour of the palmitic acid-supercritical carbon dioxide system.

INTRODUCTION

The solubility of a solid (component 2) in supercritical carbon dioxide (component 1) from its thermodynamic definition is [1]:

$$y_2 = \frac{P_2^{sat}}{\hat{\phi}_2^F P} \exp \frac{(P - P_2^{sat})\upsilon_2^S}{RT} \tag{1}$$

where P_2^{sat} and υ_2^S are the saturation pressure (sublimation pressure in this case) and the molar volume of pure solid, respectively, and $\hat{\phi}_2^F$ is the fugacity coefficient of the solid in the supercritical phase (at pressure P and temperature T).

The calculation of the solubility y_2 therefore requires a knowledge of P_2^{sat}, υ_2^S and an equation of state (with its associated mixing rules) for the calculation of $\hat{\phi}_2^F$. The fugacity coefficient is the property calculated by a thermodynamic model. The other properties of the solid (P_2^{sat} and υ_2^S) should be obtained from independent information. These equations are summarized in Table 1. Cubic equations of state are the basic tools for supercritical fluid-solid equilibria calculations [2]. This program has been designed for using three equations of state; Redlich-Kwong, Soave-Redlich-Kwong and Peng-Robinson equation [2], i.e., the program allows to choose the equation that we want to use. These equation are summarized in Table 2. The program has been developed to use the Van der Waals or the Lorenty-Berthelot mixing rules. These equations are also shown in Table 2.

There are many properties that affect the results of calculations of solid solubilities in supercritical carbon dioxide using equations of state and mixing rules. Besides the critical constants, the sublimation pressures of solids also have a significant influence on the results of the calculations. The sublimation pressures of high molecular weight compounds are too small for accurate experimental measurement. Reverchon et al. suggested that the sublimation pressure should be considered as an adjustable parameter [3]. Cortesi et al. [4] and Huang et al. [5] have reported data for the sublimation pressures of solids obtained in this way.

In the study described here, in order to calculate the fugacity coefficient, a binary interaction parameter K_{12}, that it is part of the mixing rules, must be obtained by fitting the experimental solubility data.

MATERIALS AND METHODS

The program has been realized in Visual Basic® language. The necessary properties of the both compounds: critical temperature and pressure, molar volume and acentric factor are introduced as a file, i.e., *components file*. The experimental data are introduced as a file, i.e., *experimental data file*. A components file exists for each group contribution method used to estimate these properties and the experimental data file is the solubility data for all pressure and a constant temperature.

Once both files have been opened, the program presents in screen the range of saturation pressure and of binary interaction parameter that we want to use and with which increments. Next we can choose the equation of state that we want to use. The algorithm of the process is shown in Figure 1. After carrying out the calculations, the calculated solubility data, for each P_2^{sat} and with the value of K_{12} that minimizes the error, are shown in the screen.

For each value of temperature and for the whole range of pressure, two parameters – K_{12} and the solid sublimation pressure (P_2^{sat}) – have been fitted by minimizing this error (average absolute relative deviation, AARD) between experimental and calculated solubility data.

RESULTS AND DISCUSSION

The equilibrium data of different systems [6, 7] have been correlated using this program. The most interesting system is the palmitic acid-carbon dioxide phase equilibrium because the sublimation pressures of this fatty acid are known and the results can be compared with them. The values of the sublimation pressure obtained using the Peng-Robinson equation of state with Lorentz-Berthelot mixing rules are shown in Figure 2 along with the literature data. The P_2^{sat} values obtained have been correlated using the Clapeyron equation for R^2 value above 0.9. K_{12} values increase with temperature and they can be adjusted according to a linear relationship with temperature for R^2 value above 0.9. The experimental data and the data calculated using this equation of state are represented in Figure 3. These data are in good agreement with experimental data, as can be observed from Figure 2 and Figure 3. The saturation pressure values obtained show that the thermodynamic model applied to fluid-solid equilibrium calculations is useful to predict the behaviour of the palmitic acid-supercritical carbon dioxide system. Similar results have been obtained in the correlation of the solubility experimental data of another solid-supercritical CO_2 systems [6, 7].

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Table 1. Calculation of fluid-solid equilibrium [2].

Property	Symbol	Expression
Equilibrium conditions for solid (2)-fluid (1) equilibria		$\hat{f}_2^{\,S} = \hat{f}_2^{\,F}$
Fugacity of solute in the supercritical phase	$\hat{f}_2^{\,F}$	$\hat{f}_2^{\,F} = \hat{\phi}_2^{\,F} y_2 P$
Fugacity of solute in the solid state	$\hat{f}_2^{\,s}$	$\hat{f}_2^{\,s} = P_2^{\,sat} \phi_2^{\,sat} \exp\left(\int_{P_2^{sat}}^{P} \frac{\upsilon_2^{\,s}}{RT} dP \right)$
Solubility of a solid in the supercritical fluid after simplifications	y_2	$y_2 = \frac{P_2^{sat}}{\hat{\phi}_2^{F} P} \exp \frac{(P - P_2^{sat})\upsilon_2^{S}}{RT}$
Solid sublimation pressure	P_2^{sat}	Fitting parameter
Fugacity coefficient of the solid	$\hat{\phi}_2^{\,F}$	$\ln \hat{\phi}_i = \int_0^P \left[\left(\frac{\partial z}{\partial n_i} \right)_{P, T, n_{j \neq i}} - 1 \right] \frac{d\,P}{p}$
Binary interaction parameter	K_{12}	Fitting parameter

Table 2. Summary of the equations of state (EOS) and mixing rules (MR) used in this correlation method.

EOS	Functional form	Parameters	Constants
RK	$P=\frac{RT}{V-b}-\frac{a\alpha}{V\left(V+b\right)}$	$a=\Omega_a\ R^2 T_c^{\ 2.5}\ /\ P_c\ ;\ b=\Omega_b\ RT_c\ /\ P_c$ $\alpha=T^{-1/2}$	$\Omega_a=0.42747\ ;\ \Omega_b=0.08664$
SRK	$P=\frac{RT}{V-b}-\frac{a\alpha}{V\left(V+b\right)}$	$a=\Omega_a\ R^2 T_c^{\ 2}\ /\ P_c\ ;\ b=\Omega_b\ RT_c\ /\ P_c$ $\alpha=\left[1+s\left\{1-(T\ /\ T_c)^{1/2}\right\}\right]^2$	$\Omega_a=0.42747\ ;\ \Omega_b=0.08664$ $s=0.48508+1.55171\omega-0.15613\omega^2$
PR	$P=\frac{RT}{V-b}-\frac{a\alpha}{V\left(V+b\right)+b\,(V-b)}$	$a=\Omega_a\ R^2 T_c^{\ 2}\ /\ P_c\ ;\ b=\Omega_b\ RT_c\ /\ P_c$ $\alpha=\left[1+s\left\{1-(T\ /\ T_c)^{1/2}\right\}\right]^2$	$\Omega_a=0.45724\ ;\ \Omega_b=0.07780$ $s=0.37464+1.54226\,\omega-0.26992\,\omega^2$
Mixture parameters			
		$a\alpha=\sum_i\sum_j y_i y_j\,(a\alpha)_{ij}$	$b=\sum_i y_i\ b_i$
$(a\alpha)_{ij}$ (VDW MR)	$(a\alpha)_{ij}=\left(1-k_{ij}\right)\left\{(a\alpha)_i\ (a\alpha)_j\right\}^{1/2}$	(LB MR)	$(a\alpha)_{ij}=\Omega_a\ R^2 T_{cij}^{\ 2.5}\alpha_{ij}\ /\ P_{cij}$ (RK EOS) $(a\alpha)_{ij}=\Omega_a\ R^2 T_{cij}^{\ 2}\alpha_{ij}\ /\ P_{cij}$ (SRK and PR EOS) $T_{cij}=\left(1-K_{ij}\right)(T_{ci}\ T_{cj})^{1/2}\ ;V_{cij}=\left(\frac{V_{ci}^{\ 1/3}+V_{cj}^{\ 1/3}}{2}\right)^3;P_{cij}=\frac{Z_{cij}\ RT_{cij}}{V_{cij}};Z_{cij}=\frac{Z_{ci}+Z_{cj}}{2};$ $\alpha_{ij}=(\alpha_i\ \alpha_j)^{1/2}$

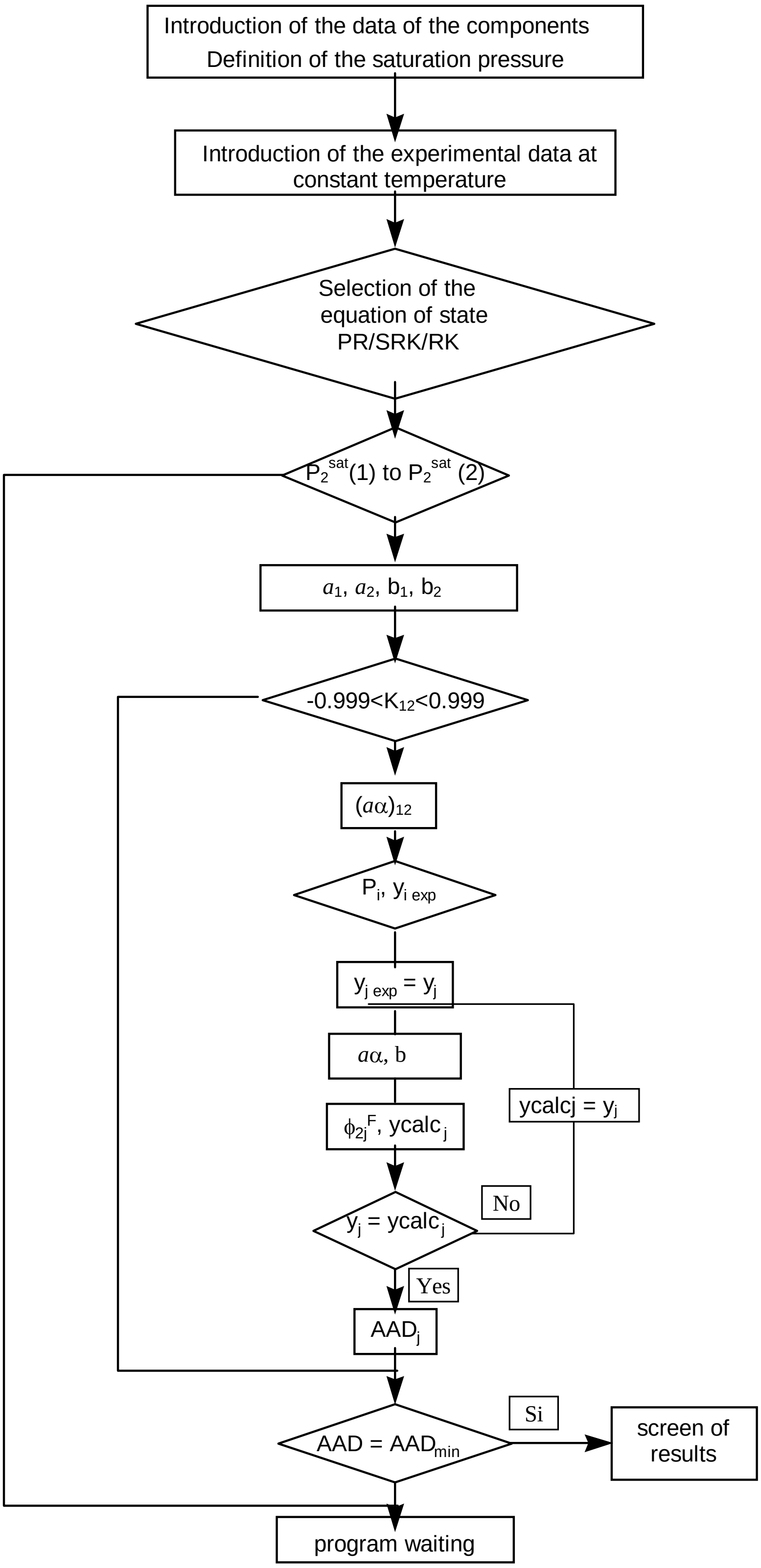

Figure 1. Algorithm of the program

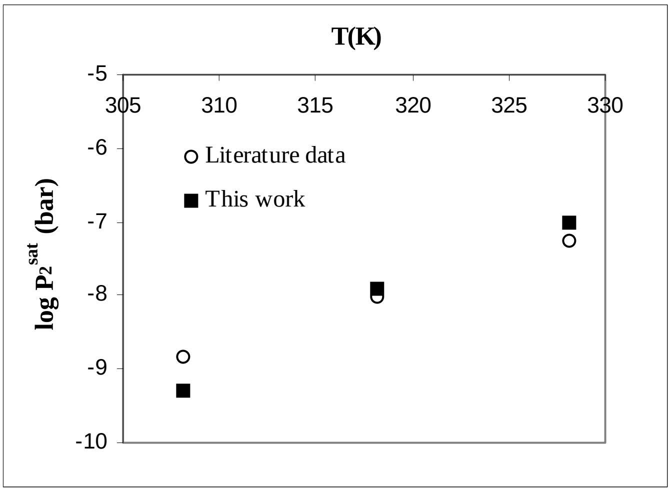

Figure 2. P_2^{sat} values *vs* temperature

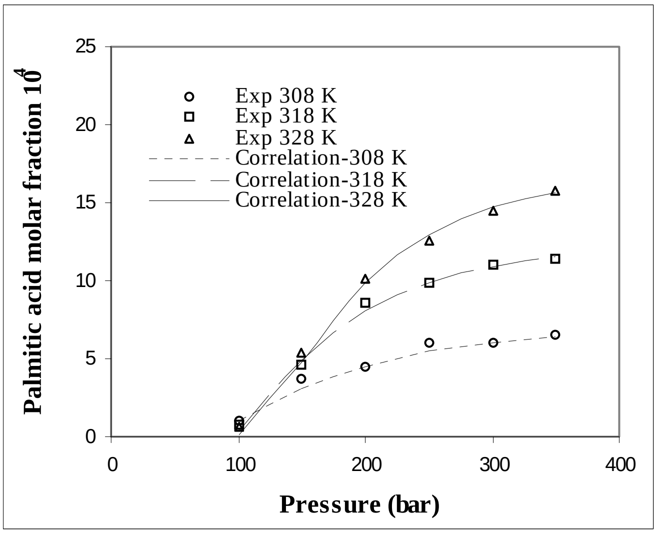

Figure 3. Solubility of palmitic acid in supercritical carbon dioxide. Experimental data and results obtained using the thermodynamic correlation program at 308, 318 and 328 K, respectively.