

Efficient flash computation of continuous sets of solid-liquid-vapor equilibria directly related to laboratory data obtained through the synthetic method

Matías J. Molina^{a,b}, José V. Mattos^d, S. Belén Rodríguez-Reartes^{a,b,c}, Lúcio Cardozo Filho^d, Marcelo S. Zabaloy^{a,b,*}

^aDepartamento de Ingeniería Química, Universidad Nacional del Sur (UNS), Avda. Alem 1253, Bahía Blanca, (8000), Argentina.

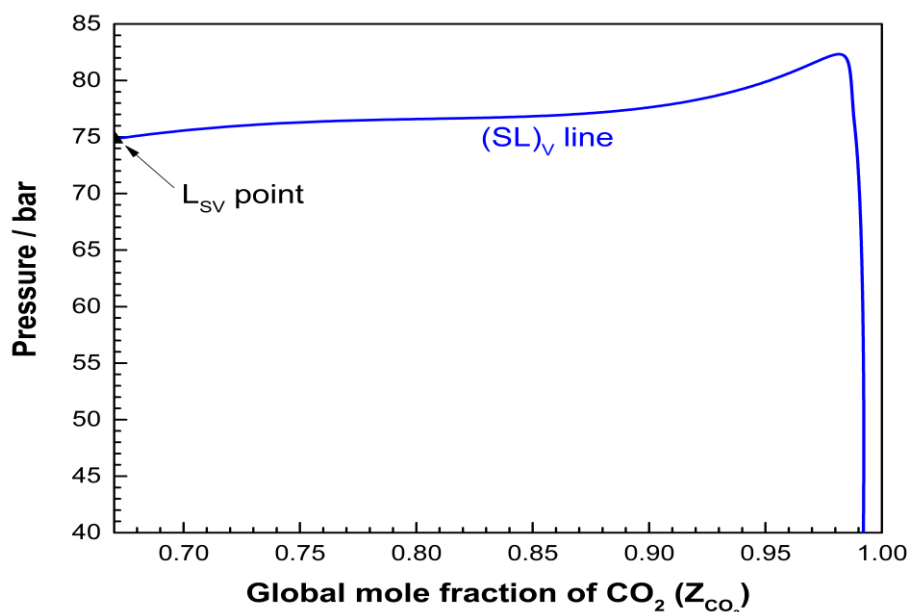
^bPlanta Piloto de Ingeniería Química – PLAPIQUI (UNS – CONICET), Camino “La Carrindanga” Km 7, Bahía Blanca, (8000), Argentina.

^cDpto de Ingeniería Química, ETSEQ, Universitat Rovira i Virgili, Av. Països Catalans 19, (43007), Tarragona, Spain.

^dUniversidade Estadual de Maringá, Departamento de Engenharia Química, Av. Colombo, 5790 - Bloco D-90, Maringá - PR, Zona 07, CEP 87020-900, Brasil

*mzabaloy@plapiqui.edu.ar

GRAPHICAL ABSTRACT



ABSTRACT

Often in the laboratory the set goal is to measure solid-fluid equilibria for systems made of CO₂(1), a drug(3) and an organic solvent(2), at supercritical conditions, by using a variable volume equilibrium cell. Frequently, it is decided to proceed as follows: a known amount of a known-composition binary liquid solution of components 2 and 3 is fed into the cell, followed by feeding a known amount of the antisolvent CO₂(1). In this way, the global composition becomes known. Then, at set temperature (T), by moving the cell piston, a high enough pressure (P) is found, at which the system is a homogeneous fluid (F). Next, P is lowered up to the appearance of an incipient solid (S) phase [fluid-solid (F_s) equilibrium]. Sometimes, already at the maximum operating pressure of the apparatus, solid-fluid coexistence (no homogeneity) is found, and hence the lowering of the pressure leads to the detection of an

incipient vapor (V) phase in the presence of a solid phase and of a fluid phase, each of finite size (solid-liquid-vapor (SL_V) equilibrium). In this case, at the end of the experiment, the only known information to be recorded is: T, the global composition, and the pressure P of SL_V equilibrium where the V phase is the only incipient one [1]. If an isothermal set of such experiments covers a range of global amount of CO₂ (same liquid solution fed), then, the experimentalist essentially obtains a curve of SL_V equilibrium pressure versus, e.g., global CO₂ mole fraction, at set T and set global drug/solvent ratio. We recognize that the right type of computation corresponding to a point of such curve is a ternary solid-liquid-vapor flash at zero vapor-phase mole fraction and set temperature T (Duhem's Theorem), being the predicted P just one of the outcomes of the calculation. Notice that none of the SL_V phase compositions is experimentally known. The purpose of this work is to develop an efficient algorithm for computing curves as the previously described, each in a single computer run. This work precedes a, strictly speaking, modeling stage in which we would seek agreement between experimental data and model predictions. The algorithm is illustrated in this work for the system CO₂(1)+ethanol(2)+acetaminophen(3) [1], where ethanol is the organic solvent. The system of equations of an SL_V flash at set temperature is built by imposing: {1} the satisfaction of the fluid PVT_x equation of state (EOS) for the L and V phases (translated Peng Robinson-EOS, with quadratic mixing rules, in this work), {2} the isofugacity condition for each of the 3 components in the L and V phases, {3} the isofugacity condition for component 3 among the V and S phases (the S phase is considered to be made of pure component 3, and the solid-state fugacity is computed according to [2]), {4} mass conservation condition in the heterogeneous system for each component, {5} summation of mole fractions equal to unity for the L and V phases, {6} specification equation that sets the value of T, and, {7} specification equation that sets the V phase mole fraction equal to zero. On the other hand, the system of equations that makes possible to compute the global mole fractions includes: {a} the constraint $z_1 + z_2 + z_3 = 1$, being z_i the global mole fraction of component i , and {b} the specification $z_3/z_2 = \text{const}$, which corresponds to the composition of the fed liquid solution. In this work we use the enlarged system of equations (ESEs) resulting from adding the two last equations to the SL_V system of equations. The ESEs has a single degree of freedom that one would tend to spend by setting the value of one of the z_i s. However, since we resort, for solving the ESEs, to a numerical continuation method (NCM), due to its efficiency, we leave the NCM algorithm to freely choose the variable to be specified, and to set its value, for each flash to be computed. The graphical abstract (GA) presents, as an illustration of the results that can be obtained, the computed SL_V flash pressure, flash where the vapor phase is incipient, as a function of z_{CO_2} (= global mole fraction of CO₂). T is constant throughout the curve (T = 313.15 K), as it is the global drug/solvent ratio (= 1.1776 mol acetaminophen/kg ethanol). The computed solid phase mole fraction decreases as z_{CO_2} decreases, tending to zero as the L_{SV} point is approached. Such point is a double saturation point where a major L phase is simultaneously at equilibrium with two incipient phases: a pure-acetaminophen S phase and a V phase. No stability tests were performed for the computed equilibria. Such tests would identify the valid segments of the curve shown in the GA. After doing that, the phase diagram would be completed by the addition of other types of curves, such as the solid-fluid equilibrium curve of incipient S phase. The NCM was able to properly capture the steep part of the curve in the GA.

Keywords: SLV flash, continuous set, computation, algorithm, numerical continuation method

[1] J.V. Mattos et al. DEQ, UEM, BRASIL. Yet unpublished.

[2] S.B. Rodriguez-Reartes, M. Cismondi, E. Franceschi, M.L. Corazza, J.V. Oliveira, M.S. Zabaloy. J. Supercrit. Fluids 50 (2009) 193–202.