The Journal of Supercritical Fluids 130 (2017) 210–229

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Characterization of solid-fluid equilibrium regions of computed constant-overall-composition phase diagrams

Sabrina Belén Rodriguez-Reartes, Jorge A. Guapacha, Marcelo S. Zabaloy*

Planta Piloto de Ingeniería Química (PLAPIQUI), Departamento de Ingeniería Química (DIQ), Universidad Nacional del Sur (UNS)-CONICET, CC 717, 8000, Bahía Blanca, Argentina

ARTICLE INFO

Keywords:
Theoretical methods
Solid-Fluid equilibrium
Asymmetric binary systems
Equation of state
Solidified fraction
Miscibility islands

ABSTRACT

In this work we studied the features of the solid-fluid region of computed binary constant-overall-composition phase diagrams (COCPDs), by resorting to calculated constant solidified-fraction curves. As generally done for constant overall composition (COC) mixtures, we computed phase envelopes (made of fluid–fluid equilibrium (FFE) and solid-fluid equilibrium (SFE) segments), together with appropriate segments of solid-fluid–fluid equilibrium (SFFE) curves. Besides, for achieving a more complete characterization of solid-fluid regions of computed COCPDs, we calculated sets of constant solidified fraction curves. A methodology to find the quantitative connection among these curves and already computed SFFE lines is proposed. The results obtained for heterogeneous regions suggest the existence of complex patterns of behavior, for phase equilibria involving fluid and solid phases. Some of them could be regarded as unexpected. The proposed approach can be applied, in general, to binary systems which present precipitation, in pure form, of the heavy compound.

1. Introduction

The phase behavior over wide pressure ranges of binary systems made of a light compound (e.g., CO_2, CH_4, C_3H_8) and an organic compound having a relatively high molecular weight is of interest in a number of applications, e.g, Refs. [1–5]. Within the ranges of conditions of interest, these systems may present fluid–fluid (FFE), solid-fluid (SFE), liquid-liquid-vapor (LLVE) and solid-fluid–fluid (SFFE) equilibria. Typically, transition pressures (temperatures) are measured at set temperature (pressure), and set overall composition (COCPDs), through the synthetic method, covering a temperature (pressure) range. The result is a set of measured points (segments) of the phase envelope of the COCPD, eventually together with sets of points (segments) of three-phase equilibrium lines. This is shown in the pressure-temperature space. Appropriate models for these complex systems may be useful to interpolate and extrapolate experimental information, and to study possible patterns of phase behavior. One of such models has been used in Refs. [1–4].

An approach for describing solubilities of solids (SFE) at high pressures is the use empirical density-based correlations (EDBCs) [5,6]. They properly correlate existing solubility data in the pressure range from 10 MPa to 30 MPa [6]. EDBCs are based on the observation that, in the mentioned region, a double logarithmic plot (i.e., logarithm of the solubility vs. logarithm of the solvent density) yields a linear relationship [6]. However, the extrapolation of EDBCs beyond the mentioned limits fails (i.e., it fails at low temperatures or at very high pressures, where liquid-like densities appear) [6]. A list of the empirical approaches most used for modeling solubilities of solids in supercritical fluids can be found in ref [5].

EDBCs provide information about situations where a solid phase coexists with a fluid phase, but without giving information on the individual phases themselves. On the other hand, equations of state (EOSs) of the van der Waals family, e.g., the PR-EOS [7], give complete information for (mixed or pure) fluid phases; while (pure) solid fugacity equations (PSFugEs, [8–12]), e.g., the one used in this work (described in Section 3.1.1), do the same for solid phases made of pure compounds. From combining EOSs and PSFugEs it is possible to calculate all kinds of multiphase-multicomponent equilibria involving fluid and solid phases, except for those equilibria where solid solutions, i.e., solid phases not made of a single component, are present. A variety of EOSs may be used for describing the properties of supercritical fluid mixtures [5], e.g., Soave-Redlich-Kwong (SRK) EOS, Peng-Robinson (PR) EOS, group contribution (GC) EOS, perturbed hard-sphere chain (PHSC) EOS, quasi-chemical nonrandom lattice fluid (QLF) EOS, multifluid non-random lattice fluid (MF-NLF) EOS, etc [5]. Care should be exercised when choosing and EOS: sophisticated EOSs can yield an inconsistent behavior [13]. Attempts have been made of defining a single relationship between pressure, temperature, density and composition to

* Corresponding author.
E-mail addresses: mzabaloy@plapiqui.edu.ar, marcelo.santiago.zabaloy@gmail.com (M.S. Zabaloy).

http://dx.doi.org/10.1016/j.supflu.2017.07.010
Received 29 March 2017; Received in revised form 6 July 2017; Accepted 13 July 2017
Available online 25 July 2017

Nomenclature

Symbols and acronyms

1st CEP	1st critical end point
2nd CEP	2nd critical end point
C_1, C_2, C_3	Constants that characterize the pure heavy component SLE curve
CEP	Critical end point
COC	Constant overall composition
COCPD	Constant-overall-composition phase diagram
DL	(vertical) dashed line
EDBC	Empirical density-based correlation
EOS	Equation of state
$\hat{f}_2(T, 1, \upsilon_o)$	Fugacity of the pure heavy component ("2"), in liquid state, at system T and P
$f_2^S(P, T, \upsilon_o)$	Fugacity of the pure heavy component ("2") in solid state at system T and P
FF	Fluid-fluid
FFE	Fluid–fluid equilibrium
FI	Full isopleth
GC-EOS	Group contribution EOS
HT	High temperature
I-C-FPF-L	**I**sopleth fluid–fluid **C**onstant **F**luid-**P**hase-**F**raction **L**ine
I-C-SPF-L	**I**sopleth solid-fluid **C**onstant **S**olid-**P**hase-**F**raction **L**ine
IE	**I**sopleth two-phase **E**nvelope
INE	**I**sopleth **N**on-**E**nveloping two-phase line
L	Liquid
LL	Liquid-liquid
LLE	LL equilibrium
LLV	Liquid-liquid-vapor
LLVE	LLV equilibrium
LT	Low temperature
MF-NLF-EOS	Multifluid nonrandom lattice fluid EOS
MPgAc	Medroxiprogesterone acetate
P	Absolute pressure
P_{crit}	Critical (absolute) pressure
%SMPgAc	Percentage of solidified heavy component (MPgAc)
PHSC-EOS	Perturbed hard-sphere chain EOS
PR-EOS	Peng-Robinson EOS
PSFugE	Pure solid fugacity equation
P_{tp}	Pure compound vapor-liquid equilibrium P at T_{tp} (consistently obtained from the PR-EOS)
PVT	Pressure-temperature-volume
QLF-EOS	Quasi-chemical nonrandom lattice fluid EOS
R	the universal gas constant
S	Solid
SF	Solid-fluid
SFE	SF equilibrium
SFF	Solid-fluid-fluid
SFFE	SFF equilibrium
SF-MD	Binary solid-fluid master diagram
SL	Solid-liquid
SLE	SL equilibrium
SLV	Solid-liquid-vapor
SLVE	SLV equilibrium
SLV-HT	High temperatur SLV locus
SLV-LT	Low temperature SLV locus
SRK-EOS	Soave-Redlich-Kwong EOS
SV	Solid-vapor
SVE	SV equilibrium
T	Absolute temperature
T_{crit}	Critical (absolute) temperature
TP	Triple point
tpd	Reduced tangent plane distance
T_{tp}	Triple point absolute temperature for the pure heavy compound
u_2	Mole fraction of component "2"
V	Vapor
υ_o	Pure heavy component molar volume in liquid state
υ_u	Molar volume of fluid phase of composition u_2
υ_x	Molar volume of fluid phase of composition x_2
w_2	Mole fraction of component "2" in the S phase
$w_{2,SLV}$	Mole fraction of component "2" in S phase at SLVE
x_2	Mole fraction of component "2" in the fluid phase
$x_{2,SLV}$	Mole fraction of component "2" in l phase at SLVE
$y_{2,SLV}$	Mole fraction of component "2" in V phase at SLVE
z_2	Overall composition (mole fraction of component "2") of the binary system

Greek letters

$\Delta\upsilon^{S-L}$	Solid-liquid molar volume difference ($\upsilon_{solid} - \upsilon_{liquid}$)
Φ_F	Fluid phase fraction (mole basis)
Φ_S	Solid phase fraction (mole basis)
Φ_S^L	Φ_S of SL system (at set z_2) under SLVE
Φ_S^V	Φ_S of SV system (at set z_2) under SLVE
ω	Acentric factor

describe simultaneously both, the fluid state and the solid state, e.g., ref [14].

In the present work we applied the PSFugE approach described by Prausnitz [10] and presented in more detail by Firoozabadi [9], but in the particular form of ref [2], to the calculation of the fugacity of the pure solid phase (see Section 3.1.1 for more details). Such form is continuous at the triple point temperature [12], and it can be applied, over wide ranges of pressure (or density), to multiphase equilibria involving pure solids coexisting with fluid mixtures.

With regard to the literature sources of high pressure experimental solid-fluid equilibrium data the reader may consult the comprehensive review in Ref. [5].

In previous works, we calculated COCPDs including the two-phase envelope and the appropriate segments of SFFE lines. The systems considered were CO_2 + medroxyprogesterone acetate (MPgAc) [2], CO_2 + progesterone [4] and CH_4 + n-triacontane [4]. On the other hand, only phase envelopes were computed in other works. In this last case the studied systems were CO_2 + Mitotane [1], C_3H_8 + n-eicosane [3] and CO_2 + n-eicosane [3]. In all cases [1–4], the phase envelopes included SFE and FFE segments. The systems in Refs. [1] and [2] present retrograde melting behavior. This is also the case for systems CO_2 + progesterone [4] and CO_2 + n-eicosane [3]. For a detailed description of retrograde melting behavior see Ref. [4].

As an illustrative example, Fig. 1 shows, for system CO_2(1) + MPgAc(2), a computed COCPD. The overall MPgAc mole fraction is $z_2 = 9.2404 \times 10^{-5}$. Fig. 1 depicts the calculated phase envelope (solid line) and it shows the appropriate segment of the calculated solid-liquid-vapor (SLV) line. This line characterizes, at least partially, the SFE region. The phase envelope has a single segment which is of the solid-fluid type. Based on the limited information it provides, the phase diagram of Fig. 1 has no FFE segments in its phase envelope, and, in principle, it would not have FFE regions either.