



# An enhanced “first freezing point” method for solid–liquid–gas equilibrium measurements in binary systems



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## ABSTRACT

This work presents an enhanced method for solid–liquid–gas (SLG) phase equilibrium measurements in binary systems. The method is mainly based on the observation of the first freezing point. It consists of the formation of first solids from fluid phase(s) by means of slow temperature decreases. In this work, additionally to the observation of the appearance of first solids, SLG equilibrium measurements were confirmed through a pressure change when the solids were formed while temperature was still decreasing at constant volume. A data acquisition system was built to allow registration of both temperature and pressure in the static-view cell in real time.

The three-phase SLG equilibria for the well-studied carbon dioxide + naphthalene system were determined in order to validate our methodology. SLG equilibria were also measured for the binary systems constituted by carbon dioxide + hexadecanoic acid, octacosane, triacantane, or dotriacontane. The experiments were performed at pressures up to 39 MPa and temperatures below the melting point of the pure solute. The reported uncertainties in temperature and pressure are  $\pm 0.02$  K and  $\pm 0.02$  MPa.

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## 1. Introduction

Supercritical fluids have been considered as alternative technology in several processes since their solvent properties are suitable, such as their density which is similar to a liquid, their viscosity comparable to those for gases, and their high diffusivity. These properties can be altered with slight temperature and pressure changes [1,2]. For this instance, knowledge of the phase behavior for mixtures constituted by supercritical solvent + solute is a fundamental factor for the design and analysis of novel processes as well as for the development and validation of thermodynamic models. Particle production using supercritical fluids (SCFs) requires information about solubility data of the solute in the SCF and solid–liquid–gas (SLG) phase transitions. This phase change is referred as the minimum pressure required for melting the solid mixed with the solvent at a fixed temperature [3,4].

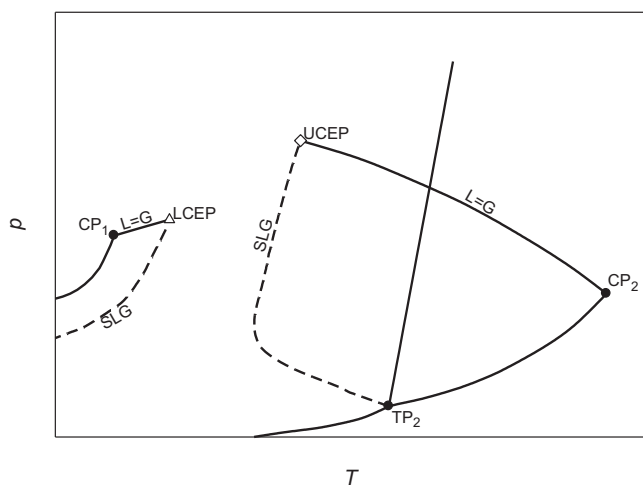
Some researches about SLG equilibria for binary systems formed by supercritical solvent + high molecular weight solute are reported

in the literature. Particularly, binary carbon dioxide + hydrocarbon systems exhibit a highly asymmetric behavior because of their large differences in molecular size, chemical structure, and interactions. The phase behavior of this kind of systems is classified as Class II-b [5], where the triple point temperature for the solute is higher than the critical temperature of the light compound. It is typically described in a pressure versus temperature graph as shown in Fig. 1. Vapor–liquid critical points of the binary mixture are split in two lines. The first curve covers from the critical point of component 1 ( $CP_1$ ) to the lower critical end point (LCEP). The second curve goes from upper critical end point (UCEP) to the critical point of component 2 ( $CP_2$ ). At the LCEP and UCEP, the gas and liquid phases become a single phase in the presence of a solid phase. SLG equilibria are described by two lines. The first line intersects the LCEP and the second path goes from the triple point of component 2 ( $TP_2$ ) to the UCEP.

The melting point depression effect, represented by a negative SLG slope, is caused by the high solubility of the solvent in the solute. This behavior ends at a minimum melting temperature. After this value, the slope becomes positive, and temperature increases up to reach the UCEP. This is attributed to the low solubility of the solvent in the solute, and mainly to the predominant influence of hydrostatic pressure [6].

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**Fig. 1.** Pressure–temperature phase behavior diagram for a highly asymmetric binary mixture.

Temperature and pressure are the common variables to represent a SLG phase behavior. Composition would be useful to describe the phase envelope completely; however, to the best of our knowledge, there is no such data reported in the literature that describes the complete SLG diagram for binary systems [4,5,7].

The most versatile methods for SLG measurements reported elsewhere are based on visual determinations through a camera. These methods are named as first melting point and first freezing point. The first melting point consists on the appearance of the first drop of liquid in the presence of solid and gas phases by means of temperature or pressure raises. The second method considers the formation of the first solids from fluid phase(s) as equilibrium criteria [8–12]. Some apparatus have been alternatively developed with slight modifications of the melting or freezing methods with successful results such as the modified capillary method [13,14]. Alternatively, SLG phase equilibrium can be experimentally obtained by other methods such as differential scanning calorimetry (DSC), high pressure microscopy, and transitiometry [15–18]. Typically, commercial DSC equipment has the limitations of working at relative moderated pressures, high pressure microscopy offers images of high resolution for visual methods, and transitiometry provides thermodynamic variables using both calorimetry and PVT measurements.

The reliability of analytical and visual methods for SLG measurements has been extensively verified in the literature. Nevertheless, visual methods are of relative low cost compared with the analytical methods. On this basis, the majority of the available visual equipment is based only on the observation of phase change to determine temperature and pressure at SLG data, no other criterion has been used to support it. Consequently, inherent errors can be attributed to users. Our interest is focused on the SLG phase equilibrium line than goes from  $TP_2$  to the UCEP. Hence, we measure the experimental solid–liquid–gas phase equilibrium data for binary systems containing carbon dioxide + solute (naphthalene, hexade-

canoic acid, octacosane, triacontane, or dotriacontane) through a reliable static visual apparatus. The first freezing method is reinforced by a pressure change noted on the data registration in our measurements.

## 2. Experimental

### 2.1. Materials

Infra Air products supplied carbon dioxide research grade. High purity hydrocarbons (naphthalene, hexadecanoic acid, octacosane, triacontane, and dotriacontane) were purchased from Sigma–Aldrich. Chemicals were used as received and no purification stage was applied before they were used. Certified purities and properties of chemicals are listed in Table 1 [19,20].

### 2.2. Apparatus and procedure

A schematic diagram of the experimental apparatus is shown in Fig. 2. The main component is a static-view cell (EC) capable to operate up to 55 MPa and 393 K. It is made of stainless steel 316 with approximately 25 cm<sup>3</sup> of volume. The cell has a sapphire window. A magnetic bar moved by an external magnetic stirring device (SD) was used for stirring purposes. Temperature of the cell was regulated by means of a circulating liquid bath (LB1, Polyscience, PD15R). A syringe pump (SP, High Pressure Equipment, 62-6-10) was used to hold the gas from the cylinder (A) and send it to the cell for increasing pressure. Temperature of the syringe pump was kept at 3 °C with the help of a second circulating liquid bath (LB2). By this way, carbon dioxide could be liquefied according to the carbon dioxide phase diagram in order to have enough solvent volume to perform SLG equilibria at high pressures. A digital camera (CAM, Net, 3icube) was placed in front of the sapphire sight window, and was connected to a personal computer (PC) to allow an enlarged observation of any phase change. 12 images per second could be captured and stored in the PC. A LEDs lamp placed around the lens was used to illuminate inside the cell.

Two platinum resistance thermometers of PT-100-Ω (Ti, Thermo-Est) inserted in two thermowells were connected to a digital thermometer indicator (TD, Automatic Systems Laboratories, F-200). A pressure transducer (PT, General Electric, Druck PMP) was connected to a digital multimeter (M, Agilent, 34401A) and a power supply (PS, Agilent, E3610A). TD and M were communicated to the PC through RS232 to USB cables in order to storage temperature and pressure measured data. A data acquisition program was developed in Python Software and plots were built with the help of Gnuplot interface. Each variable was plotted versus time quasi-simultaneously every 5 s in the interface. Instruments for temperature and pressure were previously calibrated, and the uncertainties were estimated to be ±0.02 K and ±0.02 MPa, respectively [21].

Before performing any measurement, the internal sections of the apparatus were washed with organic solvents and carbon dioxide to eliminate any contaminants. Then, nitrogen was flushed to dry the cell, tubing, and accessories.

**Table 1**  
Properties of chemicals [19,20].

Chemicals	CAS	Mole fraction purity	Supplier	$T_f$ (K)	$T_c$ (K)	$p_c$ (MPa)
Carbon dioxide	[124-38-9]	0.999999	Infra	216.58	304.12	7.374
Naphthalene	[91-20-3]	0.999	Sigma–Aldrich	351.35	748.40	4.050
Hexadecanoic acid	[57-10-3]	0.990	Sigma–Aldrich	335.66	785.00	1.510
Octacosane	[630-02-4]	0.990	Sigma–Aldrich	334.35	832.00	0.850
Triacontane	[638-68-6]	0.996	Sigma–Aldrich	338.65	844.00	0.800
Dotriacontane	[544-85-4]	0.986	Sigma–Aldrich	342.35	855.00	0.750

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