Fluid Phase Equilibria 270 (2008) 121–128

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

High-pressure phase equilibria for chlorosilane + carbon dioxide mixtures

Eduardo Vyhmeister[a,b], Anthony J. Muscat[a], David Suleiman[b], L. Antonio Estévez[b,*]

[a] University of Arizona, Department of Chemical & Environmental Engineering, 1133 E. North Campus Drive, Tucson, AZ 85721, United States
[b] University of Puerto Rico, Department of Chemical Engineering, PO Box 9046, Mayagüez, PR 00681-9046, United States

ARTICLE INFO

Article history:
Received 23 February 2008
Received in revised form 10 June 2008
Accepted 11 June 2008
Available online 4 July 2008

Keywords:
Chlorosilane
Supercritical carbon dioxide
Fluid-phase equilibrium
Critical locus
Mixture critical point
Dimethyldichlorosilane
Methyltrichlorosilane
Trimethylchlorosilane
Diethyldichlorosilane

ABSTRACT

Fluid-phase equilibria, including dew points, bubble points, and critical points were measured for four binary systems composed of a chlorosilane and carbon dioxide. The measurements were carried out in a constant-composition, variable-volume cell equipped with a sapphire window, which allowed visual observation of the phases in the cell. A syringe pump was used to inject the CO_2 into the cell and to control its pressure. Methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, and diethyldichlorosilane up to about 0.14 mol fraction were studied in this apparatus and a total of 243 phase-boundary points were obtained. Displacements in the critical point with respect to pure CO_2 of up to 11.81 MPa and 348.05 K were observed. Modeling of the fluid-phase equilibria for three of the four binary systems was done using the Peng–Robinson equation of state, standard van der Waals mixing rules with two binary interaction parameters, and a φ–φ formulation of the equilibrium. The binary interaction parameters were obtained by fitting the model to the experimental data. The model produced excellent agreement between computed and experimental data. Graphical representations of the modeling results are presented and compared to experimental results. The results indicate that the largest chlorosilane (diethyldichlorosilane) produced the largest shift in critical pressure and critical temperature with respect to pure CO_2.

1. Introduction

Supercritical fluids (SCFs) have been used in diverse applications, including pharmaceuticals, food processing, and separations. Prompted by the high volume of solvents used in the various stages of the fabrication process and increasingly stringent regulations on the use and disposal of chemicals, integrated-circuit (IC) manufacturing companies are striving to find environmentally benign replacements. Supercritical carbon dioxide ($scCO_2$) is a potential alternative solvent for use in IC manufacturing processes, such as pre-cleaning, photoresist stripping, cleaning post-etching and post-ashing residues, oxide and copper etching, low-*k* film repair and pore sealing, pattern development, metal deposition, and drying [1–7]. Carbon dioxide is nonpolar, nontoxic, inexpensive, and vastly available. Several research efforts have been aimed at using halogen-bearing silanes dissolved in $scCO_2$ as a selective repair agent in chip fabrication [8–11]. Chlorosilanes are molecules that contain a core silicon atom attached to one or more chlorine atoms and one or more hydrocarbon chains. Among the halosilanes, those bearing chlorine have proven to have a reaction that can be better controlled than that of their homologues [11]; other halosilanes react too fast and thus the repair reaction is harder to control. In thin film-repair and pore-sealing applications, chlorosilanes react with hydroxyl terminals on the surfaces and inside the pores of the material. Therefore, high diffusivity and low surface tension are desirable solvent properties. SCFs are thus especially suitable for this purpose. Chlorosilane concentrations at supercritical conditions must be known to accurately describe chemical reactions of chlorosilanes both in the fluid phase and on a surface. It is also important to ensure that the chlorosilane remains in the supercritical-fluid phase and does not condense; therefore, proper phase diagrams of the binary system being used have to be known. This research examines fluid-phase equilibria in binary mixtures of a chlorosilane and supercritical CO_2.

2. Materials and methods

2.1. Materials

Coleman grade carbon dioxide (CO_2) with a purity of 99.99% or higher was supplied by the Cryogenics & Gas Facility at the University of Arizona. Dimethyldichlorosilane (DMDCS), diethyldichlorosilane (DEDCS), methyltrichlorosilane (MTCS), and trimethylchlorosilane (TMCS), were purchased from Sigma–Aldrich (St. Louis, MO) and were used without further purification. Table 1 shows molecular formulas, purity, and properties of these

* Corresponding author. Tel.: +1 787 832 4040x2573; fax: +1 787 265 3818.
E-mail addresses: estevez@uprm.edu, estevez.antonio@gmail.com (L.A. Estévez).

0378-3812/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.fluid.2008.06.017

Table 1
Properties of compounds used

	Compound				
	TMCS	DMDCS	MTCS	DEDCS	Carbon dioxide
Molecular formula	$(CH_3)_3ClSi$	$(CH_3)_2Cl_2Si$	CH_3Cl_3Si	$(CH_3CH_2)_2Cl_2Si$	CO_2
CAS #	75-77-4	75-78-5	75-79-6	1719-53-5	124-38-9
Purity[a] (%)	99.0	99.0	99.0	98.0	99.99
T_b (°C)[a]	57	71	66	125–131	−78
T_c (K) [17,18]	498	520	518	NA[b]	304.25
P_c (kPa) [17,18]	3202	3486	5563	NA	7380
Antoine *A* [18]	6.0754	6.2684	5.9970	NA	
Antoine *B* [18]	1191	1328	1167	NA	
Antoine *C* [18]	−38.1	−32.1	−47.15	NA	
P^{sat} at 20 °C or 293.15 K (kPa)	26.7	14.5	17.9	NA	
ω[c]	0.2657	0.2751	0.4478	NA	0.224 [19]

[a] From vendor.
[b] Not available.
[c] Calculated as explained in Section 3.2.

compounds. The Antoine constants listed in Table 1 correspond to the equation:

$$P^{sat} = 10^{A-(B/C+T)} \quad (1)$$

where P^{sat} is vapor pressure in kPa and T is temperature in K. Also, naphthalene (CAS number 91-20-3) was used to validate the apparatus. It was also purchased from Sigma–Aldrich (St. Louis, MO) and with a purity of 99.0%.

2.2. Apparatus

Fig. 1 is a schematic of the solubility apparatus used to obtain the equilibrium phase boundaries. The apparatus, which is similar to that described by McHugh and Krukonis [12], consisted primarily of a syringe pump (SP) ISCO (Lincoln, NE) model 260D and a cell (SC). The pump was operated in either constant-pressure or constant-flow mode. The solubility cell was a cylindrical stainless steel vessel, 2 in. (51 mm) in external diameter and 7 1/4 in. (184 mm) in length (including end caps), with four 1/16 in. (1.6 mm) ports and two screw caps. The phases in the cell were observed through a 5/8-in. (16 mm) sapphire window (W). The cell was divided into two chambers by a piston (P). The space enclosed by valves A, D, and E, and the piston was the front-side or equilibrium chamber, and the space enclosed by the piston and valve C was the rear-side or pressure-control chamber. Two buna O-rings allowed the piston to move back and forth inside the cell without leaks between the chambers.

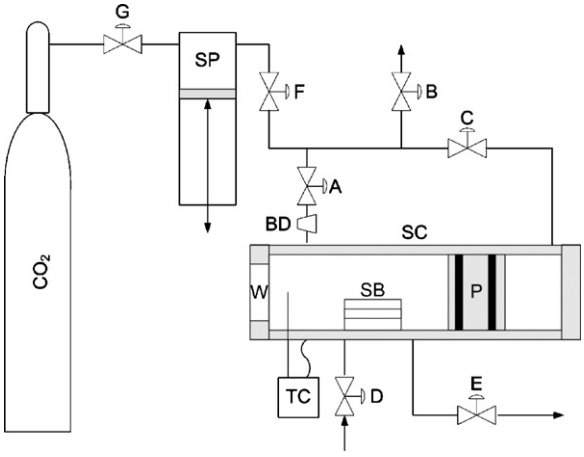

Fig. 1. Schematic diagram of the apparatus. Key to symbols: SP, syringe pump; A–G, needle valves; BD, burst or rupture disk; TC, temperature controller system connected to a heating tape; SC, solubility cell; W, sapphire window; P, piston; and SB, stirring bar.

The pump delivered pressurized CO_2 in a precise, desired amount and was used to control the pressure in the solubility cell. The ports were used to read temperature, inject the CO_2, inject the chlorosilane, and purge the contents. The solubility cell was placed on a magnetic hot plate, and a stirring bar placed inside of the cell maintained uniform concentration and temperature. Two-way needle valves from High Pressure Equipment Company (Erie, PA), model 15-11AF1, were used to control the flow of chemicals into and out of the cell. The cell temperature was maintained at a desired setpoint by an Omega Engineering Inc. (Stamford, CT) CNi temperature controller connected to a type-K thermocouple, Super OMEGACLAD® XL Probes model KMTXL-062G-6, also from Omega Engineering Inc. An adaptor mounted on the vessel allowed the thermocouple to slide into the front-side chamber of the vessel, which was covered by heating tape and wrapped with insulating foam. The thermocouple was calibrated in house using the ice-point technique. The temperature was displayed digitally to 0.1 °C (0.1 K). The stability of the reading was of ±0.05 °C (0.05 K) as reported by the temperature controller manufacturer. The pressure was displayed digitally to 0.1 bar (10 kPa) with a standard pressure accuracy of ±0.5% of the full scale (~50 MPa).

A rupture disc (4000 psi; 28 MPa) from High Pressure Equipment Company (Erie, PA) was used for safety. A 1-mL precision syringe, Hamilton (Reno, NV) 1000 Series, was used to inject chlorosilanes into the cell.

2.3. Procedure

A critical point, bubble point, or dew point was approached in the equilibrium chamber of the solubility cell by increasing the pressure at constant temperature and constant mole fraction. This was achieved by increasing the pressure in the rear chamber using the syringe pump. Chlorosilanes are known to readily react with water and form HCl, which is highly corrosive. Therefore, maintaining anhydrous conditions in both chambers of the cell (and throughout the apparatus) was extremely important. Before each run, the system was rinsed twice with near-critical CO_2 as follows. With all the valves closed, except valve G, the syringe pump was charged with CO_2 up to about 5.3 MPa at a controlled room temperature of 19 °C (~292 K). Once charged, valve G was closed and valves F and A were opened to fill the front-side chamber with CO_2. The magnetic stirrer was turned on and the temperature controller was connected and set to 35 °C (308.15 K). The syringe pump was set to work at a constant pressure of 6.5 MPa, thus the flow rate decreased