

PHASE BEHAVIOUR OF TWO BINARY SYSTEMS FORMED BY CO₂ AND A SILANE PRECURSOR: *N*-[3-(TRIMETHOXSILYL)PROPYL]ANILINE AND (3-MERCAPTOPROPYL)TRIMETHOXSILANE

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ABSTRACT

In this communication we present the phase equilibrium of the binary systems CO₂ + *N*-[3-(trimethoxysilyl)propyl]aniline (TMSPA) and CO₂ + (3-mercaptopropyl)trimethoxysilane (MPTS). The measurements were conducted in a high-pressure variable volume view cell at 313 K. The CO₂ molar fraction in the binary mixture was varied from 0.90 to 1.0. Results showed that MPTS is soluble in CO₂ at moderate pressures over 8.7 MPa whereas TMSPA solubilization requires higher pressures (24.0 MPa).

INTRODUCTION

Supercritical carbon dioxide (scCO₂) has received significant attention in the last decade as an attractive medium to functionalize the surface of inorganic materials such as silica [1]. In comparison with the conventional solution methods, scCO₂ offers a number of advantages for functionalization, particularly in porous materials: scCO₂ facilitates the transport of the precursors to the nanopores internal surface without structural damage due to its low viscosity, high diffusivity and very low surface tension. Furthermore, scCO₂ is non-toxic, non-flammable, inexpensive, relatively inert and does not leave any residue in the material.

One of the most commonly used functionalization methods consists in the covalent attachment of organosilanes to the silica surface by a sol-gel chemical reaction. A wide variety of silane precursors have been used and highly ordered and densely packed monolayers have been obtained. In particular, the modification of several silica materials with (3-mercaptopropyl)trimethoxysilane (MPTS) in scCO₂ has already been reported in the literature [2, 3]. Moreover, we are currently performing the surface functionalization of mesoporous silica SBA-15 using *N*-[3-(trimethoxysilyl)propyl]aniline (TMSPA). The materials modified with specific amine or mercapto compounds are of great interest due to their numerous applications in catalysis, enzyme immobilization and sorption of metals, anions, organics and gases [4]. This surface functionalization requires the organosilane solubilization in scCO₂. In order to develop this technology, the knowledge of the high-pressure phase equilibria for the CO₂ + organosilanes mixtures is required. Therefore, in this communication we present the phase equilibrium for the binary systems CO₂ + TMSPA and CO₂ + MPTS.

MATERIALS AND METHODS

N-[3-(trimethoxysilyl)propyl]aniline (>96.9% pure) and (3-mercaptopropyl)trimethoxysilane (99+% pure) were obtained from Sigma-Aldrich and used as received. Carbon dioxide (99.99% pure) was supplied by Air Liquide.

Phase equilibrium measurements were carried out using a high-pressure variable-volume view cell designed for temperatures from ambient to 360 K and pressures up to 35 MPa. The stainless steel cell is fitted on one side with a sapphire window for visual observation and its volume can be varied by a piston connected to a manual pressure generator using isopropanol as hydrostatic fluid. The contents in the cell are illuminated and observed through the sapphire window using a Fiebert Endoctech boroscope and a digital camera connected to a computer. A detailed description of the equipment is presented in our earlier papers [5].

The phase behaviour was determined following the synthetic method. A mixture of known composition was prepared in the cell and its phase behaviour was studied against pressure and temperature. First, the cell was closed and purged with CO₂ several times at low pressure. Then each component was separately loaded into the cell and their amounts were determined by weight. A volume of TMSPA or MPTS was introduced first using a syringe. Liquid carbon dioxide was then gravimetrically transferred into the cell by means of a 40 cm³ sample cylinder. Once the sample was loaded, the cell was heated to the desired temperature and the sample was compressed to a single phase. The contents of the cell were continuously agitated by a magnetic stirrer in order to reach the homogeneous phase. The pressure was then slowly decreased until bubbles or drops were observed which correspond to the phase separation. At this point, the temperature and pressure were registered. This procedure was repeated several times to obtain accurate temperature and pressure values. These values served to estimate the uncertainties in the pressure and temperature for each measurement. Based on this, average uncertainties in the bubble or dew-point pressure and temperature were estimated to be ±0.1 MPa and ±0.5 K, respectively. Mole fraction uncertainties were estimated to be ± 0.1 %.

RESULTS

The vapour-liquid equilibria (VLE) of the two binary systems CO₂ + TMSPA and CO₂ + MPTS were measured at 313 K in the CO₂ molar fraction (x_{CO_2}) range from 0.900 to 0.999. The bubble and dew-point pressures of both systems are shown in Figure 1. At this temperature, the dew-point pressures decrease whereas the bubble-point pressures increase as x_{CO_2} increases for both systems. These VLE data indicate that MPTS is already soluble in CO₂ at a moderate pressure (8.7 MPa) whereas TMSPA solubilization requires higher pressures (24.0 MPa). By interpolation of the bubble and dew points for CO₂ + MPTS, the critical point at 313 K can be estimated obtaining critical pressure and composition values of 8.66 MPa and $x_{\text{CO}_2} = 0.992$, respectively.

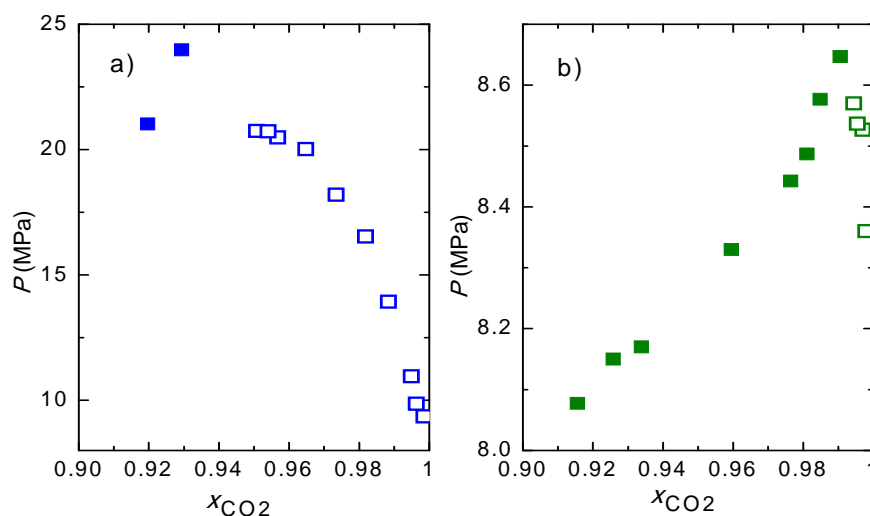


Figure 1. Vapour-liquid equilibrium at 313 K for: a) $[x\text{CO}_2 + (1-x)\text{TMSPA}]$ and b) $[x\text{CO}_2 + (1-x)\text{MPTS}]$. Empty symbols are dew-points and full symbols are bubble-points.

VLE data for $\text{CO}_2 + \text{TMSPA}$ and $\text{CO}_2 + \text{MPTS}$ had not been previously measured. Our results were compared to those reported for $\text{CO}_2 +$ other silane agents such as hexamethyldisilazane (HMDSZ) [6], octyltriethoxysilane (OTS) [7], hexamethyldisiloxane (HMDS) [8], and (*N,N*-dimethylaminopropyl)trimethoxysilane (DMAPTS) [9]. For similar compositions, bubble point and dew-point pressures of the binary system $\text{CO}_2 + \text{MPTS}$ are very similar to those reported for systems formed by HMDSZ and DMAPTS, and slightly lower than those found for $\text{CO}_2 + \text{HMDS}$, whereas the dew-point pressures for $\text{CO}_2 + \text{TMSPA}$ are of the same magnitude than those of $\text{CO}_2 + \text{OTS}$. We are currently performing phase equilibrium measurements for $\text{CO}_2 + \text{MPTS}$ and $\text{CO}_2 + \text{TMSPA}$ at temperatures up to 333 K.

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