

HIGH-PRESSURE OPTICAL CELL FOR *IN SITU* RAMAN SPECTROSCOPY

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ABSTRACT

Raman spectroscopy has been linked to a high-pressure optical cell for the *in situ* study of supercritical carbon dioxide (SC-CO₂)-solute interactions. The body of the cell is made of a stainless steel cylinder enclosing a volumetric capacity of 24 mL, allowing optical access through sapphire windows on both ends. An argon ion laser was used for the excitation and Raman spectra were collected in the back-scattering geometry. This new set-up allows *in situ* studies of SC-CO₂ adsorption by materials under pressures up to 300 bars and temperatures up to 100 °C, where only a minimal sample preparation is required. The set-up was tested in the system SC-CO₂/alkyl ketene dimer (AKD), giving adsorption values up to 7 g of CO₂ per g of AKD, as well as information about AKD solubility in SC-CO₂. As a proof of concept, a possibility to study solubility and adsorption phenomena in SC-CO₂ by the technique of Raman spectroscopy has been demonstrated.

INTRODUCTION

We present a new set-up that combines a high-pressure optical cell with Raman spectroscopic system.

In the last several decades, supercritical fluids (SCFs) have been extensively applied particularly in extraction, chromatography, crystallization, pharmaceutical drug formulation, polymer technologies and chemical reactions processes [1]. Fundamental studies of these peculiar solvents are essential to gain understanding of the different processes.

In situ monitoring is needed for the study of the solute-solute, solute-fluid, and solute-cosolvent interactions under high pressure, since these are responsible of different phenomena such as solubility of compounds in supercritical fluids and adsorption of high-pressure fluids in different

materials. The study of these phenomena is essential in processes like Rapid Expansion of Supercritical Solutions (RESS) and Particles from Gas Saturated Solutions (PGSS) [1], which can be used for material development. In addition, this set-up could be a suitable technology for the study of candidate materials for CO₂ sequestration.

Raman spectroscopy represents a powerful technique that measures the scattered light, providing information about vibrational and rotational motions [2]. Study of the nature of molecular vibrations and rotations provides information about the solute-solute, solute-fluid, and solute-cosolvent interactions under high pressure. These interactions are responsible for different phenomena such as solubility of compounds in supercritical fluids and adsorption of high-pressure fluids in different materials.

Raman spectroscopy has been used to study different phenomena related to SC-CO₂. Several applications and cell designs can be found in literature. Some of the most relevant applications are the study of catalysis in supercritical fluids [3] or the study of CO₂ density in the CO₂-rich fluid inclusions [4] and its relation with the depth of mineralization for geological deposits.

Our aim with the present set-up is to show how Raman spectroscopy coupled to a high-pressure optical cell provides *in situ* information about CO₂ adsorption by an adsorbent as well as solubility of compounds in CO₂. Raman spectroscopy has been used to study CO₂ sorption in poly methyl methacrylate [5]. However, it has not been used yet to study solubility of compounds in SC-CO₂. To our knowledge, this is the first time that the potential of Raman spectroscopy to study adsorption and solubility of a supercritical fluid system *in situ* is reported.

The set-up has been tested for the study of CO₂ adsorption by AKD. AKD is a common sizing agent used in the paper industry since long time ago [6]. AKD was chosen for this study due to our previous experience with the system CO₂/AKD for the preparation of superhydrophobic surfaces by a RESS process [7, 8].

MATERIALS AND METHODS

AKD granules (DR SF 300) with a mean particle diameter of approximately 4.5 mm were supplied by EKA Chemicals (Bohus, Sweden). AKD is not a pure compound but a combination of R1-C₄H₂O₂-R₂ molecules where R1 and R2 are random combinations of C₁₄ and C₁₆ alkyl chains,

from stearic and palmitic acids. *N*-hexane (HPLC grade) was supplied by Tianjin Chemical Reagent Factory (Tianjin, China).

Ultrapure CO₂ was provided by Air Products (Amsterdam, Netherlands)

Equipment description

The Raman spectra were recorded with an imaging spectrometer (HoloSpec f/1.8i, Kaiser Optical Systems) equipped with a holographic transmission grating and thermoelectrically cooled two-dimensional multichannel CCD detector (Newton, Andor Technology, 1600 × 400 pixels, -60 °C). The broad wavenumber range, 100-4500 cm⁻¹, which includes both high-wavenumber intramolecular vibrations and low-wavenumber translational–vibrational modes, is simultaneously collected under same physical conditions. An argon-ion laser, 514.5 nm, was used for the excitation at powers up to 10 mW. The spectrometer was calibrated by fluorescence lines of the neon lamp. Non-polarized Raman spectra were collected in the back-scattering geometry at a resolution of about 3 cm⁻¹. Accuracy of spectral measurements, resulting from the wavelength calibration procedure and experimental conditions, is estimated to be about 1.5 cm⁻¹. The acquisition time varied from 35 to 40 s.

A home-built view cell of 24 mL capacity was used (Figure 1). This cell is a stainless steel cylinder with screw caps in both ends. Both caps contain sapphire windows, with an aperture of the windows (diameter 15.9 mm) big enough to ensure an efficient collection of the scattered radiation. It allows data collection of either liquid or gas in case of coexistence of these two phases in the system. The outer seal for the sapphire window is made of Nitrile butadiene rubber (NBR). The cell was heated by an ELW-HS heating tape and the temperature was controlled by a Pyxis ATR243. A type-K thermocouple was used to measure the temperature near the inside of the vessel. For all the experiments, the sample in the cell was stirred by a magnetic stirrer coated with polytetrafluoroethylene (PTFE). A ruby sensor was placed in a fixed position inside the vessel, giving additional information about the temperature or pressure inside the vessel.

The CO₂ was delivered into the cell using an ISCO pump (model 260D from Teledyne Thousand Oaks, CA) at the desired pressure and temperature. To prepare the AKD/SC-CO₂ system, solid AKD (200 mg) was introduced in the vessel before filling it with CO₂ at the desired pressure and temperature. Raman spectra were acquired in triplicate in all cases.

A scheme of the equipment is shown in Figure 1.

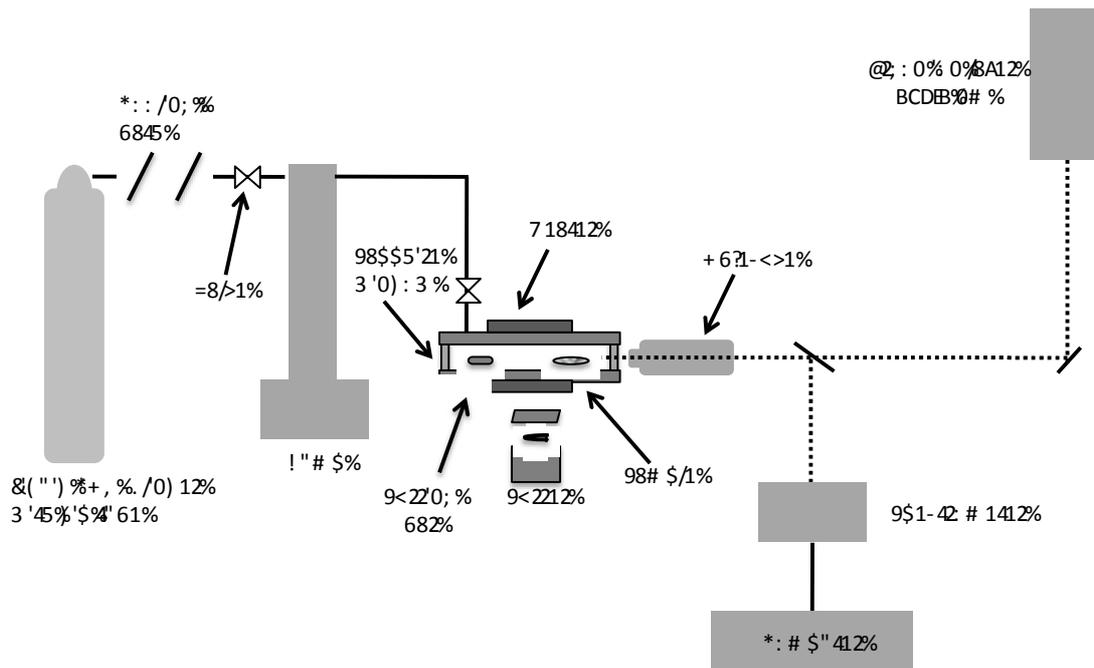


Figure 1. Scheme of the Raman-High-Pressure optical cell set-up.

Raman data analysis

The fitting of the Raman spectra was carried out using the PeakFit software.

For each Raman spectrum of CO₂, a parameter *delta* was calculated as the spectral position difference of the Fermi diads. The *delta* value was used to calculate the density of the system, by using the equation described by Yamamotos et al. [9].

The calculated density and the experimental temperature were used to calculate the pressure using the equation of state (EOS) of CO₂ described by Span and Wagner [10].

Experimental procedure

To prepare the AKD/SC-CO₂ system, solid AKD (200 mg) was introduced in the vessel through the caps. Once the vessel is closed, the heating device is placed around it and CO₂ pumped inside the vessel at the desired temperature and pressure. Two sets of experiments were carried out, each of them starting with a different initial pressure for the CO₂ (80 and 100 bar) while the initial temperature was in both cases set at 40 °C. Higher initial pressure implies a higher density/amount of CO₂ present in the vessel. Once the initial conditions of pressure and temperature are reached for

each set of experiments, Raman spectra of the CO₂ are acquired. The temperature of the system was then further increased in 10 °C intervals and Raman spectra acquired at five different temperatures: 40, 50, 60, 70 and 80 °C. For comparison, the same procedure was carried for a SC-CO₂ system, without the presence of AKD in the vessel.

Statistical data analysis

The data were statistically analyzed using the SAS 9.2 software. A two-variable regression model was used. The regression function was chosen based on the minimum values for the mean square errors, by using the method of ordinary least squares (OLS) to calculate the residuals. The goodness of the fitting was measured by the regression coefficient squared (coefficient of determination).

For the set of experiments started at 100 bar, two regression functions were obtained, one for the system with AKD and another one without AKD. These functions were compared by means of the marginal change percentage and using a t-test. In this case, a dummy variable 0 or 1 was used to indicate the absence or presence of wax respectively. An obtained value for the marginal change percentage bigger than the one described for the t-test (based on the degree of freedom) means that there is a significant difference between the curves described by the regression function, considering 95% of confidence interval. A significant difference between the curves evidences the possibility of detecting AKD dissolved in SC-CO₂.

RESULTS AND DISCUSSION

Figure 2 shows the change in pressure with temperature in the AKD/SC-CO₂ and SC-CO₂ systems. A cross-over behavior is observed. When the initial pressure of the experiment was below 100 bar, the pressures calculated for the system AKD/SC-CO₂ were lower than those for the system SC-CO₂. On the other hand, when the initial pressure of the experiment was 100 bar the calculated pressures show the opposite behavior. This observation could be explained as a competition between two phenomena, the solubility of AKD in CO₂ and the adsorption of CO₂ by the AKD. The results show that at the higher pressure the effect of solubility of AKD in CO₂ predominates.

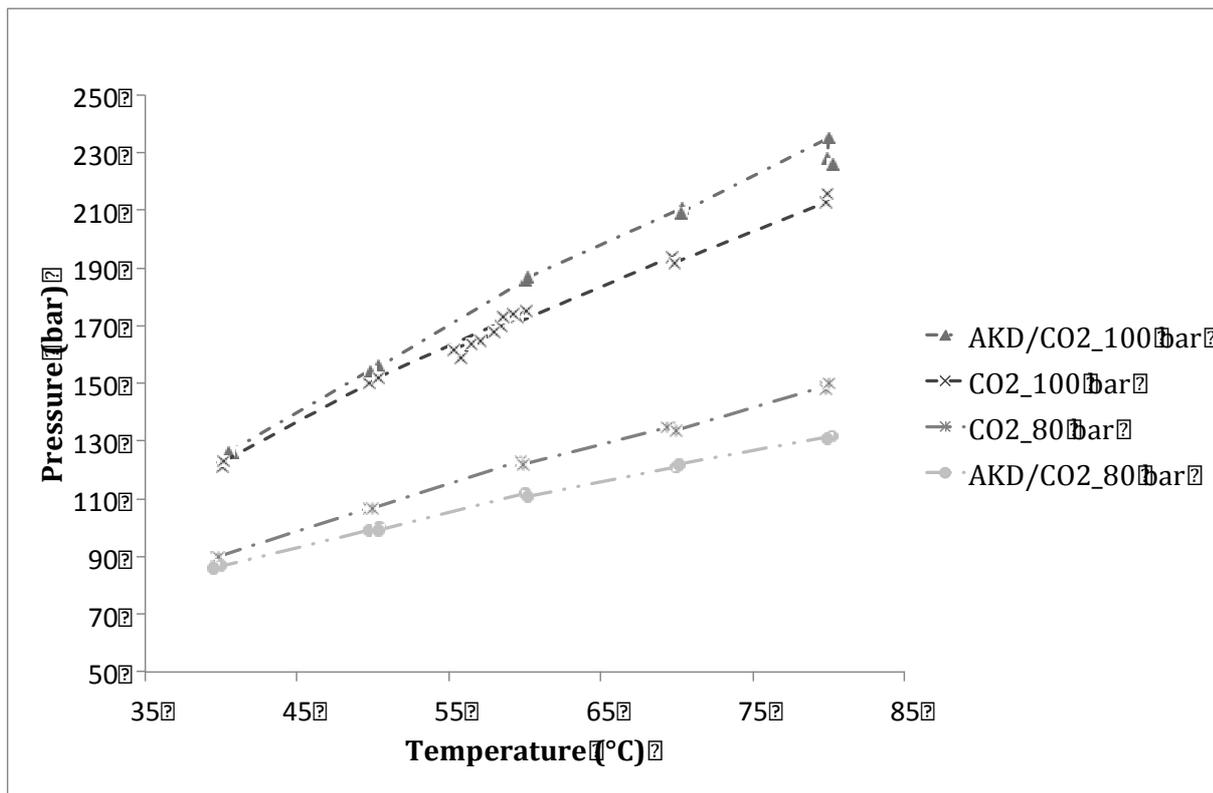


Figure 2. Variation of calculated pressure versus temperature, for the systems SC-CO₂ and AKD/SC-CO₂. The pressures shown in the legend correspond to the initial pressures of the respective experiment.

Adsorption of CO₂ by AKD

Adsorption of CO₂ by AKD can be observed when comparing the systems AKD/SC-CO₂ and SC-CO₂ at the initial pressure of 80 bars. It can be observed that the pressures reached in the presence of AKD are smaller than the ones when only CO₂ is present in the cell. This could be explained as a result of CO₂ adsorption by the AKD at those conditions. Due to its adsorption by the AKD, the density of CO₂ in the pressure vessel lowers, as evidenced by decreased pressures derived from the experimental data (see Figure 2).

The calculations of the amount of CO₂ adsorbed by AKD were done as follows:

For the system AKD/SC-CO₂, the specific volume of AKD (inverse of AKD density, considering that 3 g/mL is the density of AKD) was removed from the specific volume of CO₂. With this new data, new pressures and densities were obtained from the EOS of Span and Wagner [8]. The difference between the newly calculated densities and the original ones corresponds to the amount of CO₂ missing in the system, and therefore captured by the AKD. This density difference is used to

calculate the amount of CO₂ absorbed by 200 mg of AKD. The assumed volume was the volume of the vessel (24 mL), minus the volume occupied by 200 mg of AKD. An approximation of constant density of AKD was applied at all conditions of the study. Adsorption values up to 7 g of CO₂ per g of AKD were obtained. Note that the CO₂ densities reached in this set of experiments do not exceed 0.400 g/mL. Above this region, adsorption decreases since solubility of AKD in CO₂ becomes predominant.

Solubility of AKD in CO₂

Figure 2 shows the change in pressure when the temperature is increased for the systems AKD/SC-CO₂ and SC-CO₂ when the initial pressure was 100 bar. This can be explained as a consequence of dissolving AKD in the CO₂ at these conditions. The presence of the AKD molecules results in increase of the effective density of CO₂, as revealed by the Raman signal. Note that the densities reached in this set of experiments are above 0.500 g/mL.

In this case, a quadratic fitting of both curves turned out to be more appropriate. From the 31 points of data, the value obtained for the marginal change percentage was 6.23, while the t value for the t-test with 29 degrees of freedom was 1.699, for a 95% of confidence interval. In other words, the fitted curves for the systems AKD/SC-CO₂ and SC-CO₂ show a significant deviation from each other. This deviation evidences that the AKD is solubilized in SC-CO₂. For a quantitative analysis, Raman data in future studies should be acquired for the system AKD/SC-CO₂ using different concentrations of AKD.

CONCLUSIONS

A new set-up that combines a high-pressure optical cell with Raman spectroscopy detection has been presented. The set-up has been tested for the system AKD/SC-CO₂. As a proof of concept, a possibility to study solubility and adsorption phenomena in SC-CO₂ by the technique of Raman spectroscopy has been demonstrated.

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