

MEASUREMENT OF SOLUBILITIES OF METAL CHELATES IN SUPERCRITICAL CARBON DIOXIDE USING A QUARTZ CRYSTAL MICROBALANCE

B.A. Seifried and S.E. Guigard*

*Assistant Professor Environmental Engineering Program
Department of Civil and Environmental Engineering, University of Alberta,
Edmonton, Alberta, Canada, T6G 2M8
Email: selma.guigard@ualberta.ca fax: (780) 492-8289

The solubility measurement technique used in this work relies on a piezoelectric quartz crystal or a quartz crystal microbalance. This technique is an *in-situ* gravimetric technique, where a small amount of solute is loaded onto a piezoelectric quartz crystal. The crystal is then placed in a high-pressure cell and pressurized with supercritical carbon dioxide (SC CO₂). The solubility is quantified by the crystal's frequency change as the solute dissolves into the supercritical fluid.

In this work, the solubility of copper (II) bishenoyltrifluoroacetate (Cu(tta)₂) in SC CO₂ was measured at different pressures (10.2 MPa to 15.7 MPa) and at a temperature of 40°C. The solubilities were 0.99×10^{-6} , 2.45×10^{-6} , 3.32×10^{-6} and 3.66×10^{-6} mol/mol at SC CO₂ densities of 0.643, 0.741, 0.775 and 0.790 g/cm³, respectively. In order to verify this technique, caffeine solubilities were also measured. Caffeine solubility was determined to be 7.75×10^{-6} mol/mol at 60 °C and a SC CO₂ density of 0.322 g/cm³. This caffeine solubility is comparable to existing literature values.

INTRODUCTION

Supercritical carbon dioxide (SC CO₂) can be used to extract heavy metals from various solid matrices and to remediate heavy metal contaminated soil. In order to extract metals using SC CO₂, a chelating agent must be used. The chelating agent combines with the metal to form a neutral compound, which is soluble in non-polar SC CO₂ [1-5]. Before metals can be successfully extracted from various matrices using SC CO₂, the solubility of the metal chelate must be quantified.

Well-known techniques used to measure solubilities in supercritical fluids (SCFs) can be divided into static, dynamic and spectroscopic techniques. These techniques suffer challenges in accurately collecting and quantifying the amount of solute in the SCF and in ensuring that equilibrium conditions have been reached [6].

A piezoelectric quartz crystal technique, introduced by Guigard et al. [7], is used in this work to determine the solubility of solutes in SC CO₂. A major advantage of this *in-situ* technique over currently used solubility measurement techniques is that, with the piezoelectric quartz crystal technique, the diffusion process can be followed, guaranteeing that equilibrium is reached.

THEORY

The resonant frequency of a piezoelectric quartz crystal depends on a number of factors, including the mass loading on the crystal and properties of the surrounding fluid such as pressure, temperature and viscosity [8]. When a piezoelectric quartz crystal is used as a quartz crystal microbalance (QCM), a change in resonant frequency of the QCM is directly

related to the change in mass loaded on the quartz crystal's surface, and is independent of the material's properties loaded onto the crystal [9]. Thus, no individual calibration is required in order to quantify the amount of solute [10].

MATERIALS AND METHODS

Chemicals: Copper (II) bithenoyltrifluoroacetate ($\text{Cu}(\text{tta})_2$) was synthesized in the laboratory from cupric nitrate (Aldrich) and thenoyltrifluoroacetone (Aldrich). The method used for synthesis was similar to the method outlined by Bertrand and Kaplan [11]. Caffeine was purchased from FLUKA-Sigma Aldrich (anhydrous, = 97% purity). Supercritical fluid chromatography grade CO_2 (Praxair) was used for all experiments.

Piezoelectric Quartz Crystal, Frequency Counter and Oscillator: The crystal used in the experiments was a 9MHz AT-cut quartz crystal with wrap-around gold plated electrodes (ICM, Oklahoma City). The crystal has a diameter of 14 mm, a stiffness of $29.01 \times 10^9 \text{ N/m}^2$ and a density of 2649 kg/m^3 . An integrated *Research Quartz Crystal Microbalance* (RQCM), purchased from Maxtek (Santa Fe Springs), was used to operate the quartz crystal.

Apparatus: The supercritical fluid extraction (SFE) apparatus for the solubility measurements is shown in Figure 1. It consists of two syringe pumps (ISCO Model 500D), a circulating waterbath with a preheating coil and a stainless steel high-pressure cell (0.75mL) containing the quartz crystal and a magnetic stir bar. The quartz crystal was connected to the RQCM. The temperature of the high-pressure cell was monitored by a thermistor (YSI 406) installed in the lid of the cell. The system pressure was monitored by a pressure transducer connected to the inlet tube. Data from the thermistor and pressure transducer were collected by a data acquisition system.

Crystal Loading: A small amount of solute needs to be placed on the quartz crystals electrode area. A solution of known concentration was prepared with the solute of interest. Methanol and chloroform were used as solvents for $\text{Cu}(\text{tta})_2$ and caffeine solutions, respectively. In order to achieve a uniformly distributed layer of solute on the electrode area of the quartz crystal, a known volume of solution was slowly placed on the crystal using a microliter syringe. The solvent was allowed to slowly evaporate, leaving a uniform layer of solute on the crystal's surface. During this procedure, the crystal frequency was recorded to ensure that the frequency shift was in agreement with the amount of solute placed on the crystal. Once loaded, the crystal was placed into the high-pressure cell (see Figure 2). The high-pressure cell was then hooked up to the SFE apparatus and placed into the waterbath.

Solubility Experiments: Before pressurization, the high-pressure cell was flushed with CO_2 and heated to the desired temperature in a heated circulating waterbath. After approximately one hour, the system was pressurized, the inlet valve was opened and SC CO_2 was introduced into the cell. The pressure in the cell was monitored by a pressure transducer placed immediately upstream of the vessel. The temperature was monitored both by a thermistor placed in the steel lid of the high-pressure cell and by a thermometer placed in the waterbath. The frequency of the quartz crystal was recorded every second throughout the experiment. The experiment continued until the frequency reading remained constant. Once the frequency stabilized, the inlet valve was closed and the cell was depressurized by opening the outlet valve.

RESULTS AND DISCUSSION

The frequency readings during a typical solubility experiment are illustrated in Figure 3. Initially, the frequency of the blank quartz crystal (indicated by F1 in Figure 3) was recorded. The frequency then drops (from F1 to F2) as the solute ($\text{Cu}(\text{tta})_2$ or caffeine) is placed on the crystal. The quartz crystal is then placed in the high-pressure cell and the entire system is heated to the desired temperature for approximately one hour. This heating leads to a slight increase of the quartz crystal's frequency (from F2 to F3). The cell is then pressurized and a frequency drop (from F3 to F4) is observed. This frequency shift is attributed to the change in fluid properties surrounding the crystal [8] and to CO_2 adsorbed to the quartz crystal's and solute's surface. Once the frequency reached a minimum value (F4), the frequency began to increase as the solute dissolved into the SC CO_2 . This increase in frequency is directly proportional to the decrease of the mass of solute loaded on the quartz crystal. The slope of the change in frequency is very steep at the beginning of the experiment due to a high driving force favoring rapid dissolution. The frequency continues to increase but at a slower and slower rate until equilibrium is reached, and finally the frequency stabilizes (F5 on Figure 3). Once the frequency stabilizes, the cell is depressurized. This depressurization results in a sudden increase of frequency, again due to the change in fluid properties surrounding the crystal.

In order to calculate the solubility, the frequency shift from F4 to F5 was used in the Sauerbrey equation [9] to determine the mass dissolved in the SC CO_2 . Using this calculated mass and the volume of the high-pressure cell, the solubility was determined. The solubilities for $\text{Cu}(\text{tta})_2$ are presented in Table 1, and are plotted according to Chrastil [12] in Figure 4. Further measurements at different temperatures are currently underway in order to determine Chrastil parameter values.

In order to verify this solubility measurement technique, the solubility of caffeine was measured and compared to literature data. The solubility for caffeine found in this work was 7.75×10^{-6} mol/mol (see Table 1). The published data by Li [13] was lower than the value determined in this work. Possible reasons for this discrepancy have been discussed by Johannsen and Brunner [14]. They also found higher solubilities than Li [12] and explain that the differences may be attributed to the fact that equilibrium may not have been reached in the work by Li. In comparison with other literature data [15, 16], the values in this work seem to be higher. Again, as indicated by Johannsen and Brunner [13], it is possible that factors such as solute collection and equilibrium conditions may account for this discrepancy.

CONCLUSIONS

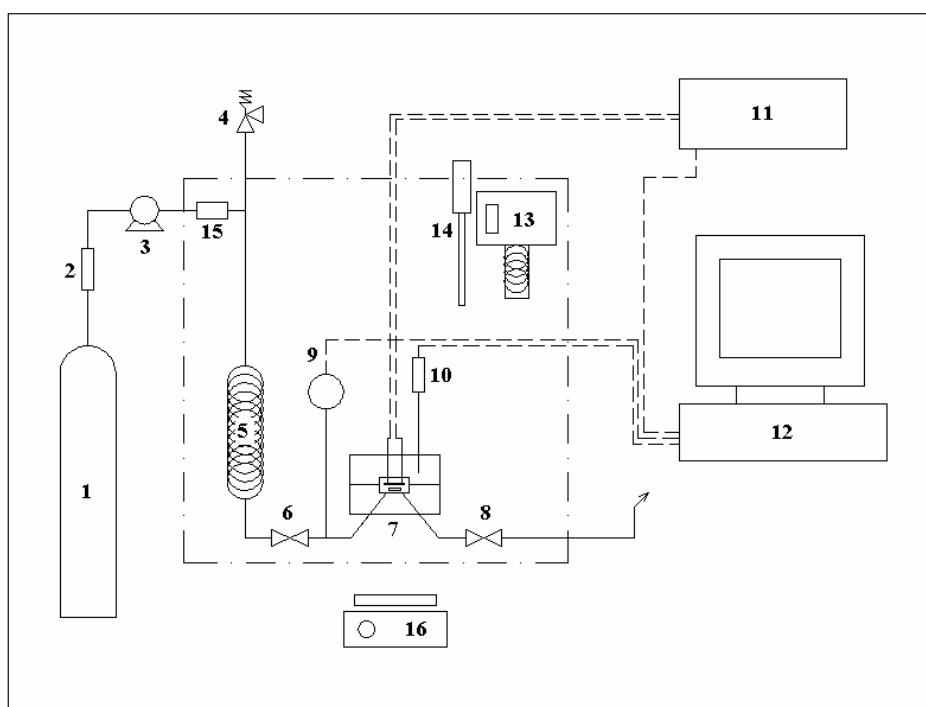
$\text{Cu}(\text{tta})_2$ and caffeine solubilities have been successfully measured using a piezoelectric quartz crystal technique. This method is a static method that allows *in-situ* measurement of solubility, with monitoring of the dissolution process, thus ensuring that equilibrium is reached. Furthermore, the need of sample collection after pressurization is eliminated with this technique. This method is of particular interest for compounds of a relatively low solubility in SC CO_2 , such as metal chelates.

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Table 1: Solubilities of Cu(tta)₂ and Caffeine

Experimental Conditions				Solubility (10 ⁻⁶ mol/mol)		
Compound	Pressure (MPa)	Temperature (°C)	Density (g/cm ³)	Average	Standard deviation (%)	Number of data points
Cu(tta) ₂	10.2	40	0.643	0.99	34.6	4
	12.9	40	0.741	2.45	17.2	3
	14.7	40	0.775	3.32	7.56	3
	15.7	40	0.790	3.66	18.8	4
Caffeine	10.5	60	0.322	7.75	19.9	3



- | | |
|-----------------------------|--|
| 1 CO ₂ Cylinder | 9 Pressure Transducer |
| 2 Filter | 10 Thermistor |
| 3 Syringe Pumps (ISCO 500D) | 11 Oscillator and Frequency Counter (RQCM) |
| 4 Safety Valve | 12 Data Acquisition - Computer |
| 5 Preheating Coil | 13 Circulating Waterbath |
| 6 Inlet Valve | 14 Thermometer |
| 7 High Pressure Cell - QCM | 15 Check Valve |
| 8 Outlet Valve | 16 Magnetic Stirrer |

Figure 1: Apparatus

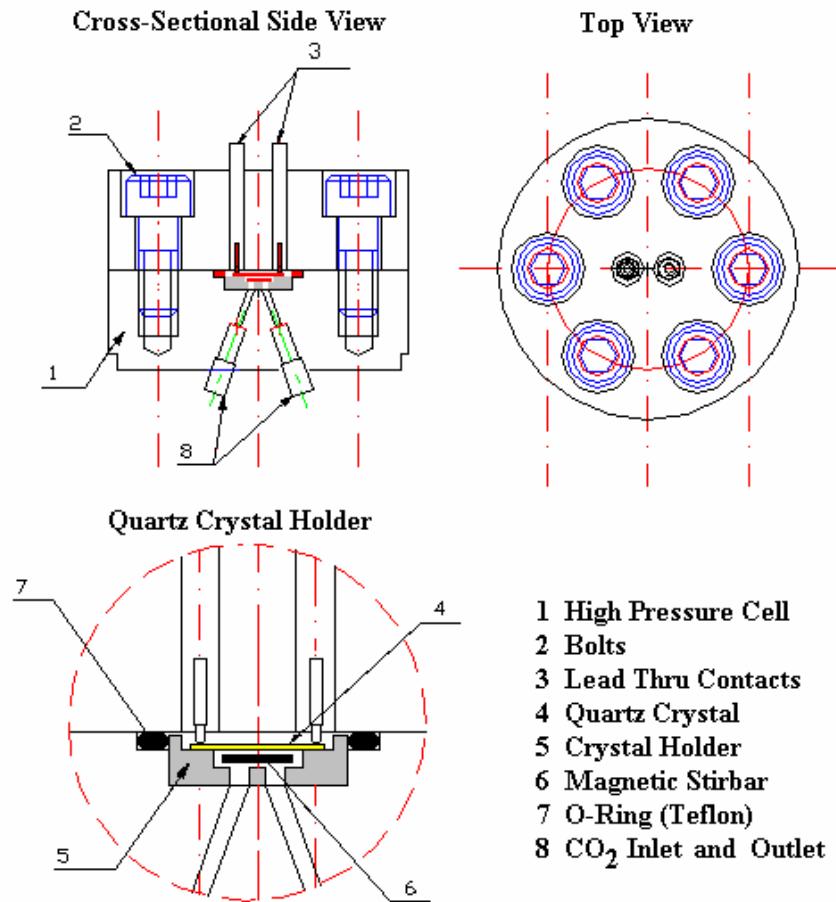


Figure 2: High Pressure Cell - QCM

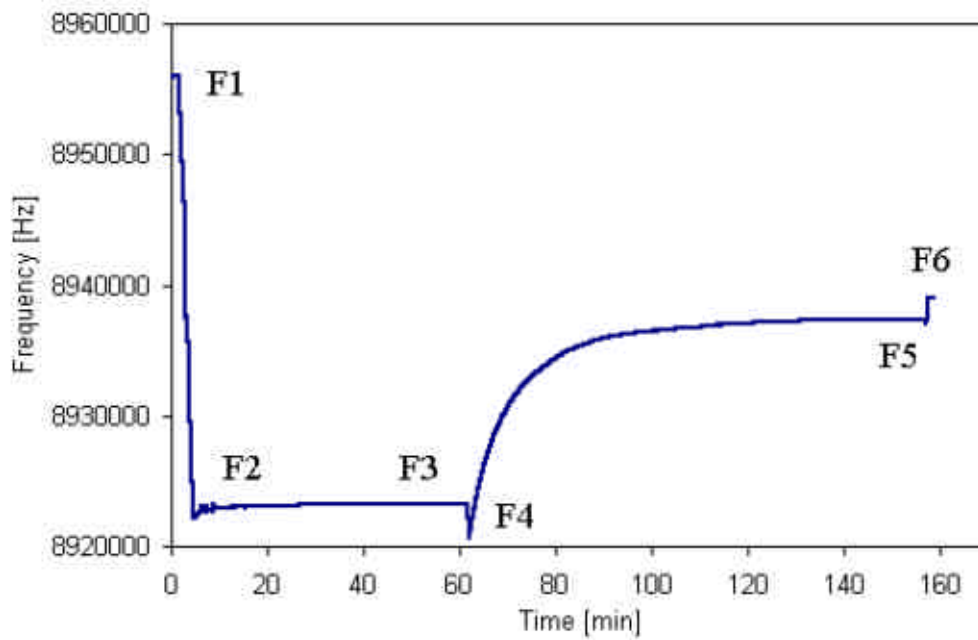


Figure 3: Frequency Reading of Quartz Crystal during a Solubility Measurement for Cu(tta)₂ at 15.7 MPa and 40°C.

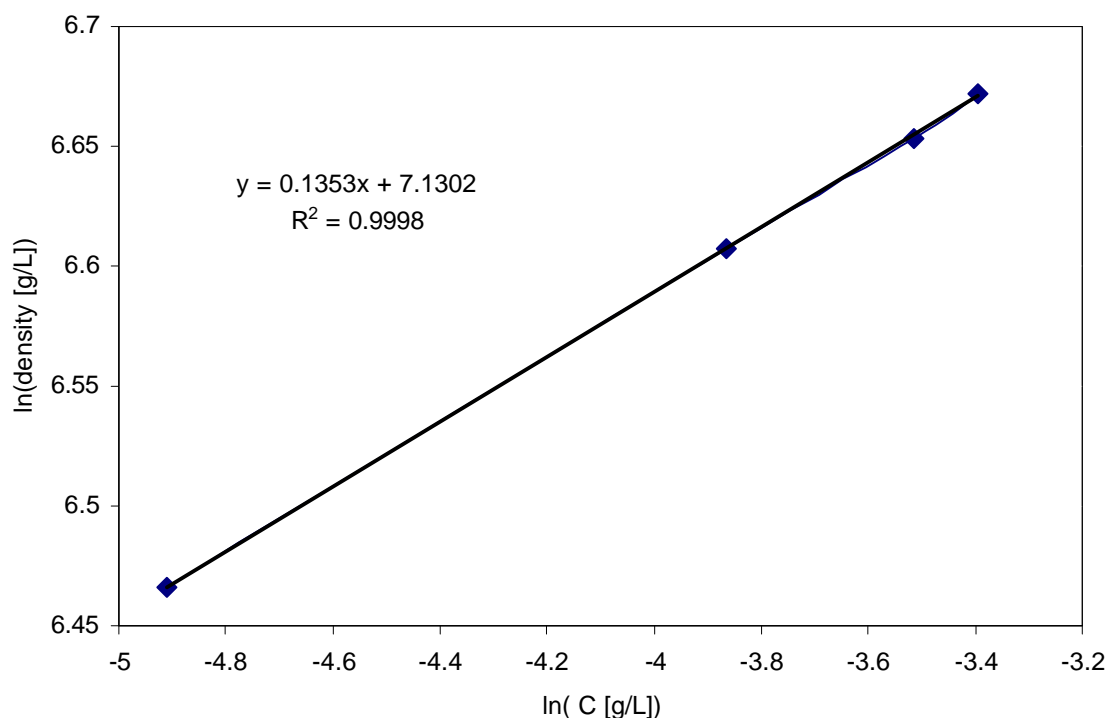


Figure 4: Chrastil fit for measured Cu(tta)₂ solubilities at 40°C

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