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Use and limitations of a quartz crystal microbalance to measure viscosity of carbon dioxide-expanded fish oil fatty acid ethyl esters

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ABSTRACT

The use of a quartz crystal microbalance (QCM) to determine the viscosity of CO_2-expanded (CX) liquids was evaluated. This study presents a calibration method for QCM to be used for viscosity measurements at elevated hydrostatic pressures, taking into account the effects of hydrostatic pressure and surrounding fluid density on the resonant frequency of the QCM in an effort to isolate the effect of viscosity. The viscosity values obtained for CX fatty acid ethyl esters and CX ethanol with increasing pressure using the QCM were lower compared to literature data, indicating that the no-slip boundary condition between the QCM surface and the CX liquid was compromised. Thus, a QCM was found not to be suitable for measuring viscosity of CX liquids but could be used to determine the viscosities of gas-free liquids at ambient and elevated pressures.

1. Introduction

Determination of viscosities of gas-expanded liquids at elevated pressures is challenging and often requires expensive or custom made equipment. Different techniques have been utilized to determine the viscosities of various lipids (fatty acids, fatty acid esters, anhydrous milk fat, cocoa butter and soybean, sunflower, corn, fish and canola oils) and alcohols saturated with CO_2 and other gases, including high pressure capillary viscometer [1,2], visual observation of the rising or sinking velocity of small saturated gas bubbles or glass beads [3], high pressure quartz viscometer [4], falling ball/weight viscometer [5,6], rolling ball viscometer [7,8] and rotational rheometer [9,10].

The use of quartz crystals oscillating in thickness-shear mode, such as a quartz crystal microbalance (QCM), for measuring viscosities at elevated pressures has not been employed extensively. QCM was used to study the viscosity of a supercritical electrolyte solution [11], consisting of quaternary ammonium salts in supercritical difluoromethane (SC-CH_2F_2) at pressures of up to 30 MPa. Furthermore, the effects of various solutes, such as salicylic acid, naphthalene, and p-methylbenzoic acid on the viscosity of SC-CH_2F_2 were investigated using a QCM [12]. However, these studies [11,12] did not seem to take into account the influence of pressure on the resonant frequency of the QCM. Investigations [13–15] on the behavior of a QCM under high pressure CO_2 have shown that the resonance frequency of a QCM is affected by mass loading, the surrounding fluid properties (viscosity, density), adsorption at the surface, hydrostatic pressure, temperature, and surface roughness of the QCM. The basic QCM theory and some of its applications were reviewed previously [16]. More recent use of QCM focuses on solubility measurements and phase behavior determination [17–20].

The main objective of this study was to assess the potential of a QCM to determine the viscosity of CO_2-expanded (CX) liquids at elevated pressures. If successful, the use of a QCM housed in a small pressure vessel can be a relatively inexpensive approach for viscosity determination, targeting CX liquids. Fish oil fatty acid ethyl esters (FAEE) and ethanol saturated with CO_2 were used to test the performance of the QCM by determining their viscosity at different pressures and comparing the results to literature data obtained with other techniques.

2. Materials and methods

2.1. Materials

Refined fish oil extracted from anchovy and sardine was purchased from Ocean Nutrition (Halifax, NS, Canada) in the form of FAEE. The fatty acid profile as provided by the manufacturer stated a level of 40% and 20% for eicosapentaenoic acid (EPA, C20:5) and docosahexaenoic acid (DHA, C22:6), respectively. FAEE were used without further treatment and stored at 4 °C in aluminum bottles. Food grade anhydrous ethanol (Commercial Alcohol, Winnipeg,

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MB, Canada) and acetone (HPLC grade, Fisher Scientific Canada, Ottawa, ON, Canada) were used for cleaning and calibration purposes of the QCM. Certified standard calibration oils of various viscosities were used to calibrate the QCM (oils S3, S6, N10, Cannon Instrument Company, State College, PA).

Bone dry CO_2 with a purity of 99.9% from a standard cylinder equipped with a dip tube (Praxair Inc., Edmonton, AB, Canada) was used for viscosity measurements. Nitrogen with a purity of 99.998% (Praxair Inc., Edmonton, AB, Canada) was used to fill the headspace of the aluminum bottles containing the FAEE after each opening to minimize degradation.

2.2. Quartz crystal microbalance apparatus

The apparatus described in detail previously for density measurements [21] was modified to incorporate the QCM for viscosity measurements (Fig. 1). The QCM was placed in an additional high pressure cell (A) with an internal volume of about 2 mL placed between the view cell (D) and the circulation pump (E). The circulation pump (E) was a magnetically driven piston pump [22], which conveyed the liquid from the bottom of the view cell (D) through the QCM cell (A) to the top of the view cell, spraying it into the upper CO_2-rich phase facilitating equilibration. The custom made high pressure cell (A) holding the QCM (Fig. 2a) was connected to the system by means of polyether ether ketone (PEEK) tubing (OD 1/16 in) to electrically insulate the QCM to minimize interference and noise in the frequency signal. An integrated oscillator and frequency counter (B) were used to determine the resonant frequency of the QCM (Research Quartz Crystal Microbalance, RQCM, Maxtek, Santa Fe Springs, CA) hooked up to a computer (C) to record frequency shifts of the crystal. The RQCM allowed capacitance adjustments over a wide range so that the QCM could be operated in liquid environments.

The resonant frequency readings were taken after minimizing the resistance of the QCM by means of fine adjustment of the capacitance of the RQCM so that a stable frequency locked by the RQCM was achieved. The sensor crystal (Fig. 2b) was a 9 MHz AT-cut quartz crystal with polished wrap-around gold plated electrodes (ICM, Oklahoma City, OK). An AT-cut quartz crystal consists of a thin quartz plate cut from a quartz crystal at an angle of 35°15′ relative to the crystal main axis [16]. The quartz crystal and electrodes had a diameter of 14 and 6.5 mm, respectively, with quartz having a stiffness of 29.01×10^9 N/m^2 and a density of 2649 kg/m^3. To determine the frequency response of the QCM in pure anhydrous ethanol at elevated hydrostatic pressures, the system was completely filled with ethanol and pressurized using an HPLC pump (Beckman Model 110A, Fullerton, CA) connected to the bottom of the view cell (D).

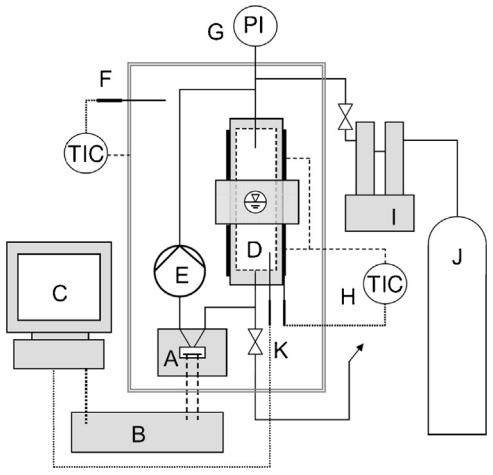

Fig. 1. Quartz crystal microbalance (QCM) setup: (A) QCM cell, (B) resonator/frequency counter (RQCM), (C) computer, (D) high pressure view cell, (E) circulation pump, (F) thermostated circulating airbath, (G) pressure indicator, (H) temperature controlled electric heaters, (I) syringe pump, (J) CO_2 cylinder, (K) thermistor.

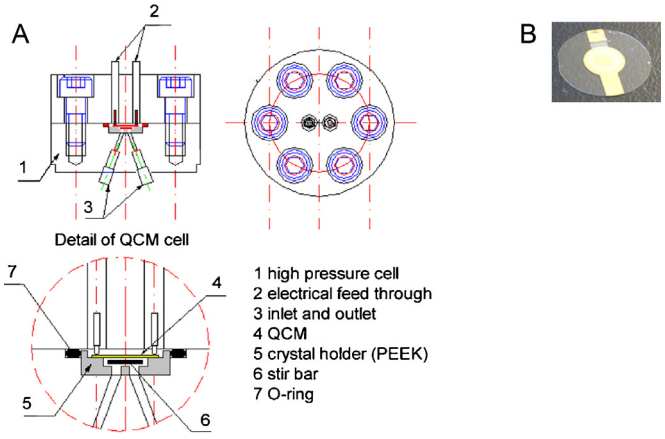

Fig. 2. (a) Details of the high pressure QCM cell. (b) QCM with wrapped around gold electrodes.

2.3. Determination of viscosity with the QCM

2.3.1. Theory and calibration of the QCM

The resonant frequency of an AT-cut quartz crystal submersed in a fluid depends on numerous factors, including the thickness of the crystal, mass loading on the crystal, pressure, temperature, surface roughness and the viscosity and density of the surrounding fluid [14,23,24]. By keeping the temperature constant, avoiding mass loading on the electrode surface and using a crystal with an optically polished surface, the factors affecting the resonant frequency are reduced down to pressure P, density ρ and viscosity η. Thus, the total frequency shift due to changes in pressure, density and viscosity are described by:

$$\Delta f = \Delta f_P + \Delta f_{\rho\eta} \quad (1)$$

The first term Δf_p describes the frequency shift due to hydrostatic pressure [25]:

$$\Delta f_p = f_0 \cdot \alpha \cdot (P - P_0) \quad (2)$$

where f_0 is the fundamental crystal frequency at a reference pressure P_0 and α is a temperature specific constant quantifying the effect of pressure on the resonant frequency [25]. The second term $\Delta f_{\rho\eta}$ in Eq. (1) represents the shift in crystal frequency due to a change in density and viscosity of the surrounding fluid compared to a reference fluid with ρ_0 and η_0. A simple relationship was proposed by Kanazawa and Gordon [24]:

$$\Delta f_{\rho\eta} = -c \cdot n \cdot f_0^{3/2} \cdot \left(\sqrt{\rho \cdot \eta} - \sqrt{\rho_0 \cdot \eta_0}\right) \quad (3)$$

In Eq. (3), c is a coefficient depending on the quartz crystal's shear modulus and density, and n is the number of crystal faces immersed in the liquid ($n = 2$ in this study). Therefore, the overall frequency shift of a QCM exposed to a pressurized liquid relative to that in a reference fluid at the same temperature can be calculated by combining and simplifying Eqs. (1)–(3) as follows:

$$\Delta f = C_1 \cdot \Delta P + C_2 \cdot \Delta\sqrt{\rho \cdot \eta} \quad (4)$$

where $\Delta P = (P - P_0)$ is the pressure increase relative to atmospheric pressure P_0 and $\Delta\sqrt{\rho \cdot \eta}$ relates to the change in the square root of the product density times viscosity relative to that of the reference fluid. In this study, the frequency shift $\Delta f = (f - f_0)$, corresponds to the increase in QCM frequency (f) caused by the effect of ΔP and