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Determination of composition of ethanol-CO_2 mixtures at high pressures using frequency response of microcantilevers

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ABSTRACT

The measurement of the composition of ethanol-CO_2 mixtures at high pressures is important in many applications involving supercritical fluids such as drying of alcogels or release of MEMs. Resonant frequency and quality factor (Q-factor) of microcantilevers immersed in ethanol-CO_2 mixtures were measured at a temperature of 308 K and pressure range from 8 MPa to 22 MPa. The measurements were carried out for different mixture compositions ranging from 0.91 to 6.16 wt% of ethanol in CO_2. At a given pressure and temperature, the resonant frequencies were found to decrease linearly with the increasing ethanol weight percent in the mixture. The sensitivity of the resonant frequency to changes in composition was found to increase with decreasing pressure. The experimental results show that ethanol-CO_2 mixture composition can be determined with good accuracy using mainly the measured resonant frequency of microcantilevers.

1. Introduction

There is a growing interest in development of microcantilever-based sensors for qualitative and quantitative detection of fluid mixtures [1–10]. The cantilever surface is usually coated with a chemically sensitive layer with a well-defined affinity to the target species of interest. Sorption of the target species into the sensitive layer results in alteration of the cantilever properties, which can be quantified by various techniques such as optical, piezoresistive, piezoelectric and capacitive [6,11]. In the static mode of operation, non-uniform surface stress caused by the sorption of the target molecule leads to deflection of the cantilever that can be related to the concentration of the molecule in the environment [6,12]. For example, palladium [13,14], palladium-nickel [15], and platinum-coated [5] cantilevers have been used to detect hydrogen in various gas mixtures and in pure state. In contrast, in the dynamic mode of operation, specific sorption of the species of interest into the sensitive coating modifies the mass of the microcantilever and, consequently, its resonant characteristics [6]. For example, the change in the resonant frequency can be related to the concentration of the target substance. Using this strategy, various volatile organic compounds (VOCs) could be detected by using microcantilevers coated with polymeric films [16–21].

There is an alternative approach for qualitative and quantitative characterization of pure fluids and binary fluid mixtures using frequency response of cantilevers without any surface preparation [22]. In this approach, detection is based on the hydrodynamic interaction between the cantilever and the surrounding fluid. Sader was able to relate the density and viscosity of the fluid to the resonant frequency, f_{fluid} and Q-factor, Q of microcantilevers immersed in the fluid using a model based on the solution of the equation of motion of a clamped elastic beam subject to hydrodynamic forces of the surrounding fluid [23]. Modified further through an analytical approximation of the complex hydrodynamic function of the cantilever describing the inertial and dissipative effects of the fluid, Sader's model can be summarized as follows [24]:

$$f_{fluid} = f_{vac}\left[1 + \frac{\pi\rho w}{4\rho_c t}\left(1.0553 + 3.7997\sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} w^2}}\right)\right]^{-1/2} \quad (1)$$

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$$Q = \frac{\frac{4\rho_c t}{\pi\rho w} + (1.0553 + 3.7997\sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} w^2}})}{3.8018\sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} w^2}} + 2.7364\frac{2\mu}{\rho 2\pi f_{fluid} w^2}} \quad (2)$$

where f_{vac} is the resonant frequency of the cantilever in vacuum, w is the cantilever width, ρ_c is the cantilever density, t is the cantilever thickness, ρ is the fluid density, and μ is the fluid viscosity. Since the density and viscosity depend on the fluid composition, changes in the resonant frequency or Q-factor can in principle be related to the changes in the composition of the fluid. Tetin et al. [22] investigated the frequency response of microcantilevers exposed to binary gas mixtures of helium (He)-nitrogen (N_2) and carbon dioxide (CO_2)-nitrogen and derived an expression that related the resonant frequency shift to the density and viscosity of the fluid and the cantilever architecture. Xu et al. [25] determined the composition of a CO_2-air mixture by relating the shift in the resonant frequency to the molar mass of the unknown gas at a specific temperature and pressure. However, the resonant frequency was found not to be too sensitive to the changes in the mixture composition; therefore, the authors suggested using shorter cantilevers to obtain higher sensitivity. Loui et al. [26] proposed a scheme for detecting pure gases and binary mixtures using dual-modality piezoresistive cantilever sensors which characterize the fluid in terms of both heat dissipation and viscous resonant damping in the fluid. Using heat conductivity and cantilever resonant frequency, they showed theoretically that the combination of the thermal and resonant response data allows more precise analysis that cannot be carried out with each detection mode used separately. Boudjiet et al. [27] determined the concentration of H_2 in N_2 by monitoring the variations in the resonant frequency and quality factor of uncoated cantilevers with concentration. They achieved high sensitivity and were able to detect 0.025% of H_2 in N_2. Lakhmi et al. [28] detected ethanol and water vapors using uncoated thick film PZT cantilevers. All of the above mentioned studies with microcantilevers were carried out at low pressures. Studies at high fluid pressures are rather limited, even though it is an important operating regime, as many industrial processes are carried out at high pressures. In our previous work, we measured the frequency response of uncoated cantilevers immersed in pure CO_2 at pressures up to 27 MPa and observed a very good agreement between the experimental data and Sader's model [29,30]. Using uncoated cantilevers, we were also able to measure simultaneously the density and viscosity of N_2 at pressures up to 24 MPa using argon (Ar) as a reference fluid [31]. These studies showed the potential of the technique for accurate fluid characterization under a wide range of operating conditions. In many high-pressure industrial processes involving various fluids, compositions of fluid mixtures must be determined with high accuracy and sufficiently fast response time compatible with the process workflow. Development of microcantilever-based systems for measuring the composition of fluid mixtures at high pressures is thus of high practical importance. In particular, high-pressure mixtures of ethanol and CO_2 are encountered in many technological processes including supercritical drying of aerogels and fabrication of Micro Electro Mechanical Systems (MEMS). Accurate monitoring of the mixture composition in such processes can help significantly in optimizing the process time and reducing the overall cost [32–35].

In this study, we investigated how the microcantilever frequency response changes with the composition of ethanol-CO_2 mixtures at high pressures. To this end, we used uncoated rather than polymer-coated microcantilevers since the polymer-coated cantilevers might swell at high pressures due to the sorption of supercritical CO_2 into the polymer layer [36]. This in turn might result in changes of the physical and mechanical properties of the cantilever and, thus, lead to systematic errors in the measurements. Moreover, long-term stability and reliability of such coatings are limited [12]. We measured the frequency response of microcantilevers at a fixed temperature of 308 K and a pressure range of 8 MPa to 22 MPa for different mixture compositions ranging from 0.91 to 6.16 wt% of ethanol in CO_2. At a given pressure and temperature, the resonant frequencies and Q-factors were found to decrease monotonically with the increasing ethanol concentration in the mixture. The presented results show that the composition of high-pressure ethanol-CO_2 mixtures can be determined with a good accuracy from the measured frequency response of an uncoated cantilever.

2. Materials and methods

2.1. Materials

CO_2 used in the experiments was supplied by Aligaz Messer and had a purity of 99.9%. Ethanol was supplied by Sigma-Aldrich and had a purity of 99.8%. Both ethanol and CO_2 were used as received.

2.2. Experimental procedure

Chips with ferromagnetic cantilevers of different lengths made out of nickel were used for the measurements. The nominal lengths of the cantilevers used in the measurements were 150 μm and 200 μm. The nominal width of 200 μm long cantilevers was 20 μm and the nominal width of 150 μm long cantilevers was 15 μm. The thickness of both cantilevers was approximately 1 μm. The design and fabrication process of these ferromagnetic microcantilevers were explained in detail in our previous study for 200 μm long cantilevers [29]. The same procedure was followed for 150 μm long cantilevers which had improved sensitivity.

The experimental setup consisted of a high-pressure fluid cell coupled to a laser, quadrant photodiode, CCD camera, lenses and other electronic equipment. A die with microcantilevers was mounted in a Teflon housing with an electromagnetic actuator – a coil made from copper wire – and placed in a 50-mL cylindrical high-pressure vessel (TharSFC 05424-4) as described in our previous studies [29,31]. The high pressure vessel had two sapphire windows on each side. These windows enabled the monitoring of microcantilevers during the experiment and the measurement of their frequency response using laser beam deflection. The electrical connection to the coil in the pressure vessel was sealed using insulated CONAX Technologies TG24T gland assemblies. Temperature of the studied fluid in the vessel was controlled by circulating water through a plastic tube wrapped around the vessel using a heating circulator (Polyscience). The temperature and the pressure in the vessel were continuously monitored using a T-type thermocouple (TC) (Omega dp462) (accuracy ± 1 K) and a pressure transducer (PT) (Omega PX409-5.0KAUSBH) (accuracy ± 0.03 MPa), respectively. The schematic of the system for the sample chamber pressurization is given in Fig. 1.

In order to drive the ferromagnetic cantilevers during the experiment, the cantilevers were actuated with varying magnetic field

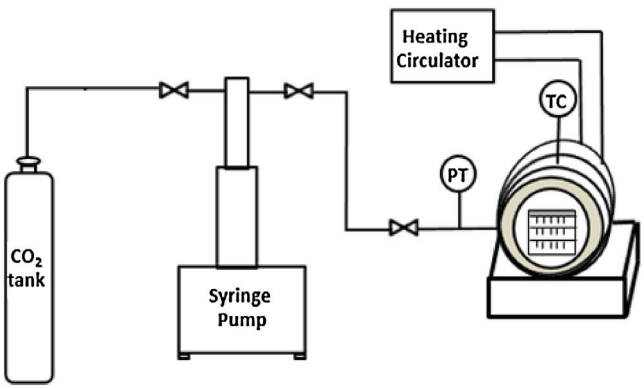

Fig. 1. Schematic of the system for the sample chamber pressurization.

produced by the coil driven by a sinusoidal voltage that was generated by a function generator (Agilent 33220A), and subsequently amplified by a factor of 50 using a high-voltage amplifier (Falco Systems WMA-300). The frequency and amplitude of the driving sinusoidal signal were computer-controlled using Instrument Control Toolbox in Matlab. The deflections of the vibrating cantilevers were detected by an AFM-like scheme. A near-infrared laser beam (wavelength 780 nm, maximal power 4.5 mW; CPS 192, Thorlabs) was transformed with a 1:1 telescope consisting of two identical lenses (f = 30 mm) and then focused on the cantilever surface with an objective. The 1:1 transformation telescope enabled changing the axial position of the laser beam focus with respect to the cantilever surface; thus, it was possible to optimize the cantilever deflection signal for studied fluids of different refractive index. The beam reflected from the oscillating cantilever was collected by the same objective and then focused on quadrant photodiode (QPD). QPD is sensitive to the beam position within its surface and, thus, it records the changes of the propagation direction of the reflected beam due to cantilever deflection. The deflection signal was sent to a lock-in-amplifier (SR530, Stanford Research Systems) together with the reference signal from the function generator in order to improve the signal-to-noise ratio. The amplitude of the deflection signal and its phase shift with respect to the driving signal produced by the lock-in amplifier were digitized with a data acquisition card (USB-6008, National Instruments) controlled using Matlab programming environment.

Ethanol-CO_2 mixtures were prepared by successive transfer of ethanol and CO_2 to the high pressure vessel. The amount of each fluid transferred to the vessel was determined gravimetrically. First, the mass of the empty vessel was measured using a balance with an accuracy of ± 0.1 g. Then, a certain amount of liquid ethanol was placed into the vessel using a micropipette. The average standard deviation in the amount of ethanol placed in the vessel was 0.008 g determined from repetitive measurements with a different balance that had an accuracy of ± 0.001 g. Subsequently, CO_2 was transferred to the vessel using a TELEDYNE ISCO D Series syringe pump (see Fig. 1) and the total resultant mass of the chamber was measured and recorded. The mass of the empty vessel and ethanol was subtracted from the total mass of the chamber to determine the amount of CO_2 placed into the vessel. Experimentally measured fluid masses and calculated mixture compositions, together with their respective uncertainties, are given in Table 1.

At the beginning of each set of measurements, the vessel was filled with the desired amount of ethanol and then charged with CO_2 to a pressure ranging between 23 and 24 MPa. The temperature of the vessel was brought to the desired value using the heating circulator. Frequency response measurements were performed when the pressure and temperature became stable; typically 3–5 h after starting the heating circulator. The cantilever frequency response measurements were performed starting from the highest pressure and then gradually decreasing the pressure for successive measurements in the set. The temperature was kept constant throughout the measurement set, and after each pressure change, we waited for approximately 5 min for the conditions in the sample vessel to stabilize. At each pressure, driving frequency of the function generator was adjusted over a range of approximately 10 kHz for 200 μm long cantilever and approximately 16 kHz for 150 μm long cantilever centered around the resonant frequency. Cantilever response was then recorded for 400 frequency values distributed evenly over this range. The amplitude of the driving sinusoidal signal before being amplified 50 times was set to 2 V peak to peak. Subsequently, the dissipation-free cantilever resonant frequency, f_{fluid} and the Q-factor, Q, were determined by fitting the measured frequency response $A(\omega)$ to the equation describing the oscillating elastic cantilever beam as a simple damped harmonic oscillator [23] as given in Eq. (3):

$$A(\omega) = \frac{A_0 4\pi^2 {f_{fluid}}^2}{\sqrt{(\omega^2 - 4\pi^2 {f_{fluid}}^2)^2 + \frac{\omega^2 4\pi^2 {f_{fluid}}^2}{Q^2}}} \quad (3)$$

where A_0 is the zero-frequency amplitude of the response and $\omega = 2\pi f$ is the angular driving frequency. At each pressure, three frequency response measurements were carried out and then the averages of the three resonant frequencies and Q-factors were taken. For the measurements with 150 μm long cantilever, the average relative standard deviations of the resonant frequency and Q-factor over the whole studied pressure range were 0.03% and 1.09%, respectively, while the maximum relative standard deviations were 0.11% and 3.87, respectively. For 200 μm long cantilever, the average relative standard deviations of the resonant frequency and Q-factor were 0.26% and 2.74% and the maximum relative standard deviation were 0.50% and 7.82%, respectively.

3. Results and discussions

The primary target of the current study is developing a technique for measuring the concentration of ethanol in a mixture of ethanol and CO_2 at the exit port of a supercritical extractor. Recently, Özbakır *et al.* [33] investigated theoretically and experimentally the extraction of ethanol from cylindrical silica alcogel monoliths and reported the ethanol concentration at the exit of the extractor as a function of time. Ethanol concentration data obtained in [33] have been converted from (kmol ethanol)/(m^3 CO_2) into the weight percent of ethanol in the mixture w_{eth} and the result of this conversion is shown in Fig. 2. The maximum ethanol weight percent in the mixture was measured to be 17% and it decreased as a function of time. In order to assess the potential of microcantilever-based sensors for the determination of mixture composition, we prepared different ethanol-CO_2 mixtures with concentrations lying within the relevant range w_{eth} = 0.91–6.16 and measured the frequency response of microcantilevers immersed in these mixtures at a temperature of 308 K and pressure range from 8 MPa to 22 MPa.

The measured resonant frequencies and Q-factors for ethanol-CO_2 mixtures of different compositions, including error bars, are given in Figs. 3 and 4 for the 200 μm long cantilever and Figs. 5 and 6 for the 150 μm long cantilever. Due to the lower mass and higher effective stiffness of the shorter 150 μm cantilever, its resonant frequencies and Q-factors are significantly higher than those of the 200 μm cantilever across the whole studied pressure range. At a constant temperature and mixture composition, the resonant frequency decreased monotonically with increasing pressure since increase in the fluid pressure resulted in an increase in the fluid density and, subsequently, an increase in the fluid mass moving along with the cantilever. The effective volume of the fluid that is affected by cantilever oscillations increases with fluid viscosity. Thus, the increase of viscosity with increasing pressure contributes further to the decrease of the cantilever resonant frequency.

Table 1
Measured values of fluid mass and calculated mixture compositions together with uncertainties in mass measurements and mixture compositions.

Empty cell mass (g)	2186.8 ± 0.1	2186.8 ± 0.1	2185.6 ± 0.1[a]	2185.6 ± 0.1[a]	2185.6 ± 0.1[a]
Ethanol mass (g)	0.545 ± 0.008	0.901 ± 0.008	0.356 ± 0.008	0.930 ± 0.008	2.417 ± 0.008
CO_2 mass (g)	36.1 ± 0.1	35.6 ± 0.1	38.8 ± 0.1	38.3 ± 0.1	36.8 ± 0.1
Total mass (g)	2223.4 ± 0.1	2223.3 ± 0.1	2224.8 ± 0.1	2224.9 ± 0.1	2224.9 ± 0.1
Ethanol weight percent	1.49 ± 0.02	2.47 ± 0.02	0.91 ± 0.02	2.37 ± 0.02	6.16 ± 0.02

[a] Empty cell mass changed due to removing of electric wire attached to the cell.

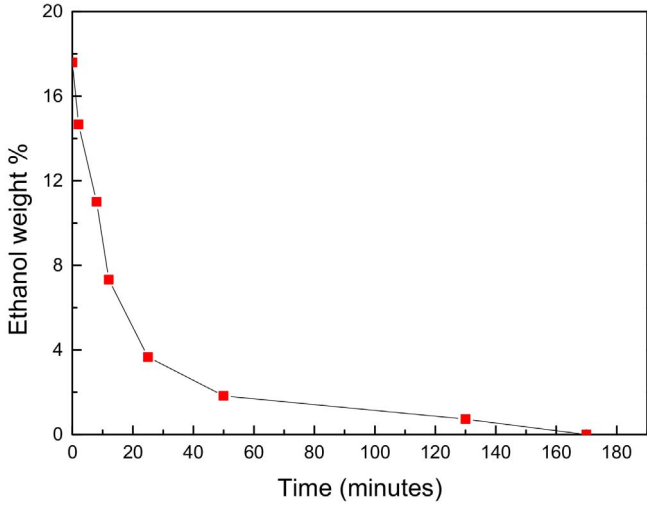

Fig. 2. Variation of ethanol weight percent w_{eth} in the exit stream of a supercritical extractor as a function of time at 10 MPa and 313 K.

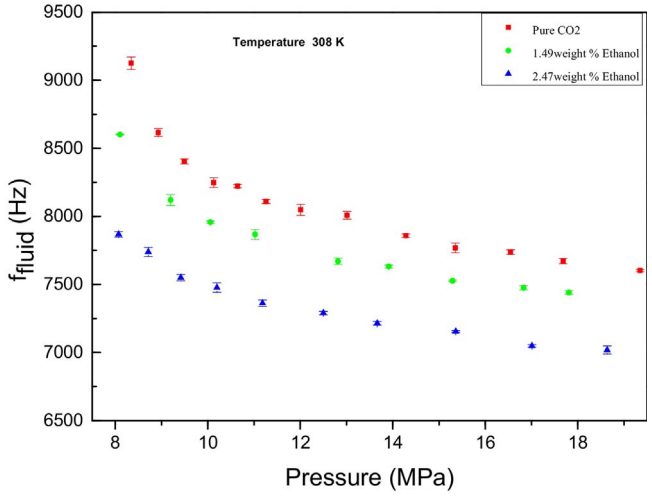

Fig. 3. Variation of resonant frequency, f_{fluid}, with pressure for different compositions of ethanol-CO_2 binary mixture at 308 K (Microcantilever length: 200 μm).

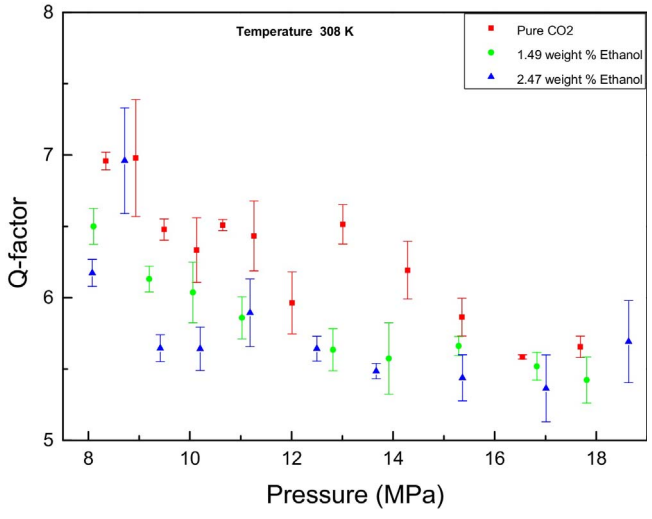

Fig. 4. Variation of Q-factor with pressure for different compositions of ethanol-CO_2 binary mixture at 308 K (Microcantilever length: 200 μm).

Increase in viscosity also causes an increase in viscous damping and energy dissipation which translates into a decrease in the Q-factor value as pressure increases.

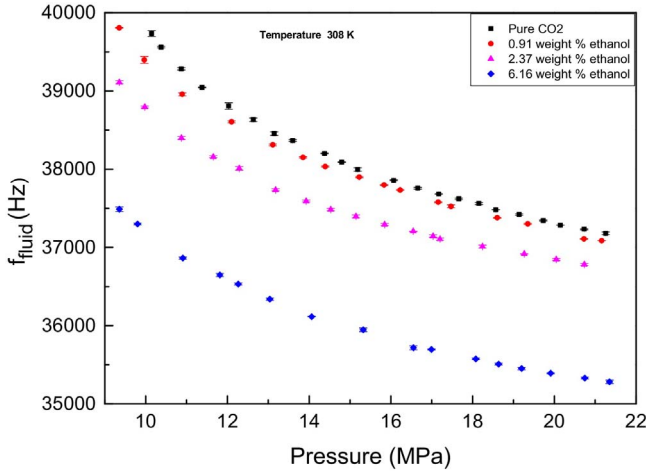

Fig. 5. Variation of resonant frequency, f_{fluid}, with pressure for different compositions of ethanol-CO_2 binary mixture at 308 K (Microcantilever length: 150 μm).

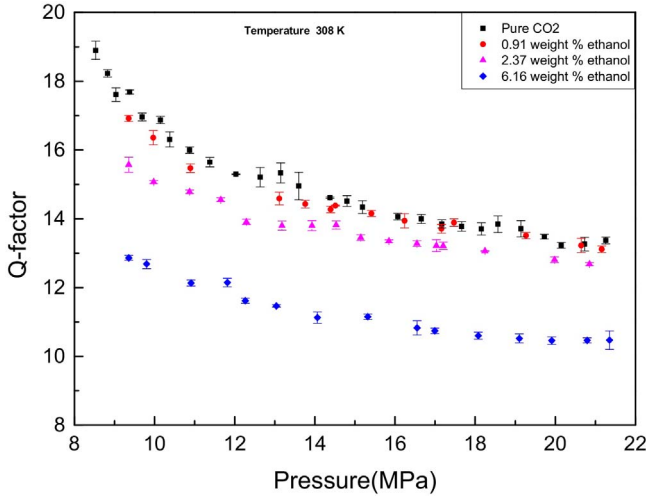

Fig. 6. Variation of Q-factor with pressure for different compositions of ethanol-CO_2 binary mixture at 308 K (Microcantilever length: 150 μm).

A close analysis of Figs. 3–6 shows that both resonant frequency and Q-factor vary with the composition of the mixture at a fixed temperature and pressure. Consequently, the frequency response measurements can be used to determine the composition of the mixture. However, the variation of the Q-factor with composition is not as pronounced and smooth as the corresponding variation of the resonant frequency with composition, especially for the 200 μm cantilever. Thus, resonant frequency is a more reliable indicator of the mixture composition. Figs. 7 and 8 show the change in the resonant frequencies of both cantilevers as a function of ethanol weight percent at different pressures and 308 K. For both cantilevers, the measured resonant frequency f_{fluid} decreases monotonically with increasing ethanol fraction in the mixture. Therefore, f_{fluid}can serve as a unique marker of the actual composition of the ethanol-CO_2 mixture. For determining the fluid composition at a particular temperature and pressure, a calibration curve has to be constructed by measuring the resonant frequencies of mixtures of known composition at that particular temperature and pressure. After obtaining a calibration curve within the desired composition range, such as the ones given in Figs. 7 and 8, then this calibration curve can be used to convert the resonant frequency measured in an ethanol-CO_2 mixture with unknown composition to the actual composition of the mixture. In our present study, we investigated the frequency response of cantilevers immersed in ethanol-CO_2 mixtures within the composition range w_{eth} = 0.91–6.16. As

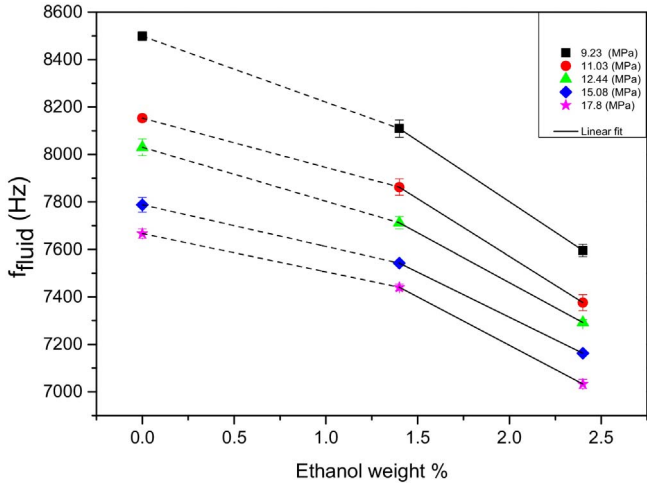

Fig. 7. Variation of resonant frequency, f_{fluid}, with ethanol weight percent, w_{eth}, at a constant temperature of 308 K and different pressures (Microcantilever length: 200 μm).

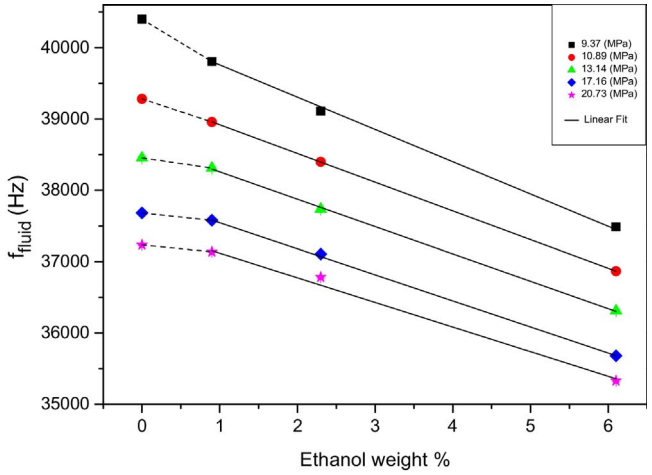

Fig. 8. Variation of resonant frequency, f_{fluid}, with ethanol weight percent, w_{eth}, at a constant temperature of 308 K and different pressures (Microcantilever length: 150 μm).

shown in Fig. 8, the change in the resonant frequency of the 150 μm long cantilever with the mixture composition at a fixed pressure displays an approximately linear trend within this composition range. From Fig. 8, it is also evident that the slopes of the lines decrease with increasing pressure for the studied mixture compositions indicating that the sensitivity of the technique decreases with increasing pressures. However, this decrease is not very pronounced. The data presented in Fig. 8 show that the difference between the values of f_{fluid} measured for pure CO_2 and ethanol- CO_2 mixture with $w_{eth} = 0.91$ is well above the standard deviation of the resonant frequency measurements across the whole studied pressure range. Thus, it should be possible to detect mixture compositions with w_{eth} lower than 0.91.

Density and viscosity of fluid mixtures depend on the mixture composition, temperature and pressure. Density at a particular temperature and pressure can be calculated using a cubic equation of state and viscosity at a particular temperature and pressure can be calculated using one of various correlations in the literature. As illustrated by Eq. (1), the cantilever resonant frequency is then related to these fluid properties in a highly nonlinear fashion. Thus, the relationship between the resonant frequency and the composition of the mixture is generally quite complex. However, it is quite interesting that the relationship between resonant frequency and composition is a linear one.

As shown in Figs. 7 and 8, the slopes of the lines relating f_{fluid} to w_{eth} for the short cantilever length (150 μm) are higher than those of the 200 μm cantilever. Thus, the detection sensitivity of the short-length cantilevers is higher. As expected, this observation indicates that the cantilever length also surfaces a factor that affects sensitivity of the composition measurement at the given temperature, pressure and mixture composition.

Alternatively, the effluent from the extractor can be analyzed using chromatography using high pressure sampling valves. Direct injection into a gas chromatograph can be problematic due to the high pressure difference between the carrier gas and the ethanol – CO_2 mixture. However, injection into a liquid chromatograph or supercritical fluid chromatograph should be possible. The accuracy of these measurements depends on the type of detector used in the chromatographic system. Generally, the accuracy of such measurements is around a few percent. High pressure spectroscopic techniques have also been used to measure compositions of mixtures of a wide variety of organic compounds with CO_2. The accuracy of these techniques depends generally on the nature of the mixture and experimental conditions. In an excellent recent study, Raman spectroscopy technique was used to determine the concentration of ethanol in CO_2 inside a gel during supercritical drying at 318.15 and 9 MPa [37] and the detection limit in mole fraction of ethanol was given as $X_{ETOH} = 0.03$. It seems that the detection limit of the proposed technique is better since the minimum mole fraction that was detected in this study was $X_{ETOH} = 0.009$ using resonant frequency of 150 μm long cantilever.

4. Conclusion

The frequency responses of cantilevers immersed in ethanol-CO_2 mixtures were investigated at a temperature of 308 K and pressure range between 8 MPa to 22 MPa. For the 150 μm long cantilever, the resonant frequency values were found to decrease linearly with increasing ethanol weight percent in composition range of $w_{eth} = 0.91 - 6.16$ at a fixed temperature and pressure. The Q-factors were also found to decrease with increasing ethanol weight percent but the scatter was high. Therefore, resonant frequency can serve as a better indicator of the actual composition of the ethanol-CO_2 mixture than the Q-factor. For determining the fluid composition at a particular temperature and pressure, a calibration curve has to be constructed by measuring the resonant frequencies of mixtures of known composition at that particular temperature and pressure. After obtaining a calibration curve within the desired composition range, then this calibration curve can be used to convert the resonant frequency measured in an ethanol-CO_2 mixture with unknown composition to the actual composition of the mixture. The lowest studied concentration of ethanol in the mixture was 0.91 wt %; however, the expected concentration detection limit is lower than this minimal value. Our study represents the first systematic attempt to use microcantilevers for the determination of the fluid mixture compositions at high pressures. We used ethanol-CO_2 binary mixtures as the model fluid but compositions of other mixtures of solvents with CO_2 can also be measured. This approach for determining mixture compositions can potentially be used in the supercritical drying process for aerogel production to measure ethanol concentration at the exit of the extractor as a function of time and enable online monitoring of the drying process.

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