

Microcantilever Based Sensor for Characterization of Ethanol-CO₂ Fluid Mixtures at High Pressures

by

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Koç University

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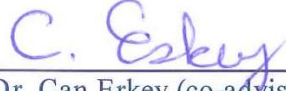
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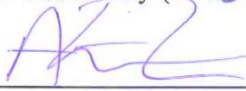
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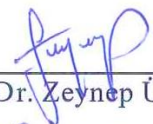
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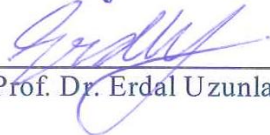

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Dedicated to my father Ali Bahar, my mother Hoor, my wife Faiza Baloch and to my
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ABSTRACT

Determination of composition of ethanol-CO₂ mixtures at high pressures is important in many applications involving supercritical fluids such as drying of alcogels or release of microelectromechanical device. Viscosity of ethanol-CO₂ mixture is also important in many applications and processes, for example, to understand the dynamics of supercritical antisolvent (SAS) and supercritical anti solvent precipitation inside the pores (SASIP) processes, to design and optimize supercritical fluid based processes, to calculate Reynolds and Schmidt numbers, and to estimate diffusion coefficients of ethanol-CO₂ mixtures from available correlations. Frequency response of an oscillating microcantilever immersed in a fluid mixture can be used to determine the composition and viscosity of the mixture over a wide range of temperatures and pressures. The resonant frequency and quality factor (Q-factor) of ferromagnetic nickel microcantilevers immersed in ethanol-CO₂ mixtures were measured in a temperature range of 308 – 333 K and pressure range of 7 – 33 MPa. The measurements were carried out with a custom built experimental setup consisting of a high-pressure vessel with temperature and pressure control, a coil for magnetic actuation of the immersed cantilevers, and a quadrant photodetector for optical readout of the cantilever displacement. In this dissertation, four types of studies were performed with the frequency response measurements of cantilevers: (i) Mixture composition determination of ethanol-CO₂ mixtures, (ii) Compositional measurement sensitivity of cantilevers, (iii) Viscosity measurement of mixtures, and (iv) Viscosity measurement sensitivity of cantilevers.

The frequency response of cantilevers immersed in ethanol-CO₂ mixtures containing 0.0091 – 0.0616 weight fraction of ethanol were measured at 308 K and within the pressure range 8 – 22 MPa. The resonant frequencies and Q-factors were found to decrease in a smooth manner with the increasing weight fraction of ethanol in the mixture. At a constant temperature, the sensitivity of resonant frequency to changes in fluid composition was found to increase with decreasing pressure. The experimental results showed that ethanol-CO₂ mixture composition can be determined with good accuracy at high pressures using mainly the measured resonant frequency of microcantilevers. The considerable changes in

the resonant frequency as a function of different compositions suggested that this approach 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 the determination of the end of the drying process.

Compositional measurement sensitivity of cantilevers defined as the derivative of the cantilever resonant frequency or quality factor with respect to the fluid mixture composition was studied. On the basis of Sader's model of hydrodynamic interaction of an oscillating immersed cantilever with the surrounding fluid, analytical expressions were derived for the sensitivity that were found to be complex functions of the density and viscosity of the mixture as well as the length, width, thickness, and density of the cantilever. Frequency response of cantilevers immersed in ethanol-CO₂ mixtures containing 0 – 0.04 weight fraction of ethanol were measured at 318 K and within the pressure range 10 – 21 MPa. Using the measured resonant frequency and quality factor together with previously published density and viscosity data for ethanol-CO₂ mixtures of various compositions, the sensitivity at each pressure and temperature was calculated and the LOD was determined. In particular, with our current setup, the LOD ranged from 0.0009 to 0.0071 weight fraction of ethanol in the mixture in the pressure range 10 – 21 MPa for a 150 μm long cantilever. The results convincingly illustrated the potential of miniature cantilever-based probes for fast and sensitive *in-situ* detection of the composition of fluid mixtures in practical technological processes carried out at high pressures.

In addition, new experimental data for the viscosity of ethanol-CO₂ mixtures of different compositions with ethanol weight fraction ranging from 0.290 to 0.882 were obtained. The experiments were carried out in the single phase region at a temperature range of 308 to 333 K and a pressure range of 7 to 33 MPa. Viscosity of ethanol-CO₂ mixtures were measured using frequency response of an oscillating microcantilever immersed in the mixture. The viscosity of the mixture increased with increasing ethanol weight fraction at a particular temperature and pressure. At a particular ethanol weight fraction, the viscosity decreased with increasing temperature at a constant density. Refutas equation could predict the viscosities of mixtures successfully that had an ethanol weight fraction greater than 0.29.

Lastly, viscosity measurement sensitivity of cantilevers defined as the derivative of the cantilever quality factor with respect to the viscosity of fluid mixture was studied. Analytical expression for the sensitivity was derived based on Sader's model. Using the frequency response data of cantilevers immersed in ethanol-CO₂ mixtures containing 0.290 – 0.882 weight fraction of ethanol at a temperature range of 308 – 333 K, together with density and viscosity data of mixtures of various compositions, the model sensitivity was determined at each mixture composition. The model sensitivity was compared with the experiment sensitivity and the relative differences were calculated. The resolution of the cantilever-based viscosity measurements was determined using the experimental sensitivity and the average standard deviations of the Q-factor at a particular mixture composition. The results indicate that with the current setup, the resolution ranged from 2.69 to 12.46 $\mu\text{Pa.s}$. The results show that cantilever-based sensors can be used as viscometers for the viscosity measurement of fluid mixtures in practical technological processes carried out at high pressures.

Keywords: Microcantilever; Frequency response; Resonant frequency; Quality factor, Mixture composition, Ethanol-CO₂; High pressure; Sensitivity; Limit of detection; Viscosity;

ÖZET

Yüksek basınçta etanol-CO₂ karışımlarının kompozisyonlarının belirlenmesi, alkojellerin kurutulması ya da mikro elektromekanik cihazların salınımı gibi süperkritik akışkanlar ile ilgili birçok uygulama için önem taşımaktadır. Etanol-CO₂ karışımının viskozitesi de süperkritik anti-çözücü (SAS) ve gözenek içinde süperkritik anti-çözücü çökmesi (SASIP) işlemlerinin dinamiklerini anlamak, süperkritik akışkanlar tabanlı süreçlerin tasarımı ve optimizasyonu, Reynolds ve Schmidt sayılarının hesaplanması ve etanol-CO₂ karışımlarının difüzyon katsayılarının mevcut korelasyonlarla tahmin edilmesi gibi birçok uygulama ve süreç için önem taşımaktadır. Akışkan karışımı içeresine daldırılmış salınımlı mikro mekanik çubukların frekans tepkisi, karışımın kompozisyonunun ve viskozitesinin geniş bir sıcaklık ve basınç aralığında belirlenmesinde kullanılabilir. Bu çalışmada etanol-CO₂ karışımlarının içine daldırılmış ferromanyetik nikel mikro-mekanik çubukların rezonans frekansını ve kalite faktörlerini (Q-factor) 308-333 K sıcaklık ve 7-33 MPa basınç aralığında ölçülmüştür. Ölçümler sıcaklık ve basınç kontrollü yüksek basınç kabı, daldırılmış mikro-mekanik çubukların manyetik aktüasyonu için gereken bir bibon, mikro-mekanik çubukların değişimini optik olarak okumak için kuadrant fotodetektörü içeren isteğe göre yapılmış deney düzeneğinde gerçekleştirilmiştir. Bu tezde mikro-mekanik çubukların frekans tepkisi ölçümlerinin kullanarak dört farklı çalışma yapılmıştır: (i) etanol-CO₂ karışımlarının kompozisyonlarının belirlenmesi, (ii) mikro-mekanik çubukların kompozisyon ölçümleri için hassasiyeti (iii) karışımların viskozite ölçümleri ve (iv) mikro-mekanik çubukların viskozite ölçüm hassasiyetleri.

Etanolün kütlece oranı 0.0091-0.0616 olan etanol-CO₂ karışımlarına daldırılmış mikro-mekanik çubukların frekans tepkimesi 308 K'de ve 8-22 MPa basınç aralığında ölçülmüştür. Rezonans frekansının ve Q faktörün, karışımdaki etanolün kütle oranı artışıyla düzgün bir şekilde azaldığı bulunmuştur. Sabit sıcaklıkta rezonans frekansının akışkan kompozisyonuna olan hassasiyetinin azalan basınçla birlikte arttığı bulunmuştur. DeneySEL sonuçlar, etanol-CO₂ karışımının kompozisyonun yüksek basınçlarda, temel olarak mikro-mekanik çubukların rezonans tepkisi ölçümü yöntemiyle iyi bir doğruluk payıyla belirlenebileceğini göstermiştir. Rezonans frekansında farklı kompozisyonların fonksiyonu olarak kayda değer değişimlerin olması, bu yöntemin aerogel üretimi için

süperkritik kurutma işleminde ekstraktör çıkışındaki etanol konsantrasyonunun zamana bağlı olarak ölçülmesinde ve kurutma işleminin sonlandığı noktayı belirlemede potansiyel olarak kullanılabileceğini önermektedir.

Sader'in salınlı daldırılmış mikro-mekanik çubuğun etrafındaki akışkan ile hidrodinamik etkileşiminin modelini baz alarak hassasiyet için, hem karışımın öz kütlesinin ve viskozitesinin hem de mikro-mekanik çubuğun boyunun, genişliğinin, kalınlığının ve öz kütlesinin kompleks fonksiyonu olarak analitik denklemler elde ettik. 318 K'de ve 10-21 MPa basınç aralığında, kütlece 0-0.04 oranında etanol içeren etanol-CO₂ karışımlarının içinde daldırılmış mikro-mekanik çubukların frekans tepkisi ölçülmüştür. Çeşitli kompozisyonlardaki etanol-CO₂ karışımı için daha önce yayımlanan öz kütle ve viskozite verileriyle birlikte ölçülen rezonans tepkisi ve kalite faktörlerini kullanarak her sıcaklık ve basınçta hassasiyet ölçülmüştür ve algılama limiti belirlenmiştir. Özellikle, şu anki sistemimizde algılama limiti, 10-21 MPa basınç aralığında 150 µm uzunluğundaki bir mikro-mekanik çubuk için karışımdaki etanolün kütlece oranı olarak 0.0009 ile 0.0071 değerleri arasında değişmiştir. Sonuçlar ikna edici bir şekilde minyatür mikro-mekanik çubuk bazlı problemlerin, yüksek basınçta gerçekleşen teknolojik proseslerde akışkan karışımlarının kompozisyonların yerinde, hızlı ve hassas olarak belirlenmesindeki potansiyelini göstermektedir.

Ek olarak, etanolün kütlece oranı 0.290 ile 0.882 arası değişen değişik kompozisyonlardaki etanol-CO₂ karışımlarının viskozitesi için yeni deneysel verileri sunulmuştur. Deneyler 308 ile 333 K sıcaklık ve 7 ile 33 MPa basınç değerleri arasında, tek faz bölgesinde gerçekleştirilmiştir. Etanol-CO₂ karışımlarının viskozitesi karışıma daldırılmış salınlı mikro-mekanik çubukların frekans tepkileri kullanılarak ölçülmüştür. Belirli bir sıcaklık ve basınçta, etanolün kütlece oranı arttıkça karışımın viskozitesi artmıştır. Belirli bir etanolün kütlece oranında, viskozite sabit öz kütlede artan sıcaklıkla birlikte azalmıştır. Refutas denklemi etanolün kütlece oranı 0.29'dan büyük karışımların viskozitelerini başarılı bir şekilde tahmin edebilmektedir.

Son olarak, mikro-mekanik çubuğun kalite faktörünün karışımın viskozitesine göre türevi olarak tanımlanan, viskozite ölçüm hassasiyeti üzerine çalışmalar yapılmıştır. Hassasiyet için, Sader'in modelini temel alan analitik bir denklem elde edilmiştir. Çeşitli

kompozisyonlardaki karışımların öz kütle ve viskozite verileriyle birlikte, 308 – 333 K sıcaklık aralığında kütlece 0.290 ile 0.882 oranında etanol içeren etanol-CO₂ karışımlarına daldırılmış mikro-mekanik çubukların frekans tepkisi verilerini kullanarak, her bir karışım kompozisyonundaki model hassasiyeti hesaplanmıştır. Model hassasiyeti deneysel hassasiyetle karşılaştırılmıştır ve göreceli farklar hesaplanmıştır. Viskozite ölçümlerinin algılama limiti deneysel hassasiyet ve belirli bir karışım kompozisyonunda Q-faktörlerin ortalama standart sapmaları kullanılarak belirlenmiştir. Sonuçlar, şu anki sistemde algılama limiti 2.69 ile 12.46 $\mu\text{Pa.s}$. aralığında değiştiğini göstermektedir. Sonuçlarımız mikro-mekanik çubuk bazlı sensörlerin, yüksek basınçta gerçekleşen teknolojik proseslerde akışkan karışımlarının viskozitelerinin ölçümü için viskometre olarak kullanılabileceğini göstermektedir.

Anahtar kelimeler: Mikro konsol; Frekans tepkisi; Rezonans frekansı; Kalite faktörü, Karışım kompozisyonu, Etanol-CO₂; Yüksek basınç; Hassasiyet; Algılama sınırı; Viskozite;

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NOMENCLATURE

f_{fluid}	Resonant frequency
Q	Quality factor
w	Ethanol weight fraction
f_{vac}	Resonant frequency in vacuum
ρ	Density
HEC	Higher Education Commission
μ	Viscosity
S_f	Derivative of f_{fluid} with respect to w
S_Q	Derivative of Q with respect to w
A_0	Zero-frequency amplitude
Re	Reynolds number
t	Thickness of cantilever
ρ_c	Cantilever density
b	Cantilever width
QPD	Quadrant photodiode
m	Mass
A_{max}	Maximum amplitude of oscillation
h	Resonance half-line width
LOD	Limit of detection
σ_f	Standard deviation of the resonant frequency

σ_Q	Standard deviation of Q-factor
S	Slope
S_μ	Derivative of the Q-factor with μ
P	Pressure
T	Temperature
σ_{Qa}	Average standard deviation of Q-factor
RD	Relative difference
R_μ	Resolution



CHAPTER 1

INTRODUCTION

Over the last two decades, research efforts were made to use cantilever-based sensors to characterize pure fluids and fluid mixtures [1-14]. Cantilevers were frequently utilized as transducer in various biological, physical and chemical sensing applications. Leading examples include chemical/biological sensors [15, 16], pressure sensors [17], Atomic Force Microscopy (AFM) [18], mass sensors [19], or viscometers and densitometers [20]. Sensing through miniaturized cantilevers have many advantages such as simple and compact architecture, fast response, high sensitivity and ultra-low sample volume requirements.

The studies in the literature involving cantilevers exposed to pure fluids and fluid mixtures can be divided primarily into two categories: (a) detection/quantification of gas/fluid species in mixtures and (b) measurement of thermophysical properties of pure fluids or fluid mixtures. The detection and/or quantification of one or more of the components of a fluid mixture is generally accomplished by coating the cantilever surface with a chemically sensitive layer with a well-defined affinity to the fluid/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 piezoresistive, piezoelectric, capacitive and optical [15, 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 [5]. In this approach, detection is based on the hydrodynamic interaction between the oscillating cantilever and the surrounding fluid. The hydrodynamic force has two components, one is pressure force (normal to the vibrating surface) and the other is viscous force (tangential to the vibrating surface). These forces on an oscillating cantilever depends on the density and viscosity of the fluid, thus, one can relate the density and viscosity of pure fluids or mixtures to the frequency response of immersed cantilever. 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 [22]. 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 gives [23]:

$$f_{fluid} = f_{vac} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + \frac{3.7997}{\sqrt{2Re}} \right) \right]^{-1/2} \quad (1.1)$$

$$Q = \frac{\frac{4 \rho_c t}{\pi \rho b} + \left(1.0553 + \frac{3.7997}{\sqrt{2Re}} \right)}{\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re}} \quad (1.2)$$

where f_{vac} is the resonant frequency of the cantilever in vacuum, b is the cantilever width, ρ_c is the cantilever density, t is the cantilever thickness, ρ is the mixture density, μ is the mixture viscosity and Re is the Reynolds number $\left(Re = \frac{2\pi f_{fluid} \rho b^2}{4\mu} \right)$.

The density and viscosity of fluids depends on the composition, therefore, change in the resonant frequency, f_{fluid} and Q-factor, Q of microcantilevers may perhaps be related to the changes in the composition of the fluid. For practical applications of detection techniques that exploit oscillating microcantilevers, it is of utmost importance to quantify their sensitivity and Limit of Detection (LOD), as these parameters directly determine the domain of usability of microcantilever-based analytical devices. For measuring the composition of a binary mixture, the sensitivity of cantilever to the changes in the mixture composition is very important and it will help to quantify the LOD of the cantilever for characterizing the mixture composition. The viscosity is also an important parameter of the fluid and using Saders model equation for the Q-factor, it can be measured.

The research results in this dissertation is divided into four parts. In part one, determination of composition of ethanol-CO₂ mixtures at high pressures using frequency response of microcantilevers is described. In part two, the compositional measurement sensitivity of high-pressure fluid mixtures using microcantilever frequency response is given. While in part three, viscosities of ethanol-CO₂ binary mixtures at high pressures are

presented. In part four, viscosity measurement sensitivity of high-pressure fluid mixtures using microcantilever frequency response is described.

In the first part, Frequency response of microcantilevers immersed in different mixture compositions ranging from 0.0091 to 0.0616 weight fraction of ethanol in CO₂ were measured at a fixed temperature of 308 K and a pressure range of 8 to 22 MPa. Ethanol-CO₂ mixtures are frequently encountered in many technological processes such as supercritical drying of aerogels or fabrication of Micro Electro Mechanical Systems. Accurate monitoring of the mixture composition in such processes can help significantly in optimizing the process time and reducing the overall cost [24-27]. In supercritical drying process of alcogels, the extraction of the solvent from the pores of the gel is performed with the usage of supercritical fluids. Supercritical CO₂ is normally used as an extraction solvent due to its favorable properties. Supercritical drying is the very important step in aerogel production as it enables preservation of the pore structure. However, the supercritical drying is a complex and the most time-consuming step in aerogel production. Therefore, drying time of the wet gel has a direct and substantial impact on the production cost on an industrial scale. The inaccurate drying time results high CO₂ utilization cost and decrease in aerogel production [24-27].

A technique for measuring the concentration of ethanol in a mixture of ethanol and CO₂ at the exit port of a supercritical extractor is suggested as shown in Fig. 1. The composition of a high-pressure ethanol-CO₂ mixture is measured using the frequency response of microcantilevers. 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-CO₂ mixtures can be determined with a good accuracy from the measured frequency response of an uncoated cantilever. This technique can be incorporated into the systems for monitoring ethanol concentration during supercritical drying process of aerogels at large scale and it will help to reduce the CO₂ utilization cost and maximize aerogel production.

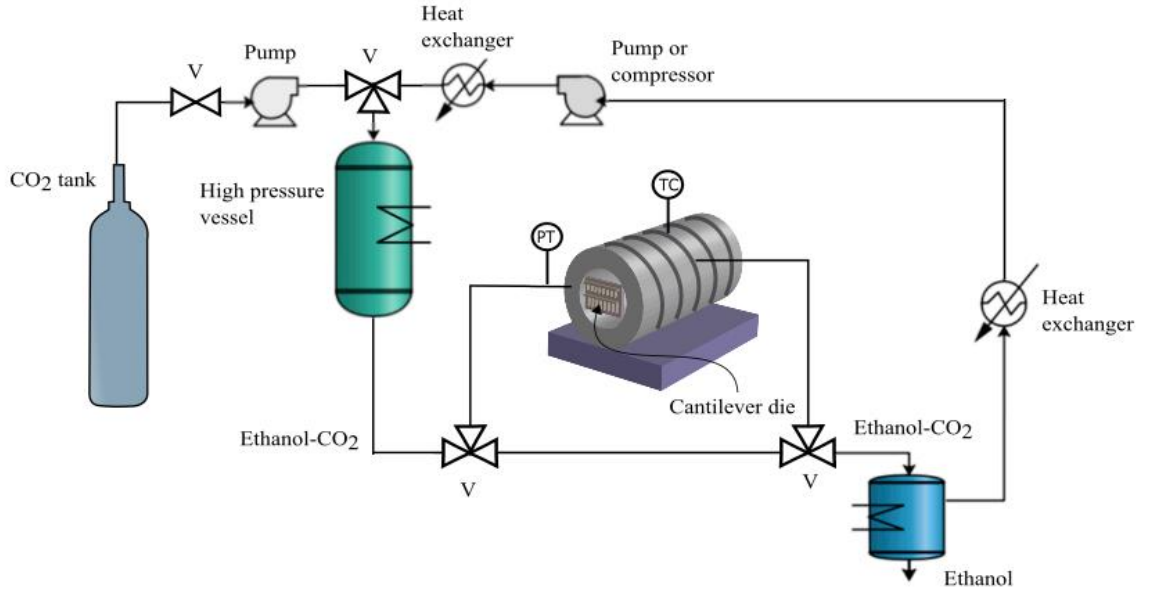


Fig. 1.1. Flowsheet of a supercritical CO₂ drying cycle of alcogels and proposed microcantilever based technique for monitoring ethanol concentration in CO₂ at the exit of extractor during supercritical drying process of aerogels [28]. PT: pressure transducer, TC: thermocouple, V: valve.

In the second part, a systematic study of the sensitivity of measurement of binary fluid mixtures' composition based on the measurement of frequency response of a microcantilever immersed in the fluid was carried out. Ethanol-CO₂ mixtures containing 0 – 0.04 weight fraction of ethanol were studied at a pressure range between 10 MPa and 21 MPa and at 318 K. The sensitivities S_f, S_Q of the compositional measurement were defined as the derivatives of the cantilever resonant frequency f_{fluid} or the Q-factor Q with respect to the weight fraction of ethanol in the mixture, w ($S_f = df_{fluid}/dw, S_Q = dQ/dw$), and analytical expressions for the sensitivity were derived from Sader's model [22] which includes the effects of viscous forces. Using the model sensitivity and the standard deviations of the resonant frequency and the Q-factor measured at given constant experimental conditions, the LOD of ethanol in ethanol-CO₂ mixtures was estimated. To the best of our knowledge, this work represents the first systematic study on the change in the resonant frequency or the Q-factor of immersed cantilevers with the mixture composition which also includes the effect of viscous forces in the sensitivity analysis.

In the 3rd part, the viscosities of ethanol-CO₂ mixtures in the single phase region containing 0.290, 0.453, 0.593, 0.747 and 0.882 weight fraction of ethanol at temperatures of 308, 313, 318, 323, 328 and 333 K and pressures from 7 to 33 MPa were measured. The viscosities were found to increase with the increasing ethanol weight fraction in the mixture and viscosities of the mixtures were found to decrease with temperature at a fixed density. Viscosities of ethanol-CO₂ mixtures are important in many processes such as supercritical extraction, supercritical antisolvent (SAS) and supercritical anti solvent precipitation inside the pores (SASIP)[29, 30]. In SAS process, ethanol is a solvent commonly for generation of fine and uniform particles of a wide variety of compounds for pharmaceutical and cosmetics applications[31-35]. A recently developed technique to load drugs or other compounds to aerogels is supercritical anti solvent precipitation inside the pores (SASIP)[29, 30] where diffusion of mixtures of ethanol and CO₂ takes place. Development of models for understanding the dynamics of supercritical extraction, SAS and SASIP processes requires data on thermophysical properties of ethanol-CO₂ mixtures. Among these, viscosity is an extremely important parameter. The viscosity data is also necessary for design and optimization of the supercritical fluid based processes[36, 37]. Knowledge of mixture viscosity is also necessary for calculation of various dimensionless numbers such as Reynolds [38] and Schmidt [39, 40] numbers. Moreover, the viscosity of mixtures of carbon dioxide with ethanol are also needed to calculate diffusion coefficients of ethanol-CO₂ mixtures from available correlations[41-45].

In the last part, the viscosity measurement sensitivity of microcantilevers for ethanol-CO₂ mixtures containing $w = 0.290, 0.453, 0.593, 0.747, 0.882$ weight fraction of ethanol at a temperature range of 308 to 333 K and pressure range between 7 and 33 MPa were studied. The sensitivity S_μ was defined as the derivative of the cantilever Q-factor with viscosity of the mixture ($S_\mu = dQ/d\mu$) and analytical expression for the sensitivity was derived from the Sader's model equations [22]. The sensitivities predicted by the model S_μ were compared with the experimentally determined values of sensitivity. Using the experimental sensitivity S_μ , and the average standard deviation of the Q-factor measured at a particular ethanol-CO₂ mixture, the resolution of viscosity measurement was estimated.

The dissertation is organized in the following manner.

The studies in the literature on cantilevers are reviewed in Chapter 2.

The experimental techniques used in this dissertation are described in Chapter 3.

The results and discussion are given in Chapter 4.

The conclusions and suggestions for future work of the dissertation are given in Chapter 5.



CHAPTER 2

LITERATURE REVIEW

2.1 Microcantilever sensors

There is a growing interest in development of microcantilever-based sensors for qualitative and quantitative detection of pure fluids and fluid mixtures [15, 46-54]. The purpose of this chapter is to review the operating modes of cantilever and available literature studies of cantilevers for the characterization of the pure fluids and mixtures and sensitivity analysis of cantilevers. In bio and chemical sensing applications, microcantilevers are generally coated with a chemically sensitive layers and the coated cantilevers are operated in static or in dynamic mode. The sensitive coating are subjected to humidity, aging and temperature affects, thus long term stability and reliability of coatings is limited [6]. Therefore, the coated cantilevers have some limitation in detecting the gases, chemical vapors or binary mixtures. There is an alternate approach to detect the pure gases and binary mixtures by using uncoated cantilevers [5].

2.2 Static mode

In static mode, microcantilevers gradually bend due to adsorption of the target molecules on the surface of the cantilevers as shown in Fig. 2.1(a). Usually, cantilever surface is 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 [15, 21]. The 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, 15]. For example,

Britton *et al.* [55], Okuyama *et al.* [56], Baselt *et al.* [57], Chou *et al.* [58], and Lang *et al.* [50] were able to detect and quantify the amount of hydrogen in various gas mixtures or in pure state using palladium, palladium-nickel, and platinum-coated cantilevers.

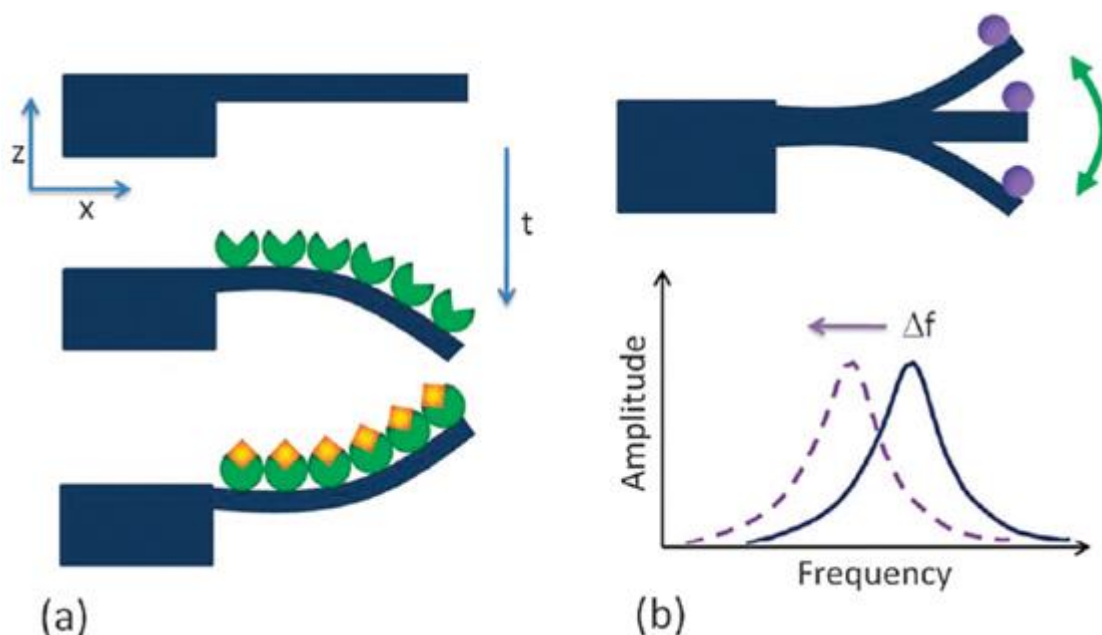


Fig. 2.1. (a) Static mode (b) dynamic mode [59].

2.3 Dynamic mode

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, as shown in Fig. 2.1(b) [15]. For example, Dong *et al.* [60], Betts *et al.* [61], Fadel *et al.* [62], Maute *et al.* [63, 64], and Kim *et al.* [65] used microcantilevers coated with various polymeric films and detected vapors of a wide variety of volatile organic compounds such as toluene, xylene, pentane, methanol, ethanol, methylene chloride, and octane. They operated microcantilevers in the dynamic mode and were able to relate changes in the resonant frequency of microcantilevers due to the sorption of the target organic compounds in the polymeric film to the concentration of the compounds. In addition to metallic and polymeric coatings, inorganic coatings have been also utilized. For example, Mertens *et al.* [66] were able to detect hydrofluoric acid (HF) in air at

concentrations ranging from 0.26 to 13 ppm using microcantilevers coated with Si_3N_4 and SiO_x .

An alternative approach to using coated cantilevers for detection and compositional analysis of pure gases and gas mixtures is to use uncoated cantilevers. With such cantilevers, the detection is not based on sorption but rather on hydrodynamic interactions of the microcantilever with the surrounding medium [1, 67, 68]. As shown in Fig. 2.2, the resonant frequency changes due to the changes in density and viscosity of the fluid surrounding the cantilever, thus resonant frequency can be related to the properties of the immersed fluid. In this dissertation, dynamic mode of the cantilever is used for the characterization of the ethanol- CO_2 mixtures.

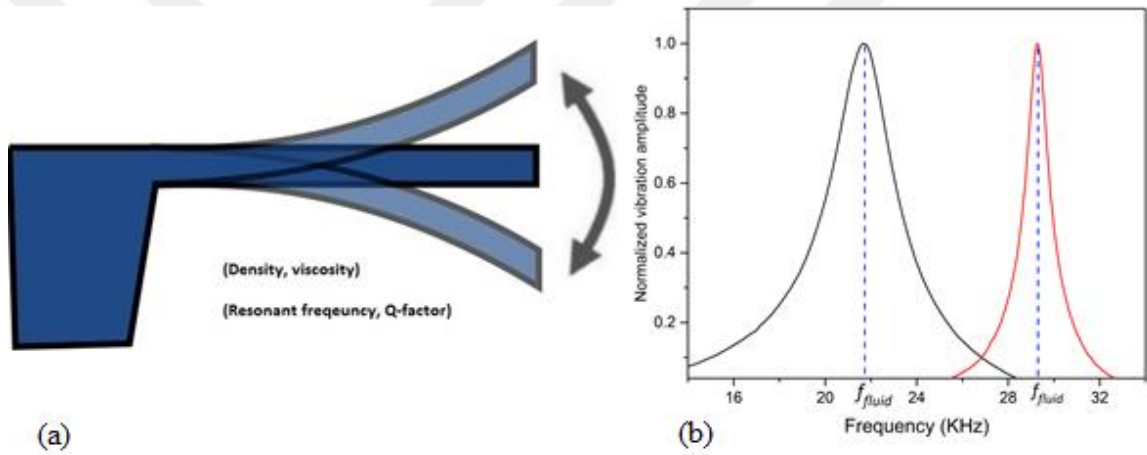


Fig. 2.2. (a) Dynamic mode of cantilever, (b) Frequency response of cantilever in fluids of different density and viscosity

2.4 Theory

In the literature, there are many studies that experimentally and theoretically studied the dynamic response of the resonating cantilevers [69]. The resonating cantilevers are described as a harmonic oscillator. This section will give a brief overview of the theoretical background of a driven damped harmonic oscillator as it was used to treat the frequency response data of cantilevers immersed in the mixtures in this study.

2.4.1.1 Simple harmonic oscillator (SHO)

In a simple harmonic oscillator, the net force (F_n) acting on the oscillating mass (m) is equal to the restoring force (F_{rest}) of the spring and it is described by Hooke's Law as [70, 71]:

$$F_{net} = F_{rest} = -kx \quad (2.1)$$

where k is the spring constant and x is the distance displaced by the mass m from its equilibrium position. Using Newton's second law Eq.2.1 can be written as:

$$F_{net} = ma = m \frac{d^2x}{dt^2} = -kx \quad (2.2)$$

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0 \quad (2.3)$$

$$\frac{d^2x}{dt^2} + \omega_0^2 x = 0 \quad (2.4)$$

Defining undamped natural frequency $\omega_0 = \sqrt{k/m}$, Eq. 2.4 can further be solved as:

$$x(t) = A \sin(\omega_0 t - \varphi) \quad (2.5)$$

where A is the amplitude and φ is the phase of oscillations which occur with frequency ω_0 .

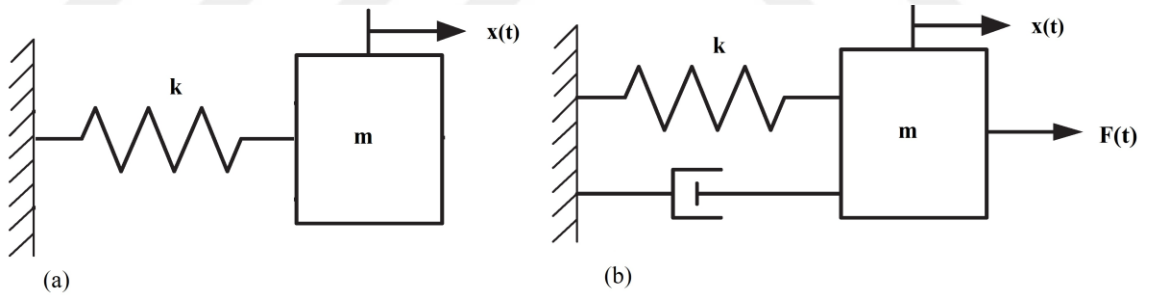


Fig. 2.3. Schematic diagram of (a) Simple harmonic oscillator (SHO) (b) Driven damped harmonic oscillator (diagram copied from [72]).

2.4.1.2 Driven damped harmonic oscillator

The equation of a damped harmonic oscillator is given as:

$$\left(\frac{d^2x(t)}{dt^2} + 2\zeta\omega_0 \frac{dx(t)}{dt} + \omega_0^2 x(t) \right) = 0 \quad (2.6)$$

When a time varying force with frequency ω and amplitude F_0 is applied on mass m , as shown in Fig. 2.3(b). The Eq.2.6 can be written as:

$$m \left(\frac{d^2 x(t)}{dt^2} + 2 \zeta \omega_o \frac{dx(t)}{dt} + \omega_o^2 x(t) \right) = F_o e^{i\omega t} \quad (2.7)$$

By introducing $x(t) = A e^{i(\omega t + \varphi)}$ into Eq. 2.7:

$$m(-\omega^2 + i2 \zeta \omega_o \omega + \omega_o^2) A e^{i(\omega t + \varphi)} = F_o e^{i\omega t} \quad (2.8)$$

Dividing by $e^{i\omega t}$ and solving it further gives:

$$A e^{i\varphi} = \frac{F_o/m}{\omega_o^2 - \omega^2 + i2 \zeta \omega_o \omega} \quad (2.9)$$

which can be further solved as:

$$\begin{aligned} A(\omega_o^2 - \omega^2) \cos \varphi + iA2 \zeta \omega_o \omega \cos \varphi - F_o/m + iA \sin \varphi (\omega_o^2 - \omega^2) - \\ A2 \sin \varphi \zeta \omega_o \omega = 0 \end{aligned} \quad (2.10)$$

Separation of the real and imaginary parts give:

$$A \cos \varphi (\omega_o^2 - \omega^2) - A2 \zeta \omega_o \omega \sin \varphi = F_o/m \quad (2.11)$$

$$A2 \zeta \omega_o \omega \cos \varphi + A(\omega_o^2 - \omega^2) \sin \varphi = 0 \quad (2.12)$$

By squaring Equations 2.11 and 2.12 and adding and solving gives:

$$\begin{aligned} (\omega_o^2 - \omega^2)^2 (\cos \varphi)^2 - 4 \zeta \omega_o \omega \sin \varphi \cos \varphi (\omega_o^2 - \omega^2) + (2 \zeta \omega_o \omega \sin \varphi)^2 + \\ (2 \zeta \omega_o \omega \cos \varphi)^2 + 4 \zeta \omega_o \omega \sin \varphi \cos \varphi (\omega_o^2 - \omega^2) + ((\omega_o^2 - \omega^2) \sin \varphi)^2 = \\ \left(F_o / Am \right)^2 \end{aligned} \quad (2.13)$$

or

$$\begin{aligned} (\omega_o^2 - \omega^2)^2 [(\cos \varphi)^2 + (\sin \varphi)^2] + (2 \zeta \omega_o \omega)^2 [(\cos \varphi)^2 + (\sin \varphi)^2] = \\ \left(F_o / Am \right)^2 \end{aligned} \quad (2.14)$$

or

$$A = \frac{F_o/m}{\sqrt{(\omega_o^2 - \omega^2)^2 + (2 \zeta \omega_o \omega)^2}} \quad (2.15)$$

By substituting $\zeta = \frac{1}{2Q}$, $\omega_o = \omega_{fluid}$ and $A_o = \frac{F_o/m}{\omega_o^2}$ in Eq. 2.15, one obtains:

$$A(\omega) = \frac{A_o \omega_{fluid}^2}{\sqrt{(\omega_o^2 - \omega^2)^2 + \frac{\omega^2 \omega_{fluid}^2}{Q^2}}} \quad (2.16)$$

Or

$$A(\omega) = \frac{A_o 4\pi^2 f_{fluid}^2}{\sqrt{(\omega^2 - 4\pi^2 f_{fluid}^2)^2 + \frac{\omega^2 4\pi^2 f_{fluid}^2}{Q^2}}} \quad (2.17)$$

where A_0 is the zero-frequency amplitude of the response and $\omega = 2\pi f$ is the angular driving frequency.

Solving Eq. 2.12 further leads to:

$$\tan \varphi = \frac{-2 \zeta \omega_{\text{fluid}} \omega}{(\omega_{\text{fluid}}^2 - \omega^2)} \quad (2.18)$$

Equation 2.17 can be used to obtain the resonant frequency, f_{fluid} , and the Q-factor, Q , of a driven cantilever immersed in a fluid from fitting of experimentally recorded data.

2.5 Mixture composition measurement and literature studies

In literature, there are some studies that used uncoated cantilevers to measure the compositions of gas mixtures. For example, Xu *et al.* [67] determined the composition of a CO₂-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.* [68] 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.* [4] determined the concentration of H₂ in N₂ 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 H₂ in N₂. Lakhmi *et al.* [73] detected ethanol and water vapors in N₂ using uncoated thick film PZT cantilevers and monitored the resonant frequency shift due to the vapor concentration. 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. Gamze *et al.* and Uzunlar *et al.* measured the frequency response of uncoated cantilevers immersed in pure CO₂, N₂ and argon (Ar) at pressures up to 27 MPa and observed a very good agreement between the experimental data and Sader's model [1, 3,

74]. Studies regarding the determination of ethanol-CO₂ mixture composition using frequency response of cantilevers are missing. Therefore, development of microcantilever-based systems for measuring the composition of fluid mixtures at high pressures is thus of high practical importance. We used uncoated rather than polymer-coated microcantilevers since the polymer-coated cantilevers might swell at high pressures due to the sorption of supercritical CO₂ into the polymer layer [75]. 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 [6].

2.6 Sensitivity analysis of cantilevers and literature studies

There have been a limited number of experimental and theoretical studies in the literature on the sensitivity of microcantilever-based detection systems. For example, Zhao *et al.* [76] studied the effect of the geometry of a microcantilever on the sensitivity of density measurements and formulated an analytical expression for the sensitivity defined as the derivative of the cantilever resonant frequency with respect to the density of the fluid. They showed that the sensitivity could be improved by decreasing the length and the width of the microcantilever and also by using a higher-order resonant mode. They measured the resonant frequency of microcantilevers immersed in n-pentane, n-hexane, n-heptane, n-octane, and cyclohexane with densities ranging from 621 to 774 kg/m³ and calculated the best resolution of their density measurements as 0.057 kg/m³ for a 1.9 mm long rectangular cantilever. Boudjiet *et al.* [7] also showed that the sensitivity of fluid-density sensors based on uncoated microcantilevers can be improved by optimizing the device geometry. They fabricated microcantilevers of different shapes (in particular, rectangular, U-shaped and T-shaped) and dimensions and measured the concentration of H₂ in mixtures of H₂ and N₂ using cantilever resonant frequencies. They found that shorter and wider rectangular cantilevers exhibited better sensitivity to density changes and cantilever thickness did not affect the sensitivity. For 1% H₂ in the mixture, the relative difference between the model and the measured resonant frequency ranged from 0.3 to 25 % for the studied cantilevers. Tetin *et al.* [5] studied the shift in the resonant frequency of uncoated microcantilevers due to the changes in the density and viscosity of the surrounding fluid. They measured the

relative shift in the resonant frequency of an immersed microcantilever due to the addition of CO₂ or He to N₂ and compared the experimentally obtained value of the shift with a theoretical model. They neglected the relatively small effect of viscosity on the observed shift of the resonant frequency and reported the sensitivity and LOD of their microcantilever system. Cox *et al.* [77] studied laterally vibrating microcantilevers immersed in water and aqueous glycerol solutions and measured the resonant frequency, the Q-factor, and the mass sensitivity of the resonant frequency. The mass sensitivities and the Q-factors of microcantilevers excited laterally were found to be higher than those of transversely excited microcantilevers, thus rendering laterally vibrating microcantilevers more suitable for operation in high-viscosity media. Beardslee *et al.* [78] studied the resonant frequency and the Q-factor of a cantilever immersed in water. They demonstrated that using the in-plane flexural mode reduces damping and mass loading due to the surrounding fluid and showed that shorter, wider, and thinner cantilevers operated with in-plane flexural modes give the best sensing characteristics. Furthermore, Loui *et al.* [79], Narducci *et al.* [80], Beardslee *et al.* [78] and Hocheng *et al.* [81] also suggested to optimize the cantilever geometry in order to increase the sensitivity of density measurements. All of the above-discussed experimental and computational studies of sensitivity of cantilever-based detection systems were carried out at a low pressure of the fluid surrounding the cantilever (typically at the atmospheric pressure) and the studies at high pressures are missing. In addition, in analyzing measurement sensitivity, these studies largely neglected the effects of the changing fluid viscosity and they did not attempt to use the measured thermophysical properties of the fluid to determine fluid's composition.

2.7 Viscosity measurement and literature studies

In addition to concentration measurements, hydrodynamic interactions between uncoated microcantilevers and the studied fluid can be exploited for the measurement of thermophysical properties of pure gases and gas mixtures, such as density and viscosity. For examples, Youssry *et al.* [9] Boskovic *et al.* [20], Gamze *et al.* [1] used Sader's model to determine the density and viscosity of the different fluids or mixtures. In our previous study [82], we measured the density and viscosity of the CO₂-N₂ mixtures using Sader's model Equations.

Furthermore, there are not many studies in the literature on the measurement of viscosities of binary supercritical mixtures (organic solvent-CO₂ mixtures) at a wide range of pressures, temperatures and compositions. Limited number of studies show that the behavior of viscosity at such conditions can be quite complex. For example, Kiran *et al.* measured the viscosities of acetone-CO₂ mixtures using a falling cylinder type viscometer [83]. The viscosities were found to increase with increasing pressure. Tilly *et al.* measured the viscosity of ethanol-CO₂ mixtures containing 2, 3, and 4 mol % of ethanol at 318 K and 328 K and at pressures ranging from 9.48 MPa to 21.8 MPa [36].

In this dissertation, the viscosities of ethanol-CO₂ mixtures in the single phase were measured by using the frequency response of an oscillating cantilever immersed in the high-pressure mixture. The viscosity was measured using Sader's model equation for the Q-factor.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Materials

CO₂ used in the experiments was supplied by Aligaz Messer with a purity of 99.9 %. Ethanol was supplied by Sigma-Aldrich with a purity of 99.8 %. Both CO₂ and ethanol were used as received.

3.2 Experimental setup and measurement procedure

3.2.1 Components in experimental setup

Chips with ferromagnetic cantilevers of different lengths made out of nickel were used for the measurements and they are classified as chip-1 and chip-2. The cantilever of the chip-1 used in the measurement had a nominal length of 200 μm , a nominal width of 20 μm , and a thickness of about 1 μm . While the cantilevers of the chip-2 had nominal lengths of 150 μm and 200 μm , a nominal width of 20 μm , and a thickness of about 1 μm . The design and fabrication process of ferromagnetic microcantilevers were explained by Uzunlar *et al.* [3, 74]. The same procedure was followed for the fabrication of the cantilevers. Chip-1 and chip-2 were used for the measurements mentioned in section 4.1, while chip2 was used for the measurements in section 4.2, 4.3 and 4.4. The SEM image of chip-2, fabricated at Micro and Nanofabrication Laboratory (Cleanroom) Koc University is shown in Fig. 3.1.

The experimental setup which was also described in detail in previous studies [1, 2, 14, 84] consisted of a high-pressure fluid vessel with sapphire windows, a laser, a quadrant photodiode, a CCD camera, lenses, and additional electronic equipment used for the readout of the cantilever frequency response. A schematic diagram of the experimental

set-up is given in Fig. 3.2(a). Before the measurements, a die with cantilevers was mounted in a Teflon housing containing an electromagnetic actuator - a coil made from copper wire- and the housing was subsequently placed in a 50-mL cylindrical high-pressure vessel with two sapphire windows on each side (TharSFC 05424-4). These windows allowed the monitoring of microcantilevers during the experiment and the measurement of their frequency response using laser beam deflection. Electrical connection to the copper coil in the high-pressure vessel was sealed using insulated CONAX Technologies TG24 T-gland assemblies. Temperature of the fluid mixture in the high-pressure vessel was controlled by circulating water through plastic tubing wrapped around the vessel, using a heating circulator with temperature control (LabO C200-H13). 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.

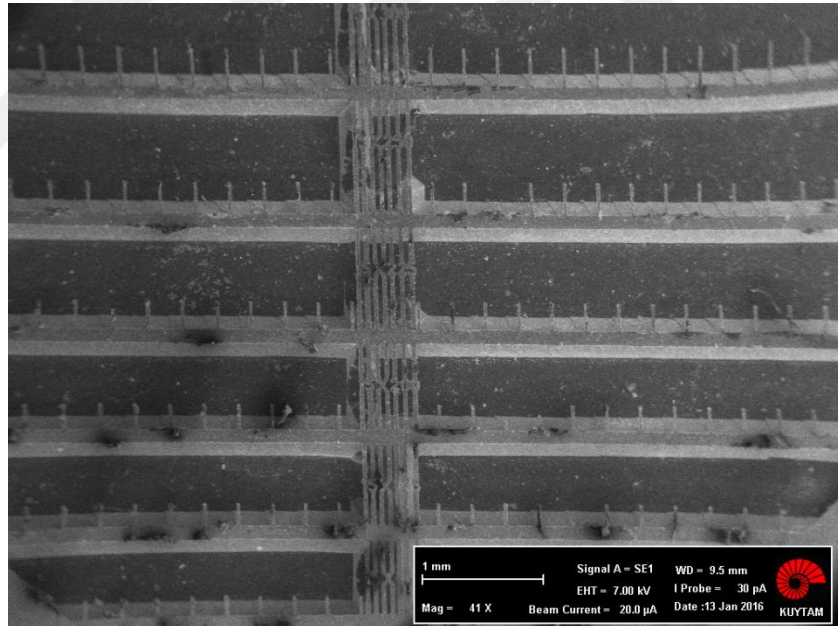


Fig. 3.1. SEM image of chip-2, fabricated at Micro and Nanofabrication Laboratory (Cleanroom) Koc University

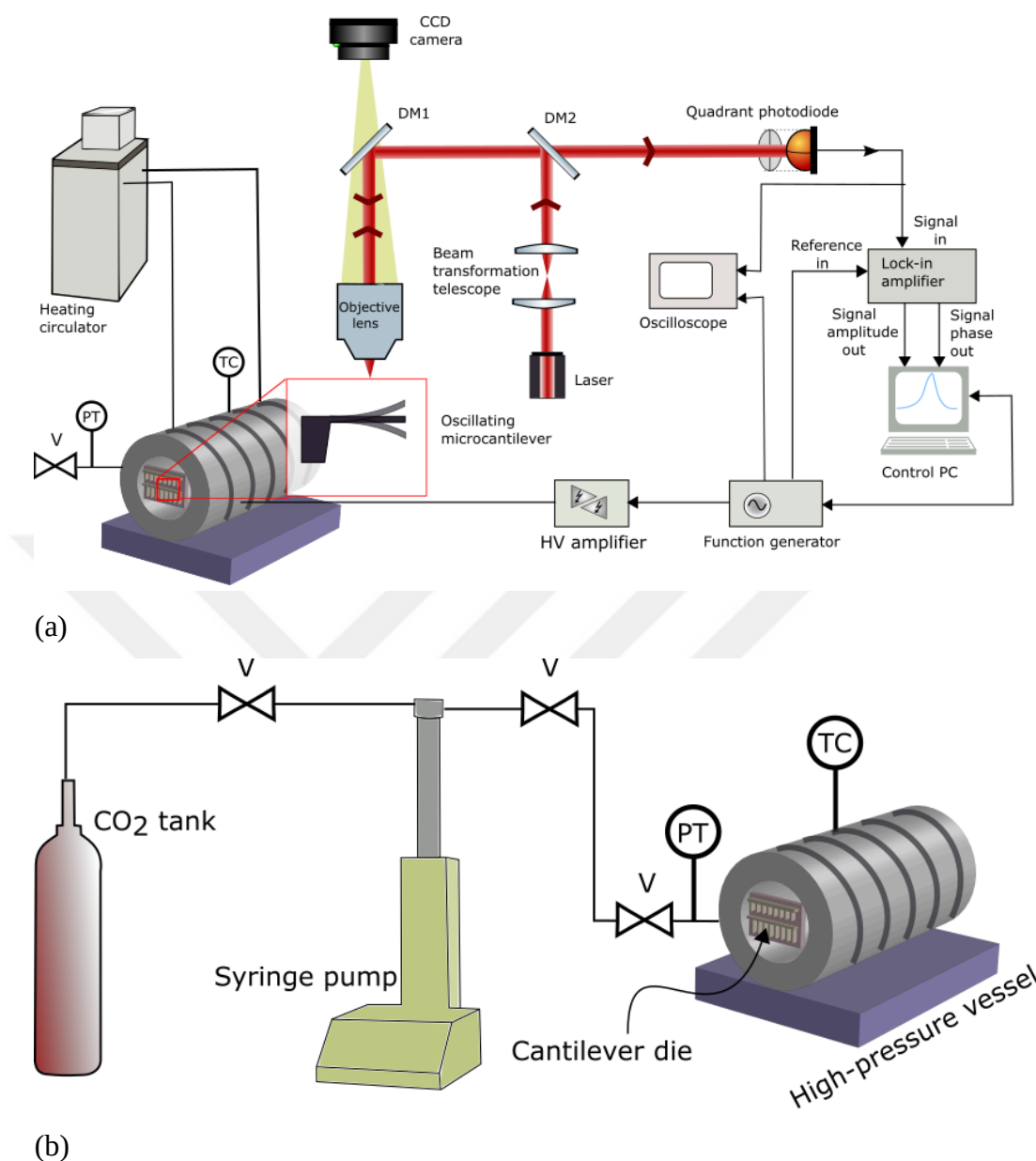


Fig. 3.2. (a) Schematic drawing of the experimental setup used for measuring the frequency response of immersed microcantilevers. DM1, DM2–dichroic mirrors. (b) Schematic drawing of the system used for sample-chamber pressurization. PT: pressure transducer, TC: thermocouple, V: valve

3.2.2 Ethanol-CO₂ mixture preparation

Ethanol-CO₂ mixtures were prepared by successive transfer of ethanol and CO₂ to the high-pressure vessel. The amount of each fluid transferred to the vessel was determined gravimetrically. Liquid ethanol was placed into the vessel using a micropipette and CO₂

was transferred to the vessel using a TELEDYNE ISCO D Series syringe pump (see Fig. 3.2(b) for illustration). Further details of the ethanol-CO₂ mixture composition preparation together with uncertainties are explained in detail in chapter 4.

3.2.3 Frequency response measurement procedure

During the measurements, the cantilevers were actuated with a time-varying magnetic field 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; see Fig. 3(a) for illustration). The frequency and amplitude of the driving sinusoidal signal were computer-controlled using Instrument Control Toolbox in Matlab. The deflections of the vibrating cantilever were detected by an atomic force microscopy-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 telescope enabled changing the axial position of the laser beam focus with respect to the cantilever surface and, thus, optimizing the cantilever deflection signal for different studied fluids. The beam reflected from the oscillating cantilever was collected by the same objective lens and then focused on a quadrant photodiode (QPD). QPD is sensitive to the position of the beam spot within its surface and can be used to record the changes of the propagation direction of the reflected beam due to cantilever deflection. In order to improve the signal-to-noise ratio, the deflection signal was sent to a lock-in-amplifier (SR530, Stanford Research Systems) together with the reference signal from the function generator. The output of the lock-in amplifier represented by the amplitude of the deflection signal and its phase shift with respect to the driving signal was digitized with a data acquisition card (USB-6008, National Instruments) controlled using Matlab programming environment.

In the beginning of each set of measurements with a given fixed mixture composition reported in section 4.1 and 4.2, the vessel was filled with the desired amount of ethanol and then charged with CO₂ to a pressure ranging between 21 MPa and 24 MPa. The temperature of the vessel was then adjusted to the desired value using the heating

circulator. Frequency response measurements were performed when the pressure and temperature became stable, typically 3-5 hours after starting the heating circulator. The measurements of the cantilever frequency response were performed starting from the highest pressure and then gradually decreasing the pressure for the successive measurements in the set. For the measurements reported in section 4.1 and 4.2, the temperature of the vessel was kept at 308 and 318 K respectively, and after each pressure change, we waited for approximately 5 minutes before starting the next measurement to ensure thermal equilibrium was restored in the vessel. At each pressure, the driving frequency of the function generator was adjusted over a range of 16 kHz for 150 μm long cantilever of chip-2, 12 kHz for 200 μm long cantilever of chip-2 and 10 kHz for 200 μm long cantilever of chip-1 with the central frequency of the studied spectral band equal to the cantilever resonant frequency.

While for the viscosity measurements reported in section 4.3, the vessel was filled with the desired amount of ethanol and then charged with CO_2 to a pressure ranging between 7 and 11 MPa. At the beginning of each set of measurements with a particular mixture, the temperature of the vessel was adjusted to the desired value using the heating circulator. The first frequency response measurement was performed typically 10-15 hours after starting the heating circulator, to ensure that ethanol and CO_2 mixed uniformly. The measurements of the cantilever frequency response were performed when the temperature and pressure became stable. For all measurements reported in section 4.3, the studied temperature range was 308 to 333 K. After frequency response measurements at a desired temperature, the temperature of the vessel was increased by 5 K for the next set of the measurement after waiting for approximately 2-3 hours to ensure that thermal equilibrium was restored in the vessel. At each studied temperature, the pressure of the vessel was recorded, and the driving frequency of the function generator was adjusted over a range of approximately 18 kHz centered around the resonant frequency of the cantilever.

For all the frequency response measurements in this dissertation, the amplitude of the driving sinusoidal signal before 50-times amplification was set to 2 V peak-to-peak and the cantilever response was then recorded at 400 equidistant points within spectral band of the studied cantilevers. According to Sader, the oscillation of an elastic cantilever beam can be approximated as a simple damped harmonic oscillator [22]. 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 Eq. 2.17 describing the oscillating elastic cantilever beam as a simple damped harmonic oscillator [22].

At each pressure, three consecutive measurements of the cantilever frequency response were carried out and the averages of the three resonant frequencies and Q-factors were reported for the measurements in section 4.1 and 4.2. While for the measurements in section 4.3, at each temperature and pressure, seven frequency response measurements were carried out and then the averages of the seven resonant frequencies and Q-factors were taken. Frequency response of an oscillating cantilever immersed in a fluid is characterized by its resonant frequency, f_{fluid} , and the Q-factor, Q . f_{fluid} is defined as the resonant frequency at which the maximum amplitude of driven cantilever oscillations is observed. Q-factor is the measure of the sharpness of the resonance peak and formulated as $Q=f_{fluid}/2h$, as shown in Fig. 3.3. It is a dimensionless parameter.

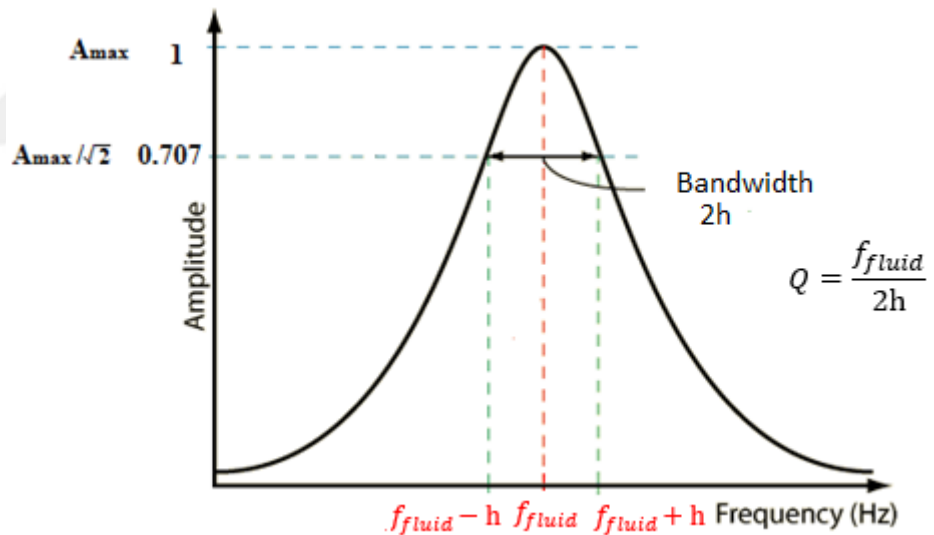


Fig. 3.3. Cantilever frequency response

CHAPTER 4

RESULTS AND DISCUSSION

Results and discussion section of this dissertation is divided in four parts. In first part, the composition determination of ethanol-CO₂ mixture is discussed. In part two, compositional measurement sensitivity of microcantilevers for high pressure ethanol-CO₂ mixtures is discussed. In the 3rd part, viscosities of ethanol-CO₂ mixture at high pressures and at different temperatures are presented. In final part, the viscosity measurement sensitivity of microcantilevers for high pressure ethanol-CO₂ mixtures is discussed.

4.1 Determination of composition of ethanol-CO₂ mixtures at high pressures

The primary target was to develop a technique for measuring the concentration of ethanol in a mixture of ethanol and CO₂ at the exit port of a supercritical extractor. Recently, Özbakır *et al.*[25] investigated theoretically and experimentally the extraction of ethanol from cylindrical silica alcogel monoliths and reported the ethanol percentage extracted from the extractor as a function of time, as shown in Fig.4.1. In order to assess the potential of microcantilever-based sensors for monitoring ethanol concentration in CO₂ as a function of time, we prepared ethanol-CO₂ mixtures with different weight fraction of ethanol, w , within the range of $w = 0.0091 - 0.0616$. Ethanol-CO₂ mixtures were prepared by successive transfer of ethanol and CO₂ 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 gram. 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 grams

determined from repetitive measurements with a different balance that had an accuracy of ± 0.001 gram. Subsequently, CO_2 was transferred to the vessel using a TELEDYNE ISCO D Series syringe pump (see Fig. 3.2 (b)) 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 4.1.

Table 4.1. 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	$*2185.6 \pm 0.1$	$*2185.6 \pm 0.1$	$*2185.6 \pm 0.1$
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	0.0149 ± 0.0002	0.0247 ± 0.0002	0.0091 ± 0.0002	0.0237 ± 0.0002	0.0616 ± 0.0002

*Empty cell mass changed due to removing of electric wire attached to the cell

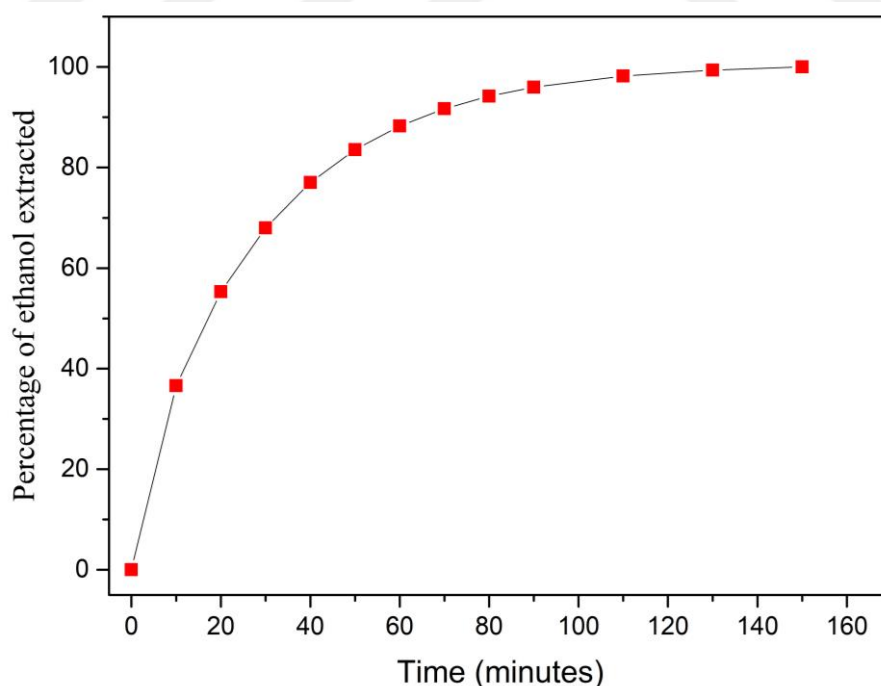


Fig. 4.1. Percentage of ethanol extracted from the extractor as a function of time at 10 MPa and 313 K [25].

We measured frequency response of microcantilevers immersed in ethanol-CO₂ mixtures at a temperature of 308 K and pressure range from 8 to 22 MPa. We used the 150 μm long cantilever of chip-2 and 200 μm long cantilever of chip-1 in this study. 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.

The measured resonant frequencies and Q-factors for ethanol-CO₂ mixtures of different compositions, including error bars, are given in Figs. 4.2 and 4.3 for the 150 μm long cantilever and Figs. 4.4 and 4.5 for the 200 μm long cantilever. At a constant temperature and mixture composition, the resonant frequency decreases due to higher added mass moving along with the cantilever as a result of the increase in the fluid density with increasing pressure. 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. 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.

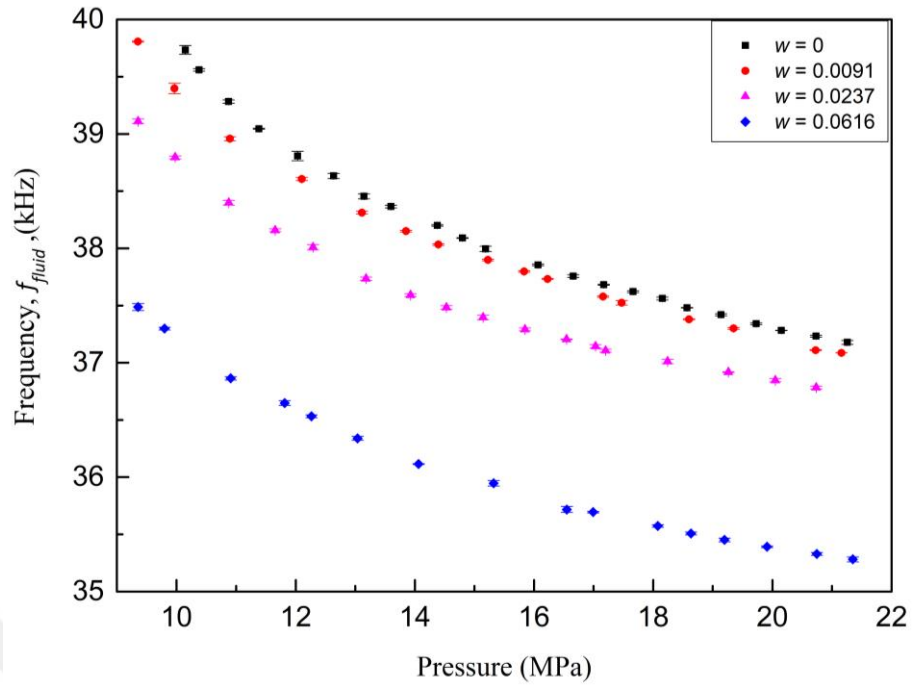


Fig. 4.2. Variation of resonant frequency, f_{fluid} , with pressure for different compositions of ethanol-CO₂ binary mixture at 308 K. Microcantilever length: 150 μ m.

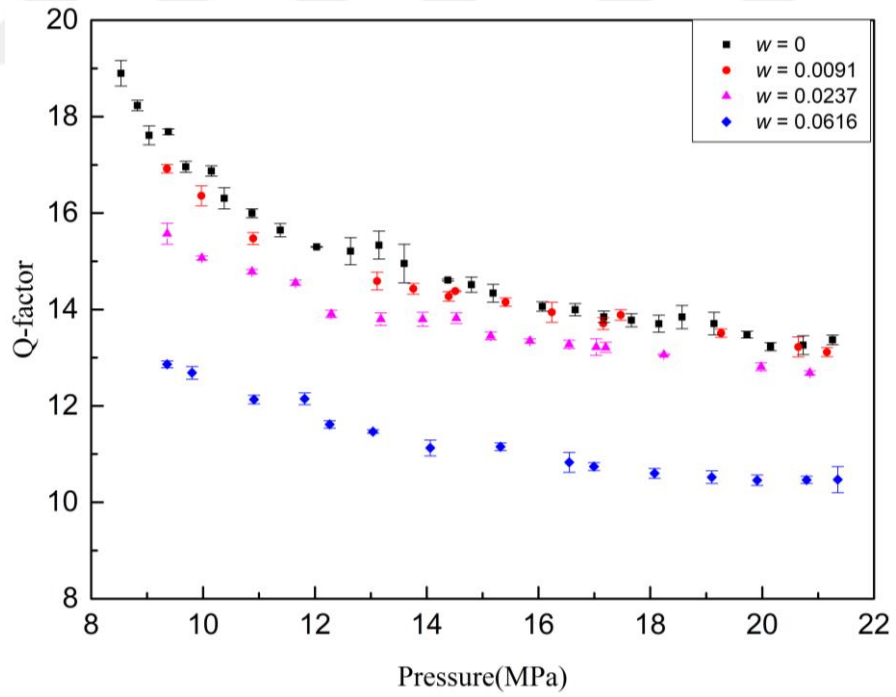


Fig. 4.3. Variation of Q-factor with pressure for different compositions of ethanol-CO₂ binary mixture at 308 K. Microcantilever length: 150 μ m.

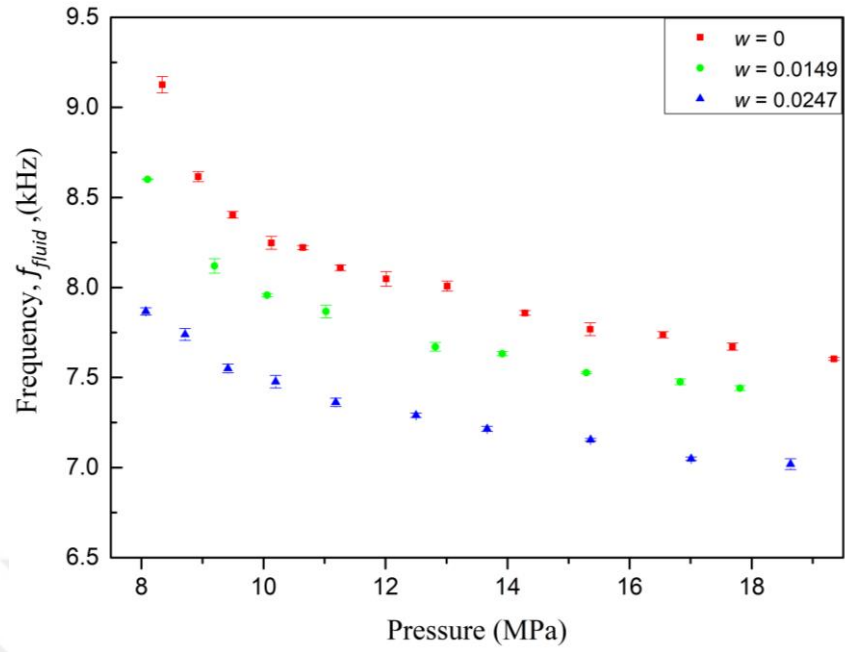


Fig. 4.4. Variation of resonant frequency, f_{fluid} , with pressure for different compositions of ethanol-CO₂ binary mixture at 308 K. Microcantilever length: 200 μ m.

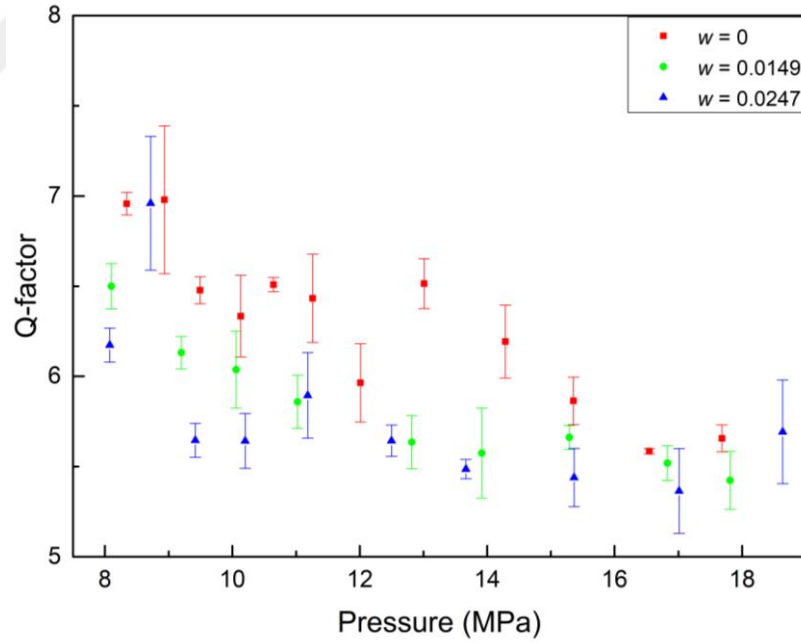


Fig. 4.5. Variation of Q-factor with pressure for different compositions of ethanol-CO₂ binary mixture at 308 K. Microcantilever length: 200 μ m.

A close analysis of Figs. 4.2-4.5 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. 4.6 and 4.7 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-CO₂ 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. 4.6 and 4.7, this calibration curve can be used to convert the measured resonant frequency in an ethanol-CO₂ mixture with unknown composition to the actual composition of the mixture. In this study, we investigated the frequency response of cantilevers immersed in ethanol-CO₂ mixtures within the composition range $w = 0.0091 - 0.0616$. As shown in Fig. 4.6, 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. 4.6, 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. 4.6 show that the difference between the values of f_{fluid} measured for pure CO₂ and ethanol- CO₂ mixture with $w = 0.0091$ 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 lower than 0.0091.

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. 1.1, 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. 4.6 and 4.7, the slopes of the lines relating f_{fluid} to w 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 is a factor that affects sensitivity of the composition measurement at the given temperature, pressure and mixture composition.

There are other techniques such as spectroscopic technique to measure the composition of the mixtures at high pressures. 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 [85] and the detection limit was 0.03 mole fraction of ethanol in mixture ($X_{ETOH} = 0.03$, where X_{ETOH} is the mole fraction of ethanol in ethanol- CO_2 mixture). It seems that the detection limit of the proposed technique is better since the minimum concentration that was detected in this study was 0.009 weight fraction of ethanol in mixture ($w = 0.009$) using resonant frequency of 150 μm long cantilever.

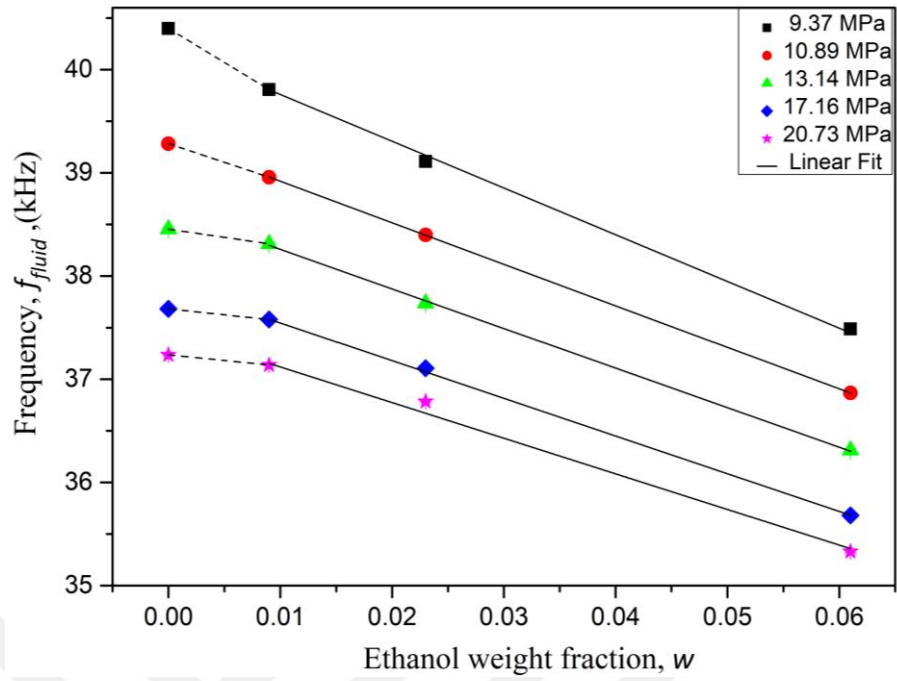


Fig. 4.6. Variation of resonant frequency, f_{fluid} , with ethanol weight fraction, w , at 308 K and different pressures. Microcantilever length: 150 μm .

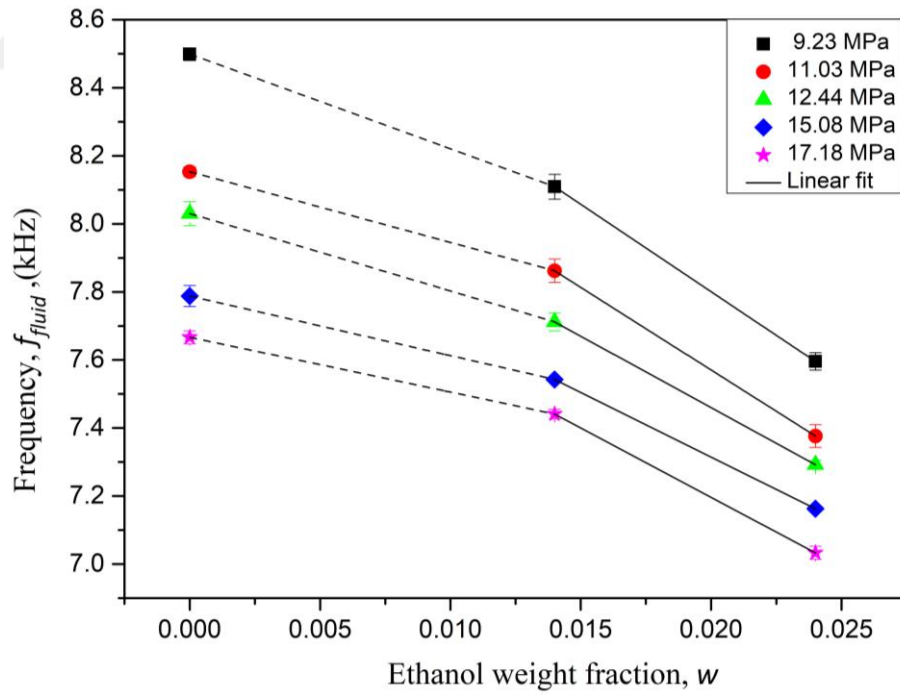


Fig. 4.7. Variation of resonant frequency, f_{fluid} , with ethanol weight fraction, w , at 308 K and different pressures. Microcantilever length: 200 μm .

4.2 Sensitivity of compositional measurement of high-pressure fluid mixtures

In this section, we study the compositional measurement sensitivity of microcantilevers for high pressure fluid mixtures using frequency response of microcantilevers. Ethanol-CO₂ mixtures were prepared by successive transfer of ethanol and CO₂ 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 amount of added ethanol was determined before the transfer into the vessel with a different balance with an accuracy of ± 0.001 g. Subsequently, CO₂ was transferred to the vessel using a TELEDYNE ISCO D Series syringe pump (see Fig. 3.2(b) for illustration) and the mass of the vessel with both fluids was again measured using the balance with an accuracy of ± 0.1 g. Finally, the masses of the empty vessel and ethanol were subtracted from the total mass of the filled vessel to determine the amount of CO₂ placed into the vessel. Measured fluid masses and calculated mixture compositions specified in terms of the weight fraction of ethanol in the mixture, w , together with their respective uncertainties, are given in Table 4.2.

Table 4.2. Measured Values of Fluid Mass and Calculated Mixture Compositions together with Uncertainties in Individual Mass Measurements and Mixture Compositions.

Measured value	Experiment #1	Experiment #2	Experiment #3	Experiment #4	Experiment #5
Empty vessel mass (g)	2185.6 $\pm$ 0.1	2185.6 $\pm$ 0.1	2185.6 $\pm$ 0.1	2185.6 $\pm$ 0.1	2185.6 $\pm$ 0.1
Ethanol mass (g)	0.791 $\pm$ 0.001	1.175 $\pm$ 0.001	1.556 $\pm$ 0.001	0.335 $\pm$ 0.001	0.509 $\pm$ 0.001
CO ₂ mass (g)	38.4 $\pm$ 0.1	38.0 $\pm$ 0.1	37.5 $\pm$ 0.1	38.7 $\pm$ 0.1	38.5 $\pm$ 0.1
Total mass (g)	2224.8 $\pm$ 0.1	2224.8 $\pm$ 0.1	2224.7 $\pm$ 0.1	2224.7 $\pm$ 0.1	2224.7 $\pm$ 0.1
Ethanol weight fraction w	0.02017 $\pm$ 0.00007	0.02997 $\pm$ 0.00011	0.03979 $\pm$ 0.00014	0.00856 $\pm$ 0.00003	0.01301 $\pm$ 0.00005

The frequency response of microcantilevers immersed in ethanol-CO₂ mixtures containing 0 – 0.04 weight fraction of ethanol was measured at a pressure range of 10 to 21 MPa and at 318 K. There are only very limited experimental data available for the density and viscosity of ethanol-CO₂ mixtures at high pressures in the literature. Viscosity and density of ethanol-CO₂ mixtures containing 2, 3, and 4 mol % of ethanol were measured and reported by Tilly *et al.* at 318 K and 328 K and a pressure range from 9.48 MPa to 21.8 MPa [36]. For the compositional measurement sensitivity of cantilevers, the density and viscosity data were available for 0 – 0.04 weight fraction of ethanol, so the cantilever frequency responses were measured in ethanol-CO₂ mixtures containing 0 – 0.04 weight fraction of ethanol. We used 150 µm and 200 µm long cantilevers of chip-2 in this study. For the measurements on 150-µm-long cantilevers, the average relative standard deviations of the resonant frequency and the Q-factor over the whole studied pressure range were 0.04 % and 1.12 %, respectively, while the maximum relative standard deviations were 0.32 % and 3.94 %, respectively. For the 200-µm-long cantilever, the average relative standard deviations of the resonant frequency and the Q-factor were 0.05 % and 0.89 %, respectively, and the maximum relative standard deviations were 0.21 % and 3.14 %, respectively.

Sensitivity S_f of the cantilever resonant frequency f_{fluid} to changes in the weight fraction of ethanol in the mixture w can be defined as the derivative of f_{fluid} with respect to w . Similarly, sensitivity S_Q of the cantilever Q-factor Q to changes in w is given by the derivative of Q with respect to w . Below, analytical expressions for S_f and S_Q were derived using Sader's model equations (Eq. 1.1 and 1.2) [22]. Equation 1.1 represents the definition of f_{fluid} as an implicit function of the fluid parameters ρ, μ that themselves depend on the ethanol weight fraction, w . The derivative of f_{fluid} with respect to w can be obtained using the implicit function theorem and applying the chain rule (see the details of the derivation in Appendix A) as:

$$S_f^m = \left(\frac{df_{fluid}}{dw} \right)_m = \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi b f_{vac}}{16f_{fluid}\rho c t \sqrt{2Re}} \right)} \times \left\{ - \left(\frac{1.0553\pi b f_{vac}}{8\rho c t} + \frac{3.7997\pi b f_{vac}}{16\rho c t \sqrt{2Re}} \right) \frac{d\rho}{dw} - \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho c t \mu \sqrt{2Re}} \right) \frac{d\mu}{dw} \right\} \quad (4.1)$$

where the subscript and superscript m stand for “model”.

Equation (4.1) is the model - or theoretical - expression for the sensitivity S_f^m ; it shows that S_f^m is a complex function of the density and viscosity of the mixture, as well as cantilever length, width, thickness and cantilever density. In order to evaluate S_f^m for a given experimental condition (pressure, temperature, and composition of the mixture), derivatives $\frac{d\rho}{dw}$ and $\frac{d\mu}{dw}$ must be determined from the dependence of density and viscosity on the mixture's composition. There are no accurate methods and correlations for estimation of the density and viscosity of fluid mixtures at high pressures. We used the data of Tilly *et al.* [36] recorded at 318 K and applied cubic-spline interpolation to obtain additional values of mixtures' density and viscosity for our particular conditions. Figs. 4.8 and 4.9 show how the density and viscosity change with pressure. In order to determine the values of compositional derivatives $\left(\frac{d\rho}{dw}\right)$ and $\left(\frac{d\mu}{dw}\right)$ at 318 K and a particular pressure, we used the data in Figs. 4.8 and 4.9 together with the data for pure CO₂ ($w = 0$) obtained from the NIST database [86]. The density and viscosity of the fluid were plotted as functions of the ethanol weight fraction w , as shown in Figs. 4.10 and 4.11, respectively. Subsequently, for each individual studied pressure, we fitted ρ and μ linearly with w and calculated the compositional derivatives $\left(\frac{d\rho}{dw}\right)$ and $\left(\frac{d\mu}{dw}\right)$ from the slopes of the fitted lines at each studied pressure. The values of $\left(\frac{d\rho}{dw}\right)$ and $\left(\frac{d\mu}{dw}\right)$ obtained at different pressures are presented in Table 4.3. As shown in Fig. 4.11, at a constant pressure and temperature, the viscosity of ethanol-CO₂ mixtures increases with increasing ethanol weight fraction in the mixture. This is a direct consequence of pure ethanol having a higher viscosity than pure CO₂ at the given experimental conditions. It also follows from Fig. 4.11 that at a constant ethanol weight fraction, w , the viscosity of the mixture increases with pressure. This increase in viscosity is primarily related to the increase of density of ethanol-CO₂ mixtures with increasing pressure (see Fig. 4.8). At higher densities, the molecules in the mixture become more closely packed and this reduced intermolecular spacing then causes the viscosity to increase [36].

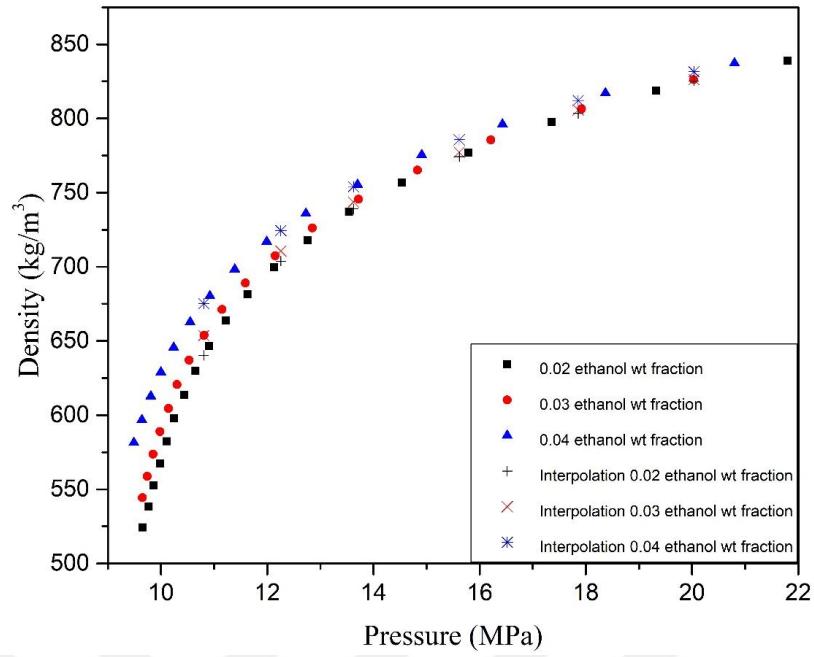


Fig. 4.8. Change of fluid density with pressure for ethanol-CO₂ mixtures with various compositions at 318 K. Data adopted from Tilly *et al.* [36], additional data points were determined by cubic-spline interpolation (see text for details).

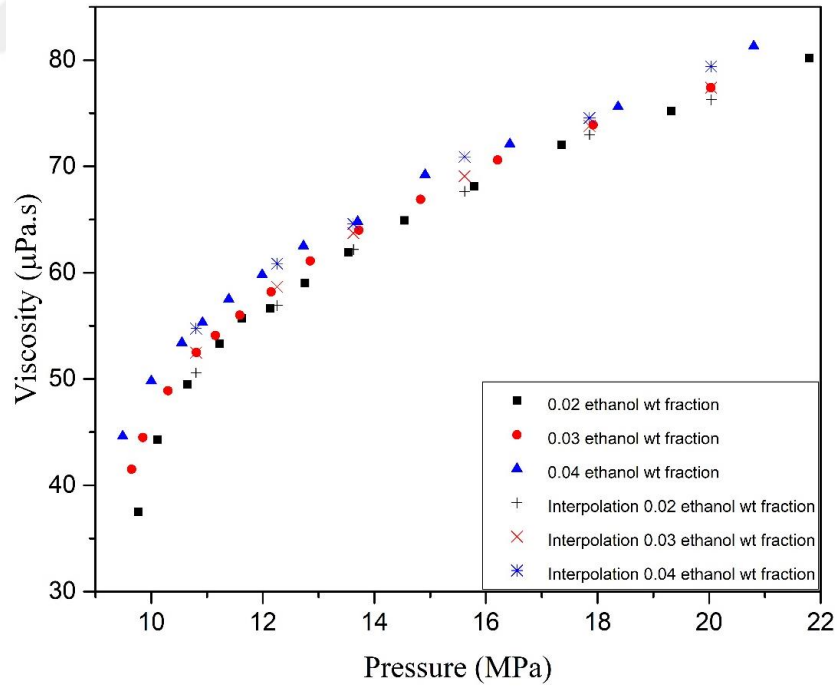


Fig. 4.9. Change of fluid viscosity with pressure for ethanol-CO₂ mixtures with various compositions at 318 K. Data adopted from Tilly *et al.* [36], additional data points were determined by cubic-spline interpolation (see text for details).

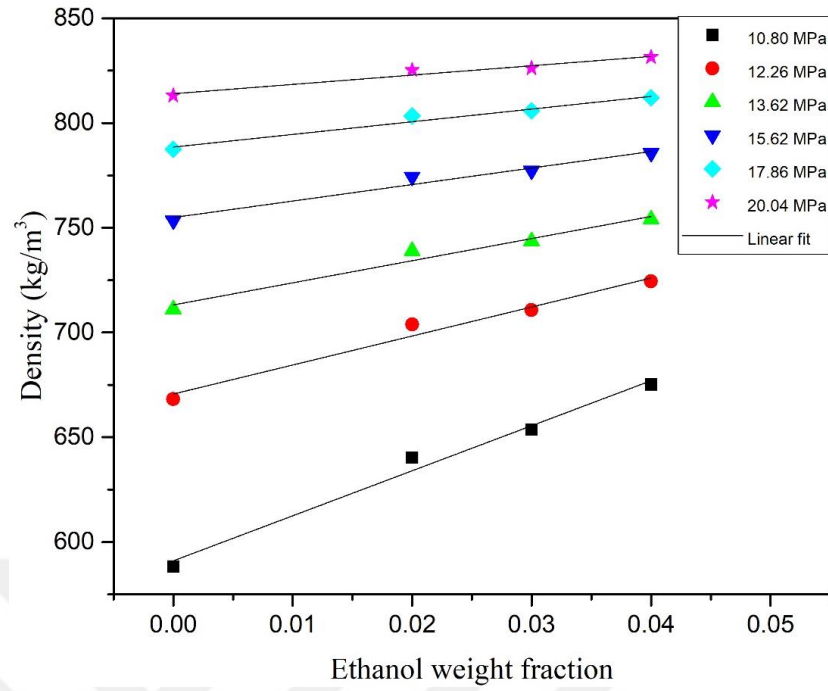


Fig. 4.10. The dependence of the fluid density, ρ , on the ethanol weight fraction, w , at different pressures and a fixed temperature of 318 K. Symbols: data points from Tilly *et al.*[36] ($w \neq 0$) / NIST ($w = 0$), solid lines: linear fits to the data.

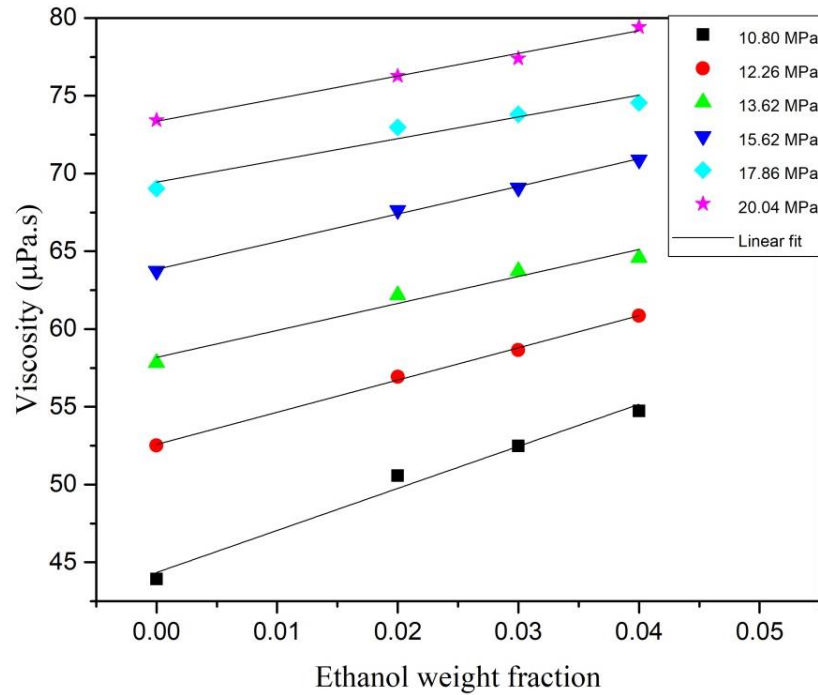


Fig. 4.11. The dependence of the fluid viscosity, μ , on the ethanol weight fraction, w , at different pressures and a fixed temperature of 318 K. Symbols: data points from Tilly *et al.*[36] ($w \neq 0$) / NIST ($w = 0$), solid lines: linear fits to the data.

Table 4.3: Derivatives of Density and Viscosity with Respect to the Weight Fraction of Ethanol in the Mixture at Different Fluid Pressures and at 318 K. Estimated Values of the Derivatives are Based on the Data Adopted from [36] and [86].

Pressure (MPa)	$\left(\frac{d\rho}{dw}\right) (\text{kg.m}^{-3})$	$\left(\frac{d\mu}{dw}\right) (\mu\text{Pa.s})$
10.80	2149.16	270.34
12.26	1384.50	207.06
13.62	1055.87	173.43
15.62	788.25	177.79
17.86	604.98	139.82
20.04	445.44	145.59

A procedure analogous to that used in deriving Eq. 4.1 for S_f^m was used to find the composition sensitivity S_Q^m of the cantilever Q-factor from model Eq. 1.2. The derivative of Q with respect to w (see the details of the derivation in Appendix B) is given as:

$$\begin{aligned}
 S_Q^m = \left(\frac{dQ}{dw}\right)_m &= \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \\
 &\times \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}}\right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}}\right)} \times \left(\frac{1.0553\pi b}{8\rho_c t} + \frac{3.7997\pi b}{16\rho_c t\sqrt{2\text{Re}}} \right) \right) \right. \\
 &\quad \left. - \frac{4\rho_c t}{\pi\rho^2 b} \frac{d\rho}{dw} \right\} \\
 &- \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}}\right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}}\right)} \times \left(\frac{3.7997\pi b\rho}{16\rho_c t\sqrt{2\text{Re}}} \right) \right) \right\} \frac{d\mu}{dw} \Bigg\}
 \end{aligned} \tag{4.2}$$

The sensitivity, S_Q^m , depends on the cantilever parameters f_{vac} , $\rho_c t$, b , cantilever Q-factor, and density and viscosity of the mixture. In addition, the derivatives of density and viscosity with respect to the weight fraction of ethanol in the mixture, $\left(\frac{d\rho}{dw}\right)$, $\left(\frac{d\mu}{dw}\right)$, are

needed to evaluate S_Q^m at a given experimental condition (pressure, temperature, and composition of the mixture).

In order to characterize the performance of our cantilever-based sensors and determine the model sensitivity of composition measurement, the resonant frequencies f_{fluid} and the Q-factors Q of uncoated microcantilevers of two different lengths (150 μm and 200 μm) immersed in ethanol- CO_2 mixtures within the composition range $w = 0 - 0.04$ were measured at 318 K and pressures varying between 10 MPa to 21 MPa. As could be already inferred from model Eqs.1.1 and 1.2, in connection with the compositional dependence of the mixture density and viscosity illustrated by Figs. 4.8 and 4.9, the values of f_{fluid} and Q were observed to change monotonically with w at a particular temperature and pressure. The measured values of f_{fluid} and Q for the two studied cantilevers as a function of w are presented in Figs. 4.12, 4.13, 4.14, and 4.15. Using these values, the model sensitivities S_f^m and S_Q^m were calculated at the particular experimental conditions.

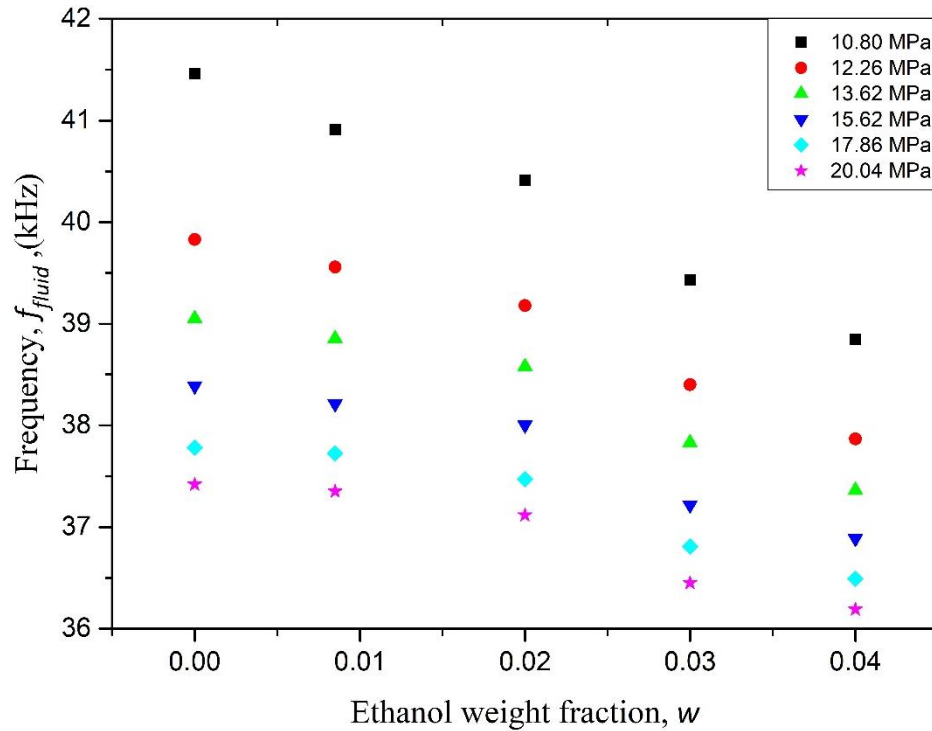


Fig. 4.12. Variation of the cantilever resonant frequency, f_{fluid} , with ethanol weight fraction, w , at 318 K and different pressures. Microcantilever length: 150 μm .

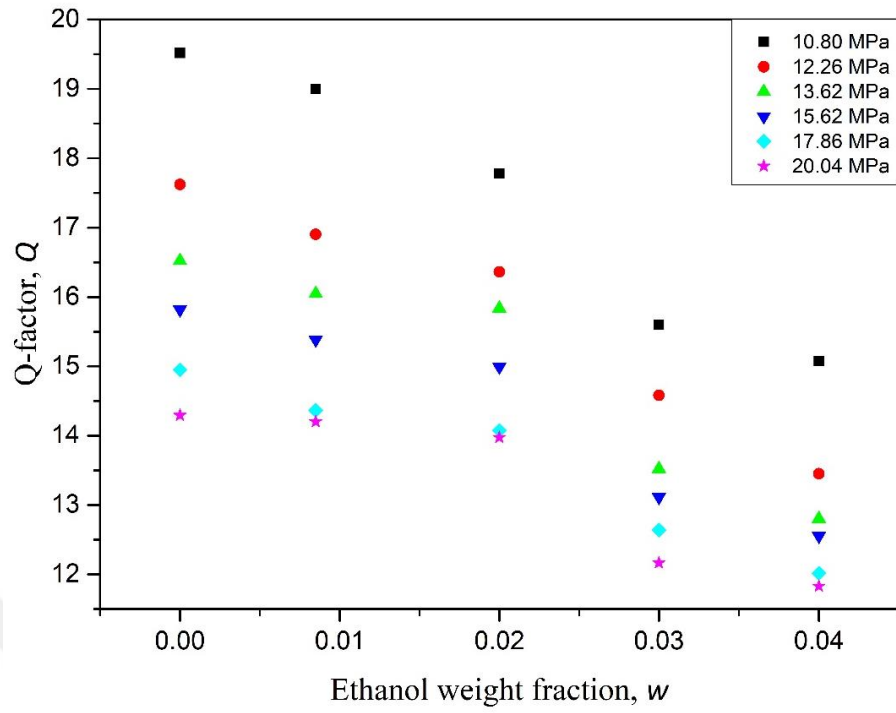


Fig. 4.13. Variation of the cantilever Q-factor, Q , with ethanol weight fraction, w , at 318 K and different pressures. Microcantilever length: 150 μm .

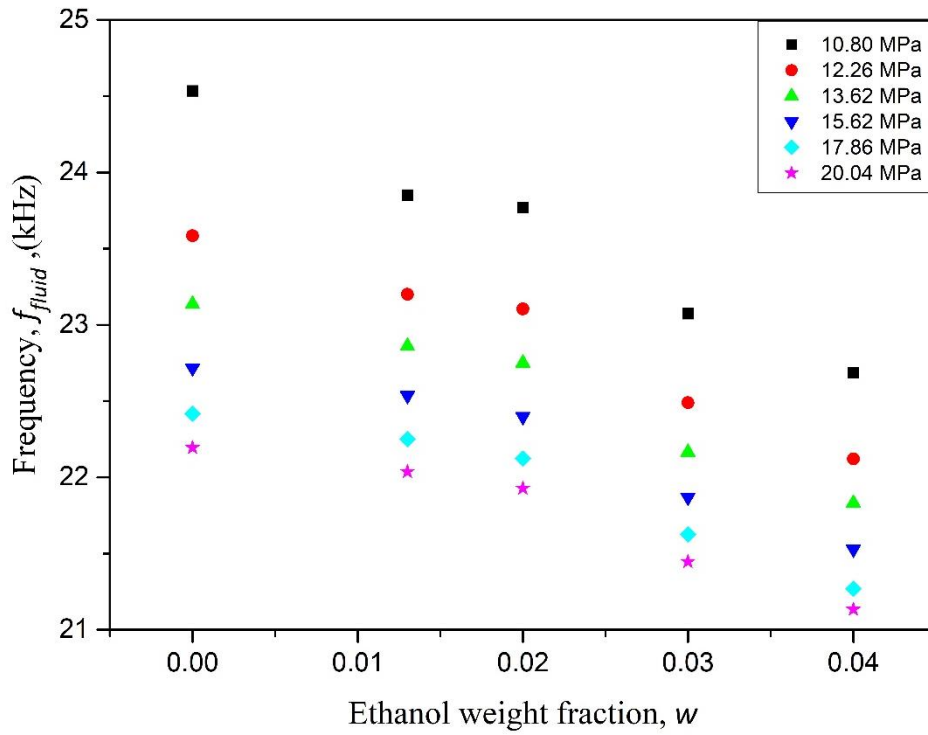


Fig. 4.14. Variation of the cantilever resonant frequency, f_{fluid} , with ethanol weight fraction, w , at 318 K and different pressures. Microcantilever length: 200 μm

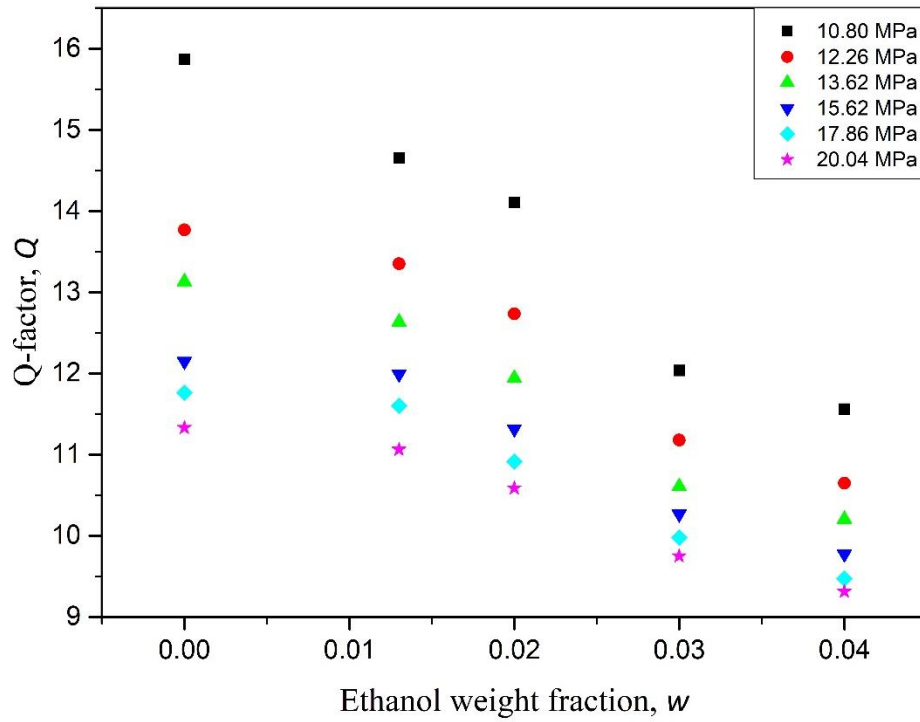


Fig. 4.15. Variation of the cantilever Q-factor, Q , with ethanol weight fraction, w , at 318 K and different pressures. Microcantilever length: 200 μm .

For completeness, the change in the cantilever resonant frequency and Q-factor with pressure for different w and the two studied cantilever lengths is illustrated in Figs 4.16-4.19. In general, the resonant frequencies and Q-factors decrease with increasing pressure at a constant temperature and composition. The resonant frequency decreases due to higher added mass moving along with the cantilever as a result of the increase in the fluid density with increasing pressure. The effective volume of the fluid that is affected by cantilever oscillations increases with the fluid viscosity; thus, the increase in viscosity with increasing pressure further decreases the cantilever resonant frequency. The increase in viscosity also causes a higher drag force and, thus, lowers the Q-factor. At a constant temperature and pressure, higher weight fraction of ethanol in the mixture leads to lowering of both the resonant frequency and the Q-factor due to above described effects of increasing fluid density and viscosity.

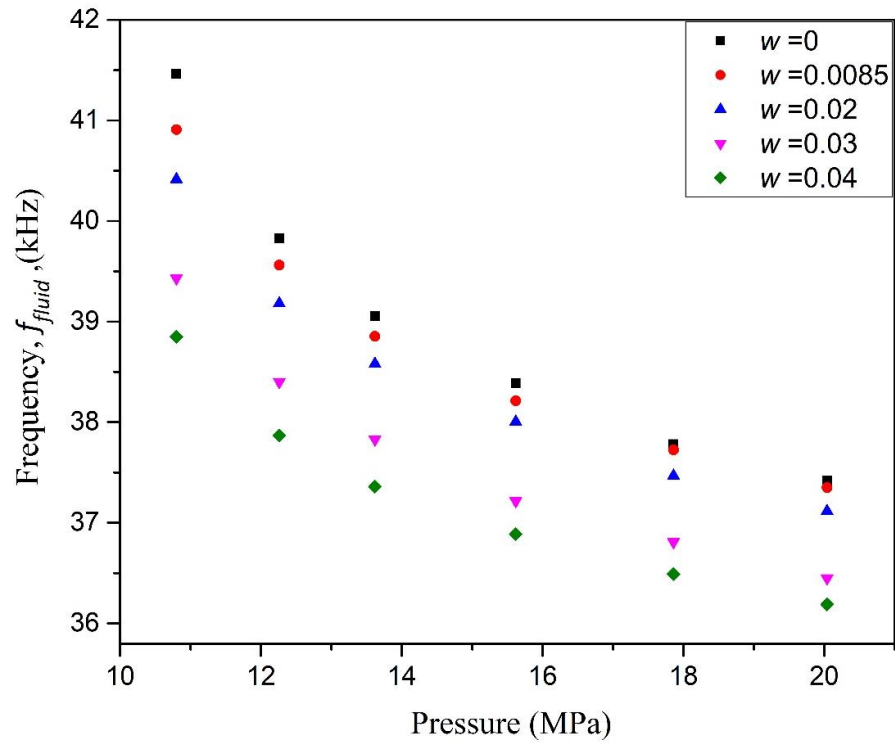


Fig. 4.16. Variation of the cantilever resonant frequency, f_{fluid} , with pressure for different compositions of ethanol-CO₂ binary mixture at 318 K. Microcantilever length: 150 μ m.

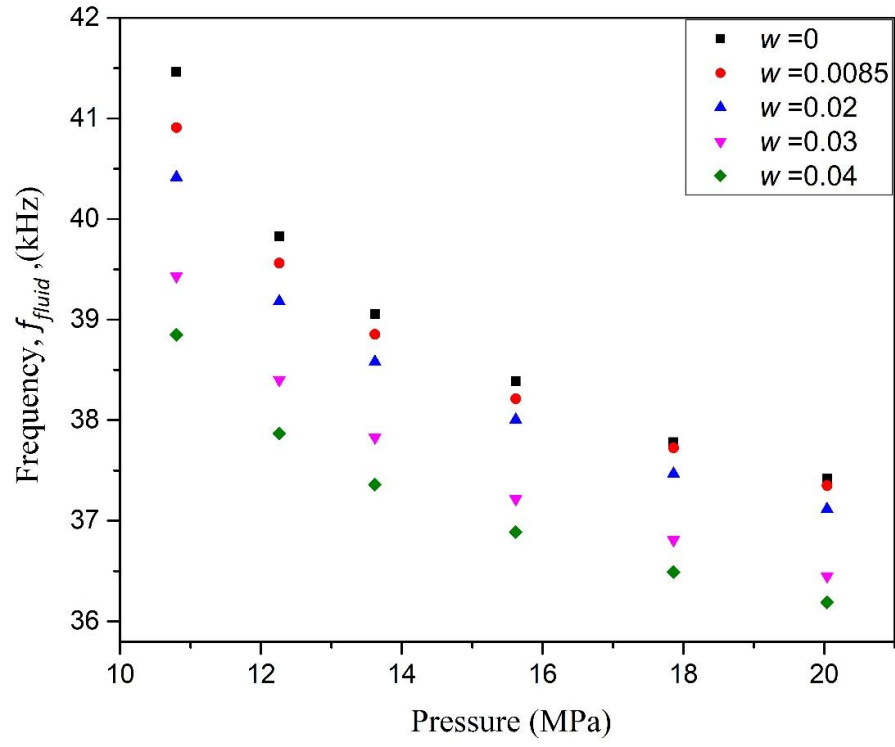


Fig. 4.17. Variation of the cantilever Q-factor, Q , with pressure for different compositions of ethanol-CO₂ binary mixture at 318 K. Microcantilever length: 150 μm .

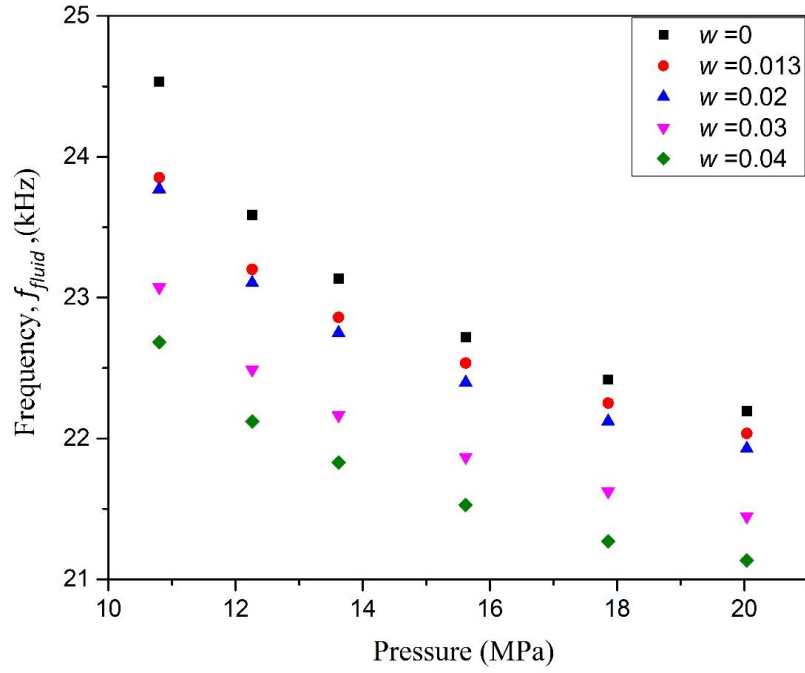


Fig. 4.18. Variation of the cantilever resonant frequency, f_{fluid} , with pressure for different compositions of ethanol-CO₂ binary mixture at 318 K. Microcantilever length: 200 μm .

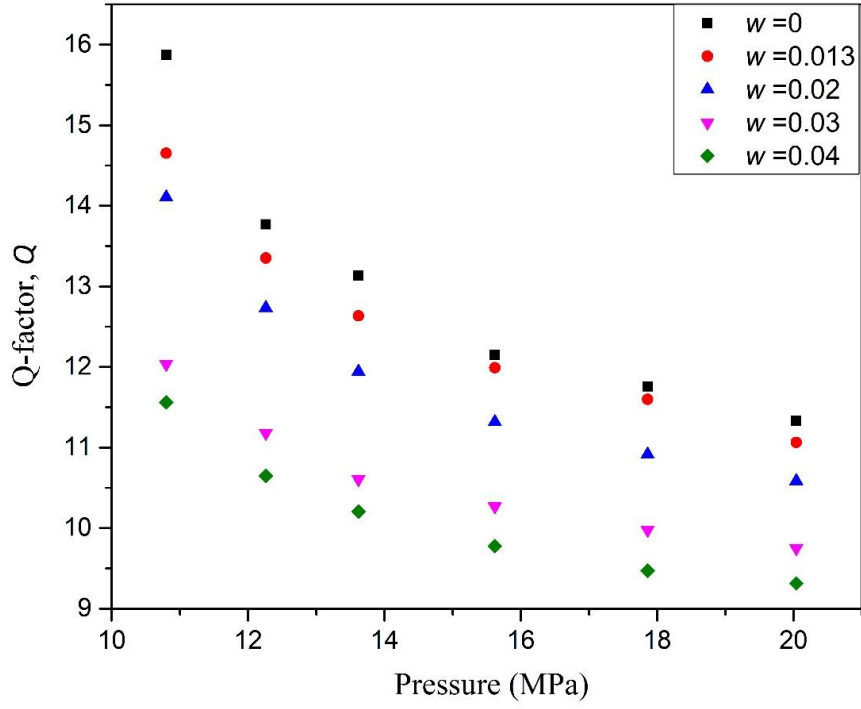


Fig. 4.19. Variation of the cantilever Q-factor, Q , with pressure for different compositions of ethanol- CO_2 binary mixture at 318 K. Microcantilever length: 200 μm .

In order to calculate the model sensitivities S_f^m and S_Q^m at a particular temperature and pressure, the cantilever-related parameters ($f_{vac}, \rho_c t, b$) are also required, in addition to the estimates of composition derivatives of mixture density and viscosity provided in Table 4.3. The necessary cantilever characteristics were obtained using the technique described in our previous study [2]. Briefly, ($f_{vac}, \rho_c t, b$) were regressed from the resonant frequency and Q-factor data recorded with cantilevers immersed in pure CO_2 at a temperature of 318 K and pressure range between 1 MPa and 21 MPa. In particular, the values of ($f_{vac}, \rho_c t, b$) were obtained by minimizing the objective function F (Eq. 4.3), using the experimental values of the cantilever resonant frequency, $f_{fluid,i}$ and Q-factor, Q_i measured in pure CO_2 and the density and viscosity of CO_2 at the given experimental pressure and temperature determined from the NIST Chemistry webbook [86]:

$$F = \sum_i \left\{ \left(f_{fluid,i} - f_{vac} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid,i} b^2}} \right) \right]^{-1/2} \right)^2 + \right.$$

$$\left(Q_i - \frac{\frac{4\rho_{ct}}{\pi\rho b} + (1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid,i} b^2}})}{3.8018 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid,i} b^2}} + 2.7364 \frac{2\mu}{\rho 2\pi f_{fluid,i} b^2}} \right)^2 \quad (4.3)$$

Here, the summation index i runs over all experimental values of $f_{fluid,i}$ and Q_i recorded for pure CO₂ at varying pressures. The resulting cantilever parameters are given in Table 4.4 for the microcantilevers of the length of 150 μm and 200 μm .

Cantilever-related parameters can be in principle determined from independent measurements; however, in practice, it is very challenging to measure these parameters accurately enough. For example, accurate determination of the cantilever density requires the thickness of individual cantilever layers and the density of each layer which are not known precisely for the given cantilever. This in turn imposes limitations on the precision of the measurement of the model sensitivity, fluid density and viscosity. Since the model sensitivity values extracted from the frequency response data using analytical expressions (Eq. 4.1 & 4.2) are very sensitive to the values of cantilever-related parameters.

An alternative to direct measurements of the cantilever characteristic parameters is obtaining these parameters by fitting, using a set of data recorded with a reference fluid of known thermophysical properties over a wide range of pressures and at a constant temperature. In recent studies [1, 2], N₂, Ar and CO₂ were used as the reference fluid to determine the cantilever parameters and it was observed that the cantilever-related parameters obtained through regressions (using Eq. 4.3) agrees well with the actual cantilever-related parameters obtained through other methods. Thus, CO₂ can be used as a reference fluid to determine the cantilever related parameters.

Table 4.4: Cantilever Parameters for the Studied Microcantilevers of Length 150 μm and 200 μm .

Cantilever parameters	Cantilever length 150 μm	Cantilever length 200 μm
$\rho_c t$ (kg/m^2)	0.01375	0.01540
f_{vac} (Hz)	56162	32206
b (μm)	22.66	21.21

Model sensitivities S_f^m and S_Q^m defined by Eqs.4.1 and 4.2 consist of a density term (DT) formed by the compositional derivative of density $\frac{d\rho}{dw}$ with its pre-factor and a viscous term (VT) given by the compositional derivative of viscosity $\frac{d\mu}{dw}$ with its pre-factor. Tables 4.5 and 4.6 summarize the contribution of DT and VT to the sensitivity S_f^m calculated using Eq. 4.1 for $w = 0.04$ and microcantilevers of 150 μm and 200 μm lengths, respectively. Evaluation of Eq. 4.1 for our particular cantilever and fluid characteristics at the studied fluid temperature and pressure shows that VT contributes ~ 8 to 19 % to the value of S_f^m of the 150 μm long cantilever and ~ 11 to 24 % to the value of S_f^m of the 200 μm long cantilever. In both cases, the viscous-term contribution is significant and its relative contribution further increases with increasing fluid pressure. Therefore, VT should not be neglected in the analysis of the compositional sensitivity of cantilever-based measurements, especially when they are carried out in high-pressure fluid mixtures. The same conclusions can be drawn for other studied ethanol weight fractions $w = 0, 0.02$ and 0.03 (data not shown). A similar analysis can be carried out for the model sensitivity S_Q^m defined by Eq. 4.2. Tables 4.7 and 4.8 summarize the contribution of DT and VT to the sensitivity S_Q^m calculated using Eq. 4.2 for ethanol weight fraction $w = 0.04$ and microcantilevers of 150 μm and 200 μm lengths, respectively. In this case, the contribution of VT is dominant in the overall value of S_Q^m , which results from the strong dependence of the Q-factor on the dissipation in the fluid and, thus, the fluid viscosity. In particular, over the studied pressure range, VT contributes ~ 81 to 92 % to the value of S_Q^m .

for the 150 μm long cantilever and ~77 to 91 % to the value of S_Q^m for the 200 μm long cantilever.

Table 4.5: Contribution of the Density and Viscous Terms to the Model Sensitivity $S_f^m(w = 0.04)$ (Hz) for the Microcantilevers of Length 150 μm .

Pressure (MPa)	*Density term (DT)	**Viscous term (VT)	$S_f^m(w = 0.04)$	***VTC contribution to model sensitivity (%)
10.80	-29474.00	-2781.20	-32255.20	8.62
12.26	-17628.00	-1964.00	-19592.00	10.02
13.62	-12931.00	-1575.90	-14506.90	10.86
15.62	-9318.70	-1525.90	-10844.60	14.07
17.86	-6932.90	-1158.50	-8091.40	14.32
20.04	-4989.70	-1159.00	-6148.70	18.85

$$* \text{ Density term (DT)} = - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right)} \times \left\{ \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{dw} \right\}$$

$$** \text{ Viscous term (VT)} = - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right)} \times \left\{ \left(\frac{3.7997\pi b f_{vac}\rho}{16\mu\rho_c t \sqrt{2Re}} \right) \frac{d\mu}{dw} \right\}$$

$$*** \text{ Viscous term contribution (VTC)} = \frac{VT}{DT+VT}$$

Table 4.6: Contribution of the Density and Viscous Terms to the Model Sensitivity $S_f^m(w = 0.04)$ (Hz) for the Microcantilevers of Length 200 μm .

Pressure (MPa)	*Density term (DT)	**Viscous term (VT)	$S_f^m(w = 0.04)$	***VTC contribution to model sensitivity (%)
10.80	-15319.00	-1973.20	-17292.20	11.41
12.26	-9182.40	-1395.30	-10577.70	13.19
13.62	-6744.20	-1120.40	-7864.60	14.25
15.62	-4846.70	-1081.70	-5928.40	18.25
17.86	-3593.30	-818.59	-4411.89	18.55
20.04	-2603.00	-823.04	-3426.04	24.02

Table 4.7: Contribution of the Density and Viscous Terms to the Model Sensitivity $S_Q^m(\mathbf{w} = \mathbf{0.04})$ for the Microcantilevers of length 150 μm .

Pressure (MPa)	$^{\circ}\text{Density term}$ (DT)	$^{\circ\circ}\text{Viscous term}$ (VT)	$S_Q^m(\mathbf{w} = 0.04)$	$^{\circ\circ\circ}\text{VTC}$ contribution to model sensitivity (%)
10.80	-8.40	-36.29	-44.70	81.20
12.26	-4.81	-22.15	-26.96	82.16
13.62	-3.33	-16.59	-19.92	83.27
15.62	-2.01	-15.19	-17.20	88.32
17.86	-1.44	-10.84	-12.28	88.31
20.04	-0.92	-10.44	-11.36	91.91

$$^{\circ}\text{Density term (DT)} = \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \times \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}}\right)^2 - \frac{3.7997\pi pb}{16\rho ct\sqrt{2\text{Re}}}\right)} \times \left(\frac{1.0553\pi b}{8\rho ct} + \frac{3.7997\pi b}{16\rho ct\sqrt{2\text{Re}}} \right) - \frac{4\rho ct}{\pi\rho^2 b} \right] \frac{d\rho}{dw}$$

$$^{\circ\circ}\text{Viscous term (VT)} = -\frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \times \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}}\right)^2 - \frac{3.7997\pi pb}{16\rho ct\sqrt{2\text{Re}}}\right)} \times \left(\frac{3.7997\pi b\rho}{16\rho ct\mu\sqrt{2\text{Re}}} \right) \right] \frac{d\mu}{dw}$$

$$^{\circ\circ\circ}\text{Viscous term contribution (VTC)} = \frac{\text{VT}}{\text{DT} + \text{VT}}$$

Table 4.8: Contribution of the Density and Viscous Terms to the Model Sensitivity $S_Q^m(\mathbf{w} = \mathbf{0.04})$ for the Microcantilevers of Length 200 μm .

Pressure (MPa)	$^{\circ}\text{Density term}$ (DT)	$^{\circ\circ}\text{Viscous term}$ (VT)	$S_Q^m(\mathbf{w} = 0.04)$	$^{\circ\circ\circ}\text{VTC}$ contribution to model sensitivity (%)
10.80	-8.21	-27.64	-35.85	77.10
12.26	-4.40	-17.45	-21.84	79.87
13.62	-3.01	-13.15	-16.16	81.35
15.62	-1.91	-11.75	-13.66	86.00
17.86	-1.33	-8.49	-9.82	86.48
20.04	-0.86	-8.16	-9.02	90.42

Tables 4.9-4.12 summarize the sensitivities S_f^m and S_Q^m calculated for ethanol weight fractions of 0.04, 0.03, 0.02, and 0 using the data summarized in Tables 4.3 and 4.4 and Figs. 4.10-4.15. From Tables 4.9-4.12, it is evident that at a given pressure, temperature, and composition, microcantilevers of length 150 μm exhibit higher values of S_f^m and S_Q^m in comparison to microcantilevers of length 200 μm . This higher sensitivity of shorter cantilevers is a direct consequence of their higher resonant frequency and higher Q-factor. For both cantilever lengths, the sensitivity values decrease with increasing pressure; this is caused by a monotonic increase of the density and viscosity of the fluid mixture with increasing pressure, which subsequently leads to the reduction of f_{fluid} and Q . At a particular temperature and pressure, sensitivity values change with composition in a nonlinear fashion, following the nonlinear dependence of f_{fluid} and Q on the ethanol concentration in the mixture, w . In general, both S_f^m and S_Q^m – or more precisely, their absolute values – increase with decreasing w . This trend then implies a better resolution of composition measurements carried out in low-concentration mixtures and it has a direct consequence for the achievable limit of detection of cantilever-based sensing.

Table 4.9: Model Sensitivity S_f^m (Hz) Calculated Using Eq. 4.1 for the Microcantilever of Length 150 μm .

Pressure (MPa)	$S_f^m(w = 0.04)$	$S_f^m(w = 0.03)$	$S_f^m(w = 0.02)$	$S_f^m(w = 0)$
10.80	-32255.20	-33683.50	-36220.40	-39032.50
12.26	-19592.00	-20414.80	-21664.00	-22732.00
13.62	-14506.90	-15044.50	-15944.60	-16526.30
15.62	-10844.60	-11133.10	-11843.00	-12205.70
17.86	-8091.40	-8299.30	-8743.10	-8967.60
20.04	-6148.70	-6284.20	-6629.20	-6794.60

Table 4.10: Model Sensitivity S_Q^m Calculated Using Eq. 4.2 for the Microcantilever of Length 150 μm .

Pressure (MPa)	$S_Q^m(w = 0.04)$	$S_Q^m(w = 0.03)$	$S_Q^m(w = 0.02)$	$S_Q^m(w = 0)$
10.80	-44.70	-48.46	-54.73	-69.58
12.26	-26.96	-29.64	-33.04	-38.43
13.62	-19.92	-21.04	-23.95	-26.98
15.62	-17.20	-18.32	-20.74	-23.16
17.86	-12.28	-12.91	-14.20	-15.83
20.04	-11.36	-11.96	-13.65	-14.52

Table 4.11: Model Sensitivity S_f^m (Hz) Calculated Using Eq. 4.1 for the Microcantilever of Length 200 μm .

Pressure (MPa)	$S_f^m(w = 0.04)$	$S_f^m(w = 0.03)$	$S_f^m(w = 0.02)$	$S_f^m(w = 0)$
10.80	-17292.20	-18166.40	-19819.90	-21734.40
12.26	-10577.70	-11102.00	-12018.30	-12759.00
13.62	-7864.60	-8218.30	-8872.30	-9319.90
15.62	-5928.40	-6208.00	-6658.50	-6944.80
17.86	-4411.89	-4629.44	-4946.85	-5148.16
20.04	-3426.04	-3578.66	-3818.53	-3959.43

Table 4.12: Model Sensitivity S_Q^m Calculated Using Eq. 4.2 for the Microcantilever of Length 200 μm .

Pressure (MPa)	$S_Q^m(w = 0.04)$	$S_Q^m(w = 0.03)$	$S_Q^m(w = 0.02)$	$S_Q^m(w = 0)$
10.80	-35.85	-39.03	-44.62	-57.59
12.26	-21.84	-23.63	-26.56	-31.01
13.62	-16.16	-16.94	-18.85	-21.93
15.62	-13.66	-14.63	-16.13	-18.25
17.86	-9.82	-10.36	-11.26	-12.69
20.04	-9.02	-9.66	-10.54	-11.64

Limit of Detection (LOD) is the lowest quantity of an analyte that can be distinguished from the blank sample value with a sufficient confidence. In our case, LOD is the smallest ethanol weight fraction in the mixture that can be unambiguously detected. In the literature, different methods can be found to estimate the LOD depending on the complexity of the data obtained from the analytical system and the relationship between the experimentally

measured parameter and the actual quantity of interest [87-99]. Two of these approaches for LOD estimation are illustrated in Fig. 4.20. For the sake of brevity, let us consider only the compositional measurements based on recording the cantilever resonant frequency f_{fluid} ; LOD estimation from the Q-factor measurements can be carried out in an analogous manner. The most rigorous method makes direct use of the known functional relationship between f_{fluid} and the mixture composition w . This non-linear function $f_{fluid} = f_{fluid}(w)$ can be derived using Sader's model Eq. 1.1, in combination with the reference data [36] on the density and viscosity of ethanol-CO₂ mixtures, and it is schematically illustrated by the solid red curve shown in Fig. 4.20. From the repeated measurements carried out with pure CO₂, we know the values of $f_{fluid}(w = 0)$ and also the standard deviations of the measurements of f_{fluid} at $w = 0$, $\sigma_f(w = 0)$ that quantify the precision with which f_{fluid} can be measured. Assuming we can distinguish with confidence greater than 99.6 % the values of f_{fluid} that are separated by $\pm 3\sigma_f$, we can calculate the resonant frequency $f_{fluid}(w = w_{LOD})$ for the minimum detectable weight fraction of ethanol w_{LOD} as:

$$f_{fluid}(w = w_{LOD}) = [f_{fluid}(w = 0) - 3\sigma_f(w = 0)] \quad (4.4)$$

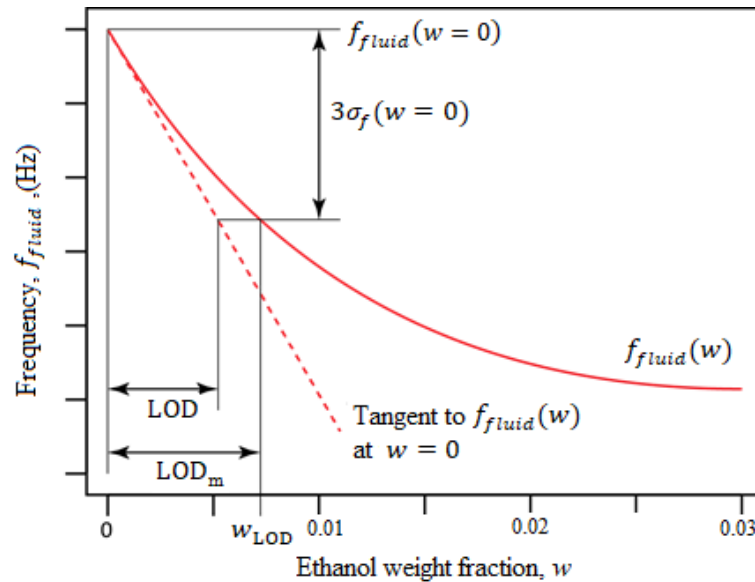


Fig. 4.20. Illustration of Determination of the Limit of Detection (LOD)

Subsequently, we can use the known functional relationship $f_{fluid} = f_{fluid}(w)$ to find the actual value of w_{LOD} corresponding to $f_{fluid}(w = w_{LOD})$; w_{LOD} is then precisely equal to

the true LOD indicated as LOD_m in Fig. 4.20. Alternatively, we can approximate the nonlinear function $f_{fluid} = f_{fluid}(w)$ in a small neighborhood of the point $w = 0$ with a line, following the approach based on IUPAC recommendation [100] and discussed in detail by Ramos *et al.* [87]. This linear approximation is illustrated in Fig. 4.20 by the dashed line which forms a tangent to the graph of $f_{fluid} = f_{fluid}(w)$ at $w = 0$, with a slope S that corresponds to the sensitivity df_{fluid}/dw evaluated at $w = 0$. Within the linear approximation, the LOD can be estimated as:

$$LOD = \frac{k_d \sigma_b}{S} \quad (4.5)$$

Here, σ_b is the standard deviation of the blank (sample with $w = 0$) and k_d is a number that is chosen according to the desired confidence level. As mentioned above, $k_d = 3$ implies 99.6% confidence level and it is strongly recommended. Consequently, in our particular case, LOD can be defined as:

$$LOD_f = \frac{3\sigma_f}{S_f^m(w=0)} \quad (4.6)$$

$$LOD_Q = \frac{3\sigma_Q}{S_Q^m(w=0)} \quad (4.7)$$

where σ_f and σ_Q are the standard deviations of the resonant frequency and the Q-factor of the cantilevers measured in pure CO_2 ($w = 0$) and the values of $S_f^m(w = 0)$ and $S_Q^m(w = 0)$ are obtained using Eq. 4.1 and Eq. 4.2. For the purpose of calculating LOD, absolute values of sensitivities are used.

Tables 4.13 and 4.14 summarize the numerical values of LOD_f and LOD_Q calculated from Eqs. 4.6 and 4.7 using the standard deviations of the resonant frequency and the Q-factor of microcantilevers immersed in pure CO_2 at different pressures. For the purpose of LOD calculations, the values of $S_f^m(w = 0)$ and $S_Q^m(w = 0)$ for the 150 μm and 200 μm long microcantilevers were taken from Tables 4.9-4.12. The comparison of Tables 4.13(a) and 4.14(a) shows that the minimum detectable weight fraction of ethanol determined from the measurement of f_{fluid} and Q at the pressure of 10.8 MPa with the 150 μm long cantilever was 0.0009 and 0.0043, respectively. Similarly, for the 200 μm long cantilever at the same pressure, the minimum detectable ethanol weight fraction determined from the

measurement of f_{fluid} and Q was 0.0018 and 0.0100, respectively (compare Tables 4.13(b) and 4.14(b)). A similar relationship between LOD_f and LOD_Q was observed at all studied pressures.

Table 4.13: Limit of Detection LOD_f of Microcantilever-Based Measurements at 318 K and Different Pressures. (a) Microcantilever Length: 150 μm and (b) Microcantilever Length: 200 μm .

(a)

Pressure (MPa)	10.80	12.26	13.62	15.62	17.86	20.04
Standard deviation σ_f (Hz)	11.58	11.21	17.44	12.35	6.35	16.14
$S_f^m(w = 0)$	-	-	-	-	-	-
	39032.50	22732.00	16526.30	12205.70	8967.60	6794.60
LOD_f (ethanol wt fraction)	0.0009	0.0015	0.0032	0.0030	0.0021	0.0071

(b)

Pressure (MPa)	10.80	12.26	13.62	15.62	17.86	20.04
Standard deviation σ_f (Hz)	13.24	20.86	13.42	21.85	12.17	16.00
$S_f^m(w = 0)$	-	-	-	-	-	-
	21734.40	12759.00	-9319.90	-6944.80	-5148.16	-3959.43
LOD_f (ethanol wt fraction)	0.0018	0.0049	0.0043	0.0094	0.0071	0.0121

Table 4.14: Limit of Detection LOD_Q of Microcantilever-Based Measurements at 318 K and Different Pressures. (a) Microcantilever Length: 150 μm and (b) Microcantilever Length: 200 μm .

(a)

Pressure (MPa)	10.80	12.26	13.62	15.62	17.86	20.04
Standard deviation σ_Q	0.10	0.13	0.15	0.11	0.11	0.10
$S_Q^m(w = 0)$	-69.58	-38.43	-26.98	-23.16	-15.83	-14.52
LOD_Q (ethanol wt fraction)	0.0043	0.0101	0.0172	0.0147	0.0206	0.0215

(b)

Pressure (MPa)	10.80	12.26	13.62	15.62	17.86	20.04
Standard deviation σ_Q	0.19	0.02	0.10	0.12	0.13	0.08
$S_Q^m(w = 0)$	-57.59	-31.01	-21.93	-18.25	-12.69	-11.64
LOD_Q (ethanol wt fraction)	0.0100	0.0019	0.0135	0.0201	0.0298	0.0213

From the above comparison of the values of LOD_f and LOD_Q , it is clear that the resonant frequency is a more sensitive indicator for measuring the mixture composition at an arbitrary fluid pressure. Thus, the model sensitivity S_f^m given by Eq. 4.1 can be used to find the true LOD of ethanol in ethanol-CO₂ mixtures. Since LOD also depends on the standard deviation of the measurements of f_{fluid} , the stability of the resonant frequency during the measurement and the precision of its determination are important. The LOD analysis shows that the shorter 150 μm cantilever has a higher measurement sensitivity and, hence, a lower achievable LOD. Therefore, short-length cantilevers are suggested for high-resolution micro-sensing of the composition of fluid mixtures.

4.3 Viscosities of ethanol-CO₂ binary mixtures at high pressures

The viscosities of five ethanol-CO₂ binary mixtures with compositions ranging from 0.290 to 0.882 weight fraction of ethanol were measured in the temperature range of 308 to 333 K and the pressure range of 7 to 33 MPa. All the measurements were carried out in the region where ethanol-CO₂ mixtures formed a single phase. This is demonstrated as E1 region in Fig. 4.21 and the region below the bubble point curves for ethanol-CO₂ mixtures is designated as E2. The bubble point curves [101-104] for ethanol-CO₂ mixtures taken from the literature are also plotted in Fig. 4.21 and the region is labelled as E2. During our measurements, we made sure that our experimental conditions were above the E2 region and measurements were performed in the single phase region.

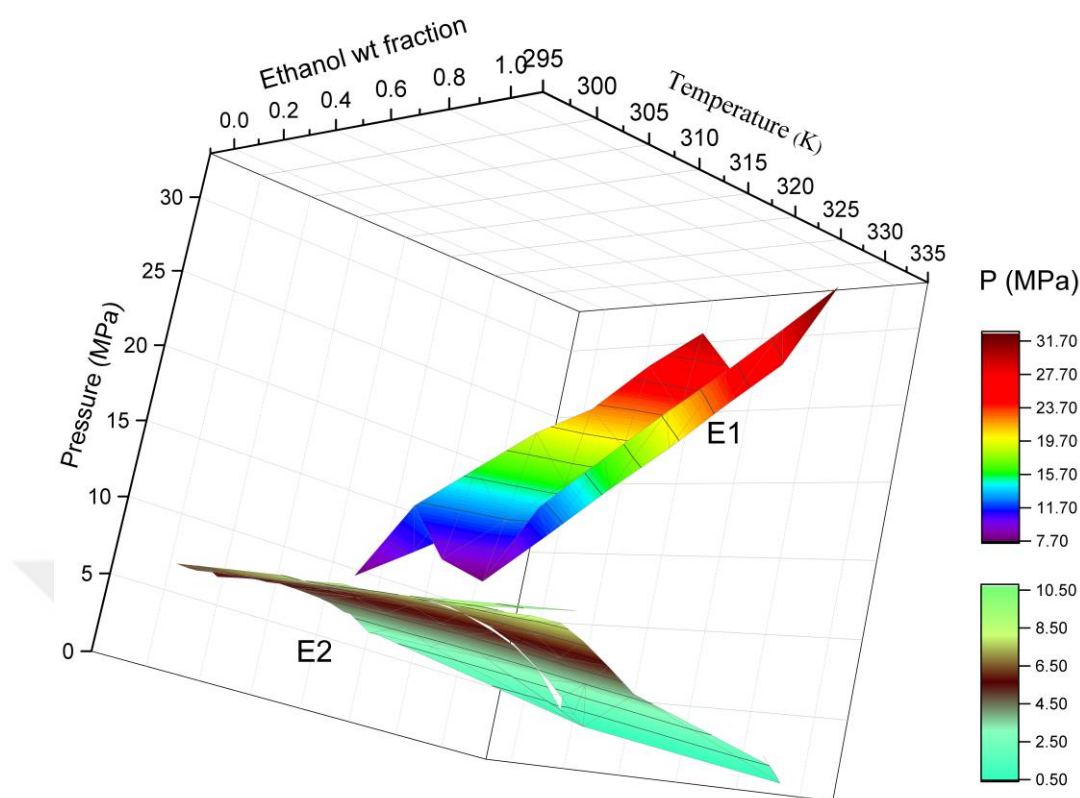


Fig. 4.21. Temperature, pressure and composition ranges of the measurements in this work (Upper region E1), bubble point curves of ethanol-CO₂ mixtures (Lower region E2: Data from literature [101-104]).

Ethanol-CO₂ mixtures were prepared by successive transfer of ethanol and CO₂ to the high-pressure vessel. The amount of each fluid transferred to the vessel was determined gravimetrically using a balance with an accuracy of ± 0.1 gram. First, the mass of the empty vessel was measured using the balance and then, a certain amount of liquid ethanol was placed into the vessel using a syringe and the mass of the vessel was measured and recorded. Subsequently, CO₂ was transferred to the vessel using a TELEDYNE ISCO D Series syringe pump (see Fig. 3.2(b) for illustration) and the mass of the vessel with both fluids was again measured and recorded. Finally, the masses of the empty vessel and ethanol were subtracted from the total mass of the filled vessel to determine the amount of CO₂ placed into the vessel. Measured fluid masses and calculated mixture compositions stated in terms of ethanol weight fractions in the mixture, w , together with their respective uncertainties, are given in Table 4.15.

In this study, the density of a particular ethanol-CO₂ mixture was determined by dividing the total mass of the fluid inside the vessel by the volume of the vessel. The volume of the empty vessel was approximately 50-mL but it decreased after placing cantilever die, Teflon housing and copper coil in it. To determine the empty available volume of the vessel, high pressure CO₂ was used. The vessel was filled with CO₂ using TELEDYNE ISCO D Series syringe pump at room temperature (298 K) and the pressure of the vessel was recorded once it was filled. The mass of the CO₂ was calculated gravimetrically by using a balance with an accuracy of ± 0.1 gram. NIST data was used to obtain the density of the CO₂ at the recorded temperature and pressure [86]. The volume was measured by dividing the mass of CO₂ (39.3 ± 0.1 g) with the density of CO₂ (915.64 kg/m^3) and the volume obtained was 42.92 ± 0.15 mL. This volume was used to determine the density of all ethanol-CO₂ mixtures used in this study. The density values of different ethanol-CO₂ mixtures are given in Table 4.15.

Table 4.15: Measured Values of Fluid Mass, Calculated Mixture Compositions and Densities together with Uncertainties in Measurements of Masses, Densities and Mixture Compositions.

Measured value	Experiment#01	Experiment#02	Experiment#03	Experiment#04	Experiment#05
Empty vessel mass (g)	2185.9 ± 0.1	2185.9 ± 0.1	2186.0 ± 0.1	2185.9 ± 0.1	2185.9 ± 0.1
Ethanol mass (g)	10.2 ± 0.1	16.5 ± 0.1	21.1 ± 0.1	26.3 ± 0.1	30.5 ± 0.1
CO ₂ mass (g)	25.0 ± 0.1	19.9 ± 0.1	14.5 ± 0.1	8.9 ± 0.1	4.1 ± 0.1
Total mass (g)	2221.1 ± 0.1	2222.3 ± 0.1	2221.6 ± 0.1	2221.1 ± 0.1	2220.5 ± 0.1
Ethanol weight fraction, w	0.290 ± 0.004	0.453 ± 0.004	0.593 ± 0.005	0.747 ± 0.005	0.882 ± 0.005
Density of ethanol-CO ₂ mixture (kg/m^3)	820.13 ± 4.39	848.09 ± 4.46	829.45 ± 4.42	820.13 ± 4.39	806.15 ± 4.36

The resonant frequencies, f_{fluid} and the Q-factors, Q of uncoated microcantilever of length $200 \text{ }\mu\text{m}$ immersed in ethanol-CO₂ mixtures within the composition range $w = 0.290 - 0.882$ were measured at a temperature range of 308 to 333 K and a pressure range of 7 to 33 MPa. We used the $200 \text{ }\mu\text{m}$ long cantilever of chip-2 in this study. The average relative standard deviations of the measured resonant frequency and Q-factor over the whole studied range of temperatures were 0.08 % and 0.31 %, respectively, while the

maximum relative standard deviations were 0.14 % and 0.84 %, respectively. The measured resonant frequency and Q-factor data for the studied conditions is given in Appendix D (Table D1).

Resonant frequencies and Q-factors measured for ethanol-CO₂ mixtures with various compositions at different temperatures are given in Figs. 4.22, 4.23 and 4.24. As shown in Fig. 4.24, the resonant frequency does not change significantly with temperature at a constant density at low ethanol weight fractions. This implies that it would be difficult to extract accurate viscosities from the resonant frequency. This is not too surprising since inspection of Eq. 1.1 shows that resonant frequency weakly depends on viscosity of the fluid. In our recent study on sensitivity analysis of cantilevers, we showed that the change in Q-factor with ethanol weight fraction is dominated by the viscous term and its contribution to the change was found to be in the range of 77 to 91 % for the 200 μm long cantilever at high pressures [84]. Therefore Q-factor is more appropriate than resonant frequency to measure the viscosity of the fluid.

Change in Q-factor with ethanol weight fraction in ethanol-CO₂ mixtures at different temperatures is shown in Fig. 4.22. As shown in Fig. 4.22, Q-factors decrease with increasing ethanol weight fraction at a fixed temperature which implies that viscosity increases with ethanol weight fraction. The Q-factor decreases because of the higher drag force due to increasing viscosity. The Q-factors were also plotted as a function of temperature at each composition in Fig. 4.23 which show that for a mixture composition of fixed density, Q-factor increases with increasing temperature. The increase in Q-factor is due to the lower drag force because of the decreasing viscosity.

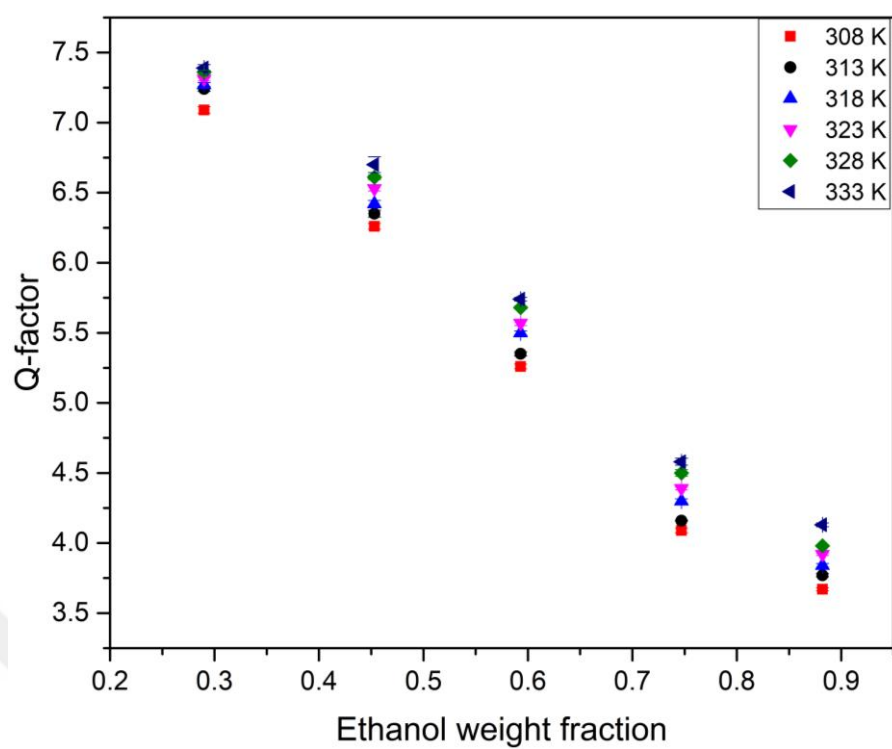


Fig. 4.22. Variation of Q-factor with ethanol weight fraction at different temperatures

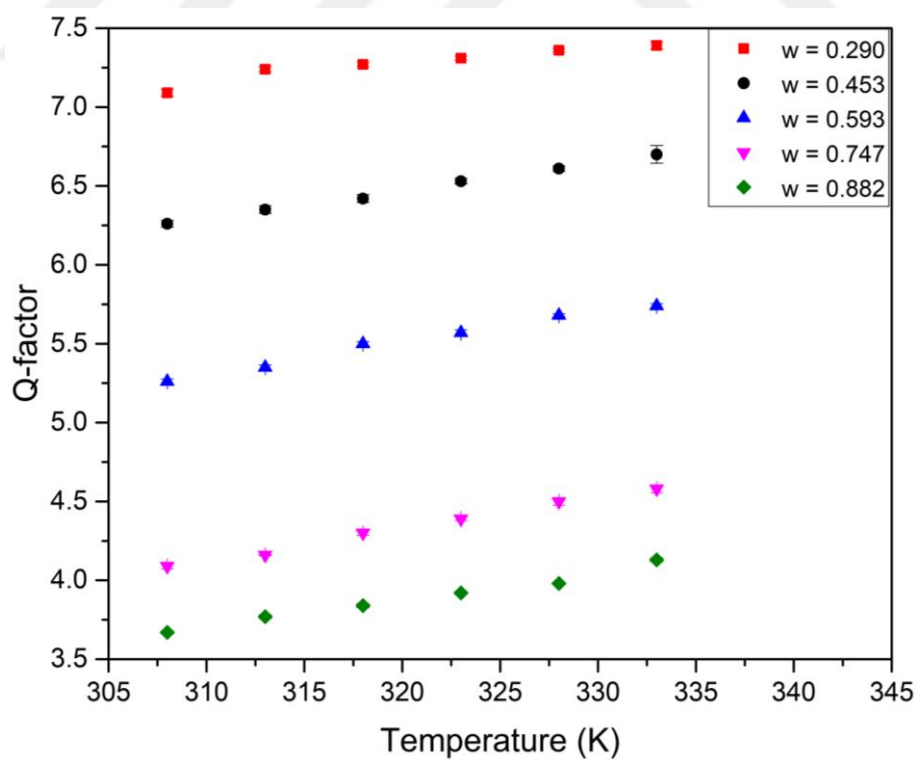


Fig. 4.23. Variation of Q-factor with temperature for different ethanol-CO₂ mixtures.

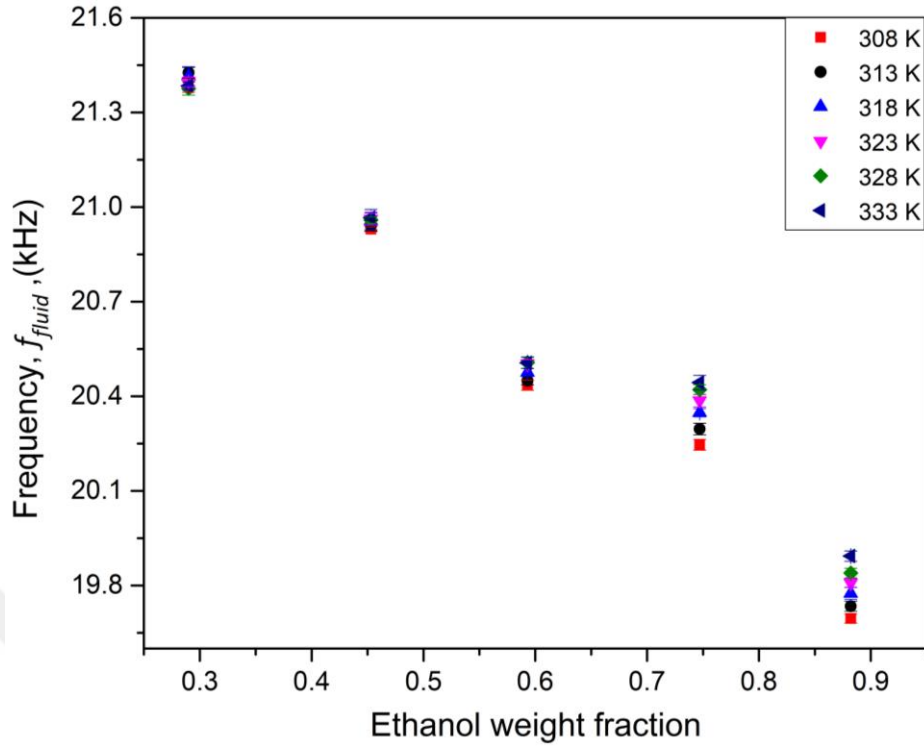


Fig. 4.24. Variation of resonant frequency with ethanol weight fraction at different temperatures.

It is possible to extract ρ and μ from Q and f_{fluid} data by solving Eqs.1.1 and 1.2 simultaneously. However, if the density of the mixture is known, viscosity can be extracted just from Eq.1.2 using the measured Q -factor and the resonant frequency. In order to extract the viscosity of ethanol- CO_2 mixtures using Eq.1.2, the cantilever-related parameters ($f_{vac}, \rho_c t, b$) are also required. The necessary cantilever characteristic parameters were obtained using the technique described in section 4.2. The cantilever parameters, ($f_{vac}, \rho_c t, b$) were regressed from the resonant frequency and Q -factor data recorded with the same cantilever immersed in pure CO_2 at a temperature of 323 K and a pressure range between 1 MPa and 21 MPa. The resulting cantilever parameters are: $\rho_c t = 0.01468 \text{ kg/m}^2$, $f_{vac} = 32231 \text{ Hz}$ and $b = 21.21 \text{ }\mu\text{m}$. With these parameters, Eq. 1.2 was solved for viscosity at each condition. The cantilever-related parameters obtained using CO_2 as the reference fluid at 323 K agrees well with the parameters obtained using CO_2 as reference fluid at 318 K.

The viscosities of the fluid mixtures extracted using Eq. 1.2 are given in Table 4.16. For a particular ethanol-CO₂ mixture composition, viscosity decreases with increasing temperature at a constant density.



Table 4.16:Viscosities of Ethanol-CO₂ Mixtures at Different Conditions and the Relative Difference Between the Experimental Measured Viscosities and Calculated by Different Equations.

					Relative difference (%) calculated by:	
Ethanol weight fraction	T/K	P/MPa	$\rho/\text{kg.m}^{-3}$	Viscosity (10^{-6} Pa.s)	Refutas equation (Eq. (4.8))	Chung equation (Eq. (4.11))
w= 0.290	308	7.83	820.13±4.39	182.73±1.04	31.43	55.32
	313	10.44	820.13±4.39	174.37±0.75	28.83	51.89
	318	13.14	820.13±4.39	173.08±0.78	29.14	51.59
	323	15.83	820.13±4.39	170.81±0.58	28.78	50.96
	328	18.64	820.13±4.39	168.35±0.54	28.01	50.04
	333	21.42	820.13±4.39	166.91±1.42	27.81	49.76
w=0.453	308	12.36	848.09±4.46	234.46±1.49	2.13	39.35
	313	15.91	848.09±4.46	227.46±1.82	2.65	37.49
	318	19.43	848.09±4.46	222.21±1.78	2.69	36.30
	323	22.23	848.09±4.46	213.89±1.17	4.41	33.76
	328	26.46	848.09±4.46	208.93±1.26	4.85	32.16
	333	30.05	848.09±4.46	202.86±3.78	5.85	30.28
w=0.593	308	9.04	829.45±4.42	335.50±2.27	8.01	47.19
	313	12.52	829.45±4.42	323.40±1.89	7.35	45.15
	318	16.02	829.45±4.42	303.95±1.51	9.60	40.87
	323	19.60	829.45±4.42	296.19±2.12	8.76	39.68
	328	23.29	829.45±4.42	284.33±1.05	9.73	36.88
	333	26.98	829.45±4.42	277.14±1.59	8.87	35.93
w=0.747	308	7.78	820.13±4.39	582.23±4.04	4.76	54.14
	313	11.67	820.13±4.39	560.89±0.82	8.82	52.64
	318	15.69	820.13±4.39	522.43±4.13	7.00	47.67
	323	19.48	820.13±4.39	501.29±2.71	7.56	45.17
	328	23.57	820.13±4.39	472.80±5.39	7.03	41.72
	333	27.49	820.13±4.39	455.49±5.24	7.80	39.68
w=0.882	308	12.28	806.15±4.36	723.31 ±4.72	0.77	25.46
	313	16.42	806.15±4.36	680.72 ±4.83	0.14	21.84
	318	20.45	806.15±4.36	654.88 ±5.57	2.79	20.13
	323	24.32	806.15±4.36	625.87 ±3.67	4.71	17.80

	328	28.39	806.15±4.36	607.56 ±2.48	7.66	16.60
	333	32.55	806.15±4.36	560.20 ±3.84	5.56	10.54

The viscosity isotherms of ethanol-CO₂ mixture are plotted as a function of ethanol weight fraction at different pressures in Figs. 4.25-4.30. The viscosity of the mixture increases with ethanol weight fraction at fixed temperatures as expected since the viscosity of pure ethanol is much higher than pure CO₂.

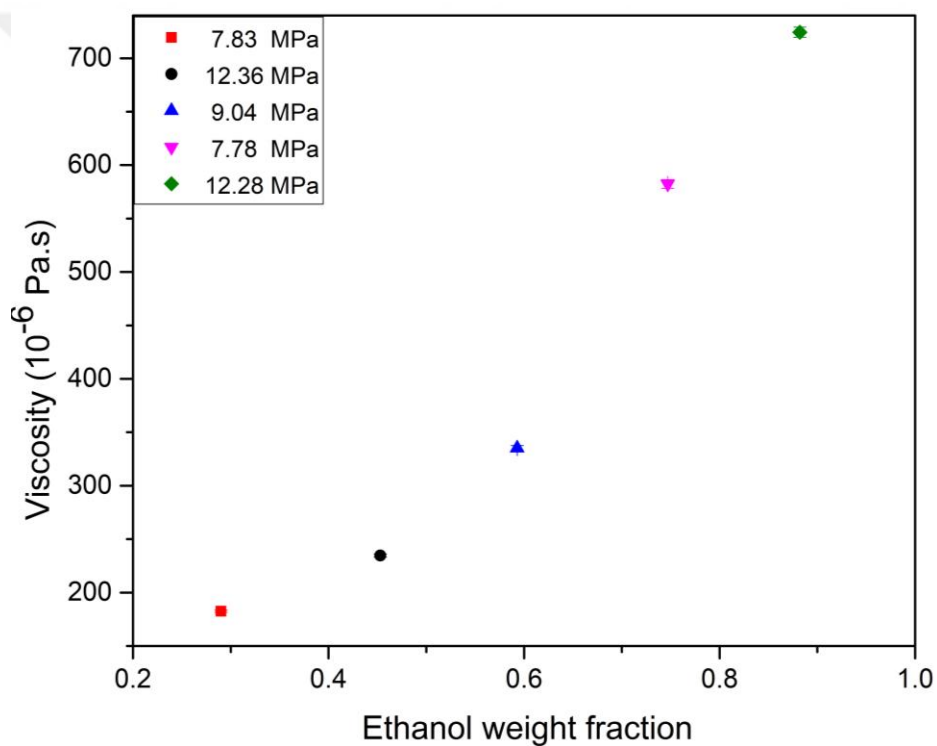


Fig. 4.25. Variation of the fluid viscosity with ethanol weight fraction at temperature of 308 K.

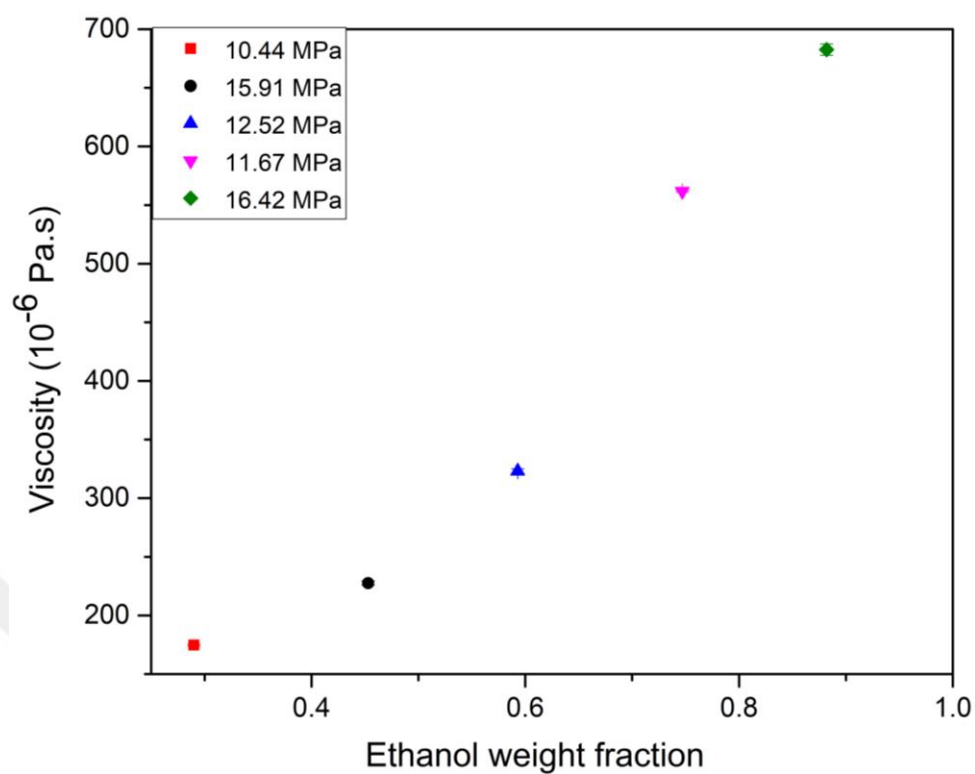


Fig. 4.26. Variation of the fluid viscosity with ethanol weight fraction at temperature of 313 K.

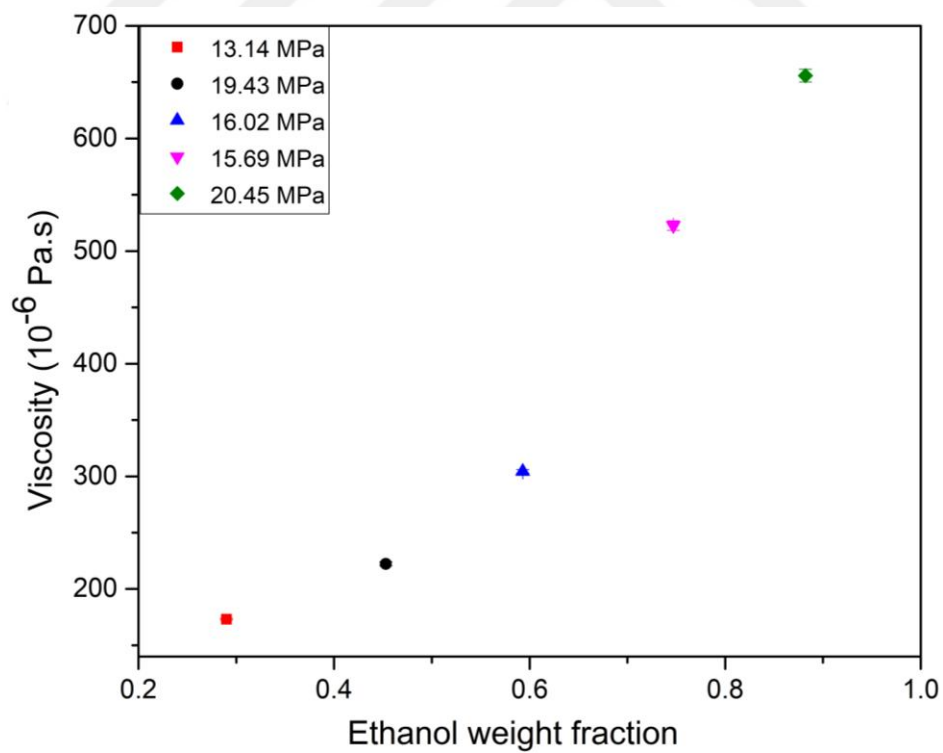


Fig. 4.27. Variation of the fluid viscosity with ethanol weight fraction at temperature of 318 K.

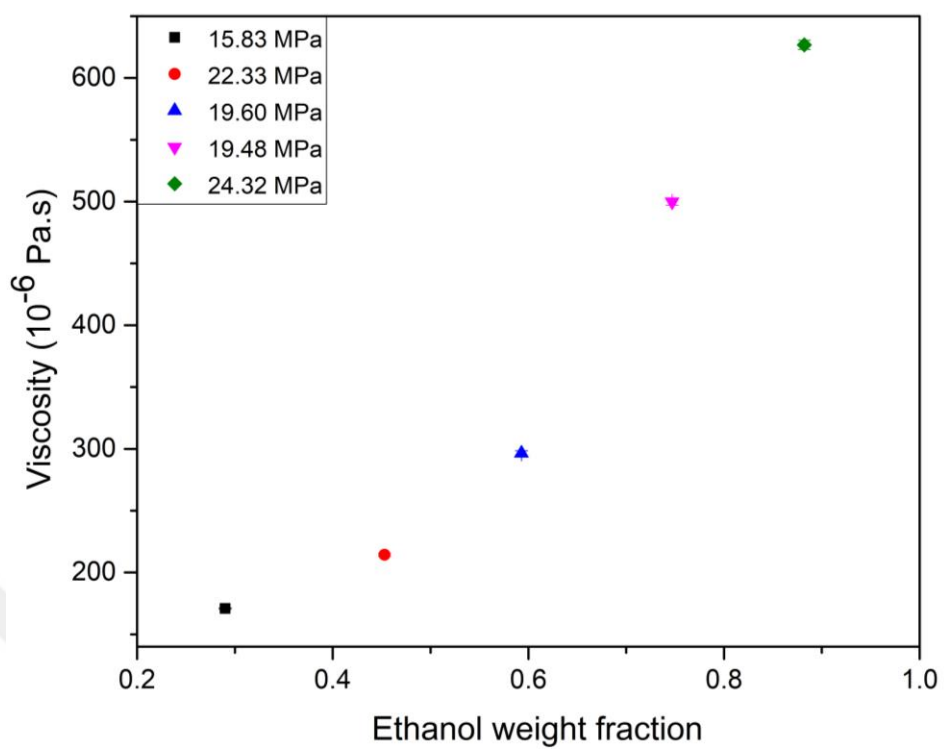


Fig. 4.28. Variation of the fluid viscosity with ethanol weight fraction at temperature of 323 K.

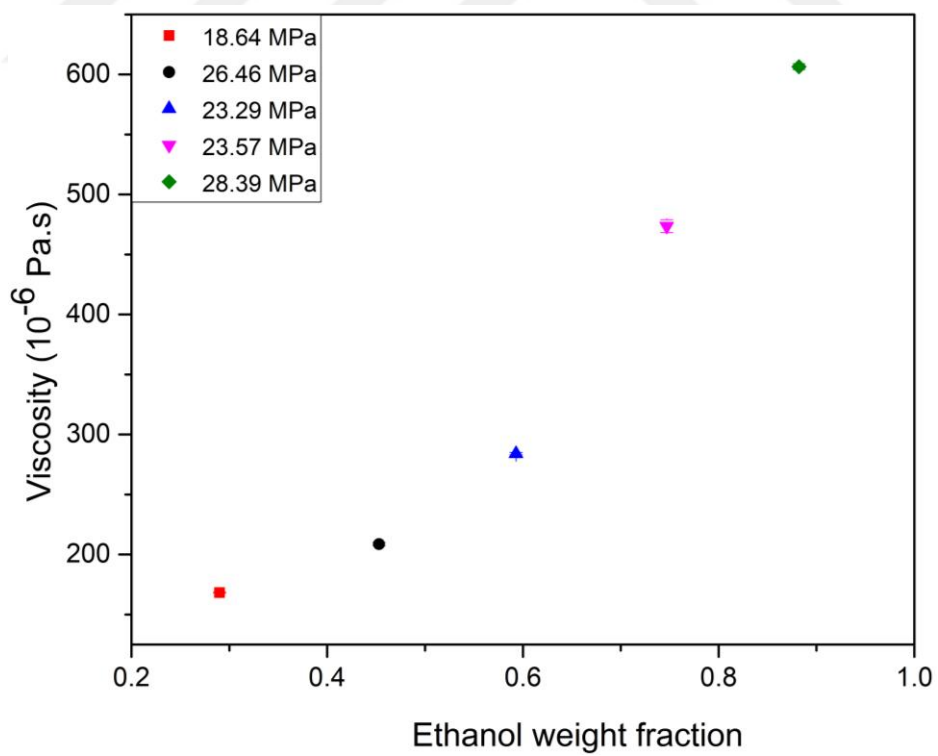


Fig. 4.29. Variation of the fluid viscosity with ethanol weight fraction at temperature of 328 K.

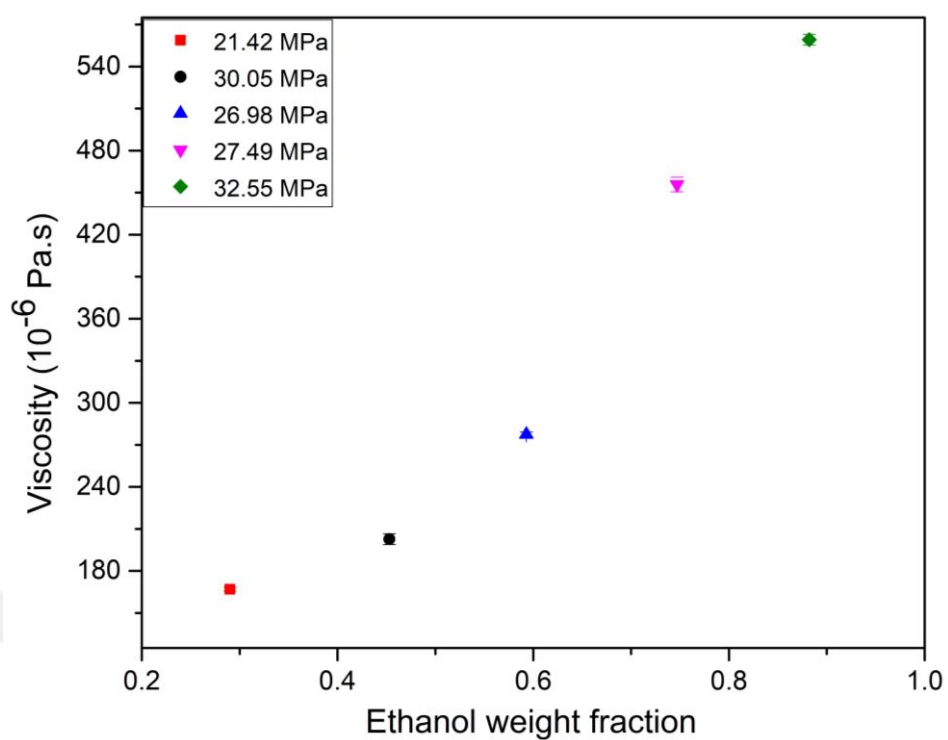


Fig. 4.30. Variation of the fluid viscosity with ethanol weight fraction at temperature of 333 K.

The temperature dependency of viscosity of ethanol-CO₂ mixtures was studied and it was observed that the viscosity decreased with increasing temperature as shown in Figs. 4.31-4.35.

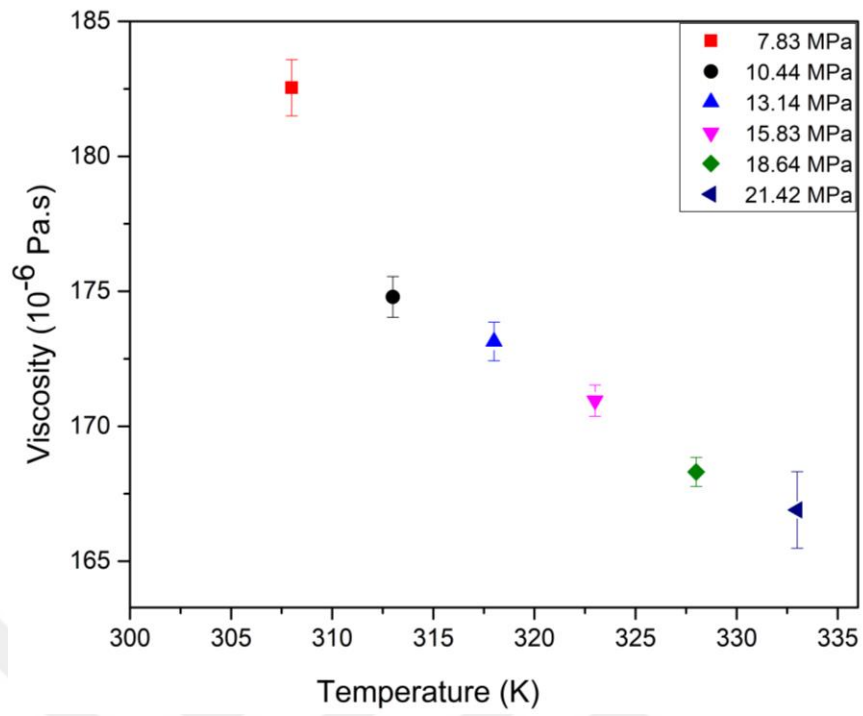


Fig. 4.31. Variation of the fluid viscosity with temperature at ethanol weight fraction, $w = 0.290$.

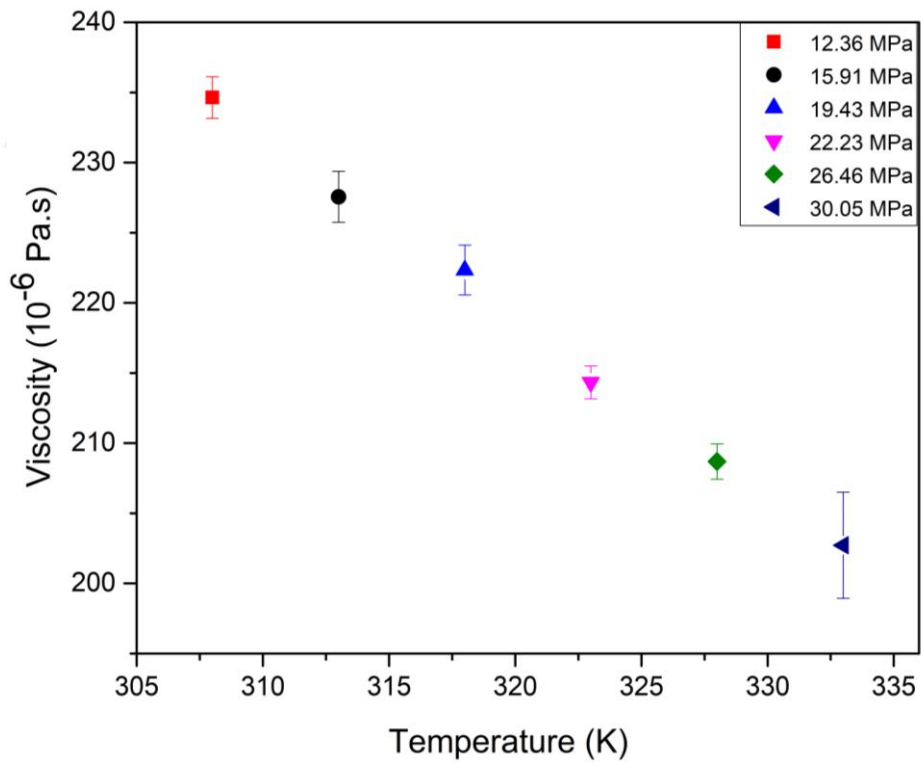


Fig. 4.32. Variation of the fluid viscosity with temperature at ethanol weight fraction, $w = 0.453$.

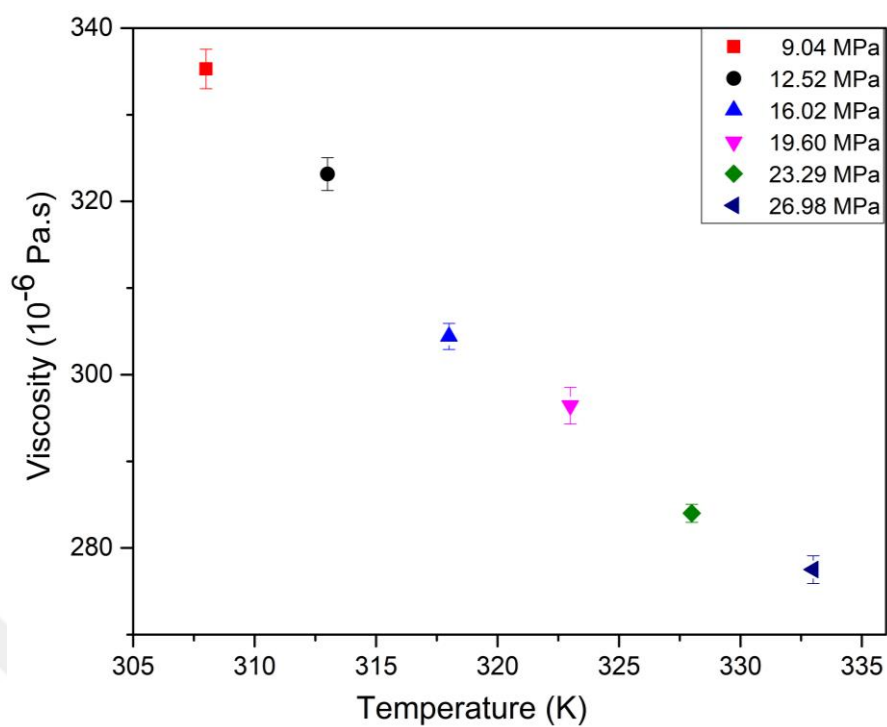


Fig. 4.33. Variation of the fluid viscosity with temperature at ethanol weight fraction, $w = 0.593$.

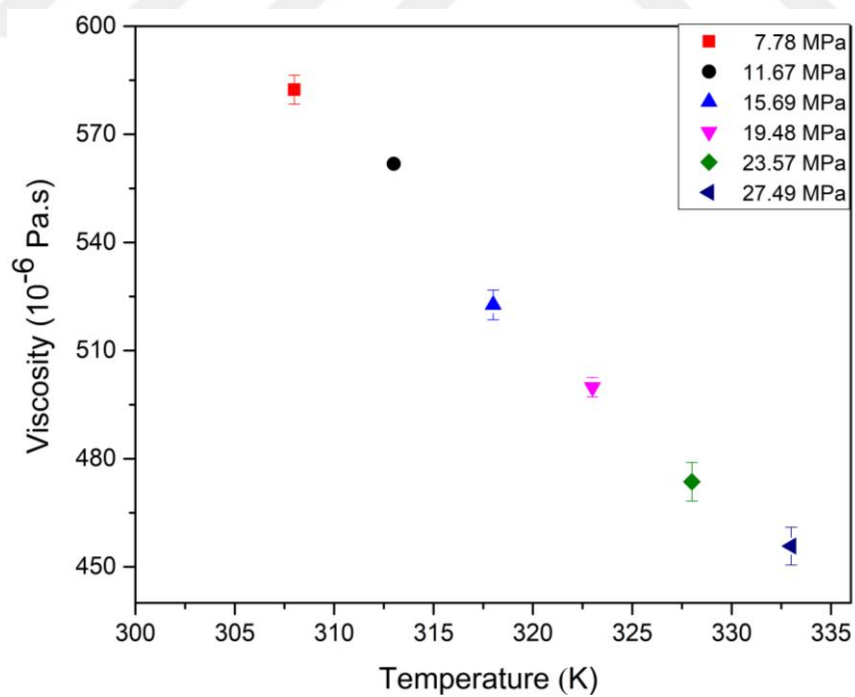


Fig. 4.34. Variation of the fluid viscosity with temperature at ethanol weight fraction, $w = 0.747$.

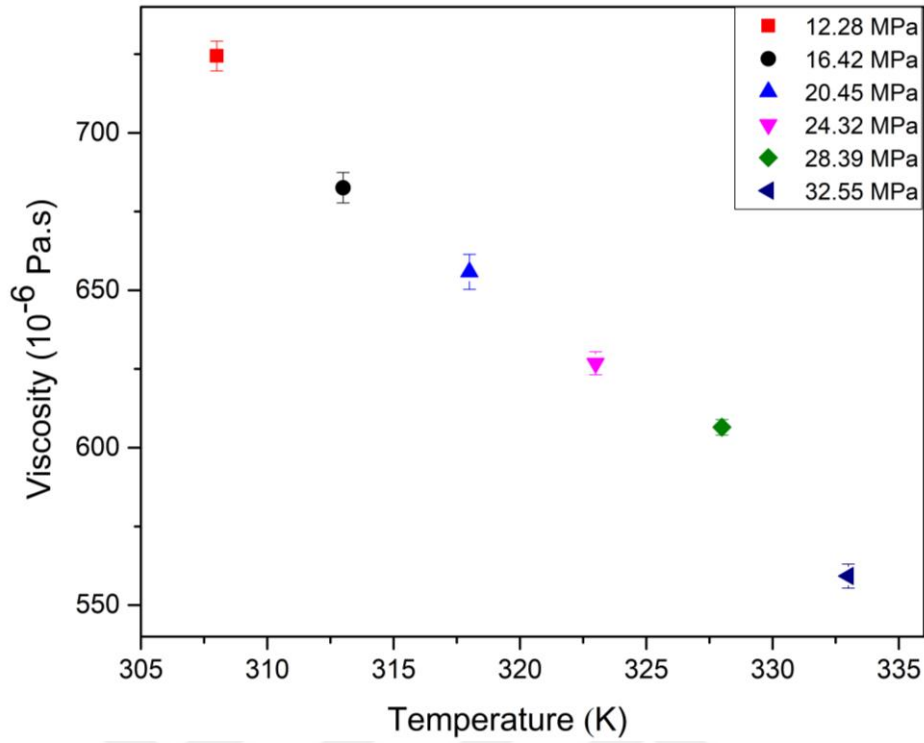


Fig. 4.35. Variation of the fluid viscosity with temperature at ethanol weight fraction, $w = 0.882$.

The experimentally measured viscosities were converted to kinematic viscosities, ν , by dividing the viscosity with the density of the mixture ($\nu = \mu/\rho$). The experimentally measured kinematic viscosities were compared with the kinematic viscosities obtained from other existing equation for binary mixtures such as Refutas equation [105].

The Refutas equation [105] for calculating the viscosity of mixture is given as:

$$\nu_{\text{mixture}} = \exp \left(\exp \left(\frac{\text{VBN}_{\text{mixture}} - 10.975}{14.534} \right) \right) - 0.8 \quad (4.8)$$

$$\text{VBN}_{\text{mixture}} = \sum_{i=0}^N x_i \times \text{VBN}_i \quad (4.9)$$

$$\text{VBN}_i = 14.35 \times \ln(\ln(\nu_i + 0.8)) + 10.975 \quad (4.10)$$

where ν_{mixture} is the kinematic viscosity of mixture, and VBN is viscosity blending number. We have calculated the viscosity blending number of pure CO₂ and pure ethanol using density and viscosity data from NIST [86] and CELSIUS company website [106].

The relative differences between the experimentally measured kinematic viscosities and the kinematic viscosities calculated using and Refutas equation are given in Table 4.16 [105]. The relative differences with Refutas equation is low at all studied mixture compositions except at low ethanol weight fraction ($w = 0.290$).

The viscosities of ethanol-CO₂ mixtures were compared with the viscosities obtained using Chung equation used for gas mixtures [107]. The Chung equation is given below:

$$\mu = \mu^* \frac{36.344(MT_c)^{1/2}}{V_c^{2/3}} \quad (4.11)$$

where, μ is the viscosity, M is the molecular weight, T_c is the critical temperature, and V_c is the critical volume. Parameters T_c , V_c and M in Eq. 4.12 are functions of the mixture composition. μ^* is a complex function and requires density and temperature of the fluid as inputs; for this purpose, densities given in Table 4.16 were used. Further details about the meaning of individual quantities used in Eq. 4.11 are given by Poling *et al.*[107].

The relative differences between measured viscosity values and the values obtained using Chung equation are given in Table 4.16 and are high even though the correlation worked well for CO₂-N₂ mixtures that we investigated in our previous study [2]. This high relative difference is not surprising, since Chung equation is basically recommended for gas mixtures.

The comparison of the measured viscosity values of ethanol-mixtures with some of the available equations in the literature shows that Refutas equation is more suitable for calculating the viscosity of ethanol-CO₂ mixtures when ethanol weight fraction is higher than 0.290. At the studied conditions, the maximum viscosity values were observed at the maximum fraction of ethanol in the mixture and which was expected because the viscosity of the pure ethanol is much higher than CO₂. The temperature dependency of ethanol-CO₂ mixtures shows that viscosity decreases with the increasing temperature at a fixed density.

Table 4.17 The Relative Difference Between Experimental Viscosity Data and Viscosity Calculated from NIST data, Shih *et al.* and Pensado *et al.* Experimental Data at Different Temperature and Pressures for Pure CO₂.

P/MPa	T/K	Relative difference (%) calculated by:		
		NIST [86]	Shih <i>et al.</i> [108]	Pensado <i>et al.</i> [109]
308	12.78	2.71	3.09	
313	14.99	3.20	3.26	5.24
318	17.18	2.09		
323	19.44	2.63		5.34
328	21.72	3.13		
333	23.97	0.64		1.51

In order to check the accuracy of the proposed technique to measure the viscosity of ethanol-CO₂ mixtures, we measured the viscosity of the pure CO₂ and compared it with the NIST data, Shih *et al.* and Pensado *et al.* experimental data [86, 108, 109]. The relative differences between the viscosity values obtained using the proposed technique and NIST data are given in Table 4.17. The low relative difference shows that viscosity of ethanol-CO₂ mixtures can be measured accurately with the proposed technique.

4.4 Viscosity measurement sensitivity of ethanol-CO₂ mixtures at high pressures

In this section, analytical expressions from Sader's model were derived for the change in Q-factor with viscosity and define sensitivity S_μ as the derivative of the cantilever Q-factor with viscosity of the fluid ($S_\mu = dQ/d\mu$). Sader's model Eq. 1.2 defines Q as a function of the fluid parameters ρ and μ , and the cantilever resonant frequency f_{fluid} . The derivative of Q with respect to μ (see the details of the derivation in Appendix C) is given as:

$$\begin{aligned}
S_{\mu}^m = \left(\frac{dQ}{d\mu} \right)_m = & \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}} \right)} \\
& \times \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} \right. \right. \\
& - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{1.0553\pi b}{8\rho_c t} + \frac{3.7997\pi b}{16\rho_c t\sqrt{2\text{Re}}} \right) - \frac{4\rho_c t}{\pi\rho^2 b} \left. \frac{d\rho}{d\mu} \right. \\
& \left. \left. - \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{3.7997\pi b\rho}{16\rho_c t\mu\sqrt{2\text{Re}}} \right) \right] \right\} \right. \\
& \left. \right\} \quad (4.12)
\end{aligned}$$

Equation 4.12 is the model - or theoretical - expression for the sensitivity S_{μ}^m ; it shows that S_{μ}^m is a complex function of the density and viscosity of the mixture, as well as cantilever length, width, thickness and cantilever density.

Equation 4.12 can be used for the viscosity measurement sensitivity of microcantilevers for high pressure fluid mixtures using frequency response of microcantilevers. In order to evaluate S_{μ}^m for a given experimental condition (at a particular composition of the mixture), derivatives $\frac{d\rho}{d\mu}$ must be determined from the dependence of density on the viscosity ethanol-CO₂ mixture. In section 4.3, we measured the viscosity and density of the ethanol-CO₂ mixtures of different compositions, $w = 0.290 - 0.882$ at a temperature range of 308 - 333 K and a pressure range of 7 to 33 MPa. We can use the data of section 4.3 to estimate the $\frac{d\rho}{d\mu}$ for different ethanol-CO₂ mixture composition. It can be observed from the data (Table 4.16) that for a particular ethanol-CO₂ mixture composition, the change in density with viscosity is zero. Therefore, for our particular case, Eq. 4.12 can be solved further as:

$$S_{\mu}^m = \left(\frac{dQ}{d\mu} \right)_m = \frac{1}{\left(\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re} \right)} \times - \left[\left(\frac{3.8018Q}{2\sqrt{2Re}} + \frac{2.7364Q}{2Re} - \frac{3.7997}{2\sqrt{2Re}} \right) \left(\frac{1}{\mu} + \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t \sqrt{2Re}} \right)} \times \left(\frac{3.7997\pi b \rho}{16\rho_c t \mu \sqrt{2Re}} \right) \right) \right] \quad (4.13)$$

In order to calculate the model sensitivity S_{μ}^m at a particular ethanol-CO₂ mixture composition, the cantilever-related parameters ($f_{vac}, \rho_c t, b$), cantilever resonant frequencies and the Q-factors (f_{fluid}, Q) and fluid parameters (ρ, μ) are required. We have used values of these parameters from section 4.3 and using these values the model sensitivity S_{μ}^m can be calculated at the particular experimental conditions. Table 4.17 summarizes the sensitivity S_{μ}^m calculated at different conditions.

Q-factor data of microcantilever immersed in ethanol-CO₂ mixtures at different temperatures given in section 4.3 was used to determine the change in Q-factor with viscosity. The change in Q-factor with viscosity for different ethanol-CO₂ mixture composition is given in Figs. 4.37-4.40. A linear fit was applied to the Figs. 4.37-4.40 to measure the slopes and the slopes $\left(\frac{dQ}{d\mu} \right)_{exp}$ (where *exp* stands for experimental) calculated for each mixture are given in Table 4.17. We have defined slopes $\left(\frac{dQ}{d\mu} \right)_{exp}$ as experimental sensitivity (S_{μ}^{exp}) and compared it with the model sensitivity (S_{μ}^m). The relative differences (RD) between S_{μ}^m and S_{μ}^{exp} are given in Table 4.17 and the average relative difference for a particular mixture composition is between 4.46 to 11.55 %. The average relative difference shows that analytical expression for the S_{μ}^m predicts fairly the change in the Q-factor with the viscosity.

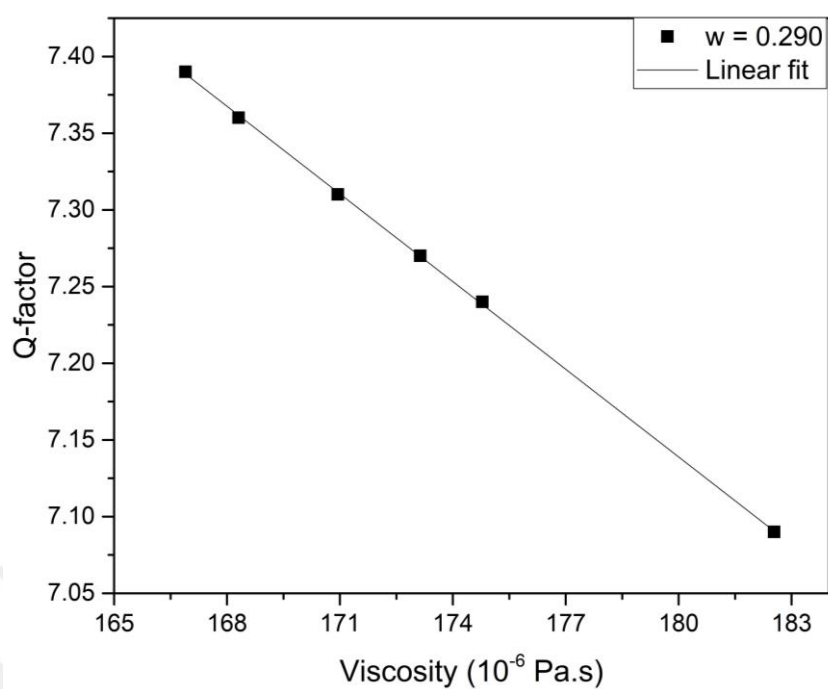


Fig. 4.36. Variation of Q-factor with fluid viscosity at ethanol weight fraction, $w = 0.290$.

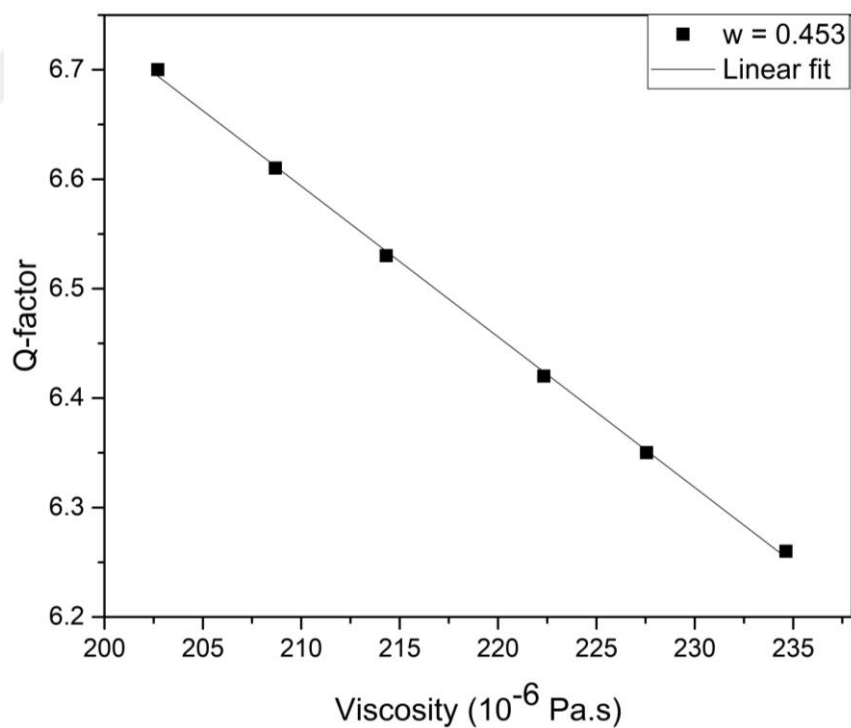


Fig. 4.37. Variation of Q-factor with fluid viscosity at ethanol weight fraction, $w = 0.453$.

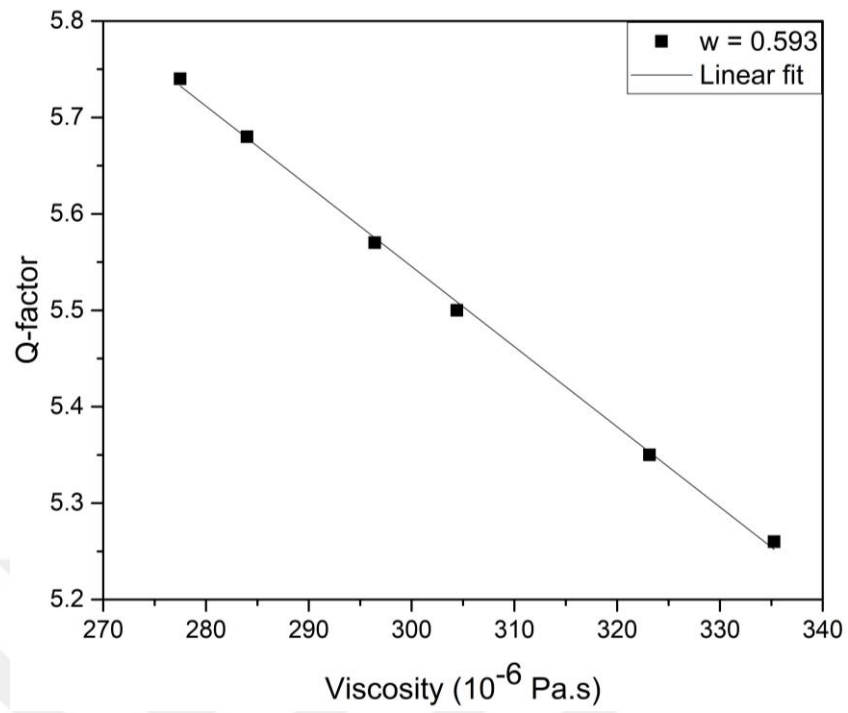


Fig. 4.38. Variation of Q-factor with fluid viscosity at ethanol weight fraction, $w = 0.593$.

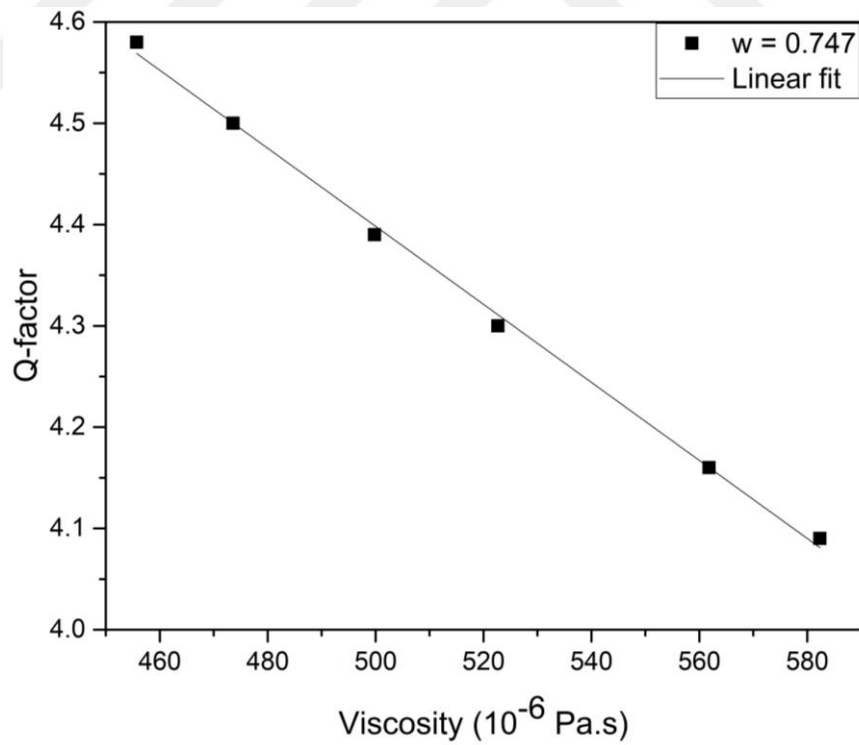


Fig. 4.39. Variation of Q-factor with fluid viscosity at ethanol weight fraction, $w = 0.747$.

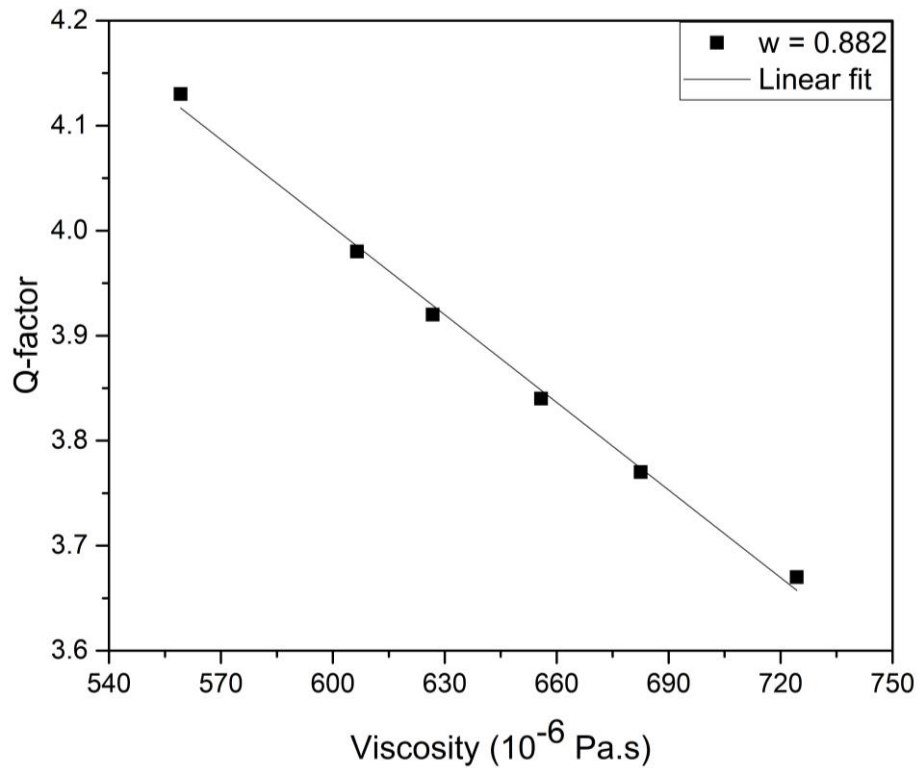


Fig. 4.40. Variation of Q-factor with fluid viscosity at ethanol weight fraction, $w = 0.882$.

S_{μ}^m and S_{μ}^{exp} sensitivities decrease with increasing ethanol weight fraction in the mixture, as the viscosity increases monotonically with the addition of ethanol in the mixture. Moreover, S_{μ}^{exp} does not change with the temperature at a particular mixture composition. On the contrary, S_{μ}^m does change with the temperature at a particular mixture composition. The relative difference between S_{μ}^m measured at different temperatures with the S_{μ}^{exp} is low, and thus we can use the S_{μ}^{exp} for calculating the resolution R_{μ} of cantilever-based measurements.

Table 4.18: Model Sensitivity S_μ^m Calculated Using Eq. 4.13 and Experimental Sensitivity S_μ^{exp} (Pa.s)⁻¹ Measured from the Slopes of Data in Figs. 4.37-4.40 together with the Relative Differences (RD) Between S_μ^m and S_μ^{exp} .

Ethanol weight fraction	w =0.290	w = 0.453	w = 0.593	w = 0.747	w = 0.882
$(S_\mu^m)_{308\text{ K}}$	-17972.3	-12216.9	-7086.17	-3096.19	-2212.6
$(S_\mu^m)_{313\text{ K}}$	-19229.5	-12792	-7489.1	-3270.12	-2419.1
$(S_\mu^m)_{318\text{ K}}$	-19462.1	-13247.9	-8192.66	-3645.35	-2569.29
$(S_\mu^m)_{323\text{ K}}$	-19827.1	-13997	-8529.61	-3900.11	-2750.21
$(S_\mu^m)_{328\text{ K}}$	-20286.4	-14564.5	-9093.68	-4229.6	-2890.3
$(S_\mu^m)_{333\text{ K}}$	-20546.8	-15213.4	-9413.23	-4481.08	-3264.95
(S_μ^{exp})	-19050	-13770	-8320	-3850	-2780
$(RD\%)_{308\text{ K}}$	5.82	11.95	16.02	21.7	22.73
$(RD\%)_{313\text{ K}}$	0.94	7.36	10.51	16.29	13.88
$(RD\%)_{318\text{ K}}$	2.14	3.87	1.54	5.46	7.88
$(RD\%)_{323\text{ K}}$	4	1.64	2.49	1.29	1.08
$(RD\%)_{328\text{ K}}$	6.29	5.61	8.89	9.4	3.89
$(RD\%)_{333\text{ K}}$	7.56	9.96	12.33	15.15	16.04

We defined resolution of cantilever-based measurements as the smallest change in the viscosity of ethanol-CO₂ mixture that can be unambiguously measured. We used Eq. 4.5 within the linear approximation to find the resolution of the cantilever-based viscosity measurements. In our particular case, Eq. 4.5 can be written as:

$$R_\mu = \frac{3\sigma_{Qa}}{S_\mu^{exp}} \quad (4.14)$$

where σ_{Qa} is the average standard deviation of the Q-factor of the cantilever measured for a particular mixture composition at different temperatures and the values of S_{μ}^{exp} are obtained from the slopes of the linear fit. For the purpose of calculating R_{μ} , absolute values of S_{μ}^{exp} are used.

Table 4.18 summarizes the numerical values of R_{μ} calculated from Eq. 4.14 using the average standard deviation of the Q-factor of microcantilevers immersed in ethanol-CO₂ mixtures of different compositions. For the purpose of R_{μ} calculations, the values of S_{μ}^{exp} for the 200 μm long microcantilever were taken from Table 4.17. Table 4.18 shows that the minimum measurable viscosity of the fluid measured from the measurements of f_{fluid} and Q was 2.69 $\mu\text{Pa.s}$ at $w = 0.29$.

Table 4.19: Resolution R_{μ} of Microcantilever-Based Measurements at Different Mixture Compositions. Microcantilever Length: 200 μm .

Ethanol weight fraction	$w = 0.290$	$w = 0.453$	$w = 0.593$	$w = 0.747$	$w = 0.882$
Average standard deviation σ_{Qa}	0.017	0.027	0.014	0.016	0.011
S_{μ}^{exp}	-19050	-13770	-8320	-3850	-2780
R_{μ} (10^{-6} Pa.s)	2.69	5.81	5.10	12.36	11.82

From the above analysis, it is clear that the Q-factor is a good indicator for measuring the viscosity of a fluid at an arbitrary fluid temperature and pressure. Since R_{μ} also depends on the standard deviation of the measurements of Q , the stability of the Q-factor during the measurement and the precision of its determination are important. The sensitivity and R_{μ} analysis shows that the cantilever has high viscosity measurement sensitivity and, hence, a lower achievable R_{μ} .

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusion

In this dissertation, the frequency responses of cantilevers immersed in ethanol-CO₂ mixtures were studied at a temperature range of 308 – 333 K and pressure range of 7 – 33 MPa. The frequency responses of cantilevers were used to measure the composition and viscosity of ethanol-CO₂ mixtures. Compositional and viscosity measurement sensitivity of cantilevers were studied, and analytical expressions were derived from Sader's model.

A new technique was developed to measure the composition of ethanol-CO₂ mixtures at high pressures from the frequency responses of cantilevers, particularly resonate frequency. As resonant frequency serves a better indicator of the actual composition of the ethanol-CO₂ 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-CO₂ mixture with unknown composition to the actual composition of the mixture. The lowest studied concentration of ethanol in the mixture was 0.0091 weight fraction; however, the expected concentration detection limit is lower than this minimal value. This study described for the first time the application of microcantilevers for the determination of the fluid mixture compositions at high pressures. Ethanol-CO₂ binary mixtures were used as the model fluid, since it is related to the supercritical drying of the aerogels.

Principally, compositions of other mixtures of solvents with CO₂ can also be measured. This technique 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.

The sensitivity of cantilever-based measurement of composition of ethanol-CO₂ mixtures at high pressures was studied and analytical expressions were derived for quantifying the change in the resonant frequency and the Q-factor of an immersed cantilever with the ethanol weight fraction in the mixture. The effects of viscous term on the sensitivity of compositional measurements were calculated and it shows that its contribution is significant and cannot be neglected in the analysis. In general, the importance of viscous term is higher at higher pressures. Using the derived model sensitivity formulas and the standard deviations of the resonant frequency and the Q-factor determined from repeated measurements of the cantilever frequency response at a particular condition, the minimum weight fractions of ethanol LOD_f and LOD_Q that can be detected in ethanol-CO₂ mixtures at various pressures were estimated. It has been demonstrated that the cantilever resonant frequency is a more sensitive indicator of the composition of fluid mixtures as compared to the Q-factor. In particular, the minimum weight fraction of ethanol that can be detected with the current setup with a 150 μm long cantilever is between 0.0009 and 0.0071 in the pressure range of 10 MPa to 21 MPa. The study represents the first attempt to derive rigorous analytical expressions which relate the change in the cantilever resonant frequency and Q-factor to the mixture composition. Ethanol-CO₂ mixtures were used as the model fluid to analyze the sensitivity of microcantilever-based compositional measurements; however, this method can be readily extended to other fluid mixtures. Thus, it can find possible applications in technological processes ranging from the synthesis of nanostructured materials to the fabrication of various functional microdevices.

Viscosity of ethanol-CO₂ binary fluid mixtures were determined by using Sader's analytical equation for the Q-factor. The viscosity of the mixture increased with increasing ethanol weight fraction in the ethanol-CO₂ mixture. The viscosity of the mixture at a fixed density decreased with increasing temperature. The relative differences between

experimentally measured viscosities and viscosities calculated from equation available in literature was investigated and it was found that the Refutas equation predicted the viscosities of mixtures with ethanol weight fraction greater than 0.29.

The viscosity measurement sensitivity of cantilevers immersed in ethanol-CO₂ mixtures was studied and analytical expression was derived for the change in Q-factor with the viscosity. The relative difference between the experimental and model sensitivity at different ethanol-CO₂ mixture compositions was calculated and the average relative difference was between 4.46 to 11.55 %. Using the experimental sensitivity and the average standard deviations of the Q-factor at a particular mixture composition, the minimum viscosity of the fluid mixture that can be measured with a sufficient confidence was estimated. In particular, the minimum viscosity of the fluid mixture that can be measured with the current setup with a 200 μm long cantilever is between 2.69 and 12.36 $\mu\text{Pa.s}$ in composition range of $w = 0.290\text{--}0.882$. The experimental results show the potential of cantilever-based viscometers for the viscosity measurement at high pressures.

5.2 Suggestions for future work

In this dissertation, the composition and viscosity of the ethanol-CO₂ mixtures were measured in batch mode. While in order to monitor the composition of ethanol-CO₂ mixtures in real time using cantilever-based sensors, there are some suggestions listed below:

1. Since cantilever-based sensors requires very small sample volumes, compact and miniature cantilever-based probes are possible for continuous monitoring of the composition of fluid mixtures and real time measurement of viscosity of fluids in practical technological processes carried out at high pressures.
2. In this study, the hydrodynamic interaction of the oscillating cantilever with the surrounding fluid was studied in the batch mode. While in real time measurements, it would be interesting to study the hydrodynamic interaction of the oscillating cantilever with the surrounding fluid. How continuous flow will affect the hydrodynamic interaction of the oscillating cantilever with the fluid.

It would be interesting to explore the effect of continuous flow on the frequency response of the cantilever.

3. Vessels of the small volumes are suggested for the real time measurements, so that the fluid surrounding the cantilever can be replaced with the new fluid in minimum/short time.
4. The frequency response measurement time can be improved. The measurement time with the current setup was about 30 milliseconds and using phase locked loop systems, it can be reduced to few milliseconds.
5. The possibility of self-oscillating cantilever to make portable sensors for real time application can be explored. For this purpose, different self-actuating mechanisms such as piezoelectric actuation can be incorporated in micro cantilevers during fabrication process.
6. Temperature measurement and control can be improved by using a thermistor (± 0.1 K) or Platinum Temperature Resistor (± 1 mK). The temperature control of the vessel can be improved by designing a new vessel surrounded by a heating bath. This will reduce the sensitivity of fluid temperature to the outside temperature.

APPENDICES

Appendix A: Derivation of formula for the sensitivity $S_f = \left(\frac{df_{fluid}}{dw} \right)$

Using Sader's model [22] of cantilever oscillations in a viscous fluid combined with Maali's analytical approximation [23], the cantilever resonant frequency f_{fluid} is given as:

$$f_{fluid} = f_{vac} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \right]^{-1/2} \quad (A1)$$

Equation (A1) defines f_{fluid} as an implicit function of the fluid parameters ρ, μ that themselves depend on ethanol weight fraction, w . Let us introduce formally an implicit function $h(f_{fluid}, \rho, \mu)$ as:

$$h(f_{fluid}, \rho, \mu) = f_{fluid} - f_{vac} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \right]^{-1/2} = 0 \quad (A2)$$

The total differential of $h(f_{fluid}, \rho, \mu)$ with respect to its variables then has the form

$$dh = \frac{\partial h}{\partial \rho} d\rho + \frac{\partial h}{\partial \mu} d\mu + \frac{\partial h}{\partial f_{fluid}} df_{fluid} = 0 \quad (A3)$$

The derivative of $h(f_{fluid}, \rho, \mu)$ with respect to ρ is given by:

$$\begin{aligned} \frac{\partial h}{\partial \rho} = & \frac{f_{vac}}{2} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \right]^{-3/2} \left[\frac{1.0553\pi b}{4 \rho_c t} + \right. \\ & \left. \frac{3.7997\pi b}{8 \rho_c t} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right] \end{aligned} \quad (A4)$$

Using Eq. (A1), expression (A4) can be further simplified as:

$$\frac{\partial h}{\partial \rho} = \frac{f_{vac}}{2} \left(\frac{f_{fluid}}{f_{vac}} \right)^3 \left(\frac{1.0553\pi b}{4 \rho_c t} + \frac{3.7997\pi b}{8 \rho_c t} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \quad (A5)$$

The derivative of $h(f_{fluid}, \rho, \mu)$ with respect to μ is given by:

$$\frac{\partial h}{\partial \mu} = \frac{f_{vac}}{2} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \right]^{-3/2} \left(\frac{3.7997 \pi b \rho}{8 \rho_c t \sqrt{\mu}} \sqrt{\frac{2}{\rho 2\pi f_{fluid} b^2}} \right), \quad (A6)$$

which, after further simplification using Eq. (A1), transforms to:

$$\frac{\partial h}{\partial \mu} = \frac{f_{vac}}{2} \left(\frac{f_{fluid}}{f_{vac}} \right)^3 \left(\frac{3.7997 \pi b \rho}{8 \rho_c t} \sqrt{\frac{2}{\rho \mu 2\pi f_{fluid} b^2}} \right) \quad (A7)$$

Finally, taking the derivative of $h(f_{fluid}, \rho, \mu)$ with respect to f_{fluid} , we obtain:

$$\frac{\partial h}{\partial f_{fluid}} = 1 + \frac{f_{vac}}{2} \left[1 + \frac{\pi \rho b}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \right]^{-3/2} \left(- \frac{3.7997 \pi \rho b}{8 f_{fluid} \sqrt{f_{fluid} \rho_c t} \sqrt{\frac{2\mu}{\rho 2\pi b^2}}} \right), \quad (A8)$$

which can be again simplified to:

$$\frac{\partial h}{\partial f_{fluid}} = 1 - \frac{f_{vac}}{2} \left(\frac{f_{fluid}}{f_{vac}} \right)^3 \left(\frac{3.7997 \pi \rho b}{8 f_{fluid} \rho_c t} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \quad (A9)$$

Inserting Eqs. (A5), (A7), and (A9) into Eq (A3) then gives:

$$\begin{aligned} dh = & \frac{f_{vac}}{2} \left(\frac{f_{fluid}}{f_{vac}} \right)^3 \left(\frac{1.0553 \pi b}{4 \rho_c t} + \frac{3.7997 \pi b}{8 \rho_c t} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) d\rho + \\ & \frac{f_{vac}}{2} \left(\frac{f_{fluid}}{f_{vac}} \right)^3 \left(\frac{3.7997 \pi b \rho}{8 \rho_c t} \sqrt{\frac{2}{\rho \mu 2\pi f_{fluid} b^2}} \right) d\mu + \left(1 - \right. \\ & \left. \frac{f_{vac}}{2} \left(\frac{f_{fluid}}{f_{vac}} \right)^3 \left(\frac{3.7997 \pi \rho b}{8 f_{fluid} \rho_c t} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \right) \right) df_{fluid} = 0 \end{aligned} \quad (A10)$$

Upon substituting for the Reynolds number $Re = (2\pi f_{fluid} \rho b^2)/(4\mu)$ and expressing the differential df_{fluid} as a function of differentials $d\rho, d\mu$, Eq. (A10) is transformed into

$$\begin{aligned}
& \left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right) df_{fluid} = \\
& = - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) d\rho - \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) d\mu
\end{aligned} \tag{A11}$$

By applying the chain rule, we can introduce the derivatives of individual parameters (f_{fluid}, ρ, μ) with respect to the ethanol weight fraction (mixture composition) w :

$$\begin{aligned}
& \left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right) df_{fluid} = - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{dw} dw - \\
& \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) \frac{d\mu}{dw} dw
\end{aligned} \tag{A12}$$

or

$$\begin{aligned}
& \left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right) \frac{df_{fluid}}{dw} = - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{dw} - \\
& \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) \frac{d\mu}{dw}
\end{aligned} \tag{A13}$$

Final rearrangement of formula (A13) gives for the sensitivity, S_f :

$$\begin{aligned}
S_f = \frac{df_{fluid}}{dw} &= \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right)} \times \left\{ - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{dw} - \right. \\
& \left. \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) \frac{d\mu}{dw} \right\}
\end{aligned} \tag{A14}$$

Appendix B: Derivation of Formula for the Sensitivity $S_Q = \left(\frac{dQ}{dw}\right)$

Sader's model [22] equation for the cantilever Q-factor Q with Maali's analytical approximation [23] is given by:

$$Q = \frac{\frac{4\rho_c t}{\pi\rho b} + \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}}\right)}{3.8018 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} + 2.7364 \frac{2\mu}{\rho 2\pi f_{fluid} b^2}} \quad (B1)$$

Equation (B1) defines Q as a function of the fluid parameters ρ and μ , and the cantilever resonant frequency f_{fluid} . Following the same approach as used in deriving the sensitivity S_f , let us introduce an implicit function $g(Q, f_{fluid}, \rho, \mu)$:

$$g = Q \times 3.8018 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} + Q \times 2.7364 \frac{2\mu}{\rho 2\pi f_{fluid} b^2} - \frac{4\rho_c t}{\pi\rho b} - \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}}\right) = 0 \quad (B2)$$

with the total differential

$$dg = \frac{\partial g}{\partial Q} dQ + \frac{\partial g}{\partial f_{fluid}} df_{fluid} + \frac{\partial g}{\partial \rho} d\rho + \frac{\partial g}{\partial \mu} d\mu = 0 \quad (B3)$$

Evaluation of the partial derivatives $\frac{\partial g}{\partial Q}$, $\frac{\partial g}{\partial f_{fluid}}$, $\frac{\partial g}{\partial \rho}$, and $\frac{\partial g}{\partial \mu}$ which appear in Eq. (B3) leads to:

$$\begin{aligned} & \left(3.8018 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} + 2.7364 \frac{2\mu}{\rho 2\pi f_{fluid} b^2}\right) dQ \\ & + \left(-\frac{3.8018Q}{2f_{fluid}} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} - 2.7364 \frac{2\mu Q}{\rho 2\pi f_{fluid}^2 b^2} + \frac{3.7997}{2f_{fluid}} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}}\right) df_{fluid} \\ & + \left(-\frac{3.8018Q}{2\rho} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}} - 2.7364 \frac{2\mu Q}{\rho^2 2\pi f_{fluid} b^2} + \frac{4\rho_c t}{\pi\rho^2 b}\right. \\ & \left.+ \frac{3.7997}{2\rho} \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} b^2}}\right) d\rho \\ & + \left(\frac{3.8018Q}{2} \sqrt{\frac{2}{\rho\mu 2\pi f_{fluid} b^2}} + 2.7364 \frac{2Q}{\rho 2\pi f_{fluid} b^2} - \frac{3.7997}{2} \sqrt{\frac{2}{\rho\mu 2\pi f_{fluid} b^2}}\right) d\mu = 0 \end{aligned} \quad (B4)$$

Substituting for the Reynolds number $Re = (2\pi f_{fluid}\rho b^2)/(4\mu)$ and rearranging the terms so that dQ is expressed as a function of df_{fluid} , $d\rho$, $d\mu$ leads to:

$$\begin{aligned} & \left(\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re} \right) dQ \\ &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2Re}} + \frac{2.7364Q}{2f_{fluid}Re} - \frac{3.7997}{2f_{fluid}\sqrt{2Re}} \right) df_{fluid} \\ &+ \left(\frac{3.8018Q}{2\rho\sqrt{2Re}} + \frac{2.7364Q}{2\rho Re} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2Re}} \right) d\rho - \left(\frac{3.8018Q}{2\mu\sqrt{2Re}} + \frac{2.7364Q}{2\mu Re} - \frac{3.7997}{2\mu\sqrt{2Re}} \right) d\mu \end{aligned} \quad (B5)$$

In order to evaluate the changes of the Q-factor Q with changing mixture composition w , we can apply the chain rule:

$$\begin{aligned} & \left(\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re} \right) dQ \\ &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2Re}} + \frac{2.7364Q}{2f_{fluid}Re} - \frac{3.7997}{2f_{fluid}\sqrt{2Re}} \right) \frac{df_{fluid}}{dw} dw \\ &+ \left(\frac{3.8018Q}{2\rho\sqrt{2Re}} + \frac{2.7364Q}{2\rho Re} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2Re}} \right) \frac{d\rho}{dw} dw \\ &- \left(\frac{3.8018Q}{2\mu\sqrt{2Re}} + \frac{2.7364Q}{2\mu Re} - \frac{3.7997}{2\mu\sqrt{2Re}} \right) \frac{d\mu}{dw} dw \end{aligned} \quad (B6)$$

which subsequently leads to:

$$\begin{aligned} & \left(\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re} \right) \frac{dQ}{dw} \\ &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2Re}} + \frac{2.7364Q}{2f_{fluid}Re} - \frac{3.7997}{2f_{fluid}\sqrt{2Re}} \right) \frac{df_{fluid}}{dw} \\ &+ \left(\frac{3.8018Q}{2\rho\sqrt{2Re}} + \frac{2.7364Q}{2\rho Re} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2Re}} \right) \frac{d\rho}{dw} - \left(\frac{3.8018Q}{2\mu\sqrt{2Re}} + \frac{2.7364Q}{2\mu Re} - \frac{3.7997}{2\mu\sqrt{2Re}} \right) \frac{d\mu}{dw} \end{aligned} \quad (B7)$$

Substituting for df_{fluid}/dw from Eq. (A14) transforms formula (B7) to

$$\begin{aligned} & \left(\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re} \right) \frac{dQ}{dw} \\ &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2Re}} + \frac{2.7364Q}{2f_{fluid}Re} - \frac{3.7997}{2f_{fluid}\sqrt{2Re}} \right) \left[- \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t\sqrt{2Re}} \right)} \times \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t\sqrt{2Re}} \right) \frac{d\rho}{dw} \right. \\ &\quad \left. - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t\sqrt{2Re}} \right)} \times \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t\mu\sqrt{2Re}} \right) \frac{d\mu}{dw} \right] \\ &+ \left(\frac{3.8018Q}{2\rho\sqrt{2Re}} + \frac{2.7364Q}{2\rho Re} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2Re}} \right) \frac{d\rho}{dw} - \left(\frac{3.8018Q}{2\mu\sqrt{2Re}} + \frac{2.7364Q}{2\mu Re} - \frac{3.7997}{2\mu\sqrt{2Re}} \right) \frac{d\mu}{dw} \end{aligned}$$

(B8)

In the next step, we can isolate the Q-factor compositional derivative dQ/dw and collect together all the terms that determine the dependence of dQ/dw on the derivative of the fluid density $d\rho/dw$ and the derivative of the fluid viscosity $d\mu/dw$:

$$\begin{aligned} \frac{dQ}{dw} = & \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \\ & \times \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} \right. \right. \\ & \left. \left. - \frac{1}{f_{\text{fluid}}} \times \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^3 - \frac{3.7997\pi\rho b f_{\text{vac}}}{16f_{\text{fluid}}\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{1.0553\pi b f_{\text{vac}}}{8\rho_c t} + \frac{3.7997\pi b f_{\text{vac}}}{16\rho_c t\sqrt{2\text{Re}}} \right) - \frac{4\rho_c t}{\pi\rho^2 b} \right) \frac{d\rho}{dw} \right. \\ & \left. - \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{f_{\text{fluid}}} \times \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^3 - \frac{3.7997\pi\rho b f_{\text{vac}}}{16f_{\text{fluid}}\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{3.7997\pi b \rho f_{\text{vac}}}{16\rho_c t\mu\sqrt{2\text{Re}}} \right) \right) \right] \frac{d\mu}{dw} \right\} \end{aligned} \quad (\text{B9})$$

Final rearrangement of formula (B9) for dQ/dw then gives the full model equation for the compositional sensitivity of the cantilever Q-factor S_Q :

$$\begin{aligned} S_Q = \frac{dQ}{dw} = & \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \\ & \times \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} - \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{1.0553\pi b}{8\rho_c t} + \frac{3.7997\pi b}{16\rho_c t\sqrt{2\text{Re}}} \right) \right. \right. \\ & \left. \left. - \frac{4\rho_c t}{\pi\rho^2 b} \right) \frac{d\rho}{dw} \right. \\ & \left. - \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{3.7997\pi b \rho}{16\rho_c t\mu\sqrt{2\text{Re}}} \right) \right) \right] \frac{d\mu}{dw} \right\} \end{aligned} \quad (\text{B10})$$

Appendix C: Derivation of Formula for the Sensitivity $S_\mu = \left(\frac{dQ}{d\mu}\right)$

Lets' start from Eq. (A11) of appendix A and it is given as:

$$\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right) df_{fluid} = - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) d\rho - \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) d\mu \quad (C1)$$

By applying the chain rule, we can introduce the derivatives of individual parameters (f_{fluid}, ρ, μ) with respect to the viscosity μ :

$$\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right) df_{fluid} = - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{d\mu} d\mu - \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) \frac{d\mu}{d\mu} d\mu \quad (C2)$$

or

$$\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right) \frac{df_{fluid}}{d\mu} = - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{d\mu} - \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) \quad (C3)$$

Rearrangement of formula (C3):

$$\frac{df_{fluid}}{d\mu} = \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t \sqrt{2Re}} \right)} \times \left\{ - \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t \sqrt{2Re}} \right) \frac{d\rho}{d\mu} - \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t \mu \sqrt{2Re}} \right) \right\} \quad (C4)$$

Similarly, Eq. (B5) is given as:

$$\begin{aligned} & \left(\frac{3.8018}{\sqrt{2Re}} + \frac{2.7364}{2Re} \right) dQ \\ &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2Re}} + \frac{2.7364Q}{2f_{fluid}Re} - \frac{3.7997}{2f_{fluid}\sqrt{2Re}} \right) df_{fluid} \\ &+ \left(\frac{3.8018Q}{2\rho\sqrt{2Re}} + \frac{2.7364Q}{2\rho Re} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2Re}} \right) d\rho - \left(\frac{3.8018Q}{2\mu\sqrt{2Re}} + \frac{2.7364Q}{2\mu Re} - \frac{3.7997}{2\mu\sqrt{2Re}} \right) d\mu \end{aligned}$$

(C5)

In order to evaluate the changes of the Q-factor Q with viscosity μ , we can apply the chain rule:

$$\begin{aligned}
 & \left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}} \right) dQ \\
 &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2\text{Re}}} + \frac{2.7364Q}{2f_{fluid}\text{Re}} - \frac{3.7997}{2f_{fluid}\sqrt{2\text{Re}}} \right) \frac{df_{fluid}}{d\mu} d\mu \\
 &+ \left(\frac{3.8018Q}{2\rho\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\rho\text{Re}} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2\text{Re}}} \right) \frac{d\rho}{d\mu} d\mu \\
 &- \left(\frac{3.8018Q}{2\mu\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\mu\text{Re}} - \frac{3.7997}{2\mu\sqrt{2\text{Re}}} \right) \frac{d\mu}{d\mu} d\mu
 \end{aligned}
 \tag{C6}$$

which subsequently leads to:

$$\begin{aligned}
 & \left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}} \right) \frac{dQ}{d\mu} = \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2\text{Re}}} + \frac{2.7364Q}{2f_{fluid}\text{Re}} - \frac{3.7997}{2f_{fluid}\sqrt{2\text{Re}}} \right) \frac{df_{fluid}}{d\mu} + \left(\frac{3.8018Q}{2\rho\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\rho\text{Re}} - \right. \\
 & \left. \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2\text{Re}}} \right) \frac{d\rho}{d\mu} - \left(\frac{3.8018Q}{2\mu\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\mu\text{Re}} - \frac{3.7997}{2\mu\sqrt{2\text{Re}}} \right)
 \end{aligned}
 \tag{C7}$$

Substituting for $df_{fluid}/d\mu$ from Eq. (C4) transforms formula (C7) to

$$\begin{aligned}
 & \left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}} \right) \frac{dQ}{d\mu} \\
 &= \left(\frac{3.8018Q}{2f_{fluid}\sqrt{2\text{Re}}} + \frac{2.7364Q}{2f_{fluid}\text{Re}} - \frac{3.7997}{2f_{fluid}\sqrt{2\text{Re}}} \right) \left[- \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{1.0553\pi b f_{vac}}{8\rho_c t} + \frac{3.7997\pi b f_{vac}}{16\rho_c t\sqrt{2\text{Re}}} \right) \frac{d\rho}{d\mu} \right. \\
 & \left. - \frac{1}{\left(\left(\frac{f_{vac}}{f_{fluid}} \right)^3 - \frac{3.7997\pi\rho b f_{vac}}{16f_{fluid}\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{3.7997\pi b \rho f_{vac}}{16\rho_c t\mu\sqrt{2\text{Re}}} \right) \right] \\
 &+ \left(\frac{3.8018Q}{2\rho\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\rho\text{Re}} - \frac{4\rho_c t}{\pi\rho^2 b} - \frac{3.7997}{2\rho\sqrt{2\text{Re}}} \right) \frac{d\rho}{d\mu} - \left(\frac{3.8018Q}{2\mu\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\mu\text{Re}} - \frac{3.7997}{2\mu\sqrt{2\text{Re}}} \right)
 \end{aligned}
 \tag{C8}$$

In the next step, we can isolate the Q-factor derivative $dQ/d\mu$:

$$\begin{aligned} \frac{dQ}{d\mu} = & \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \\ & \times \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} \right. \right. \\ & \left. \left. - \frac{1}{f_{\text{fluid}}} \times \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^3 - \frac{3.7997\pi\rho b f_{\text{vac}}}{16f_{\text{fluid}}\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{1.0553\pi b f_{\text{vac}}}{8\rho_c t} + \frac{3.7997\pi b f_{\text{vac}}}{16\rho_c t\sqrt{2\text{Re}}} \right) - \frac{4\rho_c t}{\pi\rho^2 b} \right) \frac{d\rho}{d\mu} \right. \\ & \left. \left. - \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{f_{\text{fluid}}} \times \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^3 - \frac{3.7997\pi\rho b f_{\text{vac}}}{16f_{\text{fluid}}\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{3.7997\pi b \rho f_{\text{vac}}}{16\rho_c t\mu\sqrt{2\text{Re}}} \right) \right] \right\} \end{aligned} \quad (\text{C9})$$

Final rearrangement of formula (C9) for $dQ/d\mu$ then gives the full model equation for the viscosity measurement sensitivity of the cantilever Q-factor S_μ :

$$\begin{aligned} S_\mu = \frac{dQ}{d\mu} = & \frac{1}{\left(\frac{3.8018}{\sqrt{2\text{Re}}} + \frac{2.7364}{2\text{Re}}\right)} \\ & \times \left\{ \left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\rho} \right. \right. \\ & \left. \left. - \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{1.0553\pi b}{8\rho_c t} + \frac{3.7997\pi b}{16\rho_c t\sqrt{2\text{Re}}} \right) - \frac{4\rho_c t}{\pi\rho^2 b} \right) \frac{d\rho}{d\mu} \right. \\ & \left. \left. - \left[\left(\frac{3.8018Q}{2\sqrt{2\text{Re}}} + \frac{2.7364Q}{2\text{Re}} - \frac{3.7997}{2\sqrt{2\text{Re}}} \right) \left(\frac{1}{\mu} + \frac{1}{\left(\left(\frac{f_{\text{vac}}}{f_{\text{fluid}}} \right)^2 - \frac{3.7997\pi\rho b}{16\rho_c t\sqrt{2\text{Re}}} \right)} \times \left(\frac{3.7997\pi b \rho}{16\rho_c t\mu\sqrt{2\text{Re}}} \right) \right] \right\} \end{aligned} \quad (\text{C10})$$

Appendix D: Resonant Frequency and Q-factor of 200 μm long cantilever of Chip-2

Table D 1: Measured Resonant Frequency and Q-factor of Microcantilever of Length 200 μm Immersed in Different Ethanol-CO₂ Mixture Compositions at Different Temperatures and Pressures.

Ethanol weight fraction	T/K	P/MPa	f_{fluid}/Hz	Q-factor
w= 0.290	308	7.83	21386.78	7.09
	313	10.44	21426.45	7.24
	318	13.14	21415.05	7.27
	323	15.83	21396.18	7.31
	328	18.64	21376.56	7.36
	333	21.42	21384.16	7.39
w=0.453	308	12.36	20929.83	6.26
	313	15.91	20941.41	6.35
	318	19.43	20956.16	6.42
	323	22.23	20962.23	6.53
	328	26.46	20959.06	6.61
	333	30.05	20966.41	6.70
w=0.593	308	9.04	20435.27	5.26
	313	12.52	20449.24	5.35
	318	16.02	20476.01	5.50
	323	19.60	20502.57	5.57
	328	23.29	20506.97	5.68
	333	26.98	20505.94	5.74
w=0.747	308	7.78	20246.09	4.09
	313	11.67	20296.23	4.16
	318	15.69	20348.31	4.30
	323	19.48	20386.45	4.39
	328	23.57	20420.94	4.50
	333	27.49	20443.21	4.58
w=0.882	308	12.28	19695.27	3.67
	313	16.42	19734.28	3.77
	318	20.45	19775.07	3.84
	323	24.32	19807.88	3.92
	328	28.39	19839.42	3.98
	333	32.55	19893.38	4.13

PUBLICATION RECORD

Journal Articles

- 1) S.K. Baloch, A. Jonáš, A. Kiraz, B.E. Alaca, C. Erkey, "Determination of composition of ethanol-CO₂ mixtures at high pressures using frequency response of microcantilevers", *The Journal of Supercritical Fluids*, 132 (2018) 65-70.
- 2) G.Eris, S.K.Baloch, A.A.Bozkurt, A.Jonás, A.Kiraz, B.E.Alaca, C.Erkey, "Characterization of fluid mixtures at high pressures using frequency response of microcantilevers", *Sensors and Actuators A: Physical*, 261 (2017) 202-209
- 3) S.K. Baloch, A. Jonáš, A. Kiraz, B.E. Alaca, C. Erkey, "Sensitivity of compositional measurement of high-pressure fluid mixtures using microcantilever frequency response", *Sensors and Actuators A: Physical*, 278 (2018) 111-126.
- 4) S.K.Baloch, A.Jonás, A.Kiraz, B.E.Alaca, C.Erkey, "Viscosities of Ethanol-CO₂ Binary Mixtures at High Pressures ", *The Journal of Supercritical Fluids*, In process.

Conference Presentations

- 1) "Determination of Composition of Ethanol-CO₂ Mixtures at High Pressures Using Frequency Response of Microcantilevers", with G. Eris, A. Bozkurt, A. Jonas, A. Kiraz, E. Alaca, C. Erkey, 15th European Meeting on Supercritical Fluids, May, 2016 (Essen, Germany)
- 2) "Measurement of composition of mixtures at high pressures with high sensitivity using frequency response of microcantilevers", with A. Jonáš, A. Kiraz, B.E. Alaca, C. Erkey, SPIE Photonics West, January, 2018 (San Francisco, USA)

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