Characterization of fluid mixtures at high pressures using frequency response of microcantilevers

Gamze Eriş[a], Shadi Khan Baloch[b], Asuman Aşıkoğlu Bozkurt[c], Alexandr Jonáš[d], Alper Kiraz[b,e,g], B. Erdem Alaca[f,h], Can Erkey[a,g,*]

[a] Department of Chemical and Biological Engineering, Koc University, Istanbul, 34450, Turkey
[b] Department of Electrical and Electronics Engineering, Koc University, Istanbul, 34450, Turkey
[c] Department of Physics, Yıldız Technical University, Istanbul, 34220, Turkey
[d] Department of Physics, Istanbul Technical University, Istanbul, 34469, Turkey
[e] Department of Physics, Koc University, Istanbul, 34450, Turkey
[f] Department of Mechanical Engineering, Koc University, Istanbul, 34450, Turkey
[g] Koc University Tüpras Energy Center (KUTEM), Koc University, Istanbul 34450, Turkey
[h] Koc University Surface Technologies Research Center (KUYTAM), Koc University, Istanbul 34450, Turkey

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ABSTRACT

The frequency response of ferromagnetic nickel microcantilevers immersed in binary mixtures of carbon dioxide (CO_2) and nitrogen (N_2) at 308 K and pressures up to 23 MPa was investigated. Experimental data were analyzed using the model developed by Sader for a clamped oscillatory beam immersed in a fluid and a very good agreement between the measured resonant frequencies and quality factors (Q-factors) and the theoretical predictions of the model with cantilever characteristic parameters regressed from experimental data was observed. This suggested that the data could be used to simultaneously measure the density and the viscosity of fluid mixtures over a wide range of pressures. Subsequently, density and viscosity of binary mixtures of CO_2 and N_2 were determined using N_2 as the reference fluid and compared to the predictions of Gerg equation of state and Chung equation, respectively. For the studied fluids with different compositions, the average relative difference between the experimental density values and the values predicted using Gerg equation of state and NIST database ranged from 1.0 to 13%. The average relative difference between the experimental viscosity values and the values obtained using Chung equation and NIST database ranged from 2.4 to 15%. Since the resonant frequency and Q-factor were found to vary with composition at a fixed temperature and pressure, the technique can in principle also be used to measure the composition of a binary mixture at a fixed temperature and pressure. The study represents the first systematic attempt to use microcantilevers for the characterization of high-pressure fluid mixtures and paves the way for devising portable sensors for in-line monitoring of thermophysical properties and composition of fluid mixtures under a wide range of environmental conditions.

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1. Introduction

Over the last two decades, microcantilevers have been frequently utilized as transducers in various chemical, biological and physical sensing applications. Leading examples include Atomic Force Microscopy (AFM)[1], chemical/biological sensors[2,3], pressure sensors[4], mass sensors[5], viscometers and densitometers [6]. The advantages associated with sensing through miniaturized cantilevers include high sensitivity, fast response, simple and compact architecture, and ultra-low sample volume requirements.

Gases and gas mixtures at high pressures represent an important class of fluids that are utilized and produced in a wide variety of technological applications such as extraction with compressed gases [7], high-pressure sterilization [8], synthesis of nanostructured materials [9], enhanced oil recovery [10], and power generation [11]. The objectives of the studies reported in the literature so far involving microcantilevers exposed to pure gases and gas mixtures can be divided primarily into two categories: (i) detection/quantification of gas species in mixtures and (ii) mea-

surement of thermophysical properties of gases/gas mixtures. The detection and/or quantification of one or more of the components of a gas mixture is generally accomplished by coating the cantilever surface with a polymeric or metallic thin film with specific affinity to the gaseous species of interest. In the static mode, the selective sorption or binding of the gas molecules of interest to the functionalized surface results in bending or deflection of the cantilever which can be detected by various techniques such as optical, piezoresistive, piezoelectric and capacitive [2,12]. Such bending or deflection can then be related to the concentration of the target species in the gas mixture. For example, Britton et al. [13], Okuyama et al. [14], Baselt et al. [15], Chou et al. [16], and Lang et al. [17] 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. Similarly, Dong et al. [18], Betts et al. [19], Fadel et al. [20], Maute et al. [21,22], and Kim et al. [23] 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. [24] 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 [25–27]. Xu et al. [26] proposed a method for measuring composition of gas mixtures using equations relating the resonant frequency shift to the molar mass of the gas mixture. However, high sensitivities could not be achieved using this method. For example, experiments revealed only a 0.05% shift in the resonant frequency of the cantilevers as a result of a 20% change of CO_2 concentration in CO_2-air mixtures. Tetin et al. [28] derived an analytical expression which relates the resonant frequency shift to the mass density and viscosity of the fluid and also the microcantilever architecture. Using this theoretical framework, they were able to detect low concentrations of both helium and carbon dioxide in nitrogen at atmospheric pressure and 298 K.

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, in particular, gas density and viscosity. The hydrodynamic force consists of two components: pressure (normal to the vibrating surface) and viscous force (tangential to the vibrating surface). This mechanical interaction with the surrounding fluid affects the resonant behavior of the cantilever through i) the added mass effect due to the inertia of the fluid and ii) the energy dissipation effect due to the viscous drag. As both effects depend on the density and viscosity of the specific fluid, this approach enables one to relate both the density and the viscosity of pure fluids or mixtures to the frequency response of immersed cantilever. Sader's theory [29] which is based on the solution of the equation of motion of a clamped elastic beam subject to hydrodynamic forces of the surrounding fluid has been widely utilized in the literature. Youssry et al. [30] incorporated Maali's approximations [31] to Sader's model and derived analytical expressions for extracting density and viscosity from the measured resonant frequency and quality factor (Q-factor). Boskovic et al. [6] described a method based on Sader's model for determining the density and viscosity of a gas using cantilever calibration with a reference fluid.

The calibration parameters – vacuum resonant frequency and linear mass density – were determined using the reference measurement in air. The measurements were carried out at atmospheric pressure and 300 K. Under these conditions, the errors for the density and viscosity of carbon dioxide (CO_2), argon (Ar), helium (He) and hydrogen (H_2) were less than 6.7% and 10%, respectively. In our previous study [32], we performed frequency response measurements with pure CO_2 in the temperature range between 298 K and 323 K and the pressure range between 0.1 MPa and 20.7 MPa with a custom-built experimental setup. A good agreement between the experimental data and Sader's model with Maali's approximations [31] was achieved suggesting that density and viscosity could be simultaneously measured at high pressures. Density and viscosity of nitrogen (N_2) at 308 K and pressures up to 24 MPa were measured in a separate study using Ar as a reference fluid [25]. The root-mean-square deviations of the measured density and viscosity of N_2 from the reference values obtained from NIST database were 2.5% and 5.2%, respectively.

In this study, we present our results on the characterization of thermophysical properties and composition of a model composite fluid: binary mixture of CO_2 and N_2. We investigated the frequency response of microcantilevers immersed in pure CO_2 and N_2 and mixtures of these gases of varied composition at 308 K and pressures up to 24 MPa using a high-pressure cell. At a constant temperature and composition, the resonant frequencies and Q-factors were found to decrease with increasing pressure as a result of increasing fluid density and viscosity. Experimental data were analyzed using Sader's model and a very good agreement between the measured resonant frequencies and Q-factors and the theoretical predictions of the model with the cantilever characteristic parameters regressed from the experimental data was observed (average relative errors of the resonant frequency and Q-factor for the studied fluids ranging between 0.1–0.6% and 1.2–4.5%, respectively). Subsequently, measured resonant frequencies and Q-factors of the cantilevers were used to determine the density and viscosity of the fluid using N_2 as the reference fluid. For the studied fluids of different composition, the average relative difference between the experimental density values and the values predicted using Gerg equation of State and NIST database ranged from 1.0 to 13%. Correspondingly, the average relative difference between the experimental viscosity values and the values obtained using Chung equation and NIST database ranged from 2.4 to 15%. The sensitivity of the cantilever frequency response to the changes in composition of CO_2–N_2 mixture was also investigated and a procedure for obtaining the composition of the mixture from the measured frequency response was proposed.

2. Materials and methods

2.1. Materials

N_2 and CO_2 used in the experiments were supplied by Aligaz Messer with purities of 99.9% and 99.5%, respectively, and used as received.

2.2. Experimental procedure

Ferromagnetic cantilevers with approximate length, width and thickness of 200 μm, 20 μm, and 1 μm, respectively, were used in this study. Cantilevers were composed of three layers: i) 10–20-nm-thick chromium (Cr) bottom layer, ii) 100–120-nm-thick gold (Au) middle layer, and iii) 850–950-nm thick nickel (Ni) top layer. The design and fabrication of these ferromagnetic microcantilevers together with the procedure used for measuring their frequency response were explained in detail in our previous study [32].
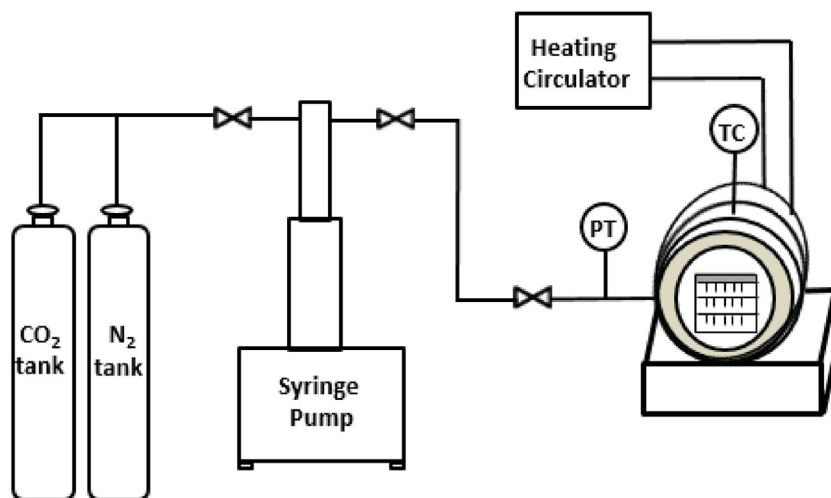
Fig. 1. Schematic of the experimental set-up.

In brief, prior to measurements, a die with microcantilevers was mounted in a Teflon housing with an electromagnetic actuator – a coil made from copper wire – and placed in a 50-mL cylindrical high-pressure vessel with two sapphire windows on each side (TharSFC 05424-4). These windows allowed both the observation of the cantilevers and the measurement of their frequency response by laser beam deflection. Electrical connection to the actuator in the pressure vessel was sealed using insulated CONAX Technologies TG24T gland assemblies. In order to control the fluid temperature inside the vessel, plastic tubing was wrapped around the vessel and connected to a heating circulator (Polyscience). Temperature and pressure were monitored throughout the experiment with a T-type thermocouple (TC) (Omega dp462) (accuracy ±1 K) and a pressure transducer (PT) (Omega PX409-5.0KAUSBH) (accuracy ±0.03 MPa), respectively. The schematic of the set-up is given in Fig. 1.

Mixtures of known composition were prepared by successive transfer of the fluids, CO_2 and N_2, to the vessel. The amount of each fluid transferred to the vessel was determined gravimetrically. First, the mass of the empty vessel was measured and recorded. Then, CO_2 was delivered to the chamber. The amount of CO_2 introduced was calculated from the difference of the actual mass and the mass of the empty chamber. Subsequently, the amount of N_2 that should be added to the chamber was calculated according to the desired composition. N_2 filling required several attempts to get a mixture with composition sufficiently close to the desired one. All mass measurements were carried out with a mass balance with an accuracy of ±0.1 g and the compositions were calculated to ±0.01-mol fraction accuracy.

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

In the beginning of each set of measurements, the vessel was filled with the desired fluid or fluid mixture to a pressure ranging between 23 and 24 MPa with the syringe pump. Then, the temperature of the vessel was adjusted to the desired value using the heating circulator. After waiting for about 1–2 h for stabilization of the pressure and temperature of the system, frequency response measurements were performed starting from the highest pressure and then gradually decreasing the pressure for successive measurements in the set. The pressure was decreased very slowly so that the temperature change in the vessel during depressurization was very small. Furthermore, after the pressure was reduced, we waited at least 5 min before starting the next measurement to make sure that thermal equilibrium with the heating circulator was restored in the vessel. Temperature was kept at 308 K throughout the measurements. At each pressure, the driving frequency of the function generator was adjusted over a range of 9 kHz approximately centered on the resonant frequency of the cantilever and the cantilever response was recorded at 400 points evenly distributed within this frequency range. The amplitude of the driving sinusoidal signal before being amplified 50 times was set to 3 V peak to peak. Subsequently, the dissipation-free cantilever resonant frequency, f_{fluid} and the Q-factor, Q, were determined by fitting the measured frequency response $A(\omega)$ to the equation describing the oscillating elastic cantilever beam as a simple damped harmonic oscillator [29] as given in Eq. (1):

$$A(\omega) = \frac{A_0 4\pi^2 f_{fluid}^2}{\sqrt{\left(\omega^2 - 4\pi^2 f_{fluid}^2\right)^2 + \frac{\omega^2 4\pi^2 f_{fluid}^2}{Q^2}}} \tag{1}$$

where A_0 is the zero-frequency amplitude of the response and $\omega = 2\pi f$ is the angular driving frequency. At each pressure, three frequency response measurements were carried out and then the averages of the three resonant frequencies and Q-factors were taken. The average standard deviations of the measured resonant frequency and Q-factor over the whole studied range of pressures were 0.1% and 3.4%, respectively, while the maximum standard deviations were 0.7% and 13.4%, respectively.
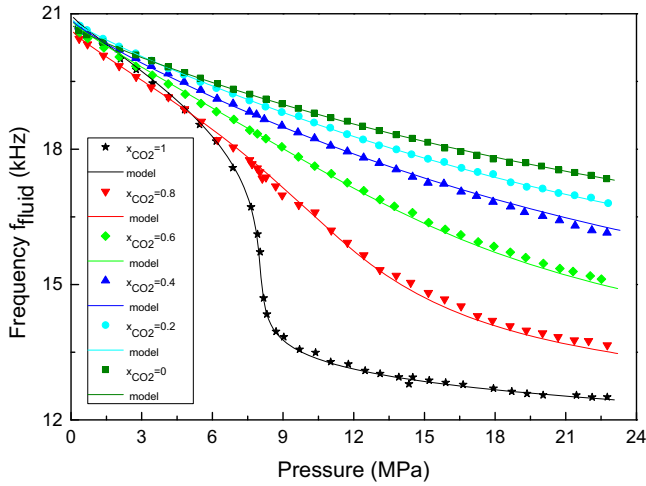
Fig. 2. Variation of resonant frequency with pressure for binary mixtures of CO_2 and N_2 at 308 K. X_{CO2}: mole fraction of CO_2, Symbols: experimental data points, solid lines: fit of experimental data to Eq. (2).

Fig. 3. Variation of Q-factor with pressure for binary mixtures of CO_2 and N_2 at 308 K. X_{CO2}: mole fraction of CO_2, Symbols: experimental data points, solid lines: fit of experimental data to Eq. (3).

3. Results and discussion

Resonant frequencies and Q-factors measured for pure CO_2, pure N_2, and mixtures of CO_2 and N_2 of varied composition at 308 K from atmospheric pressure up to 23 MPa are given in Figs. 2 and 3, respectively. 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. However, pressure dependencies of the resonant frequency and Q-factor are not identical for different compositions

of CO_2–N_2 mixture. A more substantial change in the resonant frequency and Q-factor with the fluid pressure occurs for CO_2 since the operating temperature of 308 K is close to the critical temperature of CO_2 ($T_C = 304.2$ K). In the proximity of the critical point, a small change in pressure results in a dramatic change in the density and viscosity and, thus, a dramatic change in the resonant frequency and Q-factor. As the mole fraction of N_2 in the CO_2–N_2 mixture increases, slopes of both pressure-dependent curves decrease because the studied temperature and pressure values are much higher than the critical temperature and pressure of N_2 ($T_C = 126.2$ K, $p_C = 3.4$ MPa).

Experimental data of the cantilever frequency response were analyzed using Sader's model equations with Maalli's analytical approximation [31]. The model equations are given below.

$$f_{fluid} = f_{vac} \left[1 + \frac{\pi \rho w}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} w^2}} \right) \right]^{-1/2} \quad (2)$$
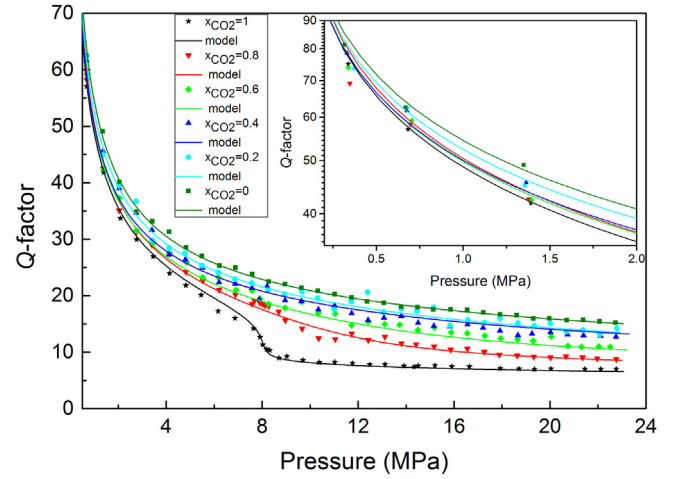
$$Q = \frac{\frac{4\rho_c t}{\pi \rho w} + \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} w^2}}\right)}{3.8018 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid} w^2}} + 2.7364 \frac{2\mu}{\rho 2\pi f_{fluid} w^2}} \quad (3)$$

where f_{fluid} is the actual resonant frequency in the fluid, f_{vac} is the resonant frequency in vacuum, w is the cantilever width, ρ_c is the cantilever density, t is the cantilever thickness, ρ is the fluid density, μ is the fluid viscosity, and Q is the quality factor.

Eqs. (2) and (3) show that the frequency response of the cantilever immersed in the fluid is dependent on the fluid density and viscosity and the cantilever characteristic parameters (f_{vac}, $\rho_c t$, w). By inserting the values of the density and viscosity of the studied fluid and cantilever characteristic parameters in Eqs. (2) and (3), theoretical resonant frequency and Q-factor can be obtained. The three cantilever characteristic parameters were regressed from the experimental data by minimizing the objective function F (Eq. (4)), using the experimental values of the cantilever resonant frequency, $f_{fluid,i}$ and Q-factor, Q_i and density and viscosity of the fluid at the given experimental conditions:

$$F = \sum_i \left\{ \left(f_{fluid,i} - f_{vac} \left[1 + \frac{\pi \rho w}{4 \rho_c t} \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid,i} w^2}} \right) \right]^{-1/2} \right)^2 + \left(Q_i - \frac{\frac{4\rho_c t}{\pi \rho w} + \left(1.0553 + 3.7997 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid,i} w^2}}\right)}{3.8018 \sqrt{\frac{2\mu}{\rho 2\pi f_{fluid,i} w^2}} + 2.7364 \frac{2\mu}{\rho 2\pi f_{fluid,i} w^2}} \right)^2 \right\} \quad (4)$$

Here, the summation index i runs over all experimental values of $f_{fluid,i}$ and Q_i recorded for the given fluid at varying pressures. Density and viscosity values for pure CO_2 and pure N_2 were determined from NIST Chemistry webbook [33]. Density and viscosity of a given CO_2–N_2 binary mixture at a particular temperature and pressure were calculated from Gerg equation of state (EoS) [34] and Chung equation [35], respectively. The Gerg EoS is recommended for predicting the density of a variety of gas mixtures including CO_2-N_2 mixtures in a wide range of temperatures (from 90 to 450 K) and pressures (up to 35 MPa). The predictions of the Gerg EOS [34] were also compared with the experimental density data of Seitz et al. [36]. For CO_2-N_2 mixtures, the deviations between the two were within 1% [34,36]. The Gerg EoS is given by Eq. (5):

$$\frac{p\left(\delta, \tau, \bar{x}\right)}{\rho_M RT} = 1 + \delta \alpha_\delta^r \quad (5)$$

where p is the pressure, ρ_M is the molar density, T is the temperature, δ is the reduced mixture density, τ is the inverse reduced mixture temperature, $\bar{x}$ is the molar composition, and α_δ^r is the residual part of the reduced Helmholtz free energy of the mixture

[34]. The molar density ρ_M predicted using Gerg EoS was converted to the mass density ρ which was then used in the model Eqs. (2) and (3). Viscosities of CO_2-N_2 mixtures were calculated using Chung equation given by [35]:

$$\mu = \mu^* \frac{36.344(MT_c)^{1/2}}{V_c^{2/3}} \tag{6}$$

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. (6) are functions of the mixture composition. μ^* is a complex function and requires density and temperature of the fluid as inputs; for this purpose, density predicted by the Gerg EoS (Eq. (5)) was used. Further details about the meaning of individual quantities used in Eq. (6) are given in [35].

Table 1 shows the summary of the characteristic parameters for the studied cantilever regressed from the experimental data for different compositions of CO_2-N_2 mixture.

Using the cantilever characteristic parameters given in Table 1 and density and viscosity values for pure CO_2, pure N_2, and mixtures of CO_2 and N_2 at 308 K from atmospheric pressure up to 23 MPa, theoretical resonant frequencies and Q-factors were determined. As shown in Figs. 2 and 3, a good agreement between the experimental data and the predictions of Sader's model was observed. The average and maximum relative differences between the experimental and theoretical resonant frequencies and Q-factors for the studied fluids of different composition are given in Table 2.

As shown in Table 1, the values of the cantilever characteristic parameters determined for pure CO_2 and N_2 and for different mixtures are close to each other; this is expected since the cantilever properties should be independent of the composition of the fluid mixture. The values for the cantilever characteristic parameters given in Table 1 were also determined independently using other methods. The cantilever width was measured with optical microscopy as 19.6 μm. The cantilever frequency response was recorded in the pressure vessel that was evacuated to 0.933 kPa, and the vacuum resonant frequency was measured as 20708 Hz. The value of $\rho_c t$ calculated by multiplying the average density of the cantilever with the total thickness of the cantilever was found to be 0.011 kg/m². In this calculation, the average density of the cantilever ρ_c was determined using:

$$\rho_c = \frac{\sum_{i=1}^{3} V_i \rho_i}{\sum_{i=1}^{3} V_i} \tag{7}$$

where ρ_i and V_i are the densities and volumes of the Cr, Au, and Ni layers of the microcantilever [25]. The values of the cantilever characteristic parameters obtained using independent methods are close to the values in Table 1. This verifies that Sader's model [29] captures well the physics of the cantilever oscillations immersed in gas mixtures at high pressures.

Since the relative differences between the experimental and theoretical resonant frequency and Q-factor values are low, as shown in Table 2, it should be possible to use the cantilever frequency response to measure simultaneously the density and viscosity of the studied fluid at a particular temperature and pressure. If the cantilever characteristic parameters are known, resonant frequency and Q-factor measured in the fluid at a certain temperature and pressure can be inserted into Eqs. (2) and (3) and the density and viscosity of the fluid can be obtained by solving simultaneously these two equations by numerical methods. As discussed above, microcantilever characteristic 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
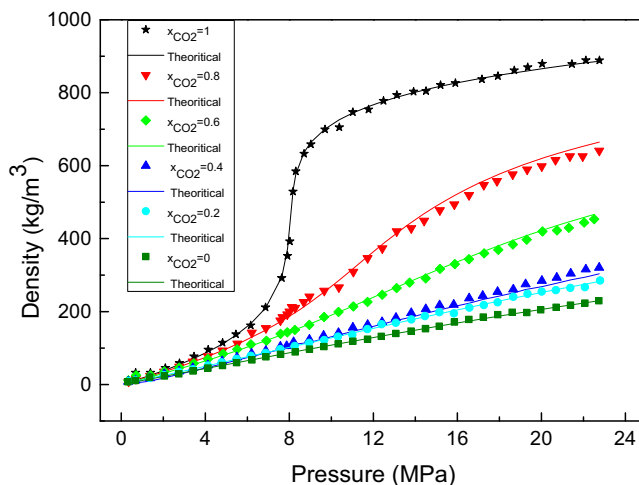

Fig. 4. Variation of fluid density with pressure for CO_2-N_2 binary mixtures at 308 K. X_{CO2}: mole fraction of CO_2, Symbols: Experimental data, solid lines: data from NIST database (pure fluids) or Gerg EoS (mixtures).

given cantilever. This in turn imposes limitations on the precision of the measurement of the fluid density and viscosity, since the density and viscosity values extracted from the frequency response data using Sader's model are very sensitive to the used values of the characteristic 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. To this end, both N_2 and CO_2 can be used as the reference fluid, since their densities and viscosities are accurately known and the experimental resonant frequency and Q-factor agree very well with the model. In our experiments, cantilever characteristic parameters were determined from a set of measurements carried out at a constant temperature using N_2 as a reference fluid. N_2 is preferred as the reference fluid since its density and viscosity do not vary considerably with the pressure, as our typical experimental conditions are sufficiently far away from the critical point of N_2.

The comparison of the measured density and viscosity of pure CO_2, pure N_2 and CO_2-N_2 mixtures with different compositions and the values obtained from the NIST database (pure fluids) and Gerg EoS and Chung equation (mixtures) are presented in Figs. 4 and 5 . The average relative differences between the measurements and expectations for the density and viscosity of the studied fluids of different composition vary between 1.0–13% and 2.4–15%, respectively. These results show that our method can measure the density and viscosity simultaneously with relatively low errors for the studied binary mixtures. From the comparison of Figs. 4 and 5, it follows that density can be measured with a higher precision compared to viscosity. One possible reason is that the resonant frequency can be determined more precisely from the measured frequency responses than the Q-factor; this is illustrated by the fact that the average standard deviation of the resonant frequency was lower than that of the Q-factor for all measurements with pure CO_2, pure N_2 and different compositions of CO_2-N_2 mixtures at the studied pressure range. Moreover, the relative differences between the experimental and theoretical Q-factor values are higher than those of the corresponding experimental and theoretical values of the resonant frequency by an order of magnitude, as shown in Table 2. In order to understand the reason for this large difference, we have to consider various sources of cantilever damping that contribute to the overall damping of the cantilever oscillations. For a cantilever immersed in a viscous fluid, the main source of damping is the

Table 1
Characteristic parameters for the studied microcantilever.

Characteristic parameters		$x_{CO_2} = 1$	$x_{CO_2} = 0.80$	$x_{CO_2} = 0.60$	$x_{CO_2} = 0.40$	$x_{CO_2} = 0.20$	$x_{CO_2} = 0$
	$\rho_c t (kg/m^2)$	0.0103	0.0106	0.0103	0.0102	0.0103	0.0105
f_{vac}	(Hz)	21007.3	20672.2	20884.0	20903.6	20919.4	20794.1
	$w (\mu m)$	20.16	20.80	20.26	21.00	19.50	19.17

Table 2
Relative difference between the experimental and theoretical values of f_{fluid} and Q-factor.

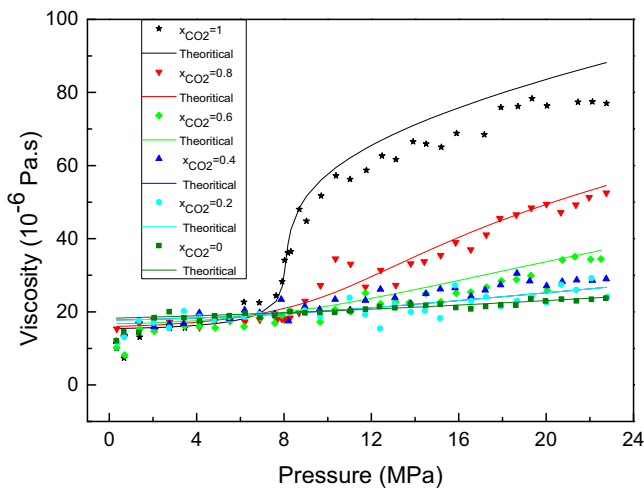| Relative difference (%)	$x_{CO_2} = 1$	$x_{CO_2} = 0.80$	$x_{CO_2} = 0.60$	$x_{CO_2} = 0.40$	$x_{CO_2} = 0.20$	$x_{CO_2} = 0$
Average f_{fluid}	0.39	0.57	0.40	0.26	0.09	0.07
Max f_{fluid}	2.25	1.22	0.85	0.87	0.36	0.26
Average Q-factor	3.89	3.81	4.49	4.37	3.55	1.28
Max Q-factor	9.95	12.70	14.20	10.43	16.26	4.60

Fig. 5. Variation of fluid viscosity with pressure for CO_2-N_2 binary mixtures at 308 K. X_{CO2}: mole fraction of CO_2, Symbols: Experimental data, solid lines: data from NIST database (pure fluids) or Chung equation (mixtures).

Fig. 6. Variation of resonant frequency with mixture composition at a constant temperature of 308 K and different pressures.

shear force acting in the fluid flowing around the cantilever; this is the damping described by Sader's model. At low fluid pressure and, consequently, low fluid viscosity, additional dissipation of the cantilever energy arising from internal friction in the cantilever material, energy loss to a compliant cantilever support, surface stresses, thermoelastic loss, and presence of additional material layers on the cantilever surface may become important [37–40]. However, these additional sources of energy dissipation are not included in the viscous damping model of Sader. As argued by Eris et al. [25], fluid viscosity is more sensitive to the measured Q-factor values than fluid density. In particular, inspection of the Sader's model equations shows that the resonant frequency depends only weakly on the fluid viscosity $\left(f_{fluid} \propto \mu^{-1/4} \right) \left(Q \propto \mu^{-1/2} \right)$ whereas the Q-factor depends strongly on viscosity

Thus, while solving the coupled Eqs. (2) and (3) of Sader's model for the fluid density and viscosity, the contribution of the Q-factor experimental values for calculating viscosity is higher than the contribution of the resonant frequencies. Therefore, any uncertainty in the measured Q-factor values will result in less precise viscosity values. On the other hand, the measured f_{fluid} and Q-factor values contribute approximately equally in calculating the fluid density; hence, the effect of the higher error of Q-factor is somewhat offset by the more precise measured values of f_{fluid}. In addition, viscosity values for mixtures predicted using Chung equation are not as accurate as the density values from Gerg EoS. For example, the average deviation between the viscosity values calculated by using Chung equation and experimental viscosity values for mixtures of CO_2 and N_2 [41,42] in the pressure range of 20–120 bar, temperature range
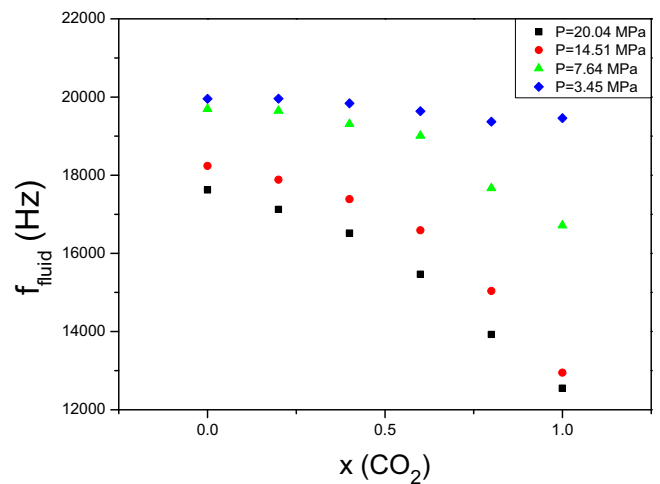
of 289–293 K, and composition range of 0.38–0.50 mol fraction of CO_2 were around 4%, while Gerg EoS predicts the density of the mixtures within a 1% error [29,31]. This may be also responsible to a certain extent for the higher relative differences observed in viscosity measurements. Furthermore, as discussed previously [25], the density and viscosity values extracted from the frequency response data are very sensitive to the values of the cantilever characteristic parameters. Thus, small changes in these parameters may lead to substantial errors in the measured thermophysical properties.

An examination of Figs. 2 and 3 shows that the resonant frequency and Q-factor vary with the composition of the mixture at a fixed temperature and pressure. Therefore, frequency response measurements can be in principle also used to determine the composition of a binary mixture. However, the variation of the Q-factor with composition is not as pronounced as the corresponding variation of the resonant frequency. Thus, resonant frequency seems to be a better indicator of the mixture composition. Fig. 6 shows the resonant frequencies for six different compositions of CO_2-N_2 binary mixture at four different pressures and 308 K. The resonant frequency was found to decrease with the increasing CO_2 fraction in the mixture. This change in the resonant frequency as a function of the CO_2 mole fraction is due to the change in density and viscosity of the fluid mixture at different compositions. From the slopes of experimental curves shown in Fig. 6, it is evident that the sensitivity of the resonant frequency to the changes in composition increases with increasing pressure. Therefore, composition of the mixture can be measured more accurately at higher pressures. In order to make this measurement, one would first need to obtain a calibration curve by measuring resonant frequencies at known

compositions at that particular temperature and pressure such as the ones presented in Fig. 6. Such a calibration curve can then be used to convert the measured resonant frequencies in a mixture with an unknown composition to the composition of the mixture.

4. Conclusions

We have characterized thermophysical properties and composition of a model binary fluid mixture of CO_2-N_2 by investigating the frequency response of microcantilevers immersed in pure CO_2, pure N_2 and four different compositions of CO_2-N_2 mixtures under a wide range of pressures (0.1–23 MPa) and a constant temperature of 308 K. A good agreement between the experimental resonant frequencies and Q-factors and the predictions of Sader's model has been obtained when the cantilever characteristic parameters (f_{vac}, $\rho_c t$, w) were regressed from the experimental resonant frequencies and Q-factors using model equations. The values of the cantilever characteristic parameters extracted from regression were close to the values obtained directly using independent methods. A procedure has been outlined for measuring simultaneously the density and viscosity of a fluid mixture and applied to determine the density and viscosity of CO_2-N_2 binary mixtures with pressures up to 23 MPa at the temperature of 308 K. The average relative difference of the density and viscosity measurements in the studied fluids with respect to the expected values ranged between 1.0–13% and 2.4–15%, respectively. It has been demonstrated that the composition of a binary mixture can also be measured using this technique.

The accuracy of the data can possibly be increased by improving the temperature control of the sample chamber, by improving the accuracy of the temperature measurements using a thermistor instead of a thermocouple, and by using cantilevers with a smaller length that are more sensitive to small variations in the fluid density and viscosity.

Our study represents the first systematic attempt to use microcantilevers for characterization of fluid mixtures at high pressures. We used CO_2-N_2 binary mixtures as the model fluid but other mixtures can also be characterized using our experimental approach. In principle, microcantilever-based sensors require only small sample volumes; thus a portable sensor can be devised to characterize the thermophysical properties of pure fluids or mixtures in applications where continuous in-line monitoring is required.

Acknowledgments

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Biographies

Gamze Eris received her B.S. and M.S degrees in Chemical and Biological Engineering from Koc University in Istanbul, Turkey in 2013 and 2015. She is currently a PhD student in the Chemical and Biological Engineering department at Georgia Institute of Technology in Atlanta, USA.

Shadi Khan Baloch received his Bachelor's degree in 2008 in Electronics Engineering from Mehran UET Jamshoro in Sindh, Pakistan and worked as Assistant Manager Transmission from 2009 to 2013 in PTCL, a leading telecom company of Pakistan. In 2013, he joined Koc University in Istanbul, Turkey as a PhD student in the Electrical and Electronics Engineering Department.

Asuman Aşıkoğlu Bozkurt received her B.S., MS and PhD degrees from Yıldız Technical University in Istanbul, Turkey in 2003, 2007 and 2013, respectively. She is currently working as a Research Associate at Yıldız Technical University. She is also working as a visiting researcher in Optofluidics and Nano-optics Research Laboratory at Koc University in Istanbul,Turkey.

Alexandr Jonas received his M.S. degree in Biophysics in 1996 from Masaryk University in Czech Republic and Ph.D. degree in Physical and Material Engineering in 2001 from the Brno University of Technology in Czech Republic. He is currently an Assistant Professor at the Department of Physics at Istanbul Technical University. His research interests include the development and applications of optical micromanipulation, microscopy, and spectroscopy techniques for characterization of complex systems and environments.

Alper Kiraz is a professor of Physics and Electrical-Electronics Engineering at Koç University. He received his B.S. degree in Electrical-Electronics Engineering from Bilkent University in 1998, M.S. and Ph.D. degrees in Electrical and Computer Engineering from the University of California, Santa Barbara in 2000 and 2002, respectively. He worked as a post-doctoral researcher at the Chemistry Department of the Ludwig-Maximilians University, Munich and as a visiting professor at the Biomedical Engineering Department of the University of Michigan, Ann Arbor. His current research interests include optofluidics, energy photonics, optical manipulation, and biomedical instrumentation.

B. Erdem Alaca received his B.S. degree in mechanical engineering from Boğaziçi University in Istanbul, Turkey in 1997 and M.S. and Ph.D. degrees in mechanical engineering from the University of Illinois at Urbana–Champaign in 1999 and 2003, respectively. He is currently an Associate Professor in the Department of Mechanical Engineering at Koç University, where he manages Mechanical Characterization and Microfabrication facilities. His research interests include small-scale mechanical behavior and testing of materials and nanowire-based devices. Prof. Alaca is a member of IEEE. He was a recipient of the 2009 Distinguished Young Scientist Award from the Turkish Academy of Sciences.

Can Erkey received his B.S. Degree in Chemical Engineering in 1984 from Boğaziçi University in Istanbul, Turkey and his Ph.D. degree in Chemical Engineering from Texas A&M University in College Station, USA. He served as an assistant professor, associate professor and professor in the Department of Chemical Engineering at the University of Connecticut. He has been a professor in the Chemical and Biological department at Koc University in Istanbul, Turkey since 2006. He is serving as the Director of the Koc University Tüpraş Energy Center. His research interests are nanostructured materials, energy and supercritical fluids.