Microcantilever Based Sensor for Characterization of Ethanol-CO_2 Fluid Mixtures at High Pressures

by

Shadi Khan Baloch

A Dissertation Submitted to the

Graduate School of Sciences and Engineering

in Partial Fulfillment of the Requirements for

the Degree of

Doctor of Philosophy

in

Electrical and Electronics Engineering

KOÇ UNIVERSITY

July 2018

ABSTRACT

Determination of composition of ethanol-CO_2 mixtures at high pressures is important in many applications involving supercritical fluids such as drying of alcogels or release of microelectromechanical device. Viscosity of ethanol-CO_2 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-CO_2 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 Limit of Detection (LOD) in such measurements carried out at high pressures is of great interest for monitoring technologically important processes. We measured the resonant frequency and quality factor (Q-factor) of ferromagnetic nickel microcantilevers immersed in ethanol-CO_2 mixtures 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-CO_2 mixtures, (ii) Compositional measurement sensitivity of cantilevers, (iii) Viscosity measurement of mixtures, and (iv) Viscosity measurement sensitivity of cantilevers.

Mixture composition of a high-pressure ethanol-CO_2 mixture can be related to the frequency response of microcantilevers immersed in the mixture fluid. We measured the frequency response of cantilevers immersed in ethanol-CO_2 mixtures containing 0.0091 – 0.0616 weight fraction of ethanol 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 show that ethanol-CO_2 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 suggest 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.

We studied compositional measurement sensitivity of cantilevers defined as the derivative of the cantilever resonant frequency or quality factor with respect to the fluid mixture composition. On the basis of Sader's model of hydrodynamic interaction of an oscillating immersed cantilever with the surrounding fluid, we derived analytical expressions 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. We measured the frequency response of cantilevers immersed in ethanol-CO_2 mixtures containing 0 – 0.04 weight fraction of ethanol 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-CO_2 mixtures of various compositions, we calculated the sensitivity at each pressure and temperature and determined the LOD of the measurement. 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. Our results convincingly illustrate 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, we present new experimental data for the viscosity of ethanol-CO_2 mixtures of different compositions with ethanol weight fraction ranging from 0.290 to 0.882. 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-CO_2 mixtures were measured using frequency response of an oscillating microcantilever immmersed 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, we studied viscosity measurement sensitivity of cantilevers defined as the derivative of the cantilever quality factor with respect to the viscosity of fluid mixture. We derived analytical expression for the sensitivity based on Sader's model. Using the frequency response data of cantilevers immersed in ethanol-CO_2 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, we calculated the model sensitivity at each mixture composition. The model sensitivity was compared with the experiment sensitivity and the relative differences were calculated. We determined the resolution of the cantilever-based viscosity measurements 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 μPa.s. Our 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-CO_2; High pressure; Sensitivity; Limit of detection; Viscosity;