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High Frequency Acoustic Reflectometry for Solid/Liquid Interface Characterization: Application to Droplet Evaporation.

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Abstract

Evolution of the local concentration in a 1 µL droplet of ethanol/water mixture during an evaporation process has been followed using high frequency acoustic reflectometry. This method has been developed for wetting characterization on micro/nanostructures and makes it possible to follow concentration evolution in a droplet deposited on a solid surface. This information gives the opportunity to predict wetting depending on surface tension linked to alcohol concentration evolution. The calibration of the method and concentration evolution in 50% and 30% ethanol droplets are presented. The evolution of a pure ethanol droplet composition is tracked so as to follow hydration process.

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1. Context:

Concentration evaluation of a mixture during an evaporation process makes it possible to determine the evolution of the properties of this mixture over the time. It is then possible to provide information for theoretical study of droplet behavior. As an example, it is a good way to determine surface tension evolution in a droplet during this process of evaporation. The local determination of this information can make easier wetting prediction at the liquid / micro-nanostructures interface because wetting state will be strongly dependent on the surface

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tension of the liquid at the interface. This can help the field of micro/nanopatterning for which cleaning and etching efficiency using chemical solutions is directly linked to wetting efficiency (Xu et al, 2012).

A very sensitive method using high frequency ultrasounds (1 GHz) has been developed and presented by Saad et al (2012) to follow wetting transition in micro and nanostructures as described by Dufour et al (2013) and Li et al (2014). In that case, the main interest of ultrasounds is due to the high contrast of mechanical impedances between air trapped at the interfaces and liquids. Moreover it does not require optical transparence. The evaluation of the reflection coefficients at the interface makes it possible to determine the properties of the reflected acoustic echoes in time domain using inverse Fourier Transform as described by Campistron et al (2011). This sensitivity has then made it possible to follow, in a first step, evaporation kinetics of drops of some water/alcohol mixtures at a plane solid/liquid interface from the tracking of the concentration evolution.

This method is based on the evaluation of acoustic reflection coefficient using thin film piezoelectric transducers (from 100 to 500 µm diameter) fabricated on the backside of the substrate on which the solid/liquid interface is characterized. These transducers are used as emitters and receivers and connected to a Vector Network Analyzer used to achieve electrical characterization of S_{ij} scattering parameters. From a theoretical point of view, considering a plane acoustic wave propagating at normal incidence at an interface separating two media of acoustic impedances Z_1 and Z_2, the absolute value of the reflection coefficient R can be calculated from the following equation:

$$|R| = \frac{Z_2 - Z_1}{Z_1 + Z_2} \quad (1)$$

$Z = \rho v$, ρ being the density of the medium and v the acoustic velocity in this medium. In our case, Z_1 is the acoustic impedance of the liquid, whereas Z_2 is the one of the (100) silicon substrate. The measurement of this reflection coefficient makes it possible to follow on line at the interface (depth in the range of the wavelength) the evolution of the mechanical impedance of the mixture and as a consequence the concentrations of the solvent and of the solute.

2. Calibration of the measurement method:

For calibrating our device, water is used as a reference liquid. One can then calculate the acoustic reflection coefficient from the values of the density and the acoustic velocity of both silicon and water found in the literature. Several precautions are taken so as to improve the accuracy of the measurements. Temporal temperature drifts are minimized by the use of 2 identical transducers, one for reference to air, the other one for measurement at silicon liquid interface. Reference to air is first measured on each. The adjustment factor $|R|_c$ is equal to the ratio of the peak amplitudes A_{22} and A_{11} of the reflection coefficients measured with each probe on each transducer

$$.|R|_c = \left(\frac{A_{22}}{A_{11}}\right)_{air} \quad (2)$$

The standardised reflection coefficient, R_{norm} at solution (sol)/ silicon interface is then deduced as:

$$|R|_{norm} = \frac{\left(\frac{A_{22}}{A_{11}}\right)_{sol}}{\left(\frac{A_{22}}{A_{11}}\right)_{air}} \quad (3)$$

Measurements are made at ambient temperature of 21°C. A drop of water of approximately 1 µL is deposited on the surface of a planar (100) silicon substrate. At a temperature of 21°C, water and silicon density and acoustic velocity are obtained from the literature in Nikanorov et al (1972) and Vatandas et al (2007) (silicon: Density =2330 kg/m^3 ; Acoustic velocity=8433.8 m/s and water : Density=997,95 kg/m^3; Acoustic velocity=1485.97 m/s. According to equation 1, one can then deduce the reflection coefficient at silicon water interface. It is found to be 0.8596. The kinetics of the reflection coefficient recorded each 30s, during 540s is reported on **Fig. 1-a**. Reliability is assessed according to the stability and the accuracy of the measurement compared to the theoretical value and evaluated to be better than 0.3%

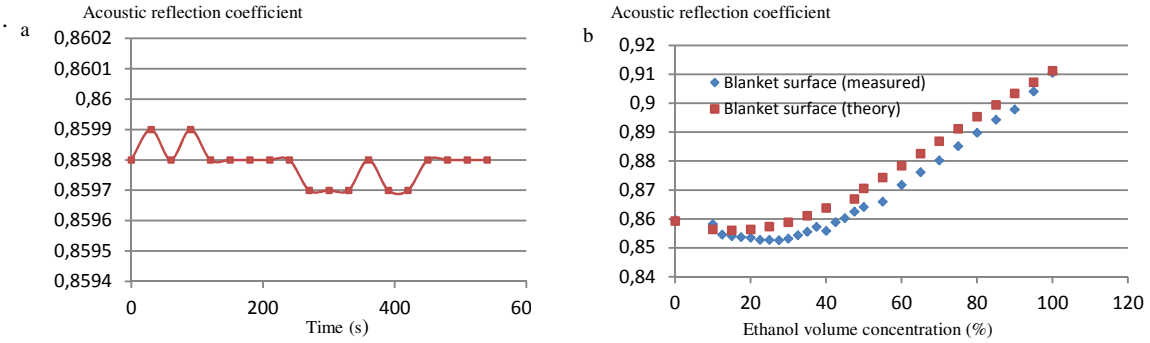

Fig. 1. Acoustic reflection coefficient $|R|_{norm}$: a) measured for water (21°C) as a function of time ; b) calculated and measured in ethanol/water mixtures as a function of Ethanol Volume Concentration .

We also calibrated the evolution of the acoustic reflection coefficient depending on the volume concentration of ethanol in water. Experiments have been achieved using ethanol/water mixtures so as to be able to obtain liquids with variable surface tension (from 72.6 for water to 22.4 mN/m for ethanol). The values of the density of ethanol-water mixtures as well as their acoustic velocity as a function of alcohol concentration are obtained from Vatandas et al (2007) and are compared to experimental results in **Fig. 1-b**. Experimental and theoretical reflection coefficient as a function of ethanol volume concentration in water, are represented for a temperature of 20°C. There is a good agreement between the theoretical values and the measured ones within a confidence range better than 1%. The reproducibility of the measurements, determined on pure water or pure ethanol droplets is estimated at 0.3% on a planar sample (blanket).

3. Evaporation effect quantification

Ethanol evaporation, as a function of time starting from a controlled concentration of ethanol/water mixture on a planar surface treated with an hydrophobic layer PFTS (PerFluoro TrichloroSilane), has been studied. To demonstrate the possibility to track the concentration evolution at the interface, we present the results, as an example with initial volume concentrations of 50% and 30% of ethanol. In a first step, the reflection coefficient evolution is tracked during the evaporation as presented in **Fig. 2**. It is then possible to interpret the kinetics of the concentration evolution of the mixture at the interface using the calibration curve given in **Fig. 1-b** presenting the acoustic reflection coefficient versus ethanol volume concentration of the mixture.

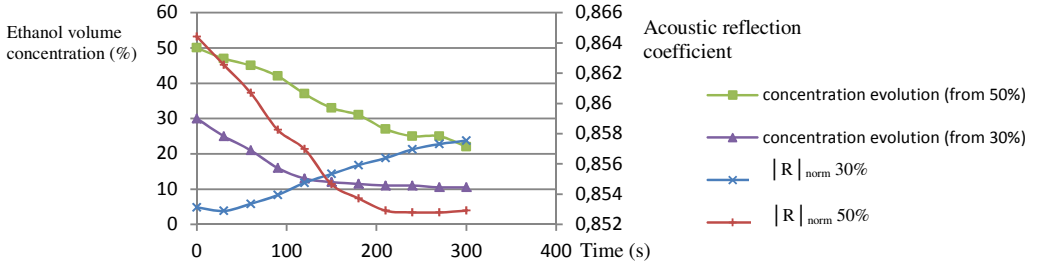

Fig. 2. Evolution of the concentration of ethanol (and of the acoustic reflection coefficient) in a 5 µL droplets of original volume concentrations 30% and 50%

The volume of the droplet was 5 µL. For these two different initial concentrations of ethanol of 30% and 50%, it was observed that the drop concentration is going down from 30 to 12% on the one hand and from 50 to 35% on the other hand in 120 seconds. Concomitantly to the measurement of the reflection coefficient during the evaporation phenomenon, lateral view images of the droplet are captured so as to measure the droplet dimensions. An image processing software makes it possible to determine the droplet's volume kinetics synchronously with

the measurement of the reflection coefficient during the evaporation kinetics. **Fig. 3-a** presents the reflection coefficient evolution under a pure ethanol droplet (volume of 1 µL) and shows that with the decrease of the volume of this droplet, the concentration of ethanol at the interface determined from the acoustic reflection coefficient, decreases. It is to be noticed that the volatility of ethanol (saturated vapour pressure of 5.8kPa at 20°C) is much higher than the one of water (saturated vapour pressure of 2.34kPa at 20°C).

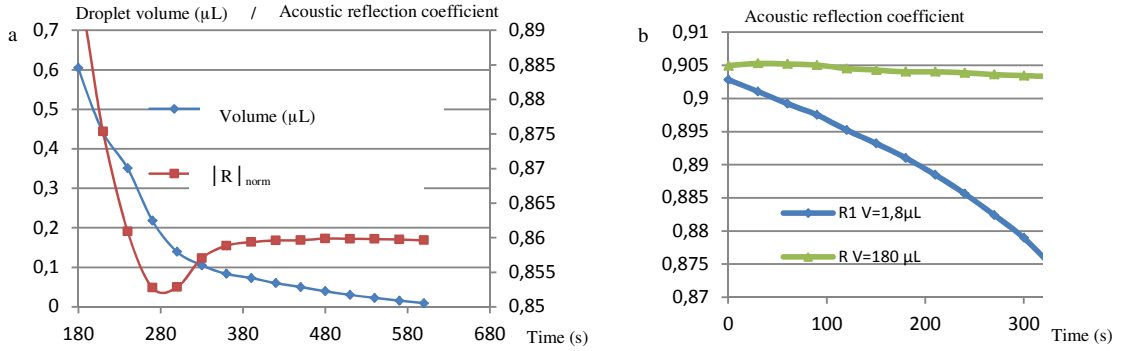

Fig. 3. Evolution of the acoustic reflection coefficient at the interface liquid/silicon: a) 1 µL droplet of pure ethanol at 99,9% (the evolution of the volume is also given) ; b) comparison between a 1µL droplet and a bigger volume of 180 µL.

It shows that it is possible to track the hydration in ambient hygrometry of 50% of this droplet with an ethanol concentration decreasing until we observe pure water at the interface (acoustic reflection coefficient close to 0.86). This is an interesting result to model wetting or fluidic evaporation behavior of a droplet on solid interface. Nevertheless, the acoustic reflection coefficient measured with a bigger volume of ethanol of 180 µL (presented in **Fig. 3-b**) will have a slower decrease because it is less sensitive to hydration from humidity in the environment in comparison to a 1 µL droplet.

As a conclusion, this method has also shown its sensitivity to track concentration evolution of a droplet/solid interface. The acoustic method we developed seems to suggest many others potentialities such as surface pollution or particles sedimentation detection. Since it is depending on the concentration of residual particles deposited on the surface when the drop is totally evaporated, the acoustic reflection coefficient may be modified.

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