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Gas-adsorption dynamics at the water–air interface, revealed by resonant droplet tensiometry

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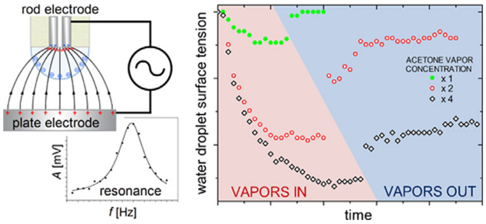
HIGHLIGHTS

- Resonant droplet tensiometry.
- Surface tension change due to vapor pressure and adsorption.
- Stimulated gas desorption at water–air interface.

GRAPHICAL ABSTRACT



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ABSTRACT

A resonant hemispherical pendant droplet tensiometry has been used to register in real time the change of surface tension of low Bond number water droplets due to evaporation of simple volatile liquids, acetone and chloroform, in a closed vessel. The contributions of the gas vapor pressure and of the gas molecules adsorption to the surface tension changes are distinguished and evaluated in time. After the initial increase of gas adsorption, a negative adsorption has been found in later time, which may be informative for the dynamics of the adsorption and desorption processes in the interface layer. The observed desorption processes are stimulated by the mechanical oscillations of the interface layer, as far as the droplet is in resonance during the measurements.

1. Introduction

The gas adsorption processes at the interface liquid droplet–air are of major importance not only in different technological processes in industry and in engines (Burger et al., 2003; Edwards et al., 1991; Dukhin et al., 1995), but also in the natural atmospheric phenomena (Finlayson-Pitts and Pitts, 2000; Djikaev and Tabazadeh, 2003; Finlayson-Pitts, 2003; Fuchs, 1964). Thus, studying the processes of structure and contents changes in time, occurring at the water–air interface induced by gas molecules adsorption, can be useful both to science and technology. Both theoretical and experimental approaches have been used recently to examine the adsorption of volatile organic compounds into the liquid–vapor interface. Most often the theoretical approach is realized by numerical simulations with the help of molecular dynamics (Canneaux et al., 2006; Vieceli et al., 2004; Morita, 2003). The experimental approach employs surface tension measurements at the water–vapor interface. A detailed critical review of the used experimental methods can be found in (Braunt, 2000). Most of the methods for surface tension measurements are based on analyzing the droplet shape deformations of large pendant or sessile drops with large Bond numbers, for which gravitational forces are dominant (Berry et al., 2015).

Numerous studies have been published recently to examine the peculiarities of the water–air interface. Mishra et al. have established different values of the pH-factor in the different regions of the interface (Mishra et al., 2012). Takahashi has examines the role of the H^+ and OH^- radicals for the charge distribution in the water–air interface, by measuring the ζ–potential of microbubbles (Takahashi, 2005). Ingram et. al. have given a detailed review of the mass-spectrometrical methods for studying the dynamics of chemical reactions on liquid surfaces, in particular, at the liquid-air interface (Ingram et al., 2015).

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In the present work the surface tension change due to solute adsorption is measured in real time by using a resonant hemispherical droplet tensiometry. The method is based on registering the resonant frequency of electrically driven small spherical or hemispherical droplets with small Bond numbers ($B_0 \leq 0.1$), for which the surface tension is dominant (Tankovsky and Zografov, 2011; Tankovsky et al., 2013; Zografov et al., 2014). The examined gas vapors are introduced into a closed transparent jar by evaporation of deposited by injection small liquid droplets. The influence of the gas vapor pressure upon the surface tension is evaluated and taken into account. The vapors of two simple volatile liquids, acetone and chloroform, have been examined.

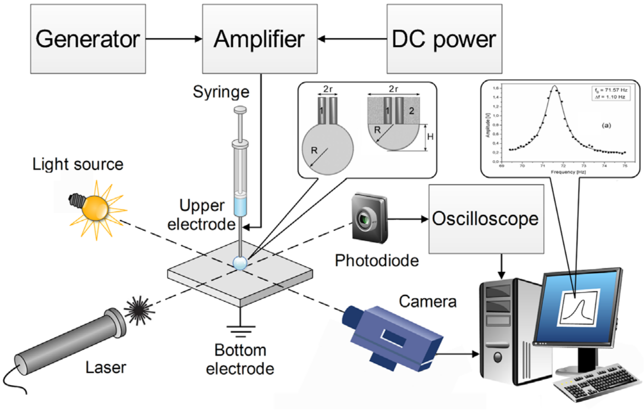

Fig. 2. Electrically driven resonant droplet tensiometry.

2. Experimental set-up and resonant hemispherical droplet tensiometry

The experimental set-up is presented schematically in Fig. 1. The hemispherical water droplet with radius $R \approx 0.9$ mm, acting as a sensor of the surface tension, is denoted with 1, 2 is a metal needle electrode and 3 is a metal plate electrode, 4 is the electrical driving source, 5 is a droplet of volatile liquid, whose vapors influence the surface tension of the sensor droplet 1, 6 is a Teflon plate over which the volatile droplet is deposited through a narrow tube 7. The volatile droplet volume is controlled by a syringe 8. The air input openings 9 are closed during evaporation and they are open when the vapors are pumped out through the opening 10.

The principle of the resonant droplet tensiometry is shown schematically in Fig. 2. A sinusoidal signal from a functional generator is amplified and is fed to the electrodes of the sensor hemispherical droplet. The electric force at the droplet interface is due to the jump of the dielectric constant at the droplet interface. The force is directed normally to the interface and is quadratic to the electric field E (Tankovsky et al., 2013)

$$F = \frac{3}{2}\varepsilon_0 E^2 \frac{\varepsilon - 1}{\varepsilon + 2} \tag{1}$$

Here ε is the dielectric constant of the liquid, while the dielectric constant of the air equals one. Additional DC electric power source is applied at the electrodes to enhance the linear component of the electric signal. Typical applied voltages are $U_{ac} = 30$ V;$U_{dc} = \pm 150$ V. The amplitude of the oscillating droplet is registered with the help of a low-power He–Ne laser, illuminating the droplet and a photodiode, as explained in (Tankovsky and Zografov, 2011). By scanning the frequency of the driving electric field a resonant curve is obtained and the resonance frequency f_0 is precisely determined. The surface tension σ can be found by the rearranged Rayleigh relation for the lowest resonant mode f_0 of a spherical droplet with radius R:

$$\sigma = \frac{f_0^2 \rho \pi^2 R^3}{2} \tag{2}$$

However, the influence of the boundary conditions at the supporting surface and the deviations of the droplet from a perfect sphere lead to a necessity to introduce correction terms in the Rayleigh relation. These correction terms can be eliminated if a hemispherical droplet is used and Eq. (2) can be applied for defining the surface tension, as described in (Tankovsky et al., 2013; Zografov et al., 2014). The droplet is also illuminated by a lamp and observed by a video camera, which allows a precise measurement and control of the droplet radius R and height H with the help of appropriate software.

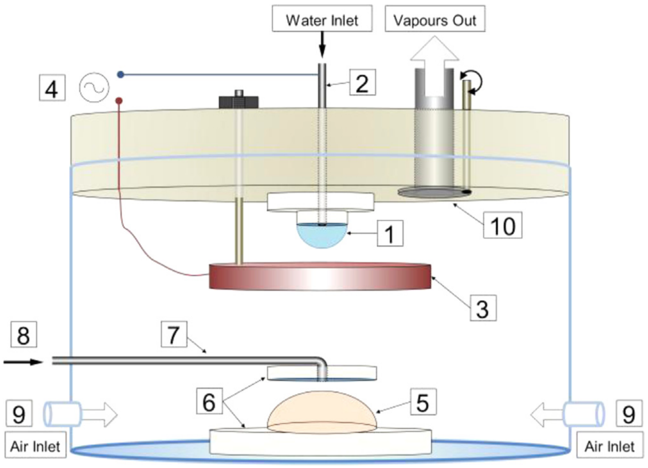

Fig. 1. Experimental set-up.

The resonant droplet tensiometry is an alternative to the other methods for measuring surface tension. Its accuracy is surpassed by some other methods e.g. droplet-shape method, which uses large-sized droplets with large Bond Number. The advantages of the resonant droplet method are its short time of performance i.e. its ability to measure in real time, the use of small sized droplets i.e. small Bond number, and the use of mechanical resonant oscillations. The method employs electrically driven cw oscillations and frequency scanning to determine the resonant frequency. However, the rapidity of the method can be improved if a short pulsed force is applied, followed by a FFT.

3. Methodology

The experimentally measured in real time surface tension $\sigma_e(t)$ of the sensor hemispherical droplet is given by the relation:

$$\sigma_e(t) = \sigma_0 - \sigma_p(t) - \sigma_a(t) \tag{3}$$

Here σ_0 is the surface tension of pure water, $\sigma_a(t)$ is the change of surface tension, caused by gas molecules adsorption and $\sigma_p(t)$ is the surface tension change caused by the gas vapor pressure.

Let us imagine that the gas vapor molecules bounce from the water surface without adsorption, exerting a pressure p_g. Then the Laplace law can be generalized in time, as follows:

$$p_l - p_0 - p_g(t) = \frac{2(\sigma_0 - \sigma_p(t))}{R} \tag{4}$$

Here p_l is the pressure in the liquid droplet, p_0 is the atmospheric pressure, $p_g(t)$ is the varying in time gas vapor pressure, R is the sensor droplet radius. When no gas vapors are present the