ELECTRIC EXCITATION OF RESONANT OSCILLATIONS OF A HEMISPHERICAL PENDANT DROPLET, USED AS A TOOL TO EXAMINE THE PROPERTIES AND DYNAMIC PROCESSES IN GAS–LIQUID INTERFACE

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Николай Танковски, Николай Зографов. ИЗПОЛЗВАНЕ НА ЕЛЕКТРИЧЕСКИ ВЪЗБУДЕНИ РЕЗОНАНСНИ ОСЦИЛАЦИИ НА ПОЛУСФЕРИЧНА ОКАЧЕНА КАПКА, КАТО ИНСТРУМЕНТ ЗА ИЗСЛЕДВАНЕ НА СВОЙСТВАТА И ДИНАМИКАТА НА ПРОЦЕСИТЕ В ИНТЕРФЕЙСА ГАЗ–ТЕЧНОСТ

Електрично възбудени осцилации на течна капка са използвани по два начина – за определяне на повърхностно напрежение и за манипулиране свойствата и процесите в интерфейса течност–въздух. Представен е обзор на научните дейности, извършени по този експериментален метод. Разгледани са получените резултати и са представени новите направления за изследване.

Nikolay Tankovsky, Nikolay Zografov. ELECTRIC EXCITATION OF RESONANT OSCILLATIONS OF A HEMISPHERICAL PENDANT DROPLET, USED AS A TOOL TO EXAMINE THE PROPERTIES AND DYNAMIC PROCESSES IN GAS-LIQUID INTERFACE

Electrically excited oscillations of pendant liquid droplets have been used in two main cases- as a means to measure the surface tension and as a means to manipulate the properties and processes in the interface liquid-air. A review of the research activities of this experimental approach is presented. Preliminary results are discussed and new fronts of research are proposed.

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1. INTRODUCTION

It can be said that the interface liquid-air resembles a crossroad of different transport processes on both sides of the interface, which meet there and interfere. Transport processes are, for example, the following: diffusion of molecules and aggregates, driven by the gradient of electrochemical potential, migration of charged molecules, driven by electric field gradients, micro-flows driven by pressure gradients, evaporation and condensation, driven by kinetic energy etc. The evaporation processes across the interface liquid-air have attracted the attention of researchers studying both static and dynamical structures in the interface [1–4]. The adsorption of molecules from the gas phase at the interface liquid droplet-air is important in different technological processes [5–7] and in natural atmospheric phenomena [9, 10]. Adsorption of molecules and aggregates, especially surfactant macromolecules, from the liquid phase at the interface are also of scientific and practical interest [11–13]. It is clear that all these processes modulate the properties of the interface and its surface tension. Hence a real time tensiometric method can reveal the dynamics of the pertinent processes in the vicinity of the interface. Resonant oscillations of a pendant liquid droplet, excited by electric field have been used to develop a tensiometric method [14].

There are several advantages when using a pendant droplet of submillimeter size, as a tensiometric tool to examine the interface liquid-gas:
• A very small amount of the tested liquid is needed
• A formula, derived by Rayleigh [15], gives a direct relation between the resonant frequency of a spherical droplet and the surface tension. Thus the momentary measured value of the resonant frequency of a droplet reveals the momentary value of the surface tension, which can be used as a tensiometric method.

$$f_2^2 = 2\frac{\sigma}{\pi^2 \rho R^3} \tag{1}$$

Here f_2 is the lowest possible resonant frequency mode, R is the droplet radius, σ is the surface tension and ρ is the liquid density.
• Due to the small size of the droplet, even weak perturbing forces can easily affect the dynamical processes in the interface. Such perturbations can be realized by mechanical resonant oscillations, by local gas pressure, by local nonhomogeneous electric field or by induced convective or diffusive micro-flows.
• Submillimeter droplets are not deformed by gravity due to the small radius, ensuring domination of tension force compared to weight force (small Bond number).

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- A pendant droplet is preferable for tensiometry, when compared with a sessile droplet since the restoring force is the tension force alone, while for the sessile droplet the restoring force is the sum of tension and gravity.
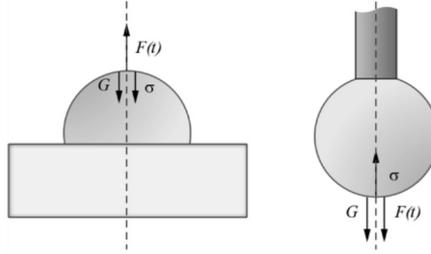

Fig. 1. Forces upon a sessile and pendant droplets: σ – surface tension, *G* – force of weight, *F(t)* – time modulated external force driving the droplet in to oscillations

2. ELECTRIC EXCITATION OF PENDANT DROPLET OSCILLATIONS

The geometry of the electrodes used to excite droplet oscillations are shown in fig. 2. The drop is attached to a thin metal needle, serving as an electrode, while the counter electrode is a plain plate. The electric field distribution in the droplet is non-homogeneous but symmetric, relative to the axes, passing through the vertical diameter of the droplet, as shown in fig. 2.
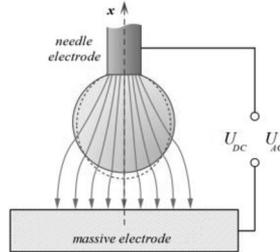

Fig. 2. Illustrative electric field distribution through the droplet

The density of the electric forces in a liquid dielectric is given by the formula:

$$f_e = \rho_c E - \frac{\varepsilon_0}{2} E^2 \nabla \varepsilon + \frac{\varepsilon_0}{2} \nabla \left(E^2 \frac{d\varepsilon}{d\rho} \rho \right) \qquad (2)$$

where ρ_c is the density of the free electric charges in the liquid, E is the electric field vector, ε_0 – vacuum permittivity, ε – liquid permittivity, ρ – liquid density.

The gradient of pressure equals the force density:

$$\nabla p = f_e \qquad (3)$$

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$$\nabla p = -\frac{\varepsilon_0}{2} E^2 \nabla \varepsilon + \frac{\varepsilon_0}{2} \nabla \left(E^2 \frac{d\varepsilon}{d\rho} \rho \right) = \frac{\varepsilon_0 \rho}{2} \nabla \left(E^2 \frac{d\varepsilon}{d\rho} \right) \tag{4}$$

Here the dielectric gradient is neglected since a non-homogeneous dielectric is not stable in liquids due to equalizing diffusion processes. Integration of equation (4) between two arbitrary points 1 and 2 gives the following relation:

$$p_2 - p_1 = \frac{\varepsilon_0 \rho}{2} \left[E^2 \frac{d\varepsilon}{d\rho} \right]_2 - \frac{\varepsilon_0 \rho}{2} \left[E^2 \frac{d\varepsilon}{d\rho} \right]_1 \tag{5}$$

Finally, after taking into account the Clausius-Mossotti relation:

$$\frac{\varepsilon - 1}{\varepsilon + 1} = \frac{N_A \rho \alpha}{3M} \Rightarrow \frac{d\varepsilon}{d\rho} = \frac{(\varepsilon - 1)(\varepsilon + 2)}{3\rho} \quad , \tag{6}$$

where N_A – Avogadro's number, α – liquids molecular polarizability and M – liquid molecular weight. Thus one can obtain:

$$p_2 - p_1 = \left[\frac{\varepsilon_0 E^2}{2} \frac{(\varepsilon - 1)(\varepsilon + 2)}{3} \right]_1^2 . \tag{7}$$

The homogeneous electric field is a constant in a liquid and is given by

$$E = \frac{3}{2 + \varepsilon} E_0, , \tag{8}$$

where E_0 is the magnitude of the external electric field.

In this case the pressure inside the droplet is zero and only across the surface is nonzero due to the different values of the dielectric constant in the liquid and in the air:

$$p = \frac{2}{3} \varepsilon_0 E_0^2 \frac{\varepsilon - 1}{\varepsilon + 2} \tag{9}$$

Thus, the electric force in homogeneous electric field has a surface component alone, while in non-homogeneous electric field the force has both bulk and surface components.

It can be seen that the force is quadratic to the electric field. Thus applying ac and dc components of the electric field will excite both first and second harmonics of oscillating pressure:

$$E = E_{DC} + E_{AC} \sin \omega t \Rightarrow E^2 = E_{DC}^2 + 2E_{DC}E_{AC} \sin \omega t + \frac{1}{2} E_{AC}^2 (1 - \cos 2\omega t) \tag{10}$$

However when $E_{DC} >> E_{AC}$

$$E^2 \approx E_{DC}^2 + 2E_{DC}E_{AC}\sin\omega t \Rightarrow f_e(t) \approx 2E_{DC}E_{AC}\sin\omega t \qquad (11)$$

Thus, the advantages of applying high *DC* component of the electric field are linearization and enhancement of the force and polarization of the interface.

3. ADVANTAGES OF A HEMISPHERICALLY SHAPED PENDANT DROPLET USED AS A TENSIOMETRIC TOOL

The Rayleigh formulae (1) for the resonance frequency of a droplet is valid for a spherically shaped droplet, unperturbed be external forces. However, in the gravitational field of the Earth the droplet should be supported by a surface from below (sessile drop) or by a surface from above (pendant drop). The real supported drop differs from an ideal free sphere because of the disturbance introduced by the supporting surface and because of gravitational shape deformations. Bisch et al [16] and later M. Perez et al [17] have proposed the following empirical formula for the resonant frequency of a sessile drop:

$$f_0(R) = \frac{\sqrt{3}}{2}\left(\frac{R_e}{R_p}\right)\sqrt{\frac{2\sigma}{\rho\pi^2 R^3}}\sqrt{\frac{r}{R}} \quad . \qquad (12)$$

Here R_e and R_p are the radiuses at the equator and at the pole of the gravitationally distorted sphere, ρ is the density of the liquid and σ is the surface tension. The first factor in the right hand side of (12) is a correction for the gravitational shape distortion of the droplet, the second factor is the Rayleigh frequency and the ratio $(r/R) \leq 1$ characterizes the boundary conditions at the supporting area. The radius of the circular region, where the drop is in touch with the supporting surface is r, and the radius of the droplet is R. One can avoid the non-spherical gravitational deformations of the droplet by choosing small drop radius, providing smaller than unity Bond number $B = \rho g R^2/\sigma$. However, the influence of the supporting element cannot be avoided. Hence, we shall ignore the shape correction term in (12) and the following generalized proportionality relation can be used:

$$f_0(R) \approx \sqrt{\frac{\sigma}{\rho R^3}\left(\frac{r}{R}\right)^x} \quad . \qquad (13)$$

In [16] the power x of the ratio (r/R) has been evaluated to be equal to one for a sessile drop, whereas in relation (13) the value of x is a generalization for pendant droplet, introduced as a free parameter, defined experimentally for different conditions. Evidently, the value of x is a measure for the influence of the boundary conditions upon the experimental value of the resonant frequency. We have found

experimentally that the value of x depends on the liquid properties with a tendency of growing when the surface tension becomes smaller. Thus, the unknown value of x is unique for every liquid, which makes it impossible to calibrate the measurements of the resonant frequency for a pendant spherical droplet. Different contact surface boundary conditions were examined, represented by three, equal in outer diameter $d = 0.7$ mm but different in design and materials, supporting electrodes. For metal needle electrode we obtained $x \approx 1.36$, for plastic needle, made from high-purity polypropylene $x \approx 1.30$ and for high-purity polypropylene rod $x \approx 1.00$.

The decision of this problem is to use a hemispherical droplet (fig. 3) for which the equivalence $r = R$ is valid, making the ratio $(r/R)^x$ equal to unity for any x.
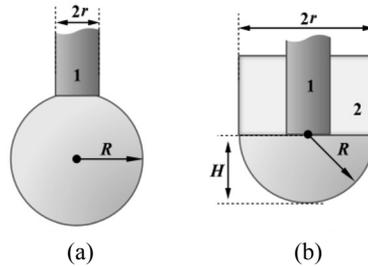

Fig. 3. Cross-sections of pendant droplets-1 needle, 2 Teflon: a) spherical droplet; b) hemispherical droplet

Thus, the correction term for the boundary conditions in (13) is eliminated [18]. Moreover, it is much easier to build a perfect hemispherical than a perfect spherical droplet. While the supporting element is a disturbance for the sphere, for the hemisphere it is a necessary existence condition. Additional advantage of the hemispherical droplet is lower weight and larger support surface, ensuring lower gravitational deformations.

We have used the advantages of a pendant hemispherical droplet to apply the Rayleigh formula and to evaluate the surface tension in real time. We have registered a lowest resonant frequency for a hemispherical pendant droplet about 3 times higher than for a pendant spherical droplet of the same radius. The ratio of mode $n = 4$ to the basic mode $n = 2$ is equal to 3. This fact suggests that the lowest excited mode for a hemispheric droplet is the fourth Rayleigh mode, $n = 4$. The obtained exact Rayleigh mode confirms the theoretical result of Lyubimov et al [19] claiming, that the resonant frequency modes of a hemispherical droplet for large wetting parameter i.e. for poor wetting of the supporting surface are, in a good approximation, the same as for an ideal sphere. The Teflon supporting surface provides the necessary poor wetting condition.

4. MAIN APPLICATIONS

4.1. RESONANT HEMISPHERICAL DROPLET TENSIOMETER, COMPARED WITH OTHER TENSIOMETRIC METHODS

The resonant droplet oscillations of a pendant droplet have been used for measuring the interfacial tension and viscosity of liquids. A technique, called „Oscillating drop surfactometer" (ODS) was proposed by Meier et al. [20]. The driving force in the ODS technique is applied indirectly upon the droplet by vibrations of the supporting needle, caused by a piezoelectric transducer. In our method the electric force has axisymmetric distribution and is applied directly upon the surface of the droplet, which favors the excitation of axisymmetric resonant modes, which are well described theoretically. Another advantage of the electric force is the flat amplitude-frequency characteristic, while the piezo-transducer has its own resonances.

Another popular tensiometric method uses the deformations of a pendant droplet, caused by gravitational field of the Earth and is called Axisymmetric Drop Shape Analysis or ADSA [21]. A software program compares the contour of a static droplet with a theoretical shape, The best fitting between real and theoretical shapes provides a means to define the surface tension

The tensiometric method ADSA uses larger droplets with Bond number $B_o>1$, while the resonant method uses droplets with small Bond number $B_o<0.5$. Despite its wide range of applications and its popularity, ADSA equipment cannot be used when micro-flows occur influencing the droplet shape. In contrast, the resonant method can be applied when the interface is manipulated by mechanical oscillations and electric field.

4.2. STUDY OF GAS PRESSURE TENSION AND SORPTION PROCESSES IN THE INTERFACE GAS–LIQUID

It is well known that the interfacial tension at the gas-liquid interface depends not only on the liquid properties, but on the partial gas pressure, as well. Thus the resonant behavior of a hemispherical water droplet located in a closed container, and exposed to vapors or gases with different concentrations, can be used as a sensor of both interface adsorption and partial gas pressure variations.

Resonant hemispherical droplet tensiometry was successfully used to study the dynamics of adsorption processes and of the partial gas pressure. A gas-cuvette was constructed for this study, as shown in fig. 4.
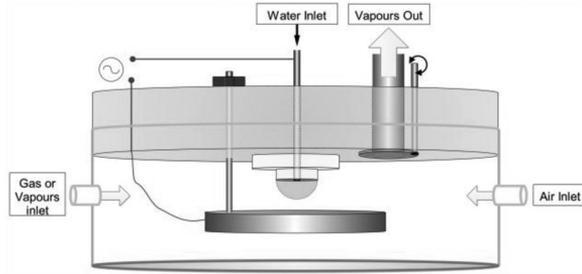
Fig. 4. Gas-cuvette for gas adsorption and pressure studies
with resonant hemispherical pendant droplet of deionized water

The closed gas-cuvette is made from glass and allows the optical detection of the droplet size and the oscillation amplitudes. The experimental set-up is shown in fig. 5.
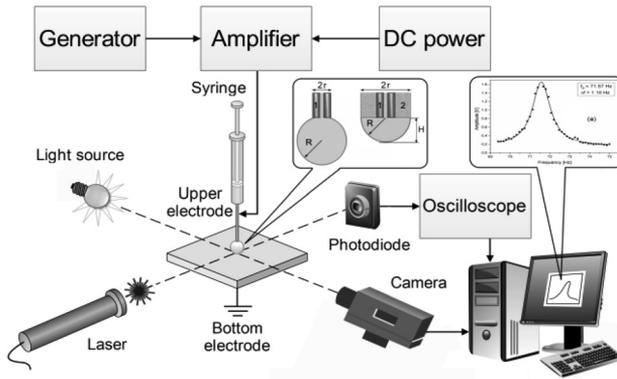

Fig. 5. Electrically driven resonant droplet tensiometry

This setup was used to study the temporal evolution of the surface tension of hemispherical pendant droplet of deionized water when vapors of a volatile liquid fill the closed cuvette.

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

$$\sigma_e(t) = \sigma_0 - \sigma_p(t) - \sigma_a(t) \tag{14}$$

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 vapour pressure.
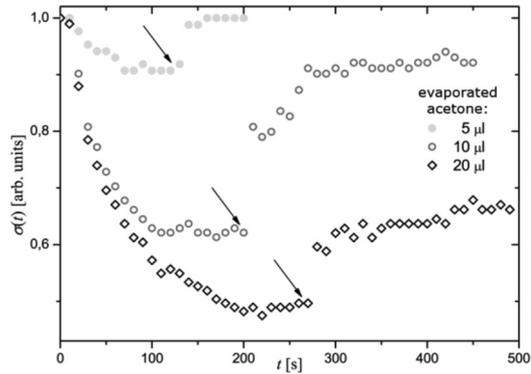
Fig. 6. Surface tension evolution $\sigma(t)$ of deionized water hemispherical droplet used as a sensor for surface tension dynamics measurements in the presence of acetone vapours

The arrows in fig. 6 represent the moment when the volatile droplet is completely evaporated and all of the vapors are evacuated from the cuvette and replaced by fresh air. The time evolution of the surface tension caused by gas pressure $\sigma_p(t)$ can be evaluated theoretically and the time evolution of adsorbed gas molecules is obtained, as shown in fig. 7.
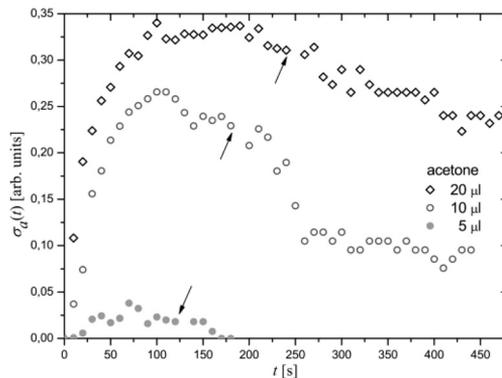

Fig. 7. Time evolution of adsorbed acetone gas molecules in the interface

It can be seen that the surface tension change, due to adsorption, reaches a maximum and then falls down. The decrease of $\sigma_a(t)$ is indicative for negative adsorption (desorption) of the gas molecules in the interface. Such behaviour should be explained with the processes, occurring in the adsorption layer. There are two possibilities, which can explain the observed negative adsorption, i.e. the decrease of $\sigma_a(t)$ in time. Either the adsorbed gas molecules evaporate back in the gas phase or they diffuse in the bulk of the sensor droplet. This problem is analysed in [22].

A curious result is obtained when a cigarette smoke is introduced in the cuvette. The surface tension falls and does not recover when the smoke is pumped out. This shows that particles of the smoke are irreversibly adsorbed in the interface.
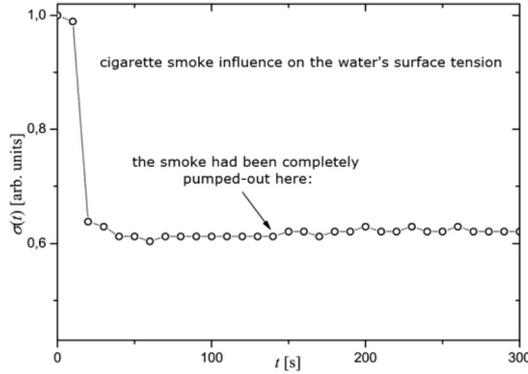

Fig. 8. Deionized water interfacial tension change under the influence of cigarette smoke

This is an interesting example of what happens in the lungs of persons having the bad habit to smoke cigarettes.

4.3. EXAMINATION OF THE INFLUENCE OF RESONANT DROPLET OSCILLATIONS AND
OF APPLIED DC ELECTRIC FIELD ON THE DROPLET EVAPORATION RATE
AND TRANSPORT PROCESSES THROUGH THE INTERFACE

The resonant oscillations of a hemispherical droplet can be used not only as a tensiometric technique but also for manipulation of the liquid gas-interface. The combined influence of mechanical oscillations and external electric field can be used as an instrument for manipulation or modification of the liquid-gas interface. Another macro-magnitude, characterizing the structure and properties of the interface, besides the surface tension, is the evaporation rate. We have developed a method, called compensated evaporation, which measures the evaporated liquid volume in real time, whereas the size of the droplet remains constant [23]. The change in time of the evaporated volume gives the evaporation rate:

$$e(t) = \rho \frac{dV(t)}{dt} \tag{15}$$

Firstly we have examined deionized water as an example of pure liquid. The results are shown in fig. 9.
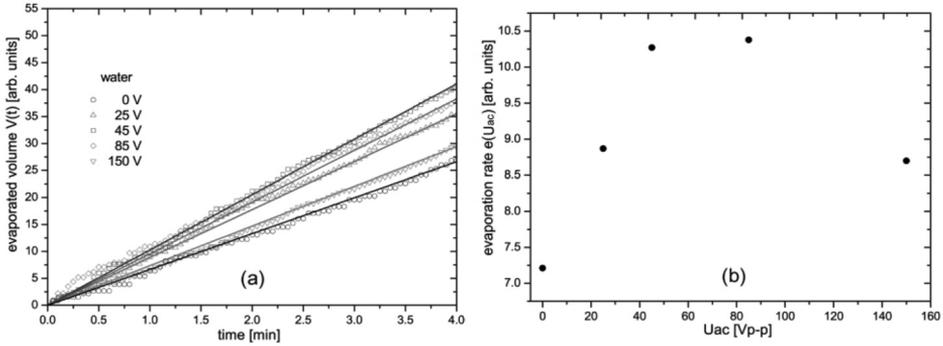
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Fig. 9. Time dependencies in pure water at different driving voltages *U*ac:
a) evaporated-volumes $V(t)$ and linear fitting approximations;
b) corresponding evaporation-rates e(*U*ac)

The evaporation curves $V(t)$ in fig. 9a are well approximated by linear trend lines, which shows that the interface properties remain constant during evaporation of pure water. The corresponding evaporation rates are determined by the slopes of the linear trend-lines (differentiation of the evaporated volume in time) and the results are shown in fig. 9b.

The following evaporation features of pure water can be noticed in fig. 9b:

For smaller oscillation amplitudes ($U_{ac} \leq 45$ V), in a linear regime, the evaporation rate is proportional to the oscillation amplitude. The increased evaporation of the oscillating droplet can be attributed to insertion of kinetic energy in the liquid by the resonant oscillations.

For higher oscillation amplitudes ($U_{ac} \geq 45$ V), in nonlinear regime, the evaporation rate reaches a maximum and then falls down. The processes occurring in a thin vapor layer, close to the oscillating interface should be considered. The velocity of the oscillating interface is higher than the vapor diffusion rate. When the oscillating droplet expands, the vapor layer is compressed. Thus, the vapor pressure rises and the vapors saturate, which favors condensation processes. In the next half-period, the droplet interface shrinks and the vapor layer expands. The vapor pressure descends and evaporation processes are favored. The net evaporation-rate is decreased, since part of the evaporated liquid returns back in the droplet. The relatively smaller evaporation rate for higher amplitudes ($U_{ac} = 150$ V), can be attributed to the balance between the counteracting stimulated evaporation and stimulated condensation.

The processes of stimulated evaporation and condensation depend on the properties of the vapor layer and on the properties of the interface. Characteristic parameters are the oscillating interface amplitude, the thickness of the vapor layer,

the oscillating interface velocity and vapor diffusivity. In this way, the described experimental method can be used for studying the structures and diffusion rates in the vapor layer.
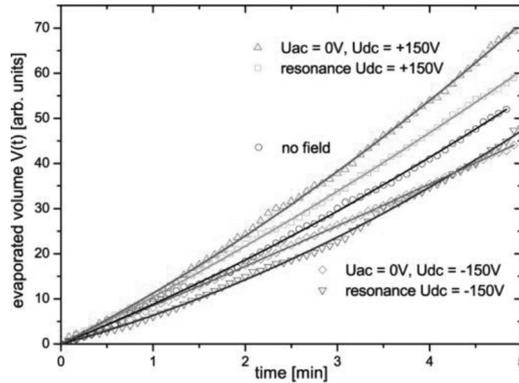

Fig. 10. Time dependencies of the evaporated volumes $V(t)$ and quadratic trend-lines in aqueous SDS surfactant mixture for static and oscillating droplet and for different dc-voltage polarization

The evaporation of solutions and complex liquids is more complicated since the mass flux of different species depends on the mole fraction of other species and diffusional interaction phenomena may occur. Evaporation of aqueous solution of Sodium Dodecyl Sulfate (SDS) surfactant has been examined under the same conditions [23]. The growing nonlinear evaporation rates suggest that the evaporation conditions in the interface and in the adjacent regions are varying monotonously during transient evaporation of complex liquids, before equilibrium is achieved.

4.4. TEMPERATURE DEPENDENCE OF THE ABILITY OF IONS TO MIGRATE IN THE INTERFACE ELECTROLYTE–AIR

The pendant droplet resonance has been applied also to examine the penetration of ions in the interface, changing its properties. The resonances of deionized water and 0.1M aqueous solution of KH_2PO_4 are compared in fig. 11 and fig. 12 for different temperatures when a dc polarizing voltage is applied. At higher temperature $T = 32°C$, the ion migration is opposed by the Brownian motion.
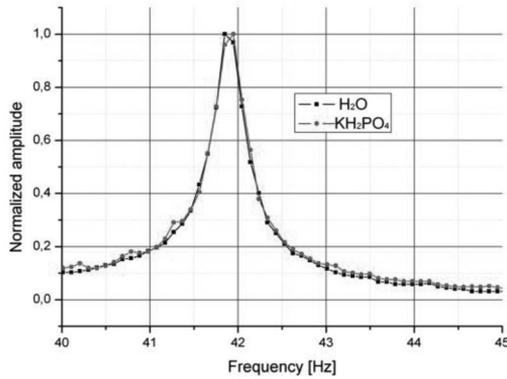
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Fig. 11. Resonance curves of droplets containing deionized H_2O and 0.1M aqueous solution of KH_2PO_4; polarizing voltage $U_{dc} = +100$ V; temperature $T = 32.5°C$
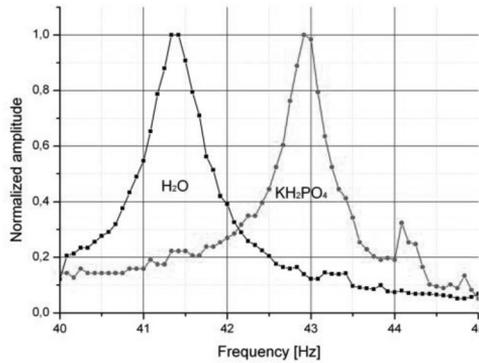

Fig. 12. Resonance curves of droplets containing deionized H_2O and 0.1M aqueous solution of KH_2PO_4; polarizing voltage $U_{dc} = +100$ V; temperature $T = 16°C$

The ions cannot reach the interface, whose structure is the same as of pure water, as far as the resonances coincide (fig. 11). At lower temperature $T = 16°C$ the ions can migrate in the interface and stiffen the intermolecular forces, shifting the resonant frequency up (fig. 12). Additionally the sign of the polarizing dc voltage can define which type of ions is adsorbed at the interface.

5. CONCLUSIONS

The measurement of surface tension and evaporation rate reveals a plenty of information about the properties and processes in the interface liquid gas. It has been shown that a hemispherical pendant liquid droplet driven in resonance by

electric force can be used as a tensiometer in real time. This allows to register transient processes in the interface gas-liquid. Moreover the properties of the interface of a pendant droplet can be easily manipulated by mechanical oscillations and by applied electric field. The reaction of surface tension and evaporation rate to perturbations is indicative for the processes in the interface. This experimental approach opens a wide front for new research.

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