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EXAMINATION OF THE LIQUID-AIR INTERFACE PROPERTIES BY OSCILLATING PENDANT DROPLET UNDER ELECTRIC FIELD INFLUENCE TECHNIQUE – A *Q*-FACTOR APPROACH

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Николай Зографов, Николай Танковски. ИЗСЛЕДВАНЕ СВОЙСТВАТА НА ИНТЕРФЕЙСА ТЕЧНОСТ-ВЪЗДУХ С ТЕХНИКАТА НА ОСЦИЛИРАЩА КАПКА ПОД ВЛИЯНИЕ НА ЕЛЕКТРИЧНО ПОЛЕ – ПОДХОД ЧРЕЗ *Q*-ФАКТОР

Резонансните трептения на висяща течна капка, възбудени от външно електрично поле, се регистрират оптически и се анализират, за да се определи механичният Q-фактор на капката. На базата на модела на Фойт-Келвин е получена опростена зависимост между Q-фактора на системата, еластичността на капката и обемната вискозност на изследваната течност. Еластичността на капка е изследвана за различни течности и условия: дейонизирана вода при различни температури, разтвори на глицерол и сърфактанта SDS с добавени различни концентрации на електролит KCL.

Nikolay Zografov, Nikolay Tankovsky. EXAMINATION OF THE LIQUID-AIR INTERFACE PROPERTIES BY OSCILLATING PENDANT DROPLET UNDER ELECTRIC FIELD INFLUENCE TECHNIQUE – A *Q*-FACTOR APPROACH

The resonant oscillations of a pendant liquid droplet, excited by an external electric field, are registered optically, and analyzed to define the mechanical *Q*-factor of the droplet. A Voigt-Kelvin model is applied to obtain a simple relation between the *Q*-factor, the droplet elasticity and the bulk

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viscosity of the examined liquid. Droplet elasticity has been examined for different liquids and conditions: deionised water at different temperatures, water and glycerol mixtures at different concentrations and aqueous solution of SDS surfactant and KCL electrolyte at different concentrations of the electrolyte.

Keywords: liquid-air interface, droplet resonance; Q-factor, surface charges
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1. INTRODUCTION

The understanding and evaluation of the viscoelastic properties of liquid-air interfaces are of major importance both for characterization of numerous soft matter materials and for proper control of different physicochemical technologies. Different experimental methods are developed and applied to examine the surface viscoelastic properties of the liquid-air interface. The mostly used ones implement: surface waves (transverse and longitudinal); oscillating drop or bubble, oscillating barrier, elastic ring, dynamic light scattering etc. [1–5]. The conventional oscillating drop methods apply an external actuator to excite drop oscillations e.g. a piezotransducer. Then, usually analysis of the drop shape dynamics is used to retrieve information about the interface properties. Drops and bubbles have been used also as sensors of dynamical pressure changes in the liquid [6, 7]. However the influence of surface charges and/or the influence of external electric field on the surface properties of the liquid-air interfaces are scarcely examined experimentally. Recently we have proposed technically simple method to excite droplet oscillations by applying external electric field, where an electrical interfacial force is acting directly upon the surface of the droplet and the oscillation amplitudes are detected with the help of a He-Ne laser [8]. In the recent work we examine the resonant oscillations of the droplet and measure its mechanical *Q*-factor. The *Q*-factor of the oscillating droplet carries information about the stored energy (i.e. the elastic modulus of liquid droplet) and the losses per cycle (i.e. the viscosity). The results are obtained and compared for the two possible signs of the applied external electric field. Thus the influence of the induced surface charge polarization on the interface properties is examined.

2. EXPERIMENTAL SET-UP AND MEASURING TECHNIQUE

The experimental set-up scheme, shown in Fig.1, is discussed in details in [8]. Here *1* is the signal generator (HP33120A), *2* is a dc voltage source, *3* is a pin-electrode, where the droplet is attached. The temperature of the droplet can be varied with the help of a Peltier element *4* and measured by a thermocouple.

5 is an earthed plane-plate electrode, *6* is a photodiode, *7* is a digital oscilloscope (HP54610B), PC is the computer, controlling the measurement and saving the measured data values. In all measurements we apply a dc voltage *U*dc = – 100 V to polarize the droplet surface negatively charged, and relatively weak ac signal *U*ac = 20 V to keep the deformations in the limits of a linear regime.

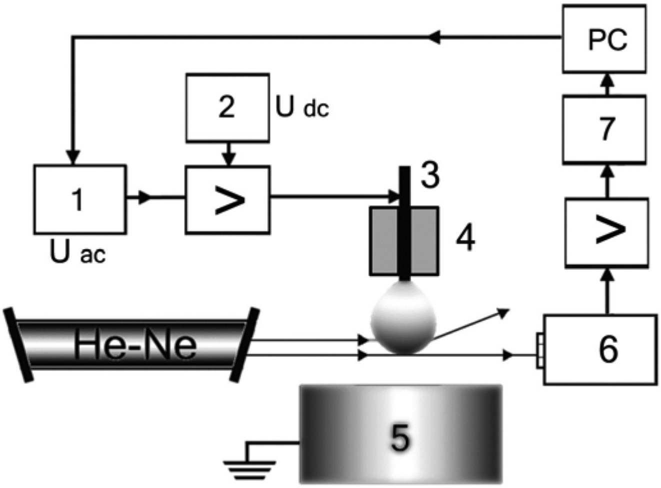

Fig. 1. Schematic of the experimental set-up

From the experimentally observed resonance curve we can define the *Q*-factor of the oscillating droplet applying the simple formula:

$$Q = \frac{f_0}{\Delta f} \, . \tag{1}$$

Here f_0 is the resonant frequency and Δf is the resonance curve width at half level of the maximal amplitude. The applied driving frequency is scanned automatically by the generator *1* and the measured signal values are saved automatically every two seconds in the computer (PC).

3. MECHANICAL MODEL OF THE OSCILLATING DROPLET

To interpret the viscoelastic behaviour of an oscillating, hanging droplet we use the Voigt–Kelvin model for a viscoelastic body [9]. The model is represented by a spring and a friction-pot in parallel, whereas the reaction force σ is the sum of the elastic and frictional forces:

$$\sigma = kx + D\frac{dx}{dt} \ . \tag{2}$$

Here *x* is the displacement or deformation along the external force direction, *k* is the elastic modulus of the spring and *D* is the friction in the pot. If we apply an external force *F*(*t*), sinusoidally varying in time in our experiment, we can write the Newton's equation of motion for the droplet with mass *m*:

$$m\frac{d^2x}{dt^2} = F(t) - kx - D\frac{dx}{dt} \tag{3}$$

We accept that the dominant component of the applied external electric force is directed vertically along the *x*-axis. The elastic properties of the droplet are defined by the stretching of the droplet surface i.e. by the interfacial molecular structure. In this way *k* represents elastic modulus of the liquid droplet. Finally, we assume that the viscous properties *D* are dominated by the bulk rheological properties of the liquid. Equation (3) describes the motion of a harmonic oscillator, whose *Q*-factor has been calculated as follows [10]:

$$Q = \frac{\sqrt{km}}{D} \ . \tag{4}$$

Certainly, the applied one dimensional approach is not very accurate when describing a droplet. However, the one dimensional oscillator can be considered only as a zero order approximation to the description of the drop dynamics. The most important result of this oversimplified treatment is that the *Q*-factor is defined not only by the bulk friction or viscosity *D* of the liquid, but also by the elastic modulus *k*, and by the droplet mass *m*. By definition the *Q*-factor is the ratio of the stored energy to the dissipated energy per cycle, so in equation (4) the stored energy is defined by the elasticity and the mass of the system, while the dissipated energy is given by the coefficient of losses *D*. However, for most of the liquids data is available for the dynamic viscosity μ and not for the friction coefficient *D*. The Stoke's Law for the frictional force of a body with linear size *a* (e.g. the radius of a sphere), immersed in the liquid, presents a proportional dependence between the frictional coefficient *D* and the viscosity μ:

$$D = Ca\mu \cdot \tag{5}$$

Here *C* is a dimensionless constant depending on the shape of the body (e.g. $C = 6\pi$ for a sphere). Thus the temperature or concentration dependencies of the elastic modulus can be evaluated only within the accuracy of a constant multiplier $L = Ca$, with dimension [m]:

$$k(T,c) = L^2 \frac{\mu^2(T,c)Q^2(T,c)}{m(T,c)} \, . \tag{6}$$

4. RESULTS AND DISCUSSIONS

Our main goal is to examine the temperature dependencies of the *Q*-factor of the oscillating droplet, for different liquids, in the temperature range 10 – 40°C. The *Q*-factor is defined experimentally in accordance with equation (1) and information about the viscoelastic properties of the examined liquid can be retrieved on the base of the model described by equations (3) and (4). The droplet is deposited to the pin-electrode with the aid of an air-displacement pipette, which gives an error in the reproducibility of the droplet mass ($\pm \Delta m$). This error is the main contribution for the experimental error ($\pm \Delta Q$) of the *Q*-factor, which can be improved by more accurate methods for control of the droplet size (dosing system), for example with the help of a piezotransducer.

4.1. TEMPERATURE DEPENDENCE ON *Q*-FACTOR AND ELASTIC MODULUS OF SPHERICAL WATER DROPLET UNDER ELECTRIC FIELD INFLUENCE

Firstly, we examine the temperature dependence $Q(T)$ of the *Q*-factor of droplets containing pure deionized water. In this case no other adsorbed molecules are present in the interface, but water molecules, whose exchange dynamics is very fast. The density of water is changing negligibly in the working temperature interval and for simplicity we take the mass to be constant versus temperature. The data for the temperature dependence of the viscosity of water $\mu(T)$ is taken from [11] and is shown graphically with filled circles in Fig. 2.

The values of the *Q*-factor are obtained experimentally and are presented with open circles in Fig. 2. Quite surprisingly the *Q*-factor is falling with temperature, while decreasing viscosity prompts an increasing *Q*-factor. It is clear that the experimental results in Fig. 2 cannot be explained with viscosity solely, but the influence of elasticity should be taken into account. The temperature dependence of elastic modulus of spherical water droplet $k(T)$ is obtained from (6) and the result is shown graphically in Fig. 3. It is seen, that the droplet elasticity decreases with temperature, steeper than viscosity. This can be explained by the progressive breaking down of the hydrogen bonds when temperature rises. The changes of elastic bonds are most radical in the temperature interval 10–17 °C. The experimental points are well approximated by a nearly quadratic power law: $k(T) \approx \frac{1}{T^{2.38}}$ (solid line in Fig. 3). Evidently pure water is more structured at lower temperatures.

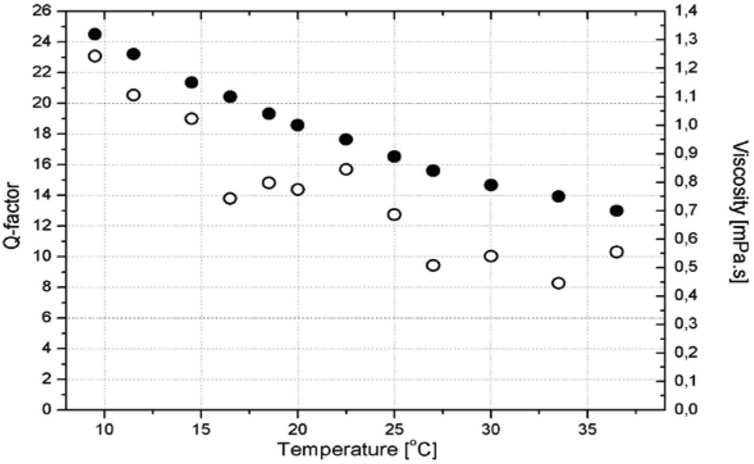

Fig. 2. Temperature dependence of the viscosity (closed circles) and *Q*-factor (open circles) for deionized water

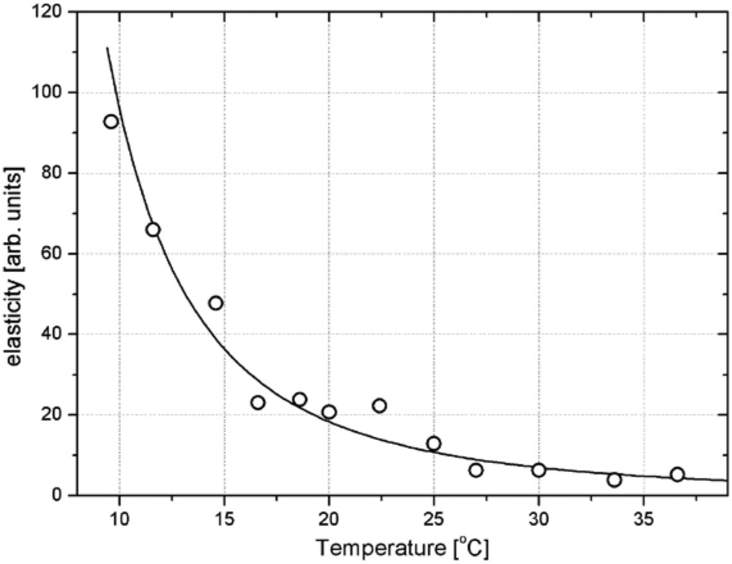

Fig. 3. Temperature dependence of the droplet elasticity of deionized water: open circles-experimental points; solid line – fitting curve

4.2. VISCOELASTIC PROPERTIES OF WATER-GLYCEROL MIXTURES UNDER ELECTRIC FIELD INFLUENCE

Glycerol mixes well with water, since its molecules interact strongly (electrostatically and via hydrogen bonds) with water molecules, thus affecting the surface properties. Moreover, glycerol has a very high bulk viscosity, influencing the overall viscosity of the solution. That is why we have examined the *Q*-factor of droplets containing solutions of water and glycerol. The measurements are performed with different concentrations of glycerol and at constant temperature of about 20°C. We have limited our measurements up to 80% concentration of glycerol. For higher concentrations the droplet resonance disappears due to high losses and the *Q*-factor can not be defined.

The viscosity of the water-glycerol mixture water-glycerol for different concentrations of glycerol is well known [12]. Viscosity values, corresponding to the experimental points have been calculated after linear interpolation of the data given in [12] and the result is shown graphically with solid line in Fig. 4.

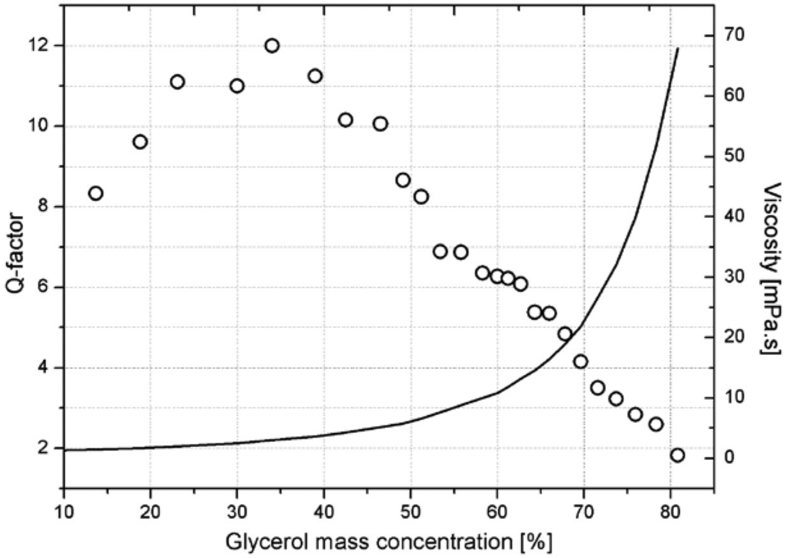

Fig. 4. Concentration dependence of the viscosity (solid line) and Q-factor (open circles) of water-glycerol mixtures

The experimentally obtained concentration dependence of the *Q*-factor is denoted with open circles in Fig. 4. A maximum of the *Q*-factor can be noticed when the mass concentration of glycerol is about 35%.

To evaluate the concentration dependence of the elasticity we use the working equation (6), where the variables now depend on the concentration *c*. The mass of the droplet is varying slightly when the concentration of glycerin changes. Data for the density of the solution at different concentrations has been taken from available data-bank [13]. The obtained concentration dependence of the elastic modulus is shown graphically in Fig. 5. The experimental points are well fitted by an exponential dependence $k(c) \approx \exp(0.057c)$ (solid line).

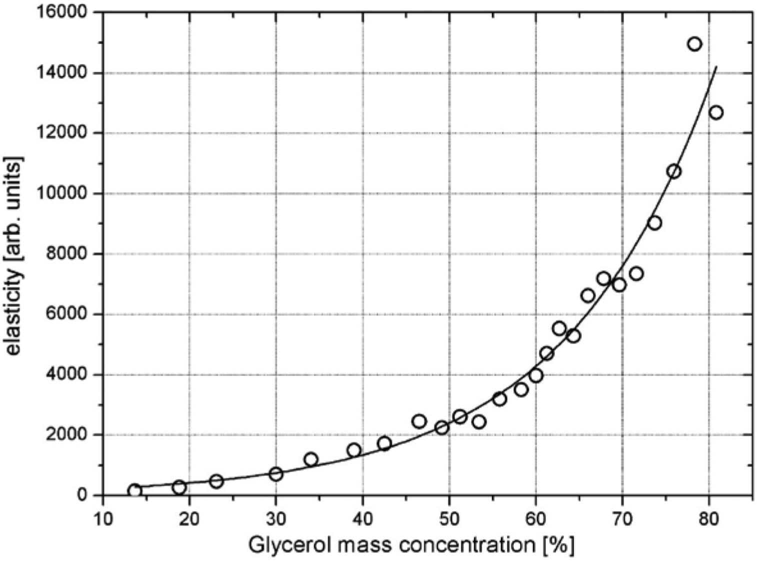

Fig. 5. Concentration dependence of the elasticity of water-glycerol mixtures: open circles-experimental points; solid line – fitting curve

The growth of the droplet elasticity when the content of glycerol rises might be due to the increasing number of hydrogen-like bonds between the glycerol and water molecules. As mentioned above, these types of bonds actually explain the perfect solubility of glycerol in water, practically in all concentrations.

4.3. VISCOELASTIC PROPERTIES OF AQUEOUS SOLUTION OF SDS SURFACTANT AND KCL ELECTROLYTE UNDER ELECTRIC FIELD INFLUENCE

Finally, we have examined the effect of adding electrolyte KCl to the aqueous solution of SDS at concentration 3.8×10^{-3} M and at temperature 25°C, near to the characteristic temperature for examination of critical micelle concentration. In this case the *Q*-factor of the solution proves to be essentially influenced by the presence of small amounts of KCl electrolyte, as shown in Fig. 6. When the electrolyte concentration is zero, the *Q*-factor is small $Q \approx 0.8$ (curve *3*). At electrolyte concentration 7×10^{-3} M the *Q*-factor reaches value $Q \approx 2$ (curve *2*) and at concentration 1.2×10^{-2} M the *Q*-factor grows further, $Q \approx 6.5$ (curve *1*). Further increase of KCl concentration leads to saturation of the *Q*-factor.

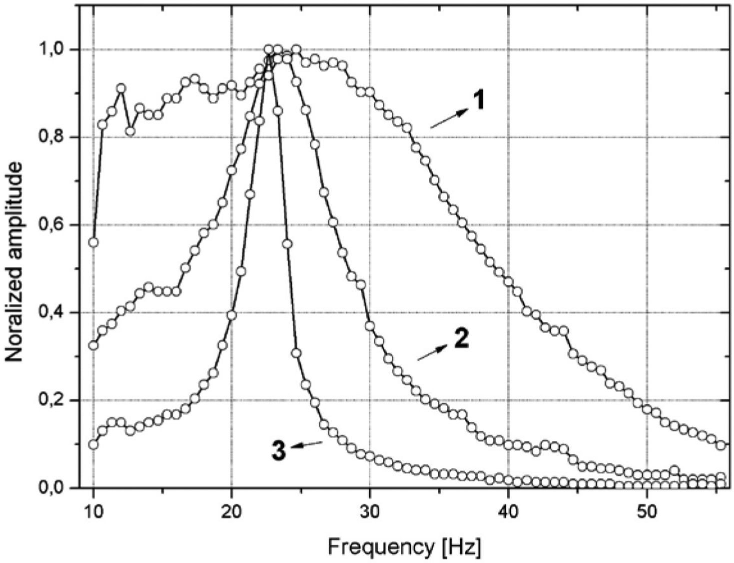

Fig. 6. Changes of the resonance curve of aqueous solution of SDS surfactant by adding small amounts of KCl electrolyte (1–12 mM KCl; 2–7 mM KCl; 3–0 M KCl)

Keeping in mind that the bulk viscosity remains almost unchanged at these small electrolyte and surfactant concentrations we can deduce that the essential increase of the *Q*-factor is due to some form of structure-making influence of the counterions K^+. Indeed, the K^+ ions have a small hydration radius and form strong bindings to the negatively charged surfactant heads. Different theoretical models for the adsorption of ionic surfactants and corresponding counterions in the surface layer, correspondingly in the electrical double layer, are reviewed by Warszynski et al. [14]. Our experimental results are in agreement with the model proposed by Warszynski et. al. (WBLF) [14, 15], in which the counterions can penetrate the Stern layer, between the charged surfactant heads. In this way the repulsion between the surfactant heads is diminished, which increases the adsorption. Moreover, the embedded in the surface layer counterions build strong electrostatic bonds with the surfactant heads and increase the dilational surface elastic modulus. Thus, the increase of *Q* when electrolyte is added to the solution is mainly due to increase of droplet elasticity.

5. CONCLUSIONS

In conclusion, we have shown that the resonance characteristics, the *Q*-factor in particular, of an oscillating droplet can supply information about the viscous and surface elastic properties of the liquid. A simplified mechanical model of the oscillating droplet is proposed, which relates the *Q*-factor with the surface elastic constant and the bulk viscosity. In case when the bulk viscosity of the examined solution is known, the *Q*-factor is defined unambiguously by the surface elastic constant of the liquid-air interface. Keeping in mind that viscosity is easily measured the proposed method can be used to study the droplet elasticity of different liquids and solutions.

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