Measurement of dynamic surface tension by the oscillating droplet method

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Abstract.   An optical measuring method has been applied to determine the dynamic surface tension of aqueous solutions of heptanol. The method uses the frequency of an oscillating liquid droplet as an indicator of the surface tension of the liquid. Droplets with diameters in the range between 100 and $200\mu m$ are produced by the controlled break-up of a liquid jet. The temporal development of the dynamic surface tension of heptanol-water solutions is interpreted by a diffusion controlled adsorption mechanism, based on the "three- layer" model of Ward & Tordai. Measured values of the surface tension of bi-distilled water, and the pure dynamic and static (asymptotic) surface tensions of the surfactant solutions are in very good agreement with values obtained by classical methods.

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List of symbols

a'	coefficient of intermolecular forces $[Nm^{-1}]$
B	adsorption constant $[-]$
c_0	bulk concentration $[mol\,m^{-3}]$
$\mathcal{D}$	apparent diffusion coefficient $[m^2 s^{-1}]$
t	time $[s]$
T	absolute temperature $[K]$
R	universal gas constant $= 8.314[J\,mol^{-1}K^{-1}]$
$\Re(\theta,t)$	droplet contour function
$\Re_0$	droplet equilibrium radius $[m]$

Greek symbols

Γ_∞	maximum surface excess concentration $[mol\,m^{-2}]$
$\delta(t)$	droplet volume normalization function
θ	azimuth of the polar coordinate system
ρ	density $[kg\,m^{-3}]$
σ	surface tension $[N\,m^{-1}]$
$\Phi(t)$	concentration in the subsurface $[mol\,m^{-3}]$
Ω	droplet oscillation frequency

1   Introduction

The surface tension of a liquid is a measurable force existing on all liquid surfaces. It arises from an imbalance of the intermolecular forces at the surface. The effects of surface tension play an important role for most processes involving liquids with free surface, such as the disintegration of liquid jets, formation of droplets and bubbles, Marangoni flow or evaporation. Surface tension is also one of the phenomena which are basic for understanding the physics of condensed matter (liquid and solids). In practical applications, beside such industries as varnish, dye or ink manufacture, the importance of surface tension is growing in many other technical, physical or medical problems. For example from the measured surface tension of amniotic fluids it is possible to get information on fetal lung

maturity or to predict neonatal respiratory distress syndromes (Masson et al. 1977). On the other hand, dynamic surface tension is an essential in modern nucleation theory (Rasmussen 1986) and helps in better understanding of crystal growth (Strani et al. 1988). A new field of interest is the analysis of increasing pollution of our water resources by surface active substances (tensides). Although during the last decades interfacial phenomena have been a chief object of several theoretical and experimental investigations, still not all of their aspects are completely understood. Particularly studies of the dynamic behaviour of surface tension seem to be far from being completed, both from theoretical and experimental points of view.

The recent progress in the high-speed imaging (Hiller et al. 1989 and Hiller et al. 1992) gave new possibilities of non-intrusive measurements of the transient behaviour of surface tension. In the following is described the application of the oscillating droplet method to measurements of the fast aging processes of the liquid surface for heptanol-water solutions.

2 Dynamic surface tension: Theoretical model and experimental method of its verification

The value of surface tension depends on the type and magnitude of intermolecular forces acting in the interfacial region. Its value can vary in time due to a change of molecular orientation or to the composition of the surface. When a liquid surface is suddenly created - for example the surface of a liquid jet discharging out of a nozzle - orientation of molecules will be totally random initially. If the liquid is polar (like water), some surface arrangements of molecules can be favoured energetically by reason of its polarity and so a process of molecular regrouping may occur. For a solution of liquids usually one of the components is preferred energetically and it accumulates on the surface. Both effects cause time-dependent changes of surface tension. As long as these variations are in progress the term "dynamic surface tension" is applied to describe intermolecular forces acting at the interface. The equilibrium (asymptotic) value of the surface tension is

termed the static surface tension (compare figure 1). The alteration of the surface tension due to pure molecular regrouping processes occurs within a time scale of less than one microsecond and cannot be analysed experimentally, whereas the modification of surface tension caused by a variation of surface composition may last milliseconds to seconds (in some special cases minutes or even hours). This time range enables an experimental analysis, however the number of reliable techniques is very limited.

The most commonly used theoretical model describing the dynamics of surface tension was introduced by Ward & Tordai (1946). To explain non-equilibrium states of the surface they introduced the three-zone model for the structure of a liquid solution. The first zone is the monomolecular surface layer. The next layer below the surface, called the sublayer, extends to a depth of some hundred molecule diameters. The third one, being further below the surface and called the bulk, is assumed to be semi-infinite. Sometimes the top molecular plain of the sublayer is called the subsurface, and is defined as a region separating the anisotropic pressure from the region of isotropic (normal) pressure in the liquid. The aging of the surface depends on the agent exchange mechanisms. On the one hand there is an adsorption of dissolved molecules (this process only takes place at the highest second or third molecular plains of the liquid). On the other hand there is diffusion, taking part in the sublayer. If a surface of a surfactant solution is newly created, the dissolved molecules being near the surface will be quickly adsorped. Thus, a strong concentration gradient between domains close to the bulk and those close to the surface arises. This is what diffusion tries to compensate. The diffusive material exchange determines the rate of the aging process of the surface, because it is much slower than adsorption. Some time after creation the surface will be saturated with adsorbed molecules. Then, the equilibrium state will adjust and the measured surface tension reaches its static value. This aging process is described through characteristic properties of the individual layers. As the demand for dissolved molecules to saturate the surface layer is negligible compared to the total amount of dissolved molecules, the bulk concentration will remain nearly unchanged. Therefore the bulk concentration c_0 is assumed constant and only the sublayer concentration $c(x, t)$ covers the demand for

molecules of the surface. For very dilute surfactant solutions the property of the surface is characterized by the surface excess concentration $\Gamma(t)$. Ward & Tordai found the following equation to describe the time-dependent surface excess concentration:

$$\Gamma(t) = 2 \left(\frac{\mathcal{D}}{\pi}\right)^{1/2} \left\{ c_0 \, t^{1/2} - \int_0^{t^{1/2}} \Phi(t - \tau) \, d\left(\tau^{1/2}\right) \right\} \tag{1}$$

To solve (1) and obtain the values of $\Phi(t)$ Ward & Tordai used a rather tedious graphical method. An easier way is given by a semi- theoretical relation found by Frumkin (1925), which relates the total concentration of the solution c to the surface excess concentration Γ :

$$c(\Gamma) \;=\; \frac{1}{B} \, \frac{\Gamma}{\Gamma_\infty - \Gamma} \, \exp\left(-\frac{2a'}{R \, T \, \Gamma_\infty} \, \frac{\Gamma}{\Gamma_\infty}\right) \tag{2}$$

Once equilibrium value of surface excess concentration is achieved, the concentration of dissolved molecules is constant throughout all liquid layers (including the subsurface) but the enriched surface. There Frumkin's equation (2) describes the relation between the surface excess concentration and the concentration of the subsurface. The question arises of how to describe the processes taking place before the surface excess concentration has achieved its equilibrium value? As was aforesaid, the rate of the molecular exchange due to the adsorption is much higher than the rate due to diffusion. It justifies the assumption that the surface and the subsurface are in thermodynamic equilibrium during the whole surface aging process. Hence, the Frumkin's equation (2) originally found for the static surface excess concentration, can also be used for the dynamic process. This leads to the following integral equation for surface excess concentration:

$$\Gamma(t) \;=\; 2 \left(\frac{\mathcal{D}}{\pi}\right)^{1/2} \left\{ c_0 \, t^{1/2} - \frac{1}{B} \int_0^{t^{1/2}} \frac{\Gamma(t - \tau)}{\Gamma_\infty - \Gamma(t - \tau)} \, \exp\left(-\frac{2a'}{R \, T \, \Gamma_\infty} \, \frac{\Gamma(t - \tau)}{\Gamma_\infty}\right) \, d\left(\tau^{1/2}\right) \right\} \tag{3}$$

For volatile liquids the influence of evaporation on surface composition must be taken into account, additionally complicating the model. However, for the dilute heptanol-

water- solutions analysed here at room temperature the effect of evaporation can be neglected.

To prove experimentally the validity of the equations (1)-(3) for the selected solution, one needs an additional relation between the measured values of the surface tension σ and the surface excess concentration Γ. Such relation is given by Gibbs' adsorption equation:

$$d\sigma = -\Gamma \, \frac{R\,T}{c} \, dc \tag{4}$$

In the present investigations the following experimental procedure has been applied to make use of the equations (1)-(4):

1. In the first step the dependence of static surface tension σ on concentration c is determined. These measured values are used to calculate the corresponding values of the static surface excess concentration Γ given by Gibbs' equation (4).

2. In the next step the function $c(\Gamma)$ is fitted to the calculated values of the static surface excess concentration Γ to determine the unknown parameters a', B and Γ_∞.

3. During the second experimental phase the dynamic surface tension is measured and corresponding values of surface excess concentration are calculated. Then, the function $\Gamma(t)$ given by the integral equation (3) is fitted to these values and so the last unknown parameter - the diffusion coefficient $\mathcal{D}$ - will be found by optimisation. If this procedure leads to a good fit of the functions (1)-(3) to the experimental data, the model can be taken as an acceptable description of the surface aging process of the tested solution. It is well known that for several substances, the simple description given by Ward & Tordai is not adequate and other models must be formulated.

3 Experimental

3.1 Measurement of static surface tension

Two classical methods - the ring method of Lecomte Du Nouy and the plate method of Wilhelmy - were used to obtain the static values of surface tension of aqueous solutions of

heptanol. At first glance measurement of the static surface tension may seem to be trivial. But a closer look at the problem reveals numerous pitfalls which my lead to error stained data, so much so that the name "comedy of errors" (Harkins & Jordan 1930) has been given to the surprising discrepancies between measurements reported in the literature. Therefore special care has been taken in ensuring high accuracy of the measured values of the surface tension of the tested solutions. The static surface tension was measured with help of a commercially available instrument K10 ST (Kruess GmbH). The device allows measurements by both the ring and the plate method. The results obtained by the ring method were corrected using the standard tables of Harkins & Jordan (1930). The estimated error of measured values of the surface tension is approximately $0.1mN/m$. The temperature of the liquid was controlled with help of a thermostat to an accuracy of $\pm0.1^oC$. To ensure accurate values of heptanol concentration in very dilute solutions relatively large amounts of investigated mixtures were prepared (typically $5-10l$). The value of heptanol concentration is assumed to be known with an accuracy of 0.02%. Additional details concerning the measuring and calibration procedures can be found in Stückrad (1992).

3.2 Measurement of dynamic surface tension by the Droplet Method

The suitability of the classical methods for measuring the aging process of surfaces is very limited. One of the reasons is the rather long period between filling the vessel with liquid and the beginning of measurement. The alteration of surface tension due to the aging process usually occurs in a much shorter time. Another disadvantage of the classical methods is the disturbance of the surface caused by its physical contact with the ring or plate. A surface already saturated with surfactant molecules will become heavily stretched at the region of its contact with the ring, i.e. there will be a strong regrouping of molecules near the surface. The measured static surface tension is not affected by these fast processes, but measured transient values are generally false. It seems, that at the present moment the oscillating droplet method is best suited to measure temporary

values of the surface tension. Although this method requires more complicated apparatus and evaluation algorithms, its non-intrusive character has several striking advantages. By forcing the break-up of the jet to occur at a very short distance from the nozzle, the period between discharging out of the nozzle and break-up of the jet can be shortened up to a few milliseconds. This enables measurements of the surface tension of very fresh surfaces. Furthermore, the oscillating droplet method can be applied for liquids at extreme temperatures, e.g. for measurements on subcooled or superheated liquids or molten metals. Due to recent achievements in the description of large amplitude non-linear oscillations of viscous droplets a proper interpretation of the experimental observations has become possible (Becker et al. 1991 & Becker 1991). As most of the details concerning theoretical and experimental aspects of droplet oscillations are available in the above cited papers, in the present report we limit our description only to a few essential points.

3.2.1 Measuring procedure

The experimental set-up is shown schematically in figure 2. The test liquid is kept under constant pressure in a reservoir. The liquid is issued through Teflon tubes and a Teflon filter to exchangeable nozzles of variable orifice diameter. The pressure in the antechamber of the nozzle can be modulated by a piezoceramic transducer. Thus artificial pressure disturbances, proportional to the applied voltage, can be super-imposed on the jet in order to control the break-up into oscillating droplets. By properly adjusting the oscillation frequency of the piezoceramic driver the jet can be forced to break up into a row of practically monodispersed droplets. As the jet discharges symmetrically from the nozzle, the droplets will oscillate in axi-symmetric modes in the absence of any external disturbances. A modification of the droplet radius is possible by changing the nozzle. The typical radius of the droplets used is in the range from 100 to $200\mu m$. Since the droplet velocity is relatively small (below 10 m/s) the influence of aerodynamic forces on the droplet shape is negligible.

The oscillations of the droplet are observed through a microscope using a CCD-camera (Sony XC77CE). Bright field illumination is applied, i.e. the projection of the droplets

appears as dark shadows in front of a bright background. To visualize the droplet oscillations a beat-frequency stroboscopic technique is applied. The droplet illumination is realized with a pulsed light emitting diode (LED) driven by a specially designed pulse generator (Hiller et al. 1987). In order to coordinate the image sequence frequency of the CCD-camera with the strobe frequency of the pulsed LED, a special trigger conditioner is applied. The video signal of the CCD is directly observable on a monitor and a video printer. For further evaluation the images are acquired by an 8- bit image processor VS100/768 (Imaging Technology Inc.) and saved on a computer hard disk. The nozzle has been installed on a computer driven shift unit. This unit enables a fully automatic tracking of the droplet along a trajectory of about 5 cm. As the position of the nozzle relatively to the CCD-camera is moved synchronous with the shift of the stroboscopic observed image, the same droplet seems to oscillate centrally in the field of vision of the camera during the whole time of recording. This is of course only possible due to the extremely high reproducibility of the droplets, which are generated by the controlled break-up of the jet. To minimize influence of the vibrations the droplet images are acquired about 3 seconds after a moving nozzle has achieved its new position. During this time the previous image is written to the computer disk. Usually sequences of 200-300 images are taken during one measuring run. As the storage of one image on the hard disk takes approximately 3 seconds, the measurement of nearly 300 images requires an exact reproducibility of the generated droplets over a period of 15 minutes. This is the chief problem of the method.

Data acquisition and storage of images are performed on a 386 personal computer (IBM compatible) equipped with a 140 MByte hard disk. Data reduction and analysis usually take place on main frame computers (IBM3090 or VAX9000).

3.2.2 Analysis of the droplet images

As only the projections of the droplets can be observed, the primary condition for an efficient measurement is that droplets are formed axi-symmetrically, with their axis of symmetry parallel to the plane of observation, i.e. to the sensor area of the CCD-camera.

Then the three-dimensional form of a droplet is completely defined by its two-dimensional projection. The contour of the droplet projection (comp. figure 3) is obtained using specially developed computer code which automatically analyses droplet images. The detected points of the droplet boundaries are fitted to theoretically given contour function

$$\Re(\theta, t) = \Re_0 \{\delta(t) + \sum_{l=2}^{lmax} a_l(t) P_l(\cos\theta)\} \quad , \tag{5}$$

comprising a series of Legendre polynomials $P_l(\cos\theta)$. Each term l of the series describes one mode of droplet oscillation, characterized by its amplitude $a_l(t)$. In practice, nearly all observed droplet deformations can be well fitted by the contour function limited to the first five oscillation modes. The droplet deformation analysis is limited to axially symmetric deformations. The validity of this assumption is proved by monitoring the equilibrium droplet radius $\Re_0$, obtained from the fitting procedure. Time dependant variations (usually observed as regular oscillations) of the $\Re_0$ indicate presence of non-axially symmetric modes of oscillations and disqualify the experimental run.

The amplitudes of the oscillation modes and droplet volume are the main parameters of the optimization procedure. The so obtained temporal variation of the oscillation amplitude a_l for a sequence of 200-300 single images of the droplet is used to calculate oscillation frequencies of the modes. The result of such an evaluation is shown in the figure 4. At first glance, the wave-form of the oscillations seems to be that of a damped harmonic oscillator. In fact, for small amplitudes the linear approximation can be applied, and oscillation frequency of each mode l is given as:

$$\Omega_l^2 = \frac{\sigma l(l-1)(l+2)}{\rho \Re_0^3} \tag{6}$$

However, a more careful analysis of figure 4 reveals variations of the oscillation period and an asymmetry between the positive (prolate) and negative (oblate) displacements. This type of oscillation can be simulated by introducing a restoring force with a symmetric term (i.e. depending on even powers of the displacement) into the equation of motion of a damped harmonic oscillator. Using an asymptotic expansion for small amplitudes, we

obtain the following time dependent approximation for a_2 (only the fundamental mode $l = 2$ has been used in subsequent evaluations):

$$a_2(t) = A \sin\{\Omega_2(\sqrt{1 - (\Omega_2\tau)^{-2} + \alpha A^2})t + \varphi\} + \beta A^2 , \tag{7}$$

where amplitude damping is given by:

$$A(t) = A_0 \exp(-t/\tau) \tag{8}$$

Here, the term with α accounts for the amplitude dependence of the oscillation frequency, β represents the asymmetry of the amplitude $a_2(t)$, and φ is the phase angle. The six free parameters: $\alpha, \beta, \tau, \Omega_2, \varphi$, and A_0 were used to fit (7)-(8) to the measured values of the momentary amplitudes a_2.

The time dependent surface tension will result in an advancing shift of the observed oscillation frequency Ω_2 of the droplet. Therefore, to obtain temporal variation of this frequency the frequency evaluation procedure is run for a time interval (typically 5 ms), and shifted step by step over the entire range of the experimental data. The asymptotic (small amplitude) frequency of the main oscillation mode Ω_2 determined for each interval is used to calculate the transient surface tension of the liquid. The damping of the oscillation amplitude additionally gives the dynamic viscosity of the liquid. The interval chosen to be analysed in each time step is a compromise between the accuracy with which the fitting procedure may determine the asymptotic form of the model function and the averaging of the short time changes of the surface tension. It must be mentioned that the applied evaluation scheme is solely an empirical method allowing an estimate of the asymptotic behaviour of the monotonous changing frequency of oscillating droplets. The combined effects of strong non-linearity and variable surface tension may make proper interpretation of the results impossible. In such a case the full non-linear model of the viscous droplet oscillations proposed by Becker (1991) and Becker et al. (1992) must be applied.

4 Experimental results

4.1 Measurement of surface tension

Initially, experiments were performed by classical methods (ring and plate) to determine the temperature dependency of the static surface tension for the tested liquids. The results are important to enable the temperature effects to be excluded from the measurements performed. They could be also used to estimate transient values of the liquid temperature (due to evaporation for example) from the measured oscillations of droplets. However, as was mentioned, the evaporation was negligible at our experimental condition. The variation of the droplet temperature is estimated at less than $\pm 1^o C$.

All performed measurements show a linear relation between static surface tension and temperature (within the measured temperature interval). It was found that for the examined surfactant solution a temperature variation of $2^o C$ will cause a maximum change of static surface tension of $0.3 mN/m$. For the solutions with the highest heptanol concentrations this corresponds to relative change of only 1%.

In the second experimental step the afore-mentioned classical methods were used to measure the effect of the heptanol concentration on the static surface tension of the solution. The result is shown in figure 5. Although the most concentrated solutions only contain 0.1% heptanol, the measured values of static surface tension hardly differs from the value of pure heptanol. It indicates that the surface of the solution is close to its saturation with heptanol-molecules. With the help of the experimentally determined relation $\sigma(c)$, Gibbs' equation (4) allows an estimation of $\Gamma(c)$, i.e. equilibrium values of the surface excess concentration as a function of the bulk surfactant concentration. Then, the so obtained $\Gamma(c)$ values are used to fit the function $c(\Gamma)$ given by equation (2), and to find the unknown free parameters a', B and Γ_∞. Figure 6 shows that the fitted curve based on the Frumkin's model are in very good agreement with the measured data. The so determined value of the maximum surface excess concentration Γ_∞ can be used to find the orientation of the heptanol-molecules at the surface. The calculated surface area occupied by a single heptanol-molecule is 26Å^2 , corresponding to a circular area of less

than 3Å radius. The single **C–O** bond extends to more than 1Å (Weast 1982). Thus, it becomes obvious that the long chains of heptanol-molecules must "stand" closely packed perpendicular to the surface.

In the last experimental step the measurements of the dynamic surface tension are performed using the oscillating droplet method. To check the experimental procedure, the control measurements of the temporal surface tension for bi-distilled water were initially performed. As it was expected, the surface tension of water remains constant in the investigated time span (compare figure 7). It is worth to notice, that the difference between the surface tension values estimated by the oscillating droplet method and the classical ones is negligible (0.5%). A quite different behaviour of the temporal values of surface tension is shown in the measurement performed for the heptanol-water solution (figure 8). A considerable decline of the surface tension in a very short period of approximately $10ms$ is firmly seen. Most striking is the relatively late beginning of the surface tension decline. Several milliseconds after the droplet separation, the measured surface tension still sustains the value of pure dynamic surface tension (i.e. that of water). It seems to be obvious that the surface degradation, which starts at the moment of the jet discharge, occurs again from the initial droplet surface created after the break-up of the jet. It points out, that after the break-up of the jet there exist a significant mass transfer process between surface and bulk liquid. At the moment we cannot offer any satisfactory explanation of this effect. One of possible sources of the additional "mixing" of liquid molecules can found in the surface disturbances generated when the droplet separates from the jet. This might cause creation of big circular eddies inside the droplet. Becker (1991) has shown, that in addition to the normal droplet oscillations, such "short living", strong dissipative oscillation modes may appear shortly after the separation. These additional modes generate eddy flows of considerable strength far into the depth of the bulk zone of the droplet, intensifying transport of the fluid molecules between surface and the bulk zone. It could justify the observed delay of the reduction of the surface tension.

4.2 Determination of the apparent diffusion coefficient

As it was mentioned it is assumed that there is the thermodynamic equilibrium between surface and subsurface during the entire period of aging. Using this assumption the relation between surface tension and surface excess concentration is given by (4). Then the diffusion coefficient $\mathcal{D}$ can be found from the integral equation (3). The equation (3) has been solved numerically. First, an analytical form of $\Gamma(t)$ has been determined, fitting second-order polynomial to the empirical points obtained by combining the results given in figures 5-8. Solving numerically the integral equation (3) the remaining unknown parameter - the apparent diffusion coefficient $\mathcal{D}$ - was found. Its mean value for the whole investigated period gives us the apparent diffusion coefficient of $4 \cdot 10^{-10} m^2/s$. The resulting curve $\Gamma(t)$ (dotted line in figure 9) is generally in good agreement with the measured data. The main differences appear at the beginning and the end of the aging process. It coincides with regions where the measurements are least accurate. Right after it's separation from the jet the droplet is oscillating at very high amplitudes. The strong nonlinear effects which appear can not be described exactly by the theoretical model used. At the end phase of the droplet oscillations their amplitudes are very low and due to the limited resolution of the experimental technique the relative errors become large. Nevertheless, the apparent diffusion coefficient found does not account for pure diffusion only, but for all processes which are responsible for the mass transfer between bulk and surface. For example, within the oscillating droplet the apparent diffusion coefficient includes the mass transfer resulting from convective transport. This causes an apparent time dependence of the estimated temporal values of $\mathcal{D}$. Because the integral equation (3) has been evaluated under the assumption that the diffusion coefficient is a time-independent constant, its applicability for the variable $\mathcal{D}$ is questionable. Therefore, the averaged value of the time dependent diffusion coefficient will be generally wrong and gives only qualitative result. This perhaps explains the 20% discrepancy between the here obtained value of $4 \cdot 10^{-10} m^2/s$ for the tested solution of $7.6 mol/m^3$ heptanol concentration, and diffusion coefficients reported in the literature by Defay & Hommelen (1959), i.e. $5.2 \cdot 10^{-10} m^2/s$ for a $3.44 mol/m^3$ heptanol-water solution and $5.3 \cdot 10^{-10} m^2/s$ for a $2.43 mol/m^3$ solution.

5 Conclusions

A method based on the analysis of droplet oscillations has been successfully applied to evaluate the transient values of surface tension for very fast aging of surfactant solutions. It seems that for the investigated dilute heptanol-water solutions this aging processes can be relatively well described by a diffusion controlled adsorption mechanism. However, the observed delay in the surface aging may suggest existence of additional processes, which modify the solute concentration driven diffusion. After the jet break-up, the eddy motion generated close to the surface may become responsible for flushing the surface sublayer with a pure solvent from the droplet core. Hence lower surfactant concentration in this layer may lead to the initial retardation of the diffusion and adsorption processes at the surface.

The model of surface kinetics is based on the assumption that equilibrium exist between the surface and the initial subsurface layer. However, at the critical micelle concentration the surface aging process may also become retarded by a parallel micelle diffusion and their breakdown into monomers. The experiments preformed to date, are of a preliminary nature and further investigations supported by a modified modelling of the surface kinetics are required to improve our understanding of the mechanisms involved.

Compared with the bubble pressure method (Garrett & Ward 1989), which also allows short time ($< 1s$) measurement of the dynamic surface tension, the method applied is characterized by a rather tedious evaluation procedure and relatively high liquid consumption (typically $0.25l$ per experimental run). Therefore in many practical applications it seems desirable to combine multi-exposed imaging (Hiller et al. 1989) with the improved theoretical description given by Becker (1991) so that the experimental observation time may be limited to a few short intervals along the droplets trajectory. Additionally, observations with a second camera at 90-degrees to the first would allow the analysis of oscillations of droplets with the axis of symmetry do not remaining in the plane of observation (i.e. being not parallel to the sensor area of the CCD-camera).

The advantages of the method include its fully non-intrusive character (the droplet surface has no contact with the nozzle), it's very low short time range ($< 10ms$), and

also the constancy of the surface investigated. Whereas the interface investigated in the bubble method permanently changes size, the oscillating droplet surface may be treated as being of practically constant area (fluctuations below 10%).

6 References

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FIGURES

- Figure 1. Typical evolution of the surface tension during the aging process.

- Figure 2. Experimental set-up.

- Figure 3. Tracking of a falling water droplet. Sequence of video images showing transient development of the droplet contours fitted with help of function (7). The equilibrium radius of the droplet $\Re_0 = 178\mu m$, time interval between images $55\mu s$.

- Figure 4. Measured oscillation amplitude $a_2(t)$: a) water droplet of equilibrium radius $\Re_0 = 185\mu m$; b) heptanol-water droplet, $\Re_0 = 174\mu m$. Time measured from the break-up moment.

- Figure 5. Measured static surface tension versus heptanol concentration for dilute heptanol-water solutions.

- Figure 6. Surface excess concentration $\Gamma(c)$ versus heptanol concentration, calculated for measured values from fig. 5

- Figure 7. Dynamic surface tension of bidistilled water measured by the oscillating droplet method. Jet age at the break-up point $0.75ms$. Dashed line - best fit of experimental points, solid line - surface tension of water measured by the static ring method.

- Figure 8. Dynamic surface tension of a dilute heptanol-water solution $(7.6mol/m^3)$ measured by the oscillating droplet method. Jet age at the break-up point $2.1ms$.

- Figure 9. Best fit for the surface excess concentration $\Gamma(t)$ (dotted line) calculated with help of (3) for measurement in figure 8. Obtained apparent diffusion coefficient $\mathcal{D} = 4 \cdot 10^{-10}m^2/s$.