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MEASUREMENT OF SURFACE TENSION OF LIQUID ALLOWING FOR THE INFLUENCE OF CAPILAR OSCILATIONS OF IDLE DROP

Instability and duration of drop transition in stationary state while measuring of surface tension by improved method of idle drop using step-wise growing voltage of electric field are analyzed.

Key words: *surface tension, method of idle drop in electric field, drop stability, capillary oscillations.*

Introduction

Nowadays many technological processes require complete and exact knowledge regarding various liquid media and surface phenomena, appearing at phase boundary. Basic property of liquid -gas boundary is surface tension, which determines specific free surface energy of the liquid and is the parameter, the value of which in many cases (gas production, chemical industry, pharmacy, food industry and other branches of national economy) is determining for evaluation of quality and quantity parameters of the liquid (1) Surface tension plays important role in technological processes, where solutions of surface-active substances are used, for instance, in the process of gas production increase, detergents fabrication, development and production of surface-active substances of various functional designations.

Problem set-up

As a result of analysis of the existing techniques and measuring facilities of surface tension of liquids it was established that measuring facilities of surface tension, operation of which is based on meniscus photographing and printing out in large scale, do not provide high accuracy of measurements. The same is true regarding microscope, since its application does not allow to make the process of measurement of liquid surface automatic and makes measurement procedure tedious for researches. Besides greater part of methods are based on empiric and approximated dependences that considerably increase measurement errors. Thus, it is necessary to improve the method, which would provide high sensitivity of measurements. One of the ways of idle drop method improvement is the impact of electric field, as a result of this impact meniscus shape changes and one of meniscus parameters, which varies, passes across extremum. The aim of the research is investigation of capillar oscillations and stability of charged drop while variation of surface tension of liquids.

Principle part

In the research, carried out, we suggested to apply the method of idle drop in electric field. The essence of the method is the following: the drop is formed in a tray. The amount of the liquid, that can be contained in a tray, exceeds the volume of internal part of a tray. The excess of liquid forms a drop, surpassing the edge of the tray.

It was established that under the impact of the electric field energy of meniscus changes and idle drop is deformed, transforming from spheric into elongated spheroid one. If intensity of external electric field grows, then according to [2], local amplification of electric field intensity near the apex of spheroid drop occurs, which is determined by dielectric constant of the liquid, surface tension, size of the drop and intensity of external field. Amplification of electric field intensity near the apex of the drop leads to its rupture or drastic reduction of curvature. Extreme geometric parameters correspond to the moment, prior to the advent of instable state. Drop of liquid in electric field becomes instable due to domination of electric forces over the forces of surface tension. Investigation of drop instability is carried on the basis of mode approach, according to which infinite set of capillar wave of infinitely small amplitude (they always exist as result of thermal motion of molecules) is considered as oscillating system with infinite number of degree of freedom.

Amplitude of m^{th} mode of meniscus capillar oscillations changes in time according to the law [3]

$$A_k(t) = A_{k0} \cdot \exp(-t \cdot \omega_m - x_m \cdot t), \tag{1}$$

where A_{k0} – is maximum value of oscillation amplitude at initial moment of time; m – is number of mode; ω_m – is frequency of oscillation; x_m – is decrement of viscous damping.

Frequencies of various modes of capillar oscillations of charged surface are defined by the formula [3]

$$\omega_m^2 = (m-1) \cdot m \cdot (m+2) \cdot \frac{\sigma \cdot (1-W)}{\rho \cdot a^3}, \tag{2}$$

where ρ – is density of the liquid; W – Relay parameter, which according to [4]

$$W = \frac{\varepsilon_0 \cdot \varepsilon_c \cdot U^2}{16 \cdot \sigma \cdot a}, \tag{3}$$

where ε_c – is dielectric constant of the environment; U – is the voltage, supplied to electrodes.

Decrement of viscous damping of capillary waves

$$x_m = (m-1) \cdot (2m+1) \cdot \frac{\nu}{a^2}, \tag{4}$$

where – kinematic viscosity.

The smallest of the possible modes has the smallest oscillation frequency and, correspondingly, the smallest period. Higher modes of capillary oscillations have time to develop on the background of the oscillation of the least of possible ones – principal mode, that is why, the period of principle mode must be taken as character time of capillary oscillations of the meniscus. The higher mode of capillar oscillations, the faster it damps.

Hence, damping of possible modes of capillary oscillations is the slowest: during the reduction of its amplitude *e* times, amplitudes of higher modes decrease to greater extent. That is why, time of viscous damping of principle – second mode must be taken as character time of viscous damping of capillary oscillations of liquid meniscus [4].

Depending on voltage value, supplied to the electrodes, characterized by Relay parameter W, two situations can be considered: 1) $W < 1$; 2) $W > 1$.

1) $W < 1$ – in this case meniscus surface performs damping oscillations, with frequencies of ω_m and damping decrements x_m. Each mode of capillar oscillations is characterized by two temporal parameters:

– time of capillar oscillations damping [3]

$$\tau_\sigma^m = \frac{2\pi}{\omega_m}, \tag{5}$$

– time of viscous damping – it is time, during which the amplitude of corresponding mode of capillary oscillation decreases *e* times [3]

$$\tau_\nu^m = \frac{1}{x_m}. \tag{6}$$

Since the period of the principle – second mode (m=2), is taken as character time of capillar oscillations of liquid meniscus, then, the expressions (5) and (6) will have the form

$$\tau_\sigma = \pi \sqrt{\frac{\rho \cdot a^3}{2\sigma \cdot (1-W)}}, \tag{7}$$

$$\tau_\nu = \frac{a^2}{5\nu}. \tag{8}$$

2) $W > 1$ – in this case monotonous increasing or damping of slight perturbation of the surface occurs, which is characterized by one of two possible character times:

– character time of development of capillar instability of liquid surface meniscus at $W > W_{cm}$ $W > W_{cm} = 1 + \frac{\rho \cdot \nu^2}{\sigma \cdot a}$ [4]

$$\tau_\sigma^{(\nu)} = \frac{1}{\sqrt{\frac{\sigma}{\rho \cdot a^3} \cdot (W-1)} - \frac{\nu}{a^2}}, \tag{9}$$

– character time of damping $1 < W < W_{cm}$

$$\tau_\nu^{(\sigma)} = \frac{1}{\frac{\nu}{a^2} - \sqrt{\frac{\sigma}{\rho \cdot a^3} \cdot (W-1)}}. \tag{10}$$

Hence, if $\tau_\sigma << \tau_\nu$ the surface performs oscillations till their amplitude considerable decreases at the expenses of their viscosity. If $\tau_\sigma >> \tau_\nu$ then almost complete oscillation damping occurs during the time, which is less than one period of principle mode.

With the increase of voltage, character time of capillary oscillations τ_σ increases. With the increase of liquid viscosity ν character time of viscous damping of capillar oscillations τ_ν decreases. Therefore, increases of voltage and viscosity leads to the fact that perturbation damping of meniscus surface occurs during less number of oscillations. To realize contact-free method of surface tension measurement in electric field, idle drop is formed in the tray with pointed edge, the form of meniscus is changed under the influence of electric field, which is accompanied by transition of drop height above the edge of the tray across extremum, surface tension is calculated by changes of geometrical parameters of the drop.

The tray with investigated liquid is placed on lower electrode. Voltage is supplied to electrodes; the voltage is formed by voltage control unit and increases step-wise. Voltage increase leads to change of meniscus form and is accompanied of drop height increase. Further strengthening of tension results in drop rupture accompanied by formation of associated drops that characterizes instable state of meniscus. In this case sharp decrease of height is observed. At each step of voltage change, supplied to electrodes, photocamera registers the image of the investigated drop, the computer performs image processing, defines ordinate z_b of drop peak and compares the given coordinate with previous value.

If $z_{i+1}<z_i$, then further one-step voltage increase occurs. In case of $z_{i+1}<z_i$ the last image remains in the memory, the image is to be processed, geometrical parameters are to be defined, and, correspondingly, surface tension of investigated liquid is to be determined.

To provide the necessary accuracy and operation rate of control facility it is required that camera actuation time be greater than the time of change and redistribution of electric field intensity between the electrodes and capillary oscillations damping on the surface of the drop

$$t_n = t_{DAC} + t_E + t_p, \tag{11}$$

where t_n – is the time of drop transition into stationary state under the voltage change by one quantum; t_{DAC} –is the time of DAP conservation; t_E – is the time of redistribution of electric field intensity between the electrodes and establishment of stationary state; t_p – is the time of achieving equilibrium on the surface of the drop.

Total duration of measuring transformation while one quantum voltage change includes DAC conservation time t_{DAC}; time of redistribution of electric field intensity between electrodes and establishment of stationary state t_E; time of achieving equilibrium on drop surface t_p; time required by photocamera to take image and its digitization t_{fc}; time of image transmission by means of USB interface to PC t_{USB} and is defined as

$$t_{tot} = t_{DAC} + t_E + t_S + t_{fc} + t_{USB} \,. \tag{12}$$

The majority of measuring devices use serial DAC due to their high conversion rate, as time setting for DAC MAX5158 is $8{\cdot}10^{-6}$ sec [5]. Time of redistribution of electric field intensity between electrodes and establishment of stationary state t_E is $2{\cdot}10^{-4}$ sec. When photocamera operates in videomode there exists the possibility of image taking with rate of 30 frames/sec, hence t_{fc}=0,03 sec. To achieve high rate of data transfer and image processing it is necessary that PC support data transfer by USB 2.0. which provides data transfer rate up to 60 Mb/sec [5, 6] that is why t_{USB}=0,03 sec.

Time of equilibrium attainment on the drop surface t_e consists of the time of capillar oscillation damping τ_σ and the time of viscouse damping τ_ν, to be defined according to (7), (8). For instance, distilled water at U=6,3 kV, Relay parameter (3) W<1, τ_ν=1,24 sec, τ_σ=$3{,}47{\cdot}10^{-2}$ sec, i. e., t_E=1,27 sec. In this case, the surface performs oscillations until their amplitude considerably drops due to viscosity. When voltage increases, character time of capillary oscillations τ_σ increases; if the liquid viscosity increases, character time of viscous damping of capillar oscillations τ_ν decreases. Thus, growth of voltage and viscosity results in acceleration of capillar oscillations damping on meniscus surface. Hence, t_{tot} does not exceed 1,5 sec.

To reduce the duration of measurement process PC performs preprocessing of drop image parallel with transition of the drop into stationary state under the condition of step-wise voltage and image taking by the camera. Time diagram of measurement transformation has the form, shown in Fig. 1.

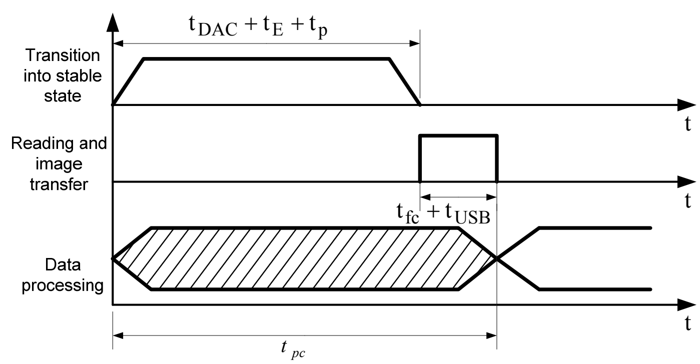

Fig. 1. Time diagram of measurement transformation

For evaluation of PC microprocessor operation rate t_{pc} it is necessary to analyze algorithm of image processing. Time of execution of image preprocessing by PC microprocessor in control device is defined

$$t_{pc} = t_1 + t_2 + t_3 + t_4 \,, \tag{13}$$

where t_1 – is duration of data loading; t_2 – is duration of z_i point ordinate determination; t_3 – is duration of z_i with z_{i-1}comparison; t_4 – duration of recording and deleting of the image from the memory; t_5 – duration of code formation for DAC.

For Intel Celeron processor with operation frequency of 2,2 GHz rate of reading from the memory is 2,5 Gb/sec, writing into memory rate – 911 Mb/sec. Since the volume of the photograph is up to one Mb, then t_{pc} does not exceed 1,5 sec.

Total duration of measuring transformation is

$$t_{\Sigma} = K \cdot t_{tot}\,, \tag{14}$$

where K – number of measurements.

Within the range of voltage variation of 450 – 700 kV/m the greatest time of measurement is 1000 sec. In order to reduce this time it is expedient to divide the voltage range depending on investigated liquid concentration into several subranges.

For instance, for concentration of 0,1 % of solutions of surface-active substances the intensity of instable state advent is within the range of 600 – 640 kV/m, for noninogenic surface-active substances (SAS) at concentration of 0,5 –1 % – 550 – 590 kV/m, for anionic SAS at concentration of 1 – 5 % – 500 – 540 kV/m. For SAS, increasing surface tension at concentration up to 2 % the intensity of instable state advent is within the range of 630 – 670 kV/m. Hence, for measurement of surface tension in certain range, it is necessary to carry out 120 measurements, that enables to reduce maximum measurement time to 180 sec.

Conclusions

The following conclusions can be made by the results of research carried out:

– drop instability based on mode approach was investigated, that enabled to evaluate the duration of capillary oscillations damping on meniscus surface, synchronize rate of drop stationary state establishment while step-wise voltage change with registration frequency of idle drop image and reduce the duration of surface tension measurement.

– it was defined that duration of drop transition into stationary sate while step-wise voltage increases does not exceed 1,3 sec. In order to reduce the duration of measurement transformation parallelly to drop transition into the stationary state and photocamera image taking, preprocessing of drop image is performed by the computer.

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