An Investigation on the Different Application and Techniques of Maximum Pressure Tensiometer

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Abstract – Here, based on the theoretical analysis of results for two ionic surfactants, sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium bromide (DTAB), we develop a new approach for quantitative interpretation of data from the maximum bubble pressure method. A given Tensiometer is characterized by an apparatus function, A(t), and by an apparatus constant. The former represents the time dependence of the bubble surface area, whereas the latter is expressed through integrals of A(t). The experiment indicates that both of them are independent of the surfactant type and concentration. Moreover, if a certain criterion is satisfied, the experimental results depend on the surface dilatation only through the apparatus constant. This makes the data interpretation much easier. The knowledge of the apparatus constant gives a general time scale (universal surface age) that makes the results independent of the specific bubble pressure setup and produces dynamic surface tension curves that are universal characteristics of the investigated solutions. A new equation for data processing is proposed, which provides excellent fits of the dynamic surface tension.

In the case of micellar solutions, the data analysis enables one to identify the kinetic regime of adsorption (among four possible regimes). For the investigated surfactant solutions, the diffusion regime "BC" was identified, for which the fast micellar process is equilibrated, whereas the slow micellar process is negligible. Upgraded with the developed approach for quantitative data interpretation, the bubble-pressure tensiometry could be a useful tool for a detailed analysis of the adsorption processes in more complex systems.

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INTRODUCTION

The Attention bubble Tensiometer is used for determination of dynamic surface tension. It is used in both academia and research institutions to study for example surfactant- or polymer-based liquid formulations. The bubble Tensiometer measures the maximum bubble pressure to calculate surface tension, but it also provides bubble lifetime and dead time information.

Integrated temperature measurement, liquid viscosity correction and optimization of the aerodynamic system ensure reliability and accuracy. Stand-alone automatic operation independent of the user as well as straightforward data analysis and saving are the key features of the bubble Tensiometer.

Portability and battery operation allow onsite measurements. Bubble Tensiometer is used to measure Dynamic surface tension. Dynamic surface tension measurements provide information on the wetting properties of the liquid. This data is useful for controlling and developing the surface active agents (surfactants) for a number of processes such as printing, spraying, cleaning and coating. It also enables direct and precise determination of bubble lifetime characteristics, providing insights on diffusion and absorption coefficient of surfactants.

With unknown liquid samples, this instrument is able to accurately correct for and estimate sample viscosity and gravitational deformation of bubble shape. In a typical measurement, a capillary is immersed into the liquid sample and air is bubbled out of the capillary. The pressure inside the capillary is measured. As the pressure increases in the capillary, a bubble is gradually pushed into the liquid.

Maximum pressure is reached when the drop is hemispherical, after which the bubble quickly grows and leaves the capillary. The maximum pressure depends on the force exerted by the liquid, and hence its surface tension. This information is useful to study, control and develop surfactants, ink jet printing, coating technologies, foam and emulsions, detergents, pharmaceuticals, cosmetics, food technologies and environmental monitoring etc.

The maximum bubble pressure method (MBPM) has found wide application for characterizing the dynamics of adsorption of various surfactants. This method is especially useful in the case of fast adsorption, which is typical for surfactant concentrations around and above the critical micellization concentration (CMC). In the first works, the MBPM was applied to pure liquids. Later, it was applied to surfactant solutions and has been refined and adapted in many ways. The history of this method, its development, and the limits of applicability are described in several reviews.

The dynamics of bubble formation has been investigated by high-speed cinematography in several studies. It was established that if the inner wall of the capillary is hydrophilic then, after the detachment of each bubble, solution enters the capillary and is further replaced by the gas flux. This phenomenon leads to a more complicated and irreproducible regime of expansion of the air-water interface. For this reason, it was recommended to use capillaries with a hydrophobic inner wall and hydrophilic tip. For such capillaries, the contact line solid water-gas is fixed at the inner edge of the capillary orifice.

The quantitative interpretation of the MBPM data demands one to take into account the fact that the surfactant adsorbs at an expanding interface. The cinematography of bubble growth provides direct evidence for the time dependence of the bubble surface area, $A(t)$. The latter dependence is different for apparatuses of different constructions of the gas supply system. For example, this system contained a reservoir and a chamber, whose volume was varied between 0.5 and 50 cm^3. For a greater chamber volume, the amplitude of pressure variations is smaller during the bubbling period, which affects the time dependence of the gas flow rate and the rate of bubble growth.

The measurement of $A(t)$ in each separate experiment renders the experimental procedure difficult. Such measurements are not used in the commercially available MBPM Tensiometer. However, if $A(t)$ is unknown, a quantitative data interpretation is impossible.

The key to resolve the above problem is the finding by Horozov et al.17 that the experimental dependence $A(t$d) is insensitive to the bubbling period and to the surfactant type and concentration. Here, *t*d) *t*/*t* age is the dimensionless time, with *t* age being the nominal surface age, i.e., the time interval between the onset of bubble growth and the moment of maximum pressure. The above finding is confirmed in the present study. Here, we make the next step: It is established that, under typical experimental conditions (with a typical bubble-pressure setup, such as Kru¨ss BP2), the experimental dynamic-surface-tension curves depend only on an integral of $A(t$d), called the apparatus constant, *ì*. For a given MBPM setup, with a given working capillary, the constant *ì* can be determined in experiments with a standard solution (calibration procedure), and further, the same value of *ì* can be used for quantitative interpretation of various data obtained with the same experimental setup. Thus, the labor consuming cinematographic determination of $A(t$d) is avoided. The procedures of data processing and interpretation demand an additional theoretical analysis, which is also presented below.

The paper is organized as follows. In this paper, we consider the two main problems encountered when applying the MBPM: (i) the fact that different kinetic curves are obtained by different apparatuses for the same surfactant solution and (ii) the fact that the bubble surface is "younger" than the nominal surface age given by the MBPM apparatuses. In this paper, we present new experimental data for the ionic surfactants sodium dodecyl sulfate (SDS) and dodecyl-trimethylammonium bromide (DTAB).

Video-frames illustrating the process of bubble growth are also shown. This paper is devoted to a new procedure for primary data processing, which involves fits of the data and determination of three adjustable parameters, one of them being the equilibrium surface tension. In this paper, the adsorption dynamics is modeled theoretically. Two independent ways for determining the apparatus constant are proposed and compared. Finally, in this paper, we give interpretation of the MBPM data for concentrations above the CMC and identify which of the four possible kinetic regimes of adsorption takes place.

MEASURING MAXIMUM PRESSURE TENSIOMETER

In the maximum pressure Tensiometer air is blown through a narrow capillary into the liquid whose surface tension is to be measured. The pressure at the inlet to the capillary, the volumetric flow of air through the capillary, and the time required for bubble formation are measured. The plot of the pressure P in the instrument gas volume against the volumetric air flow rate L through the capillary shows a significant change in the slope at a special flow rate (Fig.1). The linear range with the steepest slope which occurs at large flow rates L, corresponds to the so-called jet range. In this range there is a laminar air flow through the capillary according to the Hagen-Poiseuille Law. The magnitude of the flow rate is measured by the differential pressure across the capillary. At smaller flow rates there is, depending on the test liquid, a clear deviation from the constant slope of the curve in the linear range. This range of the graph is called the bubble range.

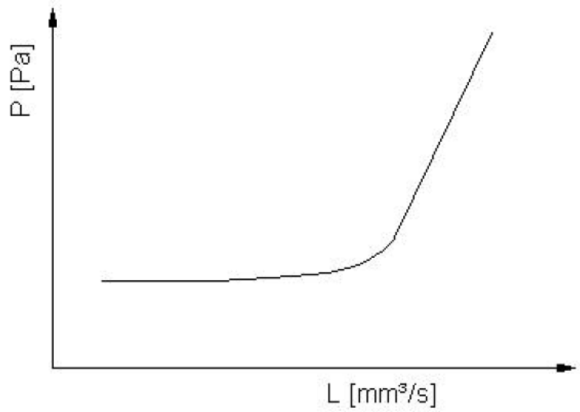

Fig. 1: Pressure P in the instrument as a function of volumetric flow rate L.

In the bubble range the pressure at the capillary outlet where the bubble is formed, rises (at constant pressure P1 at the capillary inlet) from an initial value P2 to a maximum value P1, and then rapidly falls again to the initial value P2 (Fig. 2). The maximum value P1 occurs when the radius r of the bubble at the capillary outlet is equal to the capillary radius r cap (Fig.3). The pressure is a minimum when the bubble at the capillary outlet bursts and a fresh bubble begins to form. The maximum value P1 of the bubble pressure is used to calculate the surface tension of the test liquid for the particular life of the bubble surface.

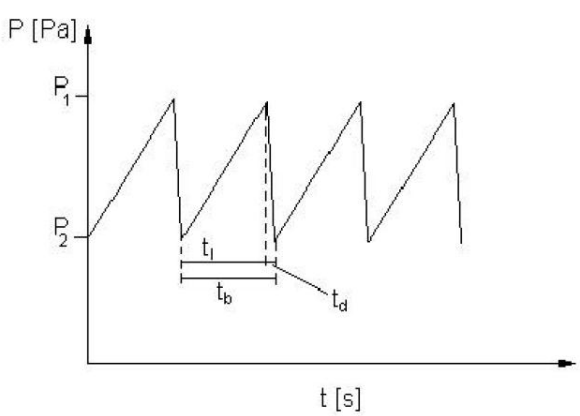

Fig. 2: Variation of system pressure P as a function of time t, tl - surface lifetime, tb – bubble lifetime, td – dead time.

The time interval from the start of bubble formation up to the moment where the bubble has the same radius r as the capillary (hemispherical size) is called the surface lifetime tl (Fig. 3). The time td required to blow up the bubble from a hemisphere until it detaches is called the dead time. The dead time is calculated by the instrument software from the transition point between the jet and the bubble ranges (Fig. 1). The bubble life tb minus the dead time td gives the surface lifetime tl.

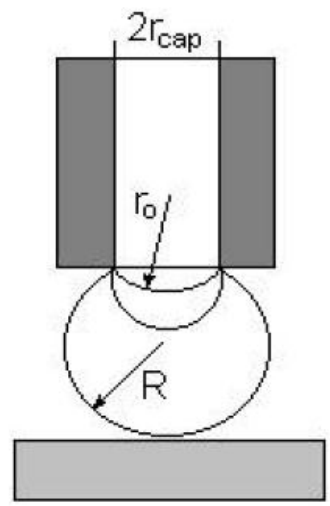

Fig. 3: Formation of the bubble at the capillary tip, R – bubble radius in the moment of detachment, ro – initial bubble radius, 2 recap - diameter of the capillary.

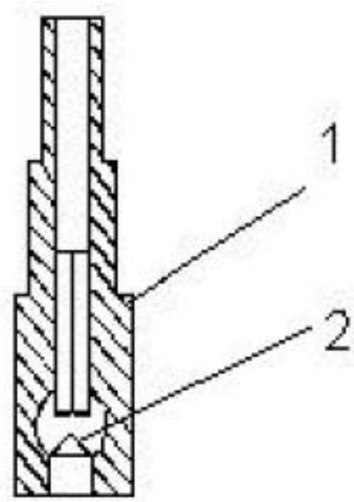

Fig. 4: Details of the capillary: 1 - capillary, 2 - rejection area.

The dead time td is determined by the geometric dimensions of the capillary and bubble. In the maximum pressure Tensiometer MPT 2 the special form of the capillary limits the growth of the bubble so that the dead time td can be calculated reliably (cf. Fig. 4). The bubble is formed at the end of a capillary (1) produced by a special process. Its growth is limited by a rejection area (2). The capillary is preceded by a chamber (humidifier) in which a few drops of the sample solvent can be placed. The size of the chamber is chosen such that the air becomes saturated with the solvent vapor as it passes through the chamber.

PRINCIPLE OF BUBBLE PRESSURE TENSIOMETRY

The maximum bubble pressure method (MBPM) was proposed in 1851 (M. Simon, Recherché Sur La Capillarité, Ann. Chim. Phys., 32(1851)5) for measuring the surface tension of liquids. Later quite a number of instruments were set up, however, the handling was difficult and the accuracy low, until modern accurate pressure sensors have been developed. During the last 30 years the method was extensively improved and hundreds of scientific articles and reviews were published. Several companies in Europe and USA produce commercial devices of this type which are widely used in the scientific studies, in a wide range of industries (from metallurgy to food), in agriculture, pharmacology, medicine and ecology. The maximum bubble pressure technique, monograph in "Drops and Bubbles in Interfacial Science", in “Studies of Interface Science”, D. Möbius and R. Miller (Eds.), Vol. 6, Elsevier, Amsterdam, 1998, p. 279-326).

The method is based on the measurement of the maximum pressure in a bubble growing at the tip of a capillary immersed into the liquid under study. When a bubble grows at the tip of a capillary, its radius of curvature decreases up to a hemisphere, and then increases again. Thus, at the hemispherical size the pressure measured is maximum. After the bubble passes this maximum pressure it grows quickly, separates from the capillary and a new bubble is formed.

The surface tension is calculated via the Laplace equation taking the capillary radius as radius of curvature:

$$P_{max} = 2\,\gamma/r$$

When the capillary is immersed into the liquid with a depth h, the respective hydrostatic pressure is measured in addition:

$$P_{max} = 2\,\gamma/r + \Delta\,\rho\,g\,h$$

$\Delta\rho$ is the density difference of the liquid to air, and g is the gravity constant. The time from the start of bubble growth to the maximum pressure at a hemispherical size is called lifetime ti, and the interval from this hemisphere until bubble departure is called deadtime t_d. Both times together give the bubble time t_b = ti + t_d. As the bubble surface grows during the experiment, the expansion has to be considered in the evaluation of the so-called effective surface age (see also the above mentioned monograph on bubble pressure tensiometry).

A schematic of the bubble pressure instrument BPA-1P is shown below. The pump produces a continuous gas flow, which is measured by the gas flow sensor. The gas flow capillary together with the gas volume damps the system and allows a smooth and regular bubble formation. The pressure sensor measures the pressure in the gas volume, which is proportional to the maximum pressure at the capillary tip. The pump and the two sensors are controlled by a computer via an electronic interface board.

The PC also collects the measured data, calculates the dynamic surface tension and effective time and presents all results online. Only data in terms of the effective time can be used for compare and for complementation with data from other instruments.

MAXIMUM BUBBLE PRESSURE METHOD

One of the useful methods to determine the dynamic surface tension is measuring the “maximum bubble pressure method” or, simply, bubble pressure method. Bubble pressure Tensiometer produces gas bubbles (ex. air) at constant rate and blows them through a capillary which is submerged in the sample liquid and its radius is already known.

The pressure (*P*) inside of the gas bubble continues to increase and the maximum value is obtained when the bubble has the completely hemispherical shape whose radius is exactly corresponding to the radius of the capillary. Figure 5 shows each step of bubble formation and corresponding change of bubble radius and each step is described below. (Image was reproduced from reference).

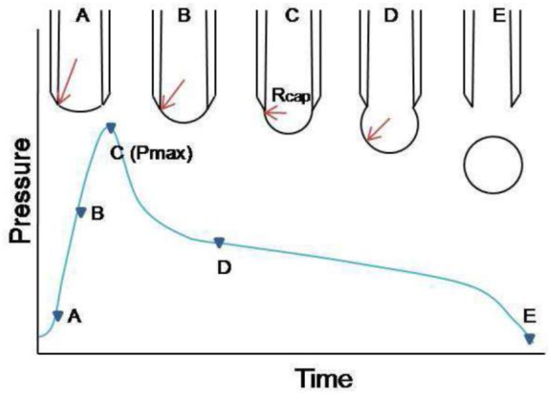

Figure 5 – Change of pressure during bubble formation plotted as a function of time.

A, B: A bubble appears on the end of the capillary. As the size increases, the radius of curvature of the bubble decreases.

C: At the point of the maximum bubble pressure, the bubble has a complete hemispherical shape whose radius is identical to the radius of the capillary denoted by Rcap. The surface tension can be determined using the Laplace equation the liquid.

$$\sigma = \frac{\Delta P_{max} \times R_{cap}}{2}$$

(σ: surface tension, ΔPmax: maximum pressure drop, Rcap: radius of capillary)

D, E: After the maximum pressure, the pressure of the bubble decreases and the radius of the bubble increases until the bubble is detached from the end of a capillary and a new cyc This is not relevant to determine the surface tension.

Currently developed and commercialized Tensiometer monitors the pressure needed to form a bubble, the pressure difference between inside and outside the bubble, the radius of the bubble, and the surface tension of the sample are calculated in one out via PC control.

Bubble pressure method is commonly used to measure the dynamic surface tension for the system containing surfactants or other impurities because it does not require contact angle measurement and has high accuracy even though the measurement is done rapidly. “Bubble pressure method” can be applied to measure the dynamic surface tension, particularly for the systems which contain surfactants to apply to biological fluids like sample for the measurements.

The maximum bubble pressure method avoids error-causing effects by measuring surface tension within the body of the fluid. It is the "Simplest Accurate Method" for measuring surface tension. A comprehensive mathematical analysis of the maximum bubble pressure method can be found in U.S. Patent No. 4,416,148 (covering the Sensa Dyne technology). Two probes having orifices of different diameters are positioned below the surface of the liquid. A pressurized process gas source forms bubbles in the liquid, and the differential pressure of the bubbles is measured and equated to the surface tension of the measured liquid.

Unlike other maximum bubble pressure methods, the Sensa Dyne's patented double probe method allows complete independence of immersion depth, for accurate repeatable results. The Tensiometer pneumatic system provides constant volumetric gas flow, making the flow independent of down-stream pressure. Flow rate to each orifice is adjustable through external valves. This allows interface formation time (bubble rate) selection from up to forty or more bubbles per second to one bubble every two minutes. Bubble rate, surface age, fluid temperature and fluid surface tension are displayed on the computer's video terminal.

CONCLUSION

Here, based on the theoretical analysis of data for two ionic surfactants. we developed a new approach for quantitative interpretation of the results of the maximum bubble pressure method (MBPM). A given MBPM tensiometer is characterized by an apparatus function. $A(t_d)$. and by an apparatus constant. λ. The former represents the time dependence of the bubble surface area. It was measured by video microscopy. and it was found to be independent of the surfactant type and concentration but dependent on the specific MBPM setup. The same is true for the apparatus constant.

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