Dynamic surface tension measured with an integrated sensor–actuator using electrolytically generated gas bubbles

Wouter Olthuis [a,*], Alex Volanschi [b], Piet Bergveld [a]

[a] *MESA Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[b] *Unilever Research Laboratory Vlaardingen, P.O. Box 114, 3130 AC Vlaardingen, The Netherlands*

Abstract

In this paper, a new, simple method to determine dynamic surface tension in aqueous solutions is reported, explained and experimentally verified. By function integration, a small device is obtained. Apart from control and interface electronics no external components or systems are necessary. Instead of the conventional sparging, we use the (cathodic) electrolysis of water at an actuator to produce gas bubbles in situ. The actuator can also function as the sensor for the bubble frequency by monitoring either its overpotential or its impedance. A simple model is given, by which the dependency of the bubble frequency on the dynamic surface tension can be predicted. Experimental results are in agreement with this model and show the feasibility of the proposed method. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dynamic surface tension; Surfactants; Electrolytically generated gas bubbles

1. Introduction

The dynamic surface tension (DST) of an aqueous solution determines its wetting and cleaning ability, e.g. in a washing process. Within the range of interest for washing, the DST is monotonously related to the concentration of surfactants, forming an important part of the formulation of washing powder. The DST decreases for increasing surfactant concentration.

An important property of surfactants is that they start clustering above a certain concentration and they form micelles. The concentration where clustering occurs is called the critical micelle concentration (CMC). Above the CMC, an equilibrium is reached between the free molecules and micelles in the solution. During the soil removal process, new surfaces become available for wetting because the bond between soil and, e.g. laundry is broken. To make sure that there are enough molecules to cover these new surfaces, the surfactant concentration has to be higher than the CMC. These are the concentrations of interest for this paper.

Conventional methods of DST determination are based on the investigation of phenomena occurring at the new interfaces produced by blowing gas bubbles (sparging) into a solution containing surfactants. One method is the determination of the maximum bubble pressure [1]. The fluctuating pressure in the bubble during growth reaches a maximum value, related to the DST and the capillary radius of the sparging device. Another method is that of the pressure-jump [2], measuring the frequency of bubble formation and subsequent release from the sparging capillary. At a constant gas flow, this frequency turns out to be related to the DST. Both methods require a separate sensing unit for the pressure measurement or the frequency determination and, moreover, some kind of gas compressor and supply unit. These units cause the conventional measuring systems to be relatively large and unsuited for, e.g. on-line monitoring of DST in washing machines.

In this paper, we propose a new method of DST determination, related to the pressure-jump method. Instead of the conventional sparging, we use the (cathodic) electrolysis of water at an actuator to produce gas bubbles in situ [3,4].

For proper operation, it is necessary to have a reproducible single gas nucleation site. Recently, we proposed to accomplish this controlled gas bubble formation during electrolysis by means of electrode surface shaping in the form of Micro Cavity Electrodes

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* Corresponding author. Tel: + 31 53 4892688; fax: + 31 53 4892287.
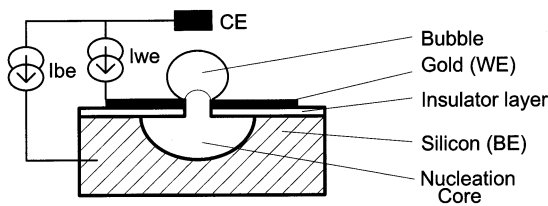
Fig. 1. Cross-sectional view of a gas phase nucleation core (GPNC) electrode with one nucleation site. I_{we} is the electrolysis current used to generate bubbles at the working electrode WE and I_{be} is the current used for the generation of the gas phase nucleation core at the bulk electrode BE.

(MCEs) [5]. It is shown there that the cavity, shaped as a reversed pyramid, works as a gas concentrator making the concentration of dissolved gas on the bottom of the cavity much higher than anywhere else in the solution before the actual nucleation. The chance that nucleation of the bubble occurs on the bottom of the cavity is thus much higher.

In this paper, we propose an alternative method of obtaining a reproducible single gas nucleation site by the integration of a small nucleation core, electrolytically filled with gas, forming a Harvey nucleus on which the subsequent formation of a single gas bubble is energetically favoured. A Harvey nucleus is basically a trace of gas that may be present in a pocket (small cavity) on the surface of an electrode or the wall of the containing vessel which is in equilibrium with the liquid environment [6]. If the concentration of dissolved gas exceeds a maximum value depending on the dimensions of such a gas containing pocket, the corresponding Harvey nucleus becomes active and a bubble will grow from that pocket. When a bubble grows from one

Harvey nucleus, its presence prevents other nucleation events in the neighbourhood of this bubble [7]. The artificial Harvey nucleus we constructed, the gas phase nucleation core electrode (GPNC), is depicted in Fig. 1.

An additional and important advantage of the device is that the actuator can also function as the sensor for the bubble frequency by monitoring either its overpotential or its impedance.

The overpotential represents the deviation of the electrode potential from the equilibrium value [8]. The overpotential accounts thus for the phenomena occurring at the electrode–electrolyte interface. The overpotential has two components, the surface overpotential due to the charge exchange mechanism at the electrode–liquid interface, and the concentration overpotential due to the concentration gradients in the electrolyte. In the particular case of gas-evolving electrodes, the concentration overpotential can be further split to account for the concentration gradient of dissolved gas and for the pH gradients.

If an alternative current with a small amplitude is superposed to the steady state current between the working and the counter electrode, the electrode impedance can also be measured. The electrode impedance is defined as the ratio of the resulting voltage variation between the working and the reference electrode to the applied current. The value of the electrode impedance is a function of the frequency of the applied small signal. Both signals, the overpotential and the impedance, contain the periodic information caused by the bubble detachment. A block diagram, showing the sub-processes of our proposed method of DST determination, including some relevant input and output parameters, is shown in Fig. 2.
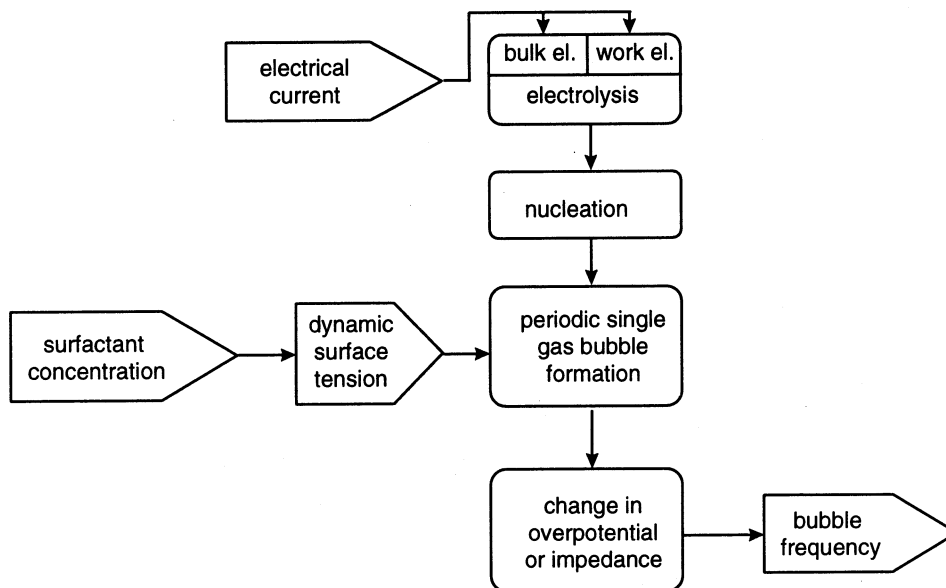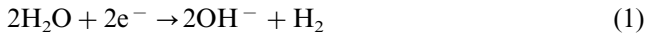

Fig. 2. Block diagram showing the sub-processes of the proposed method of DST determination with relevant input and output parameters.

2. Theory

The cathodic electrolysis of water at an actuator is used to produce gas bubbles:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{1}$$

A simplified expression for the gas production rate Q_g is

$$Q_g = \frac{i}{zF} V_m \tag{2}$$

where i is the electrolysis current, F the Faraday, z the number of electrons involved in the hydrogen evolution reaction: $z = 2$, and V_m the molar volume (being a constant at fixed pressure). Assuming a bubble volume V at the moment of detachment from the actuator, the bubble frequency, v, then becomes

$$v = \frac{Q_g}{V} \tag{3}$$

Assuming a horizontal actuator and with some additional simplifications, an equilibrium exists at the moment of detachment between the detaching force, being the buoyancy only, and the attaching force, containing the surface tension of the liquid [9]:

$$V(\rho_1 - \rho_2)g = \pi\phi\sigma \tag{4}$$

with ρ_1, ρ_2 the densities of the hydrogen gas and the liquid, respectively, g the gravitational acceleration, ϕ the diameter of the gas bubble at the actuator, and σ the surface tension of the liquid. The combination of Eqs. (2)–(4) yields for the bubble frequency v

$$v = \frac{g(\rho_1 - \rho_2)}{\pi\phi\sigma} \cdot \frac{iV_m}{zF} = \text{constant} \cdot \frac{i}{\sigma} \tag{5}$$

Using Eq. (5), the frequency of bubble release is plotted in Fig. 3a as a function of the surface tension, σ.

The relation between the surface tension, σ, and the surfactant concentration is described by adsorption. The adsorption equilibrium is governed by two equations. Firstly, the Gibbs relation specifies the change of the equilibrium surface tension, σ, due to the adsorption of surfactant at the surface [10]:

$$d\sigma = -\Gamma d\mu = -\frac{\Gamma RT}{c_0} \cdot dc_0 \tag{6}$$

where Γ [mol/m^2] is the surface density of the surfactant, μ is the chemical potential of the surfactant [J/mol], R is the gas constant [J/(mol·K)], T is the absolute temperature [K], and c_0 is the concentration of the surfactant in the subsurface layer [mol/m^3]. The subsurface is defined as being a film that directly borders the surface. At equilibrium, the subsurface concentration is also the bulk concentration of the surfactant.

Secondly, an equation is needed to relate the surfactant concentration in the subsurface layer, c_0, to the
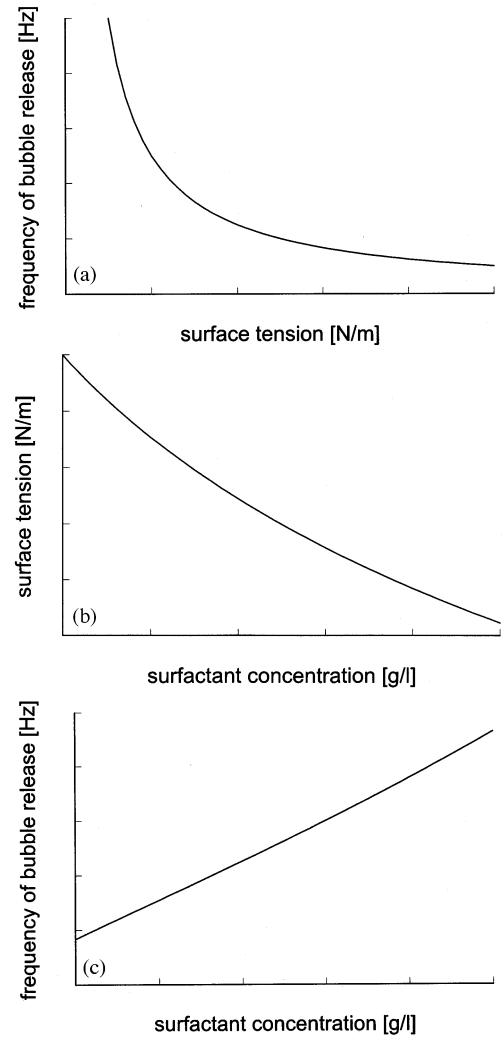

Fig. 3. (a) Dependence of the bubble release frequency on the surface tension, according to Eq. (5), (b) dependence of the surface tension on the surfactant concentration, according to Eq. (8), and (c) the resulting theoretical dependence of the bubble release frequency on the surfactant concentration.

surface density, Γ, hence an adsorption isotherm. Many nonionic surfactants are found to satisfy the empirical Langmuir adsorption isotherm [11]

$$\Gamma = \Gamma_\infty \frac{c_0}{c_0 + C_{1/2}} \tag{7}$$

where Γ_∞ is the saturation surface density [mol/m^2] and $C_{1/2}$ is the concentration at which the equilibrium surface density becomes half its saturation value. Γ_∞ is an interface-specific parameter. A characteristic of this equation is the fact that $\Gamma = \Gamma_\infty$ only if $c_0 \gg /C_{1/2}$.

The combination of Eqs. (6) and (7) yields after integration a relation between the surface tension and the surfactant concentration (the Szyszkowski equation) [11]:
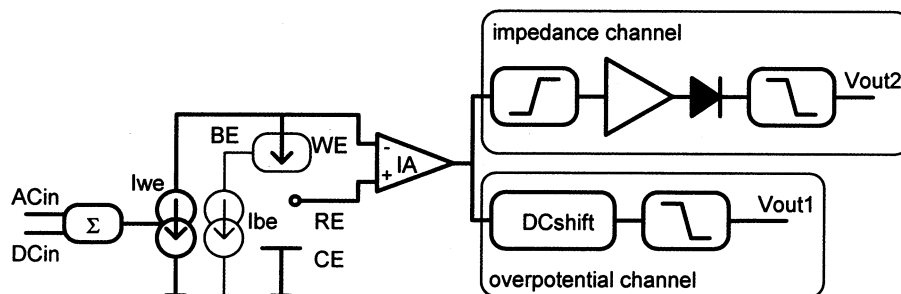
Fig. 4. Measurement set-up. WE is the working electrode, CE is the counter electrode, RE is the reference electrode, BE is the bulk electrode. I_{we} is the electrolysis current used to drive the working electrode and I_{be} is the current used for the generation of the gas phase nucleation core. AC_{in} and DC_{in} are the control voltages applied to the current source by means of the summing amplifier Σ. IA is the instrumentation amplifier. V_{out1} corresponds to the measured overpotential and V_{out2} corresponds to the measured impedance fluctuations.

$$\sigma - \sigma_0 = -\Gamma_\infty RT \cdot \ln\left(\frac{c_0}{C_{1/2}} + 1\right) \qquad (8)$$

where $\sigma 0$ is the surface tension of the solvent (water in this case). Eq. (8) predicts a decreasing surface tension with increasing surfactant concentration, c_0, at constant temperature T, as plotted in Fig. 3b. The combination of Eqs. (5) and (8) yields the expected dependence of the bubble release frequency, v, on the surfactant concentration, c_0. This non-linear dependence is plotted in Fig. 3C.

Essentially, two processes take place to reach equilibrium in a surfactant solution, not only the adsorption at the surface as described above, but also the transport of surfactant to the surface. If the surfactant adsorption process is fast compared to the transport, the concentration in the subsurface layer is in equilibrium with the surface density and there is a concentration gradient from the bulk towards the subsurface layer. Under these conditions, the relations for adsorption equilibrium are still valid, but for a time-dependent concentration in the subsurface layer, $c_0(t)$. The treatment of these time-dependent coupled processes as well as additional effects, such as electrostatic interactions (influenced by pH and the ionic strength) is beyond the scope of this paper.

3. Experimental

3.1. Device preparation

The gas phase nucleation core electrodes (Fig. 1) were made in silicon technology. Silicon wafers with a $\langle 100 \rangle$ crystal orientation were used. The cavities were isotropically etched using reactive ion etching in silicon through a SiO_2 mask (insulator layer in Fig. 1). Devices with mouth diameters of 2, 3, 5, or 10 μm were fabricated.

A sandwich of Ti/Au/Ti with a thickness of 25/250/25 nm, respectively, was evaporated and patterned on the wafers. The active area of the electrodes was defined by a passivation layer consisting of a sandwich of SiO_2,

Si_3N_4, and photocurable polyimide. The SiO_2, Si_3N_4 interlayers were included as a passivation for the polyimide layer, which otherwise can undergo redox reactions. At the end of this patterning process, the titanium top-layer was removed in the active area, allowing the gold surface a free contact with the aqueous solution. The active area of the microelectrodes used during the experiments was determined by the $SiO_2/Si_3N_4/$polyimide window to a circle with the diameter of 35 μm.

The wafers were then cut into pieces and the chips were glued on 8×100 mm² printed circuit board carriers. The metal strip was wire bonded and the silicon bulk was contacted with silver glue. The devices were then encapsulated by hand with Hysol resin.

3.2. Measurement set-up

A schematic of the complete measurement set-up used for the electrical monitoring of the gas bubbles is shown in Fig. 4.

With this specially designed set-up overpotential and impedance fluctuations due to bubble evolution could be measured simultaneously. The overpotential channel automatically removed the mean value of the measured potential, making it possible to monitor only the absolute value of the fluctuations around this mean value. For the impedance measurements, a signal (AC_{in}) with a frequency of 100 kHz and a small amplitude (typically 50 mVpp) was added to the control voltage of the current source (DC_{in}) by means of a summing amplifier, Σ. The outputs of the two channels (V_{out1} and V_{out2}) were monitored and recorded on a dual channel digital oscilloscope. The bubble frequency was estimated from these recordings.

The experiments were done in a 10 mM solution of sodium acetate (NaAc, Merck, analytical grade), at different concentrations of nonionic surfactant (Novel EO 4.5, courtesy of Unilever). Where needed, the pH was adjusted by adding small amounts of sodium hydroxide (NaOH, Merck, analytical grade).

4. Results and discussion

The need for the initial creation of a gas phase nucleus for proper operation of the device (i.e. with stable and periodic bubble evolution) was experimentally verified by testing the device deliberately before the formation of a gas phase nucleus. The result of the experiment, carried out at a fixed surfactant concentration without an initially created gas phase nucleus, is shown in Fig. 5. The reproducibility of the bubble evolution turned out to be very bad, without showing a constant periodicity. By optical observation of the gas evolution process it could be seen that several bubbles evolved at the same time, even from this small electrode surface (35×35 μm^2). It can be concluded that the reproducibility of the gas bubble evolution process is not good enough in case the gas phase nucleus is not previously generated in-situ.

The reproducibility was improved when the gas phase nucleus was generated from the bulk silicon electrode by means of a small constant current I_{be}. A typical experiment was carried out at a fixed surfactant concentration to measure the frequency and determine its stability. The result is shown in Fig. 6. The periodicity of the signal is obvious. It can be deduced from this periodicity that indeed the gas generated with the gold top electrode diffuses to the already existing gas phase in the nucleation core leading to a growing bubble rather than nucleating an independent bubble. It should be stated that the reproducibility greatly depends on the materials used and the experimental conditions. Standardization of these aspects are items for further research.

To illustrate the possibility of simultaneous monitoring of the overpotential and impedance fluctuations, a gas bubble evolution process with an estimated frequency of approximately 0.5 Hz was recorded at an electrolysis current $I_{we} = 0.37$ μA and $I_{be} = 0$ μA. Note

Fig. 6. Constant frequency during the bubble evolution from GPNC electrodes illustrated by means of the recording of the overpotential fluctuations. Measurement in 10 mM NaAc with 0.25 g/l Novel EO4.5 surfactant. The estimated frequency is 8.25 Hz. The experiment was performed at $I_{we} = 1$ μA and $I_{be} = 0.8$ μA. The origin of the overpotential fluctuations is arbitrary.

that $I_{be} = 0$ μA during these measurements, but the nucleation core was filled with gas by electrolysis just before the experiments by means of a small current of ≈ 1 μA for a number of seconds. The results are given in Fig. 7. It can be seen that, when a bubble grows on the electrode, both the absolute value of the overpotential and the impedance increase. The maximum is reached just before bubble detachment. This is due to the continuously increasing surface screening of the electrode during the bubble growth. The abrupt fall occurs when the bubble detaches from the electrode. It can be concluded from Fig. 7 that either the overpotential or the impedance fluctuations can be used for the monitoring of the bubble evolution process. The difference between the shapes of the overpotential fluctuations in Figs. 6 and 7 is due to the different frequency of the two signals that is caused by a different current injected through the electrodes.
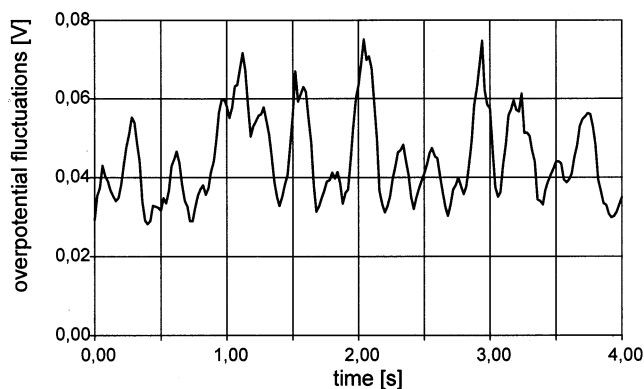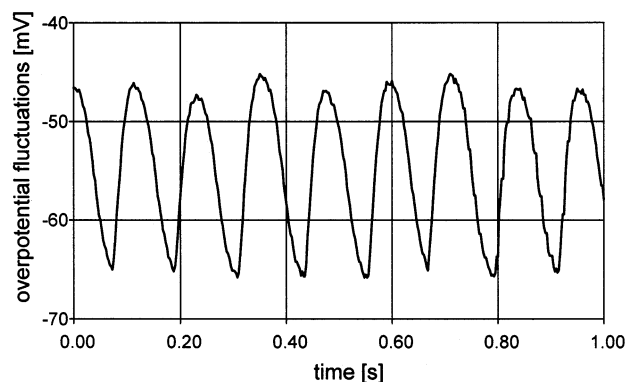

Fig. 5. Recording of the overpotential fluctuations at GPNC electrodes before the creation of the gas phase nucleus (artificial Harvey nucleus). $I_{we} = 0.58$ μA, BE not connected. Measurement in 10 mM NaAc with 0.1 g/l Novel EO4.5 surfactant (courtesy of Unilever).
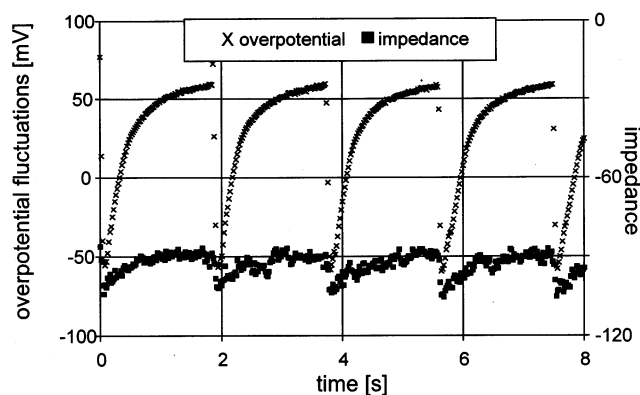

Fig. 7. Simultaneous recording of the absolute value of the overpotential and of the impedance fluctuations due to bubble evolution on GPNC electrodes, pH = 9.15. The estimated bubble frequency is 0.5 Hz. The experiment was performed at $I_{we} = 0.37$ μA and $I_{be} = 0$ μA (see text); overpotential (left scale, arbitrary origin), impedance (right scale, arbitrary impedance units).
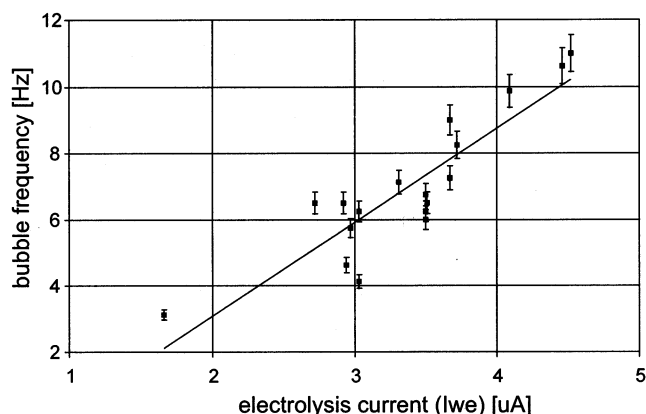
Fig. 8. Dependence of the bubble frequency on the electrolysis current through the working electrode of a GPNC electrode (I_{we}); $I_{be} = 0.9$ μA.

The influence of the electrolysis current injected through the working electrode of a gas phase nucleation core electrode (I_{we}) on the bubble frequency at constant surfactant concentration is shown in Fig. 8. As was expected, a higher bubble frequency corresponds to a higher current I_{we}, and thus a higher amount of gas produced by electrolysis.

Finally, the effect of the surfactant concentration on the bubble frequency is presented in Fig. 9 for a constant electrolysis current. At a constant current of $I_{we} = 0.6$ μA through the working electrode, an increase of the bubble frequency is observed for a higher surfactant concentration and thus for a lower dynamic surface tension. This increase in the bubble frequency was expected from Eq. (5) because by increasing the surfactant concentration, the surface tension of the solution decreases, according to Eq. (8) and the attachment force that keeps the bubble on the electrode becomes smaller, according to Eq. (4). Note, that direct comparison between Fig. 3C and Fig. 9 is not possible, because additional mass transport of the surfactant as well as electrostatic interactions are not included in the simple
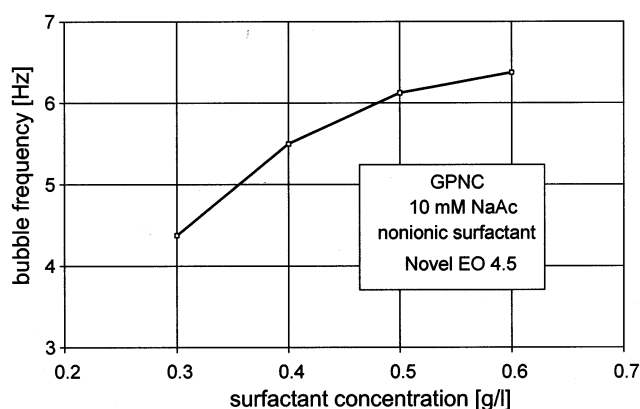
model of Fig. 3C. It can be concluded from Fig. 9 that the GPNC electrodes can be used as sensors for measuring the surface tension in aqueous solutions. Note, that the frequency of bubble release is a direct measure for surface tension and not for surfactant concentration. For any other surfactant than the one used here, there is a unique relation between surface tension and composition and concentration of the surfactant.

5. Conclusions

We have proposed a new method of DST determination, using electrolysis of water at an actuator to produce gas bubbles in situ.

It has been shown that a gas nucleation site is necessary for proper operation. This site, guaranteeing single bubble generation, is accomplished by integrating a small nucleation core, electrolytically filled with gas.

The actuator also functions as the sensor for the detection of the bubble frequency by monitoring either its overpotential or its impedance.

Simplified equations are derived, indicating the relation between the bubble frequency and the surface tension, as well as the relation between the surface tension and the surfactant concentration.

Measurement results show the expected monotonous relation of bubble frequency as a function of surfactant concentration.

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Fig. 9. Dependence of the bubble frequency on the surfactant concentration; pH = 11.38; $I_{we} = 0.6$ μA; $I_{be} = 0$ μA (see text).

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6. Biographies

Wouter Olthuis was born in Apeldoorn, the Netherlands, on October 23, 1960. He received the M.S. degree in electrical engineering from the University of Twente, Enschede, the Netherlands in 1986, and the Ph.D. degree from the Biomedical Engineering Division of the Faculty of Electrical Engineering, University of Twente, in 1990. The subject of his dissertation was the use of iridium oxide in ISFET-based coulometric sensor–actuator devices. Currently he is working as an Assistant Professor in the Biosensor Technology Group, part of the MESA Research Institute, of the University of Twente.

Alexandru Volanschi was born in Bucharest, Romania, on May 6, 1967. In 1991, he received the M.S. degree in Microelectronics of the Faculty of Electronics and Telecommunications from the Polytechnical Institute of Bucharest, Romania. His M.S. thesis was on Chemical Sensors in MOS technology. As a junior researcher, in 1991, he visited the University of Twente, The Netherlands in the EC Tempus exchange programme. He was offered a Ph.D. position in 1992 at the Biomedical Engineering Division of the Faculty of Electrical Engineering, University of Twente. In 1996, he received the Ph.D. degree on the subject 'Dynamic Surface Tension measured with Single Nucleation Site electrodes'. In 1996, he joined the Advanced Manufacturing Technology Group of the Unilever Research Laboratory, Vlaardingen, The Netherlands.

Piet Bergveld was born in Oosterwolde, The Netherlands, on January 26, 1940. He received the M.S. degree in electrical engineering from the University of Eindhoven, the Netherlands, in 1965 and the Ph.D. degree from the University of Twente, the Netherlands, in 1973. The subject of his dissertation was the development of ISFETs and related devices, the actual invention of the ISFET, since then also investigated by many international research groups of Universities as well as industry.

Since 1965, he has been a member of the Biomedical Engineering Division of the Faculty of Electrical Engineering (University of Twente) and was in 1984 appointed Full Professor in Biosensor Technology. He is one of the project leaders in the MESA Research Institute. His research subjects still concern the further development of ISFETs and biosensors based on ISFET technology as well as physical sensors for biomedical and environmental applications, resulting up to now in over 250 papers.