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Triton X-100 as an Effective Surfactant for Micropump Bubble Tolerance Enhancement

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Abstract: Improvement of bubble tolerance and priming in micropumps based on Triton X-100 surfactant is investigated. Transparent membrane piezoelectric micropumps were fabricated. Precise air volumes were introduced into the micropump chamber to emulate micropump bubble disturbance. Micropump recovery time decreased with increased addition of Triton X-100 surfactant between 50-100 ppm. Effective recovery is mainly a consequence of the air bubble dispersion into a foam of small bubbles. Small bubbles are then readily removed by liquid flow, leading to significant enhancement of micropump bubble tolerance.

Key words: piezoelectric micropump, bubble tolerance, bubble decay, priming, surfactant, Triton X-100

Triton X-100 za izboljšanje zanesljivosti mikročrpalke pri črpanju dvofaznega medija

Povzetek: V prispevku predstavljamo metodo za preprečevanje odpovedi mikročrpalke v primeru črpanja mešanice kapljevine in plina in izboljšanje omočljivosti pri začetnem polnjenju z medijem. Boljša omočljivost prepreči nastanek zračnih žepov pod membrano in omogoči začetni zagon mikročrpalke. Metoda temelji na dodajanju majhnih količin sredstva za zmanjševanje površinske napetosti (Triton X-100) neposredno v medij. Izdelali smo PZT difuzorsko mikročrpalko s stekleno membrano, ki nam je omogočila opazovanje mešanja kapljevine in plina med njenim delovanjem. Dodajanje majhnih količin sredstva za zmanjševanje površinske napetosti v črpan medij (50 ppm ut. Triton X-100) povzorči pod vplivom nihajoče membrane razpad plinskih mehurčkov v množico manjših mehurčkov, ki lažje zapustijo mikročrpalko. Z večanjem koncentracije Tritona (do 100 ppm ut. Triton X-100) smo dosegli hitrejše izločanje plina iz mikročrpalke in močno povečali zanesljivost črpanja.

Ključne besede: piezoelektrična mikročrpalka, dvofazni tok, sredstvo za zmanjševanje površinske napetosti, Triton X-100

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1 Introduction

Mircoscale pumping technology has attracted a great attention in recent years. With the increasing demand of industrial and medical fields, micropumps have been applied to numerous applications. Some of the potential applications are drug delivery systems, biochemistry, lab-on-a-chip, controlled fuel delivery in engines and fuel cells, localized cooling in electronics, micromixing [1]. Although peristaltic, reciprocating and rotary pumps all ever show up in literatures on micro mechanical driving systems, the reciprocating type micropumps are always in the majority. The most popular reciprocating type micropumps applied in MEMS are piezoelectric, electrostatic, thermo-pneumatic, bimetallic, shape memory alloy (SMA) and ionic conductive polymer film (ICPF) [2]. The application of a micropump requires maximum reliability, which means that the device should be tolerant towards gas bubbles and able to prime itself. Pumping over long time periods, during which small gas bubbles can be introduced in the pumping liquid, should not degrade the device performance [3]. To prevent entrapment of gas bubbles inside micropump chamber before micropump startup, complicated and unreliable manual priming procedures had to be performed in the first time [3]. A more practical approach was made with a CO_2-purge of the dry device [4]. Residual CO_2 inside the pump was easily dissolved in the following aqueous priming solution, which resulted in a complete filling. The problem of bubbles travelling towards the micropump in the inlet tubing, however, remained unsolved. These problems were discussed quite early sometimes even with the pessimistic argument that a microdiaphragm pump would not be able to be self-priming at all due to several physical reasons [3]. This discussion was set in 1996 with the first "self-filling" polymer-fabricated micropump by Döpper et al. [4]. A first comprehensive treatment of the subject was performed in 1998 by Richter et al [5]. They proposed increasing of compression ratio in order to improve self-priming and bubble tolerance in reciprocating type micropumps.

An alternative approach for enhancing bubble tolerance and priming in reciprocating type micropumps is proposed. It will be shown that even small quantities of appropriate surfactant additive in liquid medium facilitate priming and significantly enhance bubble tolerance. Presented approach is useful in many specific applications e.g. in living cells manipulation where micropump high-compression ratio and check valves could lead to permanent cells damage. In such micropumps, bubble tolerance can be increased by reducing chamber depth in order to decrease the dead volume and consequently increase the compression ratio. [6]. However, by reducing the chamber depth under a critical point, the deflected diaphragm could damage living cells by compressing them to the chamber floor. Typical diameter of living cells is 10 – 50 µm [7] which dictates the minimum chamber depth. In case of larger cells, obviously deeper chamber is required, deteriorating the compression ratio. In this very specific area, the proposed approach could fill the gap: by adding small amounts of surfactant in cell transportation medium.

In this study fluid was DI water and as surfactant, Triton X-100 (Merck™ / Darmstadt / Germany, $C_{34}H_{62}O_{11}$, 646.9 g/mole, purity 98–100%) was applied. The micropump applications that allow use of Triton as surfactant includes pumping suspensions with microcapsules and localized cooling in electronics. Furthermore, Triton can be added into medium (water) used in initial micropump prothotypes characterisations in order to simplify priming procedure and enhance validity and repeatability of micropump performance measurements.

There are also other appropriate non-toxic surfactants on the market, including e.g. pluronic polyols [8], Tween 80 [9], Pluronic® nF68 [10] and natural surfactants derived from animal sources containing surfactant proteins B (SP-B) and C (SP-C) [11].

2 Experimental

2.1 Micropump fabrication

To get a detailed insight into micropump operation and related bubbles problems, a low-compression ratio diffuser piezoelectric micropump with transparent membrane was fabricated. Micropump consists of 380 µm thick (100) silicon substrate (Fig. 1, A), thinned glass membrane from Pyrex 7740 (Fig. 1, B), piezoelectric actuator (Fig. 1, C) bonded on Pyrex and inlet/outlet stainless steel connections (Fig. 1, D). Micropump fabrication steps are shown on Fig. 2.

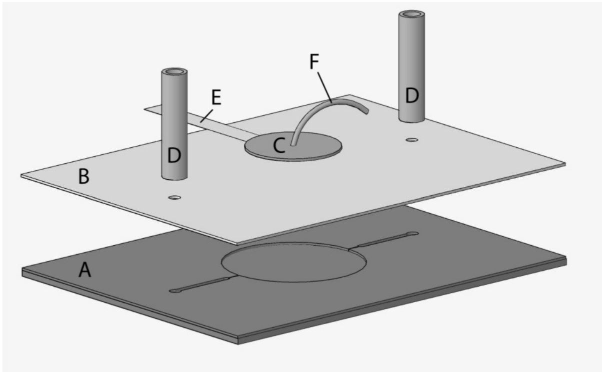

Figure 1: Micropump schematics.

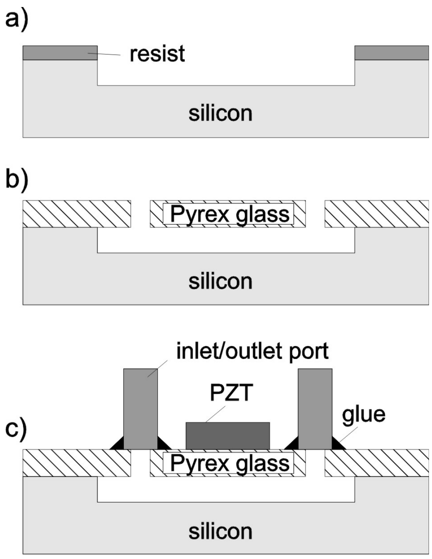

Figure 2: Schematic presentation of fabrication steps: a) mask pattering and DRIE etch of chamber/diffusers/microchannels b) Pyrex cover to Si c) gluing of fluid ports and PZT actuator.

Starting substrate was single-side mechanically polished 380 µm thick (100) silicon wafer. Silicon oxide of thickness 2.5 µm obtained by LPCVD deposition and photoresist AZ 9260, Clariant, USA, of thickness 6.5 µm were used for the fabrication of mask for silicon etching [12]. DRIE system Plasmalab System 100 – ICP 180 based on Bosch process was used for etching deep silicon micropump structures such as chamber, diffuser elements and microchannels (Fig. 2, a). Etched microstructures on silicon chip were finally sealed by anodic bonding of Pyrex glass [13], (Fig. 2, b).

In a previous work [14], it was found that PZT/Pyrex thickness ratio around 1:1 results in good micropump performance (backpressure of 61 mBar and flow-rate of 0.29 ml/min at the resonant frequency of 200Hz). A 200 µm thick PSM23 Noliac piezoelectric disc attached to the glass membrane was used for micropump actuation.

2.2 Characterization methods

To investigate the influence of surfactant additive on micropump bubble tolerance, an appropriate measurement setup was realized (Fig 3). First, micropump flow-rate vs. time characteristic was measured for pure DI water and then measured again for DI water with surfactant addition. To emulate real-world operation conditions, in both cases air bubbles were introduced into the system by a syringe pump.

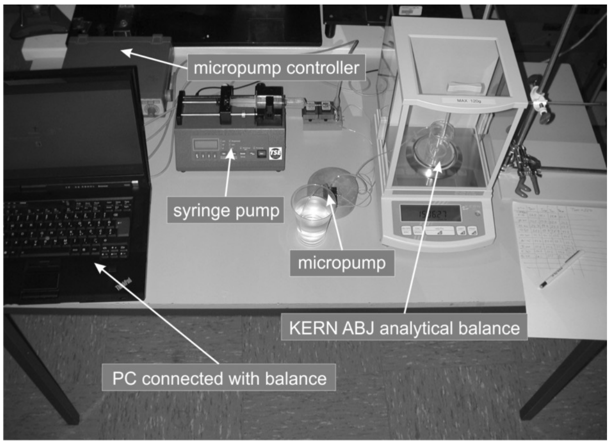

Figure 3: Measurement setup for bubble tolerance investigation.

For studying liquid/gas interaction in micropump chamber as well as micropump operation after bubble entered the pump, a microcamera for continuous monitoring and a real-time flow-rate measurement method were applied.

In initial micropump characterizations, classic volumetric method was used for micropump flow-rate measurements. However, this method is complex and depends on operator related factors [15], so real-time measurement with high data rate acquisition needed in our case can not be performed accurately.

Therefore, flow-rate measurement by micro weighing method was introduced. Micro weighing method is based on the measurement of the liquid mass change somewhere in the liquid path, measured by a sensitive digital microbalance over the unit of time. Based on our experiences, this approach may be considered as an accurate method for flow-rate measurement since both mass and the time can be evaluated fast with high precision. For this purpose, KERN ABJ 120-4M analytical balance with RS232 interface was utilized. The balance offered precise measurements up to 120g with 0.1 mg readout. Furthermore, acquired data were stored in a computer with 240 ms sample rate. To minimize dynamic measuring errors caused by liquid dropping into the tank, the output tube was submerged into the tank medium. In order to completely prime the pump, inlet tube was first submerged into the pumping medium while outlet tube was connected to a syringe pump running in the reverse mode.

To introduce controlled quantity of bubbles for bubble tolerance investigation, micropump inlet tube was taken out of the filling tank, by further running syringe pump connected on micropump outlet tube in reverse mode with very low flow-rate setting (cca. 0.05 ml/min). Air bubble volume entering into the liquid system was determined by the filling rate and time. After the air bubble was created in the inlet tube, the syringe pump was disconnected from micropump outlet tube, inlet tube submerged back into the pumping medium and the running micropump itself sucked the air bubble into the chamber. Before micropump flow-rate measuring with microweighing method, air bubble volume can also be determined by measuring air bubble length in micropump inlet tube with known diameter.

Micropump bubble tolerance was investigated for different volumes of introduced air bubbles (1-10 µl) and various concentrations of surfactant additives, expressed as the weight mixture of Triton X-100 / DI water and given in ppm units.

For flow-rate Φ determination, every 240 ms weight measuring data were acquired by a PC what enabled fast flow-rate measuring. Flow-rate Φ is determined from the first derivative of mass *m* with respect to time:

$$\Phi(t) = \frac{1}{\rho}\frac{dm(t)}{dt} \qquad (1)$$

The transparent glass pump cover made it possible to inspect visually micropump priming and surfactant effects in the chamber.

3. Results and discussion

In the following investigations, for micropump actuation sine-wave 200V / 200 Hz excitation signal was applied. As expected, initial measurements with DI water as liquid medium without surfactant additives revealed that bubble tolerance was rather low. Therefore, the influence of surfactant additive on micropump operation such as priming and bubble tolerance was investigated.

3.1 Micropump priming enhancement

Micropump in case of pure DI water was not self-priming, due to the mentioned diffuser valves and low-compression ratio design. It was observed that it is difficult to fill the entire micropump chamber with pure DI water, without entrapping air bubbles. To prime completely the pump, the support of external priming system was required. In most cases, incomplete priming decreased low-compression ratio diffuser micropump performance or even fully prevented micropump start-up.

By addition of Triton X-100 surfactant in DI water, micropump was easily primed. Fluid filled the entire micropump chamber, without entrapping air bubbles. It was found that even small quantities of surfactant additive significantly facilitate micropump priming procedure. Surfactant addition can be used only for initial micropump priming, and can then be removed from the medium.

Therefore, the proposed approach with surfactant addition to the medium results in a simple, reliable and complete priming of the micropump.

3.2 Micropump bubble tolerance enhancement

Micropump bubble tolerance is a critical effect limiting micropump use in many applications. Real-world micropump applications require maximum reliability which is closely related to the micropump insensitivity on gas bubbles in pumping medium. Therefore, effects during bubble traveling through the pump were studied in detail. For this purpose, a transparent membrane micropump was conceived, as described in chapter 2.

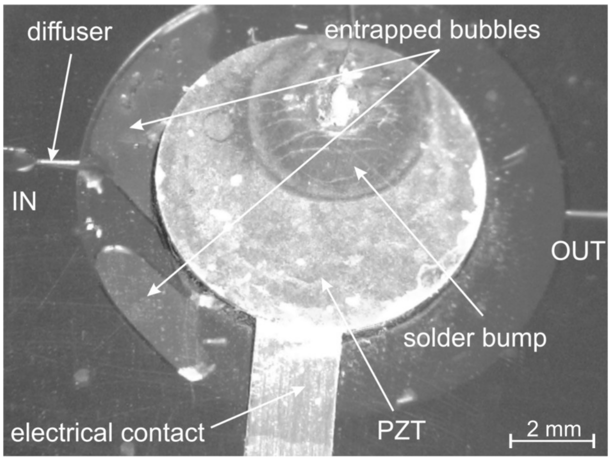

Figure 4: Micropump chamber during micropump actuation (medium: DI-water). Entrapped bubbles (on the left side) prevented further operation.

When a bubble entered into micropump chamber, filled with pure DI water, it split in several smaller bubbles which adhere on the chamber wall. They remained fixed there and due to air compressibility the micropump can not pump out the bubbles by itself (see Figure 4 at the left side).

PZT actuating energy is lost in compressing and decompressing bubbles, what results in significant liquid flow decrease, as can be seen from flow-rate vs. time measurements (Fig. 5, thin line).

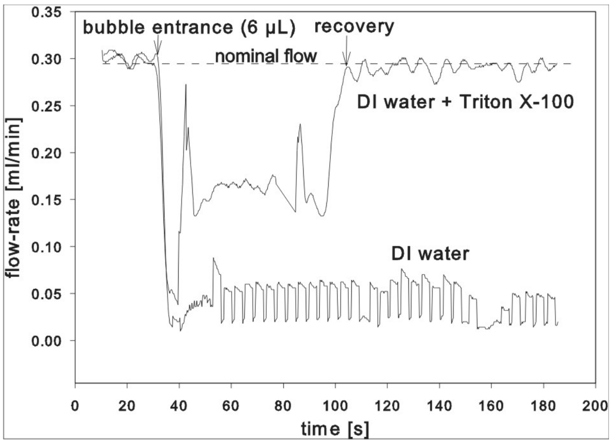

Figure 5: Pump flow-rate vs. time for pure DI water and for mixture of 1000 ppm Triton/DI water. In each case, 6 µL air bubble was introduced.

According to the literature [16], 1000 ppm Triton/DI water mixture has the lowest surface tension coefficient (0.030 N/m). For this reason, this liquid/surfactant mixture was used in our initial investigations to assure low pumping medium surface tension and consequently maximum bubble tolerance enhancement. Later on, also lower Triton/DI water concentrations with higher surface tension coefficients were taken into consideration.

When we introduced a mixture of certain concentration of surfactant in DI water, in this specific case 1000 ppm of Triton, the entrapped air bubble was instantly dispersed into a fine foam of very small air bubbles (see Figure 6, at the left side).

The foam cloud spread from the micropump inlet diffuser into the micropump chamber and consequently, due to air compressibility, micropump flow-rate in the first moment dropped almost to zero (see Fig. 5, bold line, at the bubble entrance point). Then, rapid mixing of the foam with liquid was observed, and fractions of the foam were gradually torn away from the main cloud and transported along the micropump chamber toward micropump outlet. Finally, all the foam was drained out from the system and consequently micropump recovered (see Fig. 5, bold line). Pump recovery

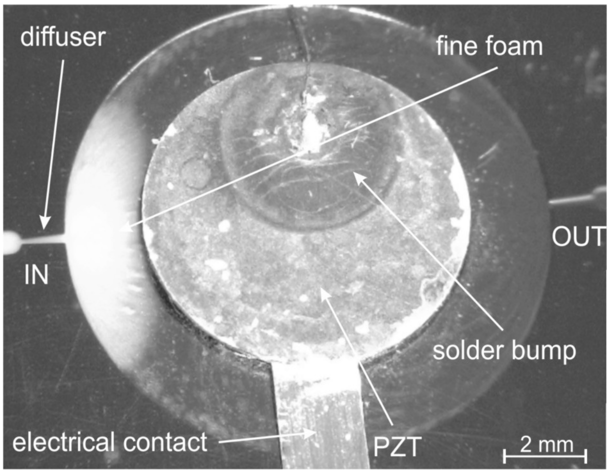

Figure 6: Micropump chamber during micropump actuation (medium: 1000 ppm Triton/DI water mixture). Bubble was dispersed into fine foam (at the left side).

time was defined as the time needed for the pump flow-rate to recover to the nominal flow value within ±5%.

Micropump also recovered when subjected to a series of bubbles introduced in the system pumping a 1000 ppm Triton/DI water mixture. The time dependent behavior and recovery of flow-rate due to these sequential disturbances is presented in Fig. 7.

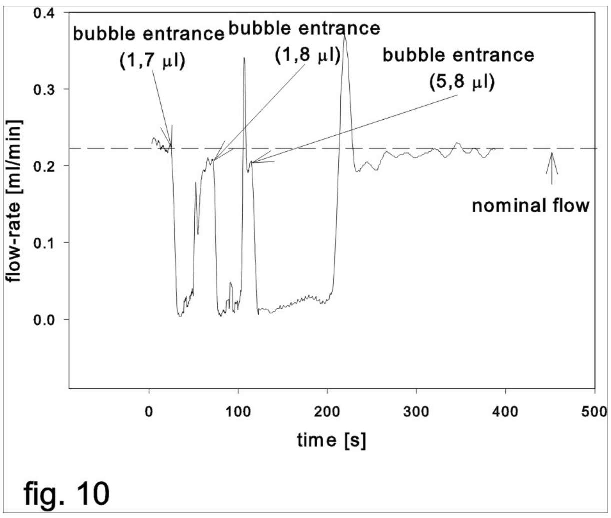

Figure 7: Micropump recovery after a series of 3 sequential bubbles (medium: 1000 ppm Triton/DI water mixture).

Recovery effects were observed also by Richter et al. [1] with bubbles injection in piezoelectrically actuated bubble resistant micropump comprising of improved thinner valve design. Injection of 8 μl air bubble also led to a rapid decrease of pump flow-rate, followed by slow recovery to the baseline within about one minute. The authors described that rather long time interval needed to recover to the original pump flow-rate had not been understood. Micropump also in this case recovered after a series of bubbles, but when two bubbles were transported into the pump chamber shortly after each other, pump failed.

To investigate micropump flow rate recovery dependence on the volume of air bubble, we introduced in separate experiments three different volumes of air bubbles in the system pumping 1000 ppm Triton/DI water mixture. Recovery time depends in this case strongly on the introduced air bubble volume, as seen in Fig. 8.

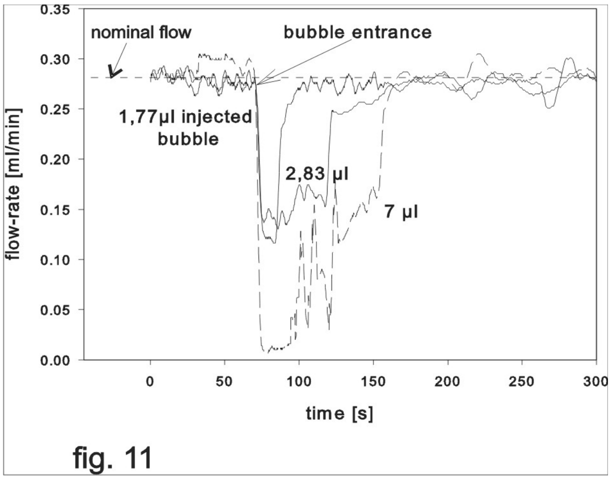

Figure 8: Micropump flow-rate recovery for three different bubble volumes, introduced separately (medium: 1000 ppm Triton/DI water mixture).

To determine micropump recovery time dependency on introduced air bubble volume in a more detail, additional measurements were performed. Due to the transparent micropump diaphragm it was possible to determine the time in which all the foam left the chamber. With a combination of microweighing method for pump flow-rate measuring and optical inspection, it was concluded that immediately after foam was no longer observed in the chamber, micropump flow-rate reached the nominal flow-rate value within ±5%. The time in which the foam had left the chamber therefore determines the recovery time.

Micropump recovery time vs. introduced air bubble volume is shown in Fig. 9. It is seen that two different regimes of recovery time dependencies exists. In both regimes, the recovery dependence was almost a linear function of time, but with lower slope for smaller bubbles (< 7μl) and with higher slope for larger bubbles (> 7 μl).

This implies that two different mechanisms for recovery could be involved. When small air bubbles with volume up to 7 µl entered the chamber, they dispersed immediately into a fine foam cloud, spreading from micropump inlet diffuser and expanding deep into the micropump chamber. The phenomenon was fully visible through transparent glass diaphragm. Initial foam cloud size in the chamber was proportional to the introduced air bubble size. During micropump operation, foam fractions were gradually removed by the liquid away from the pulsating foam cloud and traveling with the liquid along the micropump chamber toward micropump outlet and finally out of the pump. The amount and velocity of traveling foam fractions were independent of air bubble size. Constant amount and velocity of foam fractions indicated constant foam drain-rate. Therefore, the time in which all the foam had left the chamber (i.e. recovery time) was linearly proportional to the air bubble volume, as seen in Fig. 9 (the part with the lower slope).

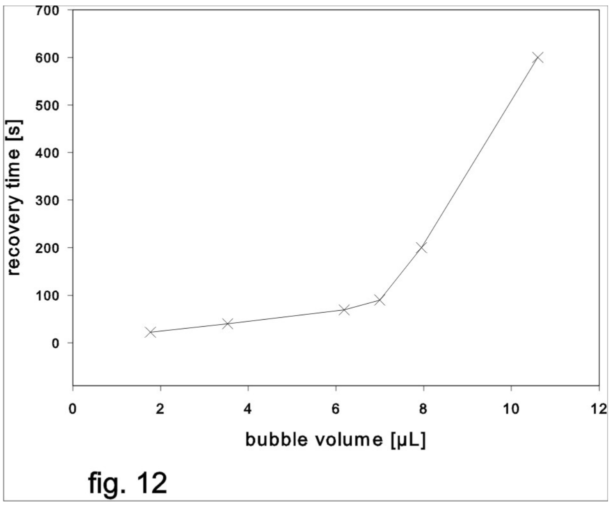

Figure 9: Micropump recovery time vs. introduced bubble volume (medium: 1000 ppm Triton/DI water mixture).

When large bubbles with volumes over 7 µl were introduced in the micropump inlet, an interesting phenomenon was optically observed. Increase of introduced air bubble volume did not additionally increase foam cloud size in the chamber. It seemed that maximum foam amount in the chamber was limited to a dispersion of 7 µl air bubbles and the rest of the bubble remained undispersed at the micropump inlet diffuser, which significantly deteriorated pump performance. At the same time, a reduction in foam fractions removed away from the pulsating foam cloud was observed and fluid velocity declined. Undispersed air bubble was waiting at the inlet diffuser until some of the foam had slowly left the pump chamber. Then a part of undispersed air bubble was transformed into foam etc. When entire air bubble had dispersed into the foam, foam drain-rate increased. And the foam cloud size started to reduce. When it disappeared, the micropump finally recovered. We assume that the maximum foam amount allowed in the chamber at a time (margin bubble volume of 7 µl, see Fig. 9) is closely linked with the micropump geometry (especially with chamber volume) and Triton/DI water concentration.

3.3 Surface tension influence on micropump recovery

In the last part of this investigation, medium surface tension influence on micropump recovery was studied. For this purpose, various low Triton/DI water mixtures were prepared (100 ppm, 75 ppm, 50 ppm, 25 ppm, 10 ppm). In order to assure complete dissolution of Triton, every dilution was followed by two hours of mixing with magnetic stirrer. Surface tension coefficients of mixtures were not measured, but rather calculated using proposed mathematical model. Liquid surface tension coefficient vs. Triton/DI water concentration model was obtained by curve fitting to four known Triton/DI water concentration data [16], as suggested in [17] (Fig. 10).

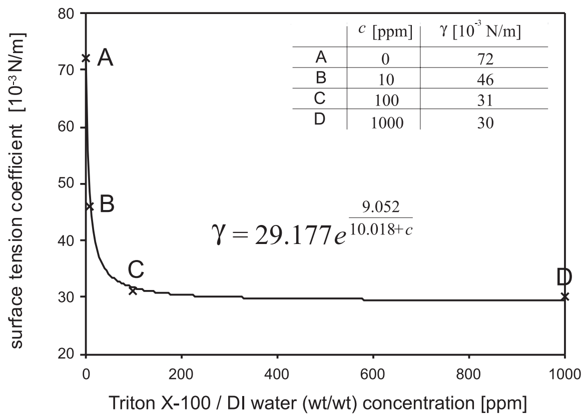

Figure 10: Liquid surface tension coefficient vs. Triton/DI water concentration model [16].

Surface tension coefficients for prepared Triton/DI water mixtures were calculated by using surface tension coefficient vs Triton X-100 / DI water concentration model (Fig. 10):

$$\gamma = 29.177 e^{\frac{9.052}{10.018+c}} \qquad (2)$$

Calculated medium surface tension coefficient exponentially decreased from 0.046 N/m (10 ppm Triton/DI water mixture) to 0.031 N/m (100 ppm Triton/DI water mixture), as shown in Table 1.

Table 1: Calculated surface tension coefficient for various Triton/DI water mixtures.

Triton X-100 / DI water (wt/wt) concentration c [ppm]	Calculated surface tension coefficient γ [10-3 N/m]
10	0.0460
25	0.0378
50	0.0338
75	0.0323
100	0.0310

By introducing surface tension coefficient instead of surfactant concentration, the pump recovery behavior can be easily compared also to other types of surfactants.

Measured micropump flow-rate recovery with respect to different surface tension coefficient and introduced air bubble with 10 µl volume is given in Fig. 11.

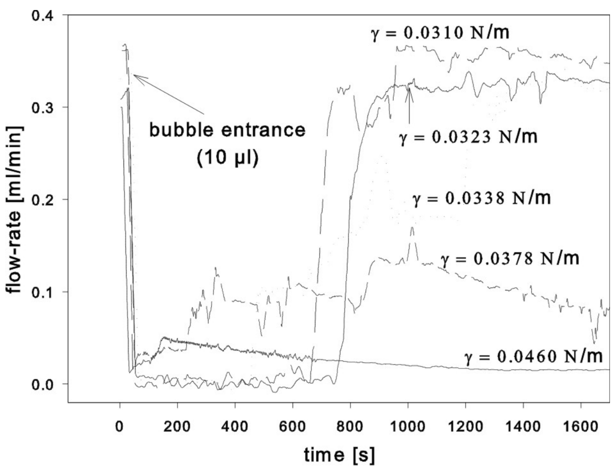

Figure 11: Micropump flow-rate vs. medium surface tension coefficients (10 µl introduced air bubble).

As observed in Fig. 11, micropump recovery begins at a critical medium surface tension of 0.0338 N/m (50 ppm Triton/DI water mixture). Liquid medium surface tension higher than critical surface tension resulted in micropump bubble intolerance. It is assumed that micropump recovery time could be further improved by decreasing medium surface tension below 0.031 N/m which was the limit in our case of Triton/DI water mixtures.

Furthermore, it was observed that also foam structure was dependent on surfactant concentration. At low Triton concentrations, there was rough foam with some larger bubbles which were trapped on chamber wall and permanently deteriorated micropump performance. At higher Triton concentrations, more fine bubbles foam texture resulted and consequently higher foam drain-rate and recovery.

Measurements presented here were all taken for micropump zero-load. Additional experiments revealed that surfactant addition also enhanced bubble tolerance in the case of micropump with load pressure on the outlet. For example, it was found that micropump with 33 mBar output load pressure recovered in 82 s when air bubble with volume of 1,9 µl was introduced in the micropump chamber, for 1000 ppm Triton X-100/DI water mixture.

4. Conclusion

An approach for enhancing micropump priming and bubble tolerance by the application of an appropriate surfactant, such as Triton X-100 is proposed. For detailed investigation of bubble related effects, micropumps with transparent membrane were fabricated by silicon/Pyrex micromachining processing. For emulation of micropump bubble disturbance, precise air volumes were introduced into the micropump chamber. Due to air compressibility the entrapped bubbles in the chamber decreased the micropump performance significantly. By adding a small amount of surfactant in the pumping DI water medium, micropump recovery time was improved. Recovery time was found to be strongly dependent on Triton addition and volume of introduced air bubble. It was determined that application of Triton disperses air bubble into fine foam of small bubbles which do not adhere to the walls and are consequently drained out of the pump by the pumped liquid. After recovery, the micropump performance is completely restored. Regarding enhanced priming, it is shown that only a short initial injection of Triton at pump start-up is sufficient for complete priming.

Acknowledgments

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