Surface acoustic wave based analytical system for the detection of liquid detergents

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Abstract

A novel analytical sensing system has been designed for the characterization and discrimination of different detergents in water. This micro-sensor system could play a key role in the development of more efficient and environmentally-friendly washing machines by enabling the measurement of residual detergents. The sensing system comprises a dual shear-horizontal surface acoustic wave (SH-SAW) resonator sensor housed within a poly-dimethylsiloxane (PDMS) microfluidic chamber. Free and electrically-shorted SAW designs were used to analyze synthetic samples of liquid detergents with varying concentrations. Two anionic surfactants, namely sodium dodecylbenzene sulfonate and sodium laureth sulphate, and one non-ionic surfactant, polyoxyethylene (9.5) t-octylphenol have been studied. Dilution tests have been performed in order to determine the sensitivity or detection limit of this liquid sensing system and have been found to be *ca*. 10 ppm. The SAW based sensor system correctly classified all three detergents through the use of the transient signal response. Because the sensor operates without the need for a selective chemical or biological coating, it should be both robust and reliable. We believe that such technology could be used to make environmentally-friendly and greener washing machines by minimizing the use of detergents and hot water.

Keywords
Surface acoustic wave; chemical sensor; two-port resonator; detergents

1. Introduction

As a result of increasing environmental awareness, consumers demand "green products" that contribute to a sustainable society, and household washing machines are no exception [1]. The most significant environmental demands of washing machines are high energy and water consumption [2]. In recent years, the development of more energy efficient and environmentally-friendly washing machines has significantly progressed. The production

weighted average consumption of washing machines in 2004 was 0.95 kWh/kg per wash for a 5 kg cotton load at 60ºC cycle. It is worth noting that in the period 1996 to 2004 there had been an efficiency improvement of about 20% [3]. The remarkable improvement in wash efficiency would not have been possible without the increased use of sensors to control the process parameters of wash cycles. Simple sensors, such as temperature sensors for controlling water heaters, pressure and weight sensors for regulating water levels, have been in use for a considerable time. However, more sophisticated smart sensor systems that enable the washing machine to 'make decisions' have been developed as a result of increasing performance and decreasing cost of sensors and microcontrollers. For example, a load-adjustment program is a frequently occurring function that is capable of reducing water and electricity consumption by up to 25%; from simply adjusting the amount of water needed according to the mass of laundry in the washing drum [4]. Monitoring and controlling washing processes via smart sensor systems enable lower water usage and precise dosing of detergents that, in combination with consumer education, will lead to reduced environmental impact and increased customer savings [5]. The common practice of users to over-dose detergents can be prevented by automatic dosage systems. Correct dosage of detergents raises the rinsing quality and reduces the amount of chemicals released to the environment [6].

A laundry detergent composition generally comprises six groups of substances: surfactants, builders, enzymes, bleaching agents, fillers and other minor additives such as dispersing agents, fabric softening clay, dye-transfer inhibiting ingredient, and optical brighteners. Laundry detergents and household/personal-care products account for over half the use of all surfactants [7]. Incidentally, the term surfactant is an abbreviation for surface active agent, which literally means active at a surface [8]. Surfactants are the single most important ingredients in laundry and household cleaning products, comprising from 15% to 40% of the total detergent formulation [9]. According to the polar head group, surfactants used in detergent formulations can be classified chemically into four groups: anionics, non-ionics, cationics, and zwitterionics. Nowadays, laundry detergents often contain a certain mixture of different types of surfactants to both strengthen their cleaning performance capability and remain mild to the skin of hands [10].

Natural alkyl sulfates were first introduced in laundry detergents around 1932. Then, the low-cost class of surfactant called alkyl benzene sulfonates became the work-horse among synthetic surfactants. Originally, branched-chain alkyl benzene sulfonates (ABS) were replaced by linear alkyl benzene sulfonates (LAS), such as sodium dodecylbenzene sulfonate and sodium xylenesulfonate, which are readily biodegradable. In today's market, LAS is still a key low-cost surfactant and alkyl sulfates (AS) are simultaneously in use [8,9].

Non-ionic surfactants have been extensively used in the area of the laundry detergents and personal-care formulations in combination with anionic surfactants. The non-ionic surfactants are represented mostly by linear alcohol ethoxylates, with the alcohols being derived from either petrochemical raw materials or natural resources. They include alcohol ethoxylate (AE), alkylphenol ethoxylate (APE), methyl ester ethoxylate (MEE), ethoxylated amine, ethoxylated amide, alkyl polyglycoside (APG), polyethylene oxide-polyalkylene oxide diblock copolymer, etc. Different from anionic surfactants, the detergency of compositions containing non-ionic surfactants is not sensitive to hard water since no precipitation occurs in the presence of divalent ions. Furthermore, non-ionic surfactants can be used to deterge animal fibres (such as silk and wool) in order to avoid the ionic adsorption of surfactant on the amino groups in the fibres since electrostatic force does not work for non-ionic surfactants. Here we report on the study of the aqueous solutions, namely two anionic surfactants, sodium dodecylbenzene sulfonate (SDBS) and sodium laureth sulphate (SLS), and one non-ionic surfactant, polyoxyethylene (9.5) t-octylphenol (Triton X 100). Generally, the mixture of anionic and non-ionic surfactants is tuned according to the specific applications and consumer needs [11]. Olsson indicated that the main surfactant in the standard detergent used is ABS, at about 7.5% of the dry weight of the detergent [1]. In their work Ivarsson et al. reduced concentrations of detergents starting from 11 to 6 (g/L), thus in turn resulting in a reduced concentration of ABS in the range of 870 – 490 ppm [19]. But this could be further improved using only 360 ppm of SDBS and 120 ppm of SLS. As regards to the non-ionic surfactant etoxylated fatty alcohol (EOA), it is normally used at a concentration of *ca*. 200 ppm.

Chemical sensor systems have been designed that utilize partially-specific sensors, signal processing and pattern recognition algorithms; this has led to the emergence of rapid, low-cost and simple instruments for characterizing and classifying liquids [13]. Although a single chemical sensor normally have limited selectivity, employing a combination of sensors or sensor features that belong to different specificity classes can enhance performance. The sensing principle of liquid sensors is most commonly based on either electrochemical potentiometry [14] or voltammetry [15] more recently, upon acousto-electric sensing [16].

The motivation for the work presented here is the development of environmentally-friendly washing machines by constructing a low cost, integrated sensor system that accurately and reliably detects residual detergent or surfactant concentrations. Such a sensor system enables the optimization of the rinsing and detergent dispensing processes in wash cycles and as a result, water consumption is decreased and safe levels of residual detergents in the laundry can be maintained. Significant research efforts have been directed towards the development of improved sensors that can measure residual detergents and surfactants [1] via titration [17],

chromatography [18], voltammetry [19] and potentiometry [20]. Both titration and chromatography systems are difficult to integrate with washing machines; however, other sensor techniques such a voltammetric-based electronic tongue [19] or conductivity sensors have been proposed as solutions. But conductivity sensors can give reasonably accurate predictions about detergents, but perform poorly for non-conducting surfactants while the prediction of non-ionic surfactants using a voltammetric electronic tongue proved difficult [1].

In this work, we investigate the feasibility of SAW microsensors being employed in a household washing machine to supervise rinsing cycles. This is of great interest because significant water and energy resources could be saved if not of all the rinses are necessary. Of equal importance is to detect the cases when the user puts too much detergent in the washing machine; this could be detected and extra rinses inserted in order to remove all the harmful detergent. In these cases the user can be alerted to avoid the unnecessary waste of detergent and, in addition, water and energy.

Here we report on the application of surface acoustic wave (SAW) sensors that have been widely used as liquid sensors due to their simplicity and versatility. Since the piezoelectric potential of the SAW extends into the adjacent liquid, its electrical (e.g. conductivity) and mechanical (e.g. density, viscosity) properties can be characterized by measuring the changes in the propagation characteristics (e.g. attenuation, phase and frequency) as the wave travels along the sensor surface. The extent of the penetration of this potential is equal to *ca.* 0.16 wavelengths [21]. For electrically-shorted (i.e. metalized) sensing surfaces, the electric field potential penetration is practically zero. Such devices are only sensitive to changes in the mechanical properties of the adjacent liquid.

The two main types of SAW device configuration are as delay line and resonator. Although delay lines have been successfully used to detect low concentration analytes [22], their sensitivity is limited by low phase slope and issues regarding stability and reproducibility [23]. Resonator configurations, however, offer perhaps a simpler, more robust and stable solution with minimal subsystem complexity [24]. Two-port resonators have been reported [25] to respond to both the conductivity σ and the square root product of the density ρ and viscosity η of the liquid [25].

Frequency response in a non-conducting viscous liquid

The basic theory of a piezoelectric sensor is that the frequency shift Δf from the unloaded crystal at base frequency f_0 for a viscous liquid l is approximately given by:

4

$$\Delta f = -f_0^{3/2} \sqrt{\frac{\eta_l \rho_l}{\pi \rho_p \mu_p}} \qquad\qquad (1)$$

Where μ_p is the shear modulus of the piezoelectric crystal and f_0 is the fundamental frequency of the piezoelectric device.

Because the density and shear modulus of the piezoelectric substrate are constants, we can re-write equation (1) as simply:

$$\Delta f_l = k \sqrt{\eta_l \rho_l} \qquad\qquad (2)$$

where $k = -f_0^{3/2} \sqrt{\frac{1}{\pi \rho_p \mu_p}}$

Frequency response in an ionic liquid

The change in frequency has also been investigated for a conductivity ionic liquid and has been shown to be linear, i.e.

$$\Delta f_l = a \Delta \sigma_l + b \qquad\qquad (3)$$

Where *a* and *b* are constants.

A detailed description of both the effects of the mechanical and electrical properties of a liquid on the attenuation and velocity of a two-port resonator has been reported by Nomura *et al.* [25].

SH-SAW sensors have been successfully used in the food industry to test milk [16], tea [26] and fruit juices [16], and to characterize flavors [16]; in healthcare to analyze blood [27] and urine [28] samples; and also to identify biologically relevant molecules [29], to detect protein concentrations [30], to characterize electrolytes in aqueous solutions without selective coatings [31], and to detection of potassium ions [32] and pH changes [21] in liquids.

We have developed a robust, high sensitivity liquid phase acoustoelectric sensing system based on shear-horizontal surface acoustic wave (SH-SAW) devices to characterize detergents and surfactants at very low concentrations. The sensor comprises two dual two-port SH-SAW resonators and a miniature PDMS fluidic chamber to handle the liquid under test. Synthetic samples of different liquids/surfactants (baseline, SDBS, SLS and Triton X-100) were characterized.

2. Materials and methods
2.1. Principle of operation

SAW sensors measure the change of the propagation characteristics of the surface acoustic wave travelling along the sensor surface due to either electrical or mechanical changes in the adjacent medium. The SH-SAW wave generated on the lithium tantalate surface has an electric field that extends several micrometers into the liquid and the acousto-electric interaction with the liquid affects the velocity and/or attenuation of SH-SAW wave.

The changes in velocity v (proportional to phase ϕ) and attenuation α can be related to both the conductivity σ and dielectric permittivity ε of the liquid, and also the viscosity η and the density ρ of the liquid (relative to a reference or baseline liquid) [25].

$$\frac{\Delta v}{v} = -\frac{K_s^2}{2}\frac{(\sigma_l/\omega)^2 + (\varepsilon_l - \varepsilon_{ref})(\varepsilon_l + \varepsilon_{piezo})}{(\sigma_l/\omega)^2 + (\varepsilon_l + \varepsilon_{piezo})^2} \tag{4a}$$

$$\frac{\Delta\alpha}{k} = \frac{K_s^2}{2}\frac{(\sigma_l/\omega)(\varepsilon_{ref} + \varepsilon_{piezo})}{(\sigma_l/\omega)^2 + (\varepsilon_l + \varepsilon_{piezo})^2} \tag{4b}$$

And for a non-conducting viscous liquid this can be simplified to:

$$\frac{\Delta\alpha}{k} = C\left(\sqrt{\eta_l\rho_l} + \sqrt{\eta_{ref}\rho_{ref}}\right) \tag{5a}$$

$$\frac{\Delta v}{v} = -C\left(\sqrt{\eta_l\rho_l} - \sqrt{\eta_{ref}\rho_{ref}}\right) \tag{5b}$$

Where K_s, k, and C are the coupling coefficients. A detailed description of these equations and the associated parameters in terms of sensitivity and temperature dependence can be found in [33]. Moreover the frequency shift of a piezoelectric material in a liquid gas has a similar form as was defined above in equation (2).

For electrically shorted lithium tantalate surfaces, the electrical potential penetration into the surroundings is practically zero, thus, such devices are only sensitive to the mechanical changes in the adjacent liquid (equations 5a and 5b). By simultaneously employing both free and shorted devices, it is possible to gain insight into the chemical and physical phenomena responsible for the sensor responses to various liquid samples. The amplitude and phase response of the two sensor variations can be expressed as a complex function of the liquid physical properties. Since the shorted sensor measures mass loading and viscosity, while the free sensor measures permittivity and conductivity as well, the difference between the responses of the two sensors can identify whether mechanical or electrical perturbations are the primary factors in the sensor response.

Response to dissimilar liquids

The same principle applies to measuring the resonant frequency rather than the delay line characteristics of a SAW sensor with the simplified version of the frequency behaviour given by equation (2). In this case the response of a shorted SAWR sensor is given by equation (2) and we can now determine the shift in frequency when we <u>change</u> from one liquid (perhaps a reference) to a second dissimilar liquid, as given by:

$$\Delta f_{12} = \Delta f_2 - \Delta f_1 = k \left[\sqrt{\eta_2 \rho_2} - \sqrt{\eta_1 \rho_1} \right] \tag{6}$$

For the free devices we need to also consider the frequency shift for conductivity and that becomes from equation (3) (Yao *et al.* [34]):

$$\Delta f_{12} = a(\sigma_2 - \sigma_1) \tag{7}$$

Response to a very similar liquid

If we make a small change to the properties of the liquid *l*, then we can determine the approximate frequency response of a <u>shorted</u> SAW device by applying the total differential theorem to equation (2) and we obtain two separate terms:

$$d\Delta f_{ls} = \left\{ \frac{\partial f_l}{\partial \rho_l} \Delta \rho_l + \frac{\partial f_l}{\partial \eta_l} \Delta \eta_l \right\} \tag{8}$$

And so substituting into equation (8) for the two partial derivatives obtained from equation (2), we should observe that for a small change in the physical properties of a liquid:

$$d(\Delta f_{ls}) \approx k \frac{\sqrt{\eta_l \rho_l}}{2} \left[\frac{d\eta_l}{\eta_l} + \frac{d\rho_l}{\rho_l} \right] \tag{9}$$

For the free SAW device, we can also have a change in conductivity and so need to combine it to give an overall frequency response of:

$$d(\Delta f_{lf}) \approx a \left[\frac{d\sigma_l}{\sigma_l} \right] + k \frac{\sqrt{\eta_l \rho_l}}{2} \left[\frac{d\eta_l}{\eta_l} + \frac{d\rho_l}{\rho_l} \right] \tag{10}$$

The difference in frequency response between the free and shorted SAW devices is related to only the electrical properties of the liquid where:

$$d(\Delta f_{lf}) - d(\Delta f_{ls}) \approx a \left[\frac{d\sigma_l}{\sigma_l} \right] \tag{11}$$

Response to a similar liquid as a binary mixture

If we now make liquid 3 a mixture of liquid 1 (say reference) with *x* parts per million of liquid or compound 2, then the properties of liquid 3 can be approximately related to the physical properties of liquids 1 and 2 by:

$$\eta_3 = x\eta_2 + (1 - x)\eta_1 \tag{12a}$$

$$\rho_3 = x\rho_2 + (1-x)\rho_1 \tag{12b}$$

$$\sigma_3 = x\sigma_2 + (1-x)\sigma_1 \tag{12c}$$

So substituting into equation (10) for $d\eta_l$ as $(\eta_3 - \eta_1)$ using equation (12a) etc gives:

$$d(\Delta f_{13}) \approx k\frac{\sqrt{\eta_1\rho_1}}{2}\left[\frac{(\eta_2-\eta_1)}{\eta_1}x + \frac{(\rho_2-\rho_1)}{\rho_1}x\right] + a\left[\frac{(\sigma_2-\sigma_1)}{\sigma_1}x\right] \tag{13}$$

To summarise, the shifts in the frequency of shorted s and free f SAW sensors are <u>linearly</u> proportional to the parts per million x_d of compound 2 (e.g. detergent/surfactant d) and are given by:

$$d(\Delta f_{ls}) \approx \alpha x_d \qquad \text{(Shorted device)} \tag{14}$$

$$d(\Delta f_{lf}) \approx [\alpha + \beta]x_d \quad \text{(Free device)} \tag{15}$$

where the coefficients are related to the physical properties of the liquids and piezoelectric parameters by,

$$\alpha = k\frac{\sqrt{\eta_1\rho_1}}{2}\left[\frac{\eta_2-\eta_1)}{\eta_1} + \frac{(\rho_2-\rho_1)}{\rho_1}\right] \quad \text{and} \quad \beta = a\left[\frac{\sigma_2-\sigma_1}{\sigma_1}\right]$$

And the difference in signal between the two devices being dependent on only the conductivity.

$$d(\Delta f_{lf}) - d(\Delta f_{ls}) \approx \beta x_d \qquad \text{(Dual device)} \tag{16}$$

In the general case of discriminating between different liquid detergents (or surfactants) with free and shorted SAW devices, it will depend upon the relative importance of the density and viscosity coefficient α, and the ionic conductivity term β.

We can estimate the weightings of the frequency response for dissimilar liquids from equations (6) and (7), and for a similar liquid from equation (15) and the physical properties of different liquids or added compounds. The physicochemical properties of detergents solutions and reference (i.e. baseline) at 35 °C are given in Table 1. Supposing that the intrinsic viscosity [11] which considers viscosity relative where limit to zero concentration is linear in diluted solutions, and using 1.8, 2.62 and 5.5 cm^3g^{-1} for SLS [35], SDBS and Triton X-100 respectively, it is possible to obtain viscosity values of 100 ppm solutions (1.00018, 1.000262 and 1.00055 relative viscosity, respectively). It can be seen from this table that the difference in conductivity from SLS and SDBS from the baseline solution is much greater than the density or viscosity (or their product difference) and so likely to dominate the frequency response of the devices. For Triton X-100, the conductivity is the same as the baseline solution and so its response will be dominated by the viscosity and density terms.

Insert Table 1

2.2. Sensors design and fabrication

The sensing elements of our analytical system are surface acoustic wave resonators (SAWR) designed to operate at a frequency of 60.6 MHz (wavelength of 68 μm) and fabricated from Au/Ti electrodes on a 36° rotated Y-cut X-propagating LiTaO$_3$ piezoelectric substrate. Lithium tantalate was chosen due to its efficient electromechanical coupling constant (K_S^2=0.047) and comparatively low temperature coefficient of delay of approximately 32 ppm/°C [37]. The interdigitated transducers (IDTs) consist of 5.5 split finger pairs with 8.5 μm finger width and have an acoustic aperture of 3400 μm. The width of the sensing area is 5015 μm and the overall die size is 13.2 mm × 8.8 mm. The IDTs are surrounded by 100 reflector gratings of 17 μm pitch to create a standing wave pattern. In order to facilitate the simultaneous measurement of mechanical and electrical properties of liquids, device configurations with both free and shorted sensing areas were implemented. Figure 1 shows an optical micrograph of a free (a) and a shorted (b) dual SAW resonator sensor.

Insert Figure 1

The main advantage of the wide (~ 5 mm) sensing area is that the resonator sensors can be used in a delay path configuration where changes in the attenuation and the phase velocity of the surface acoustic wave propagating from one IDT to the other is measured. This enables rapid characterization of sensor responses to the target analytes using a network analyzer without the need for additional circuitry. In practice there is a strong correlation between SAW frequency and delay line attenuation.

In order to test the SH-SAW sensors in delay path configuration, the devices were mounted on a custom designed PCB and below a PDMS cell that contains the liquid under test. A 12 mm × 12 mm × 5 mm miniature PDMS chamber with a central reservoir of 7.6 mm × 2.3 mm × 5 mm and a volume of ~90 μl was mounted on top of the SAW sensors to contain the liquids under test using Perspex clamps. This arrangement, shown in Figure 2, provided a leak-free mounting while enabling easy chamber removal for device cleaning.

Insert Figure 2

Although measuring the SAW attenuation and phase velocity changes provides a simple and easy method of detergent characterization, real-time monitoring and processing these characteristics require complex circuitry not suitable for low-cost integrated sensor systems. By placing the SH-SAW sensor as a resonating element in the feedback loop of a radio-frequency amplifier, the circuit will oscillate at a frequency set by the sensor if the gain and phase

conditions of the feedback loop are satisfied [38]. This allows the indirect measurement of changes in the SAW attenuation and phase velocity with great precision in a continuous manner.

For detergent characterization utilizing SAWR sensors in oscillator configuration, a miniature PDMS chamber with two reservoirs of volume ~ 104 µl was mounted on the devices using plastic clamps. The two reservoirs were connected with a microchannel to allow the liquid samples to pass from one sensor to the other (Figure 3(a)).

The liquid cell is positioned accurately over the sensing area between the IDTs with the aid of guiding pins that fit into holes in the PCB and rests on the device without any sealant. This enables easy removal of the cell to clean the device and yet hold the liquid samples without leaking. The complete sensing device setup is shown in Figure 3(b).

Insert Figure 3

2.3. Experimental

The experimental procedure for SAWR sensors in delay path configuration involved the measurement of the attenuation and phase characteristics of both the shorted and the free devices using an Agilent E50718 network analyzer. In this, an electrical signal is fed from one port of the network analyzer to the input IDTs and the amplitude ratio, ΔA, and the phase difference, $\Delta \varphi$, between the input and output signals of both sensors were measured.

A custom liquid delivery system (Figure 4) comprising a micro diaphragm liquid pump (FMM20TTCD, KNF Neuberger Ltd, UK), manifold mounted solenoid valves (Bio-Chem Fluidics, UK), C-Flex® tubing and a Dri-bloc^{TM} heater (Techne Dri-Block DB-2D, Bibby Scientific Ltd, UK) was constructed for detergent measurements. The components were chosen based on their chemical inertness. The measurements were taken at a controlled temperature (22 ±0.1 ºC) and the test sequence of the samples was randomized to minimize any aging or memory effects. The temperature and humidity of the measurement setup was monitored using a digital temperature and humidity sensor (SHT75, Sensirion AG, Switzerland). The sensor surfaces were cleaned before each measurement using a wash cycle with the baseline solution.

Insert Figure 4

For the SAWR sensors in oscillator configuration, a similar experimental setup was used, however, instead of the micro diaphragm pump, a nanolitre accuracy pulsation-free syringe pump (neMESYS, cetoni GmbH, Germany) was used for analyte delivery. The measurements were taken at a controlled temperature (35 ±0.1 ºC) in an incubator.

The temperature coefficient of frequency (TCF) of the LiTaO$_3$ substrates was measured with the SH-SAW sensor and the E5071B ENA RF Network Analyzer (300 kHz to 8.5 GHz). The sensor was loaded with baseline solution (NaOH and KOH with 65 and 22 ppb concentrations) at room temperature using an automated system. The temperature was changed between ambient to about 60°C with the aid of a commercial Dri-Bloc™ (DB-2D) heater.

The experimental results obtained with the frequency shift on the free resonator in the range 55 to 65 MHz at the minimum attenuation of the device showed that the TCF computed from the results to be approximately -32 ppm/°C on the delay line.

3. Results and discussion
3.1. Delay path configuration results

After the initial characterization of the devices, experiments were carried out in order to discriminate between the different detergent samples. Aqueous solutions of sodium dodecylbenzene sulfonate (SDBS), sodium laureth sulphate (SLS) and Octylphenol ethylene oxide condensate (Triton X-100) with 100 ppm concentration were prepared in a baseline solution (NaOH and KOH with 65 and 22 ppb concentrations). The baseline solution was used as the reference and the setup temperature regulated at 22 ± 0.1°C. The measurements were repeated by randomly introducing the samples to the sensors. The sensing surface was cleaned before every measurement using a wash cycle of baseline solution.

Simple discrimination of the different liquid samples could be achieved plotting just two of the four acoustic parameters, i.e. the attenuation of the shorted device vs. the attenuation of the free device as shown in Figure 5.

Insert Figure 5

However sample separation could be further improved by employing more parameters in a principal components analysis (PCA) which is a linear, nonparametric multivariate method (see Figure 6). The principal components or scores were calculated from all four measured sensor characteristics: the attenuation (in dB) and phase difference (in degrees) of both the free and the shorted SAW sensors.

Insert Figure 6

These preliminary tests suggest that is possible to discriminate between different surfactants using a SAWR based sensor system. They also show that both the mechanical and electrical properties of the liquids are important in the discrimination of the liquids. As the theory predicted, the difference in conductivity separates out the SDBS from the SLS (free device)

from the baseline whereas only the shorted device can separate out the Triton X-100 from the baseline. The relative separation of the clusters in PCA space also indicates that the conductivity term is larger than the density/viscosity one and is consistent with the basic theory (equations 14 and 15) and our measured liquid parameters (Table 1). However both terms are need to discriminate between different liquids as demonstrated by the cluster plot shown in Figure 5.

3.2. Oscillator configuration results

Further experiments were performed on the SAWR devices in a resonator configuration, in order to quantify the different concentrations of detergents. Aqueous solutions of sodium dodecylbenzene sulfonate (SDBS), sodium laureth sulphate (SLS) and octylphenol ethylene oxide condensate (Triton X-100) with concentrations between 10 and 100 ppm were prepared in baseline (NaOH and KOH with 65 and 22 ppb concentrations). Baseline was again used as the reference liquid and the setup temperature regulated at $35 \pm 0.1°C$. The measurements were repeated by randomly introducing the samples to the sensors. The sensing surface was cleaned before every measurement using a wash cycle of baseline solution. Measurements were carried at a flow rate of 0.6 ml/min. Baseline solution was used as a carrier liquid and controlled at a constant flow rate. A total of 3 ml of the sample liquid was injected into chamber at 0.6 ml/min. Figure 7 shows the typical time series plot of a free SAWR (Hz) sensor response to different concentrations of SLS solutions. Figures 8, 9 and 10 show SAWRs frequency response to different concentrations of SLS, SDBS and Triton X-100 solutions, respectively.

Insert Figure 7

The concentrations of the detergents solutions used here are comparable to those used in a practical washing application. Nevertheless further dilution tests have been performed to determine the SH-SAW sensors limit of detection. Figures 8 and 10 show that it is possible to measure solutions above ca. 20 ppm for both SLS and Triton X-100 solutions. In contrast, Figure 9 shows that for SDBS solutions it is possible to measure concentrations above only 30 ppm.

Insert Figures 8, 9 and 10.

In each of the Figures from 8 to 10, a linear model in ppv x has been fitted to the experimental data based upon the theory given by equation (15) for similar liquids. The actual frequency response for Triton X-100 is perhaps larger than expected but, when considering Table 1, it can be seen that this compound changes its viscosity by a factor of more than 2 unlike SLS and SDS; so the large change in viscosity compensates for the negligible change in ionic conductivity.

3.3. Transient response of SAWR detergent sensors

It has been shown elsewhere that the response of polymer-based chemical sensors can be approximated by a first-order exponential model [39]. Similarly, the frequency response of the SH-SAWR sensors can be simply expressed in terms of the rise time as shown in equation (17):

$$f = f_{max}\left(1 - e^{-t/\tau}\right) \tag{17}$$

where f_{max} is the frequency shift and τ is the rise time. After rearranging equation (17) and plotting the sensor responses to each detergent solution as $-\ln[(f_{max}-f)/f_{max}]$ vs. time, each τ can be calculated as the reciprocal of the trend line slopes. As an example, Figure 11 shows the measured frequency response of a free SAWR sensor to SLS, SDBS and Triton. The plot shows good linearity for all of the curves and the rise times are clearly different for the three different detergents. There appears to be a correlation with the viscosity of the liquid (see Table 1) and the response time with the more viscous liquid (i.e.Triton X-100) having the slowest response time.

Insert Figure 11

This approach is used to compare the response times of different detergents. Figure 12 shows the effect of velocity on the growth coefficient (i.e. rise time) of the sensors.

Insert Figure 12

Results showing the discrimination of different liquid samples using a scatter plot of frequency shift of free SAWR (dB) against the rise time (τ), are given in Figure 13.

Insert Figure 13

This shows that a single free SAWR device should be capable of not only discriminating between different detergents but also determining their concentration through the use of the transient response.

4. Conclusions

A sensing system based on liquid phase surface acoustic wave (SAW) devices has been developed for the characterization of surfactants in household detergents at low concentrations in aqueous solutions. 60 MHz SH-SAW sensors together with the PDMS housings containing the liquid under test have been micro-fabricated for this purpose. Both free and shorted SAW sensors have been studied in which their acoustic properties such as velocity (related to phase), attenuation, and frequency are related by simple theory to the electrical and/or mechanical properties of aqueous solutions. Measurements have shown that it is possible to discriminate

between different anionic and non-ionic surfactants with limits of detection ranging between 20 and 30 ppm. It has also been shown that a basic linear model describes well the frequency response on the addition of small volumes of detergent in a baseline liquid. The resolution of the SAW sensors was found to be a surfactant concentration of between 10 and 30 ppm, which is an encouraging result. consequently, it is possible to find out whether the detergent has been removed. Finally, it was also found that the transient response of the sensors can be fitted to a simple first order equation, and varied considerably with time constant from 23 s to 100 s. This means that unknown surfactants can be classified by the transient response of a single free SAW device. Furthermore, the combination of the SAW frequency shift and the time constant not only allows the determination of their concentrations but should also permit the analysis of simple mixtures of surfactants in water.

We believe that the practical application of the SAW sensor will require additional measures to ensure repeatability and reliability. For example, although the wash temperature is controlled, there will be some variation in its precise value, and piezoelectric sensors are sensitive to operating temperature. Therefore, it will be necessary to compensate the output of the SAW sensor according to the actual wash temperature with an accuracy of about ±0.2ºC. Furthermore, the precise detergent concentration may change with time depending on the mixing efficiency and wash conditions. Sampling at 100 Hz is possible and so the signals can be averaged and filtered to improve repeatability and enhance the signal to noise ratio (that in itself appears to depend upon acoustic load).

In conclusion, we have shown that a SAW based sensor system can be used to determine the concentration of surfactants and detergents in water. This low cost and robust sensor system could be used to design a new generation of greener and smarter washing machines, i.e. domestic appliances that use less detergent, less water and hence less energy. We believe that having successfully conducted a feasibility study demonstrating the ability of smart SAW microsensors to detect synthetic samples of liquid detergents with varying concentrations in a washing machine, more work is now needed to explore the effect of different formulations and commercial brands of detergents.

Acknowledgements

References

[1] J. Olsson, P. Ivarsson, F. Winquist, Determination of Detergents in Washing Machine Wastewater with a Voltammetric Electronic Tongue, Talanta 76 (2008) 91-95.

[2] European Commission. Commission Regulation (EU) No 1015/2010 of 10 November 2010 implementing Directive 2009/125/EC of the European Parliament and of the Council with regard to Ecodesign requirements for household washing machines. In: Official Journal of the European Union, 11. 11. 2010.

[3] P. Bertoldi, B. Atanasiu, Electricity consumption and efficiency trends in the enlarged European Union, EUR 22753 EN, European Community, Joint Research Centre, Institute for the Environment and Sustainability, 2007. ISSN 1018- 5593.

[4] I. Rüdenauer, C. Gensch, D. Quack, CECED, European Committee of Domestic Equipment Manufactures, 2004, Eco-efficiency analysis of washing machines, Öko-institut e.V., Freiburg, Germany.

[5] P. Järvi, A. Paloviita, Product-related information for sustainable use of laundry detergents in Finnish households, J. Clean. Prod. 15 (2007) 681–689.

[6] B. Josephy, E. Bush, J. Nipkow, S. Attali. Washing machines: Key criteria for best available technology. ECEEE 2011 Summer Study, Energy efficiency first: The foundation of a low-carbon society Conference proceedings ISBN 978-91-633-4455-8 ABA Intercopy, Stockholm, Sweden, 2011

[7] D.R. Karsa, R.M. Bailey, B. Shelmerdine, S.A. McCann, "Overview: A decade of change in the surfactant industry", In: Industrial Applications of Surfactants IV, Karsa, D.R., ed., The Royal Society of Chemistry, Cambridge (1999).

[8] B. Jönsson, B. Lindman, K. Holmberg, B. Kronberg, Surfactants and Polymers in Aqueous Solution, John Wiley & Sons, Chichester (1998).

[9] J.J. Scheibel, The evolution of anionic surfactant technology to meet the requirements of the laundry detergent industry, J. Surfactants Deterg. 7 (2004) 319-328.

[10] Y. Yu, Z. Jin, A.E. Bayly, Development of surfactants and Builders in Detergent Formulations, Chin. J. Chem. Eng. 16 (2008) 517-527.

[11] A.H. Saiyad, S.G.T. Bhat, A.K. Rakshit, Physicochemical properties of mixed surfactant systems: sodium dodecyl benzene sulfonate with triton X 100, Colloid. Polym. Sc. 276 (1998) 913–919.

[12] I. Campos, L. Gil, R. Martínez-Mañez, J. Soto, J.L. Vivancos, Use of a Voltammetric Electronic Tongue for Detection and Classification of Nerve Agent Mimics, Electroanalysis 22 (2010) 1643-1649.

[13] F. Winquist, J. Olsson, M. Eriksson, Multicomponent analysis of drinking water by a voltammetric electronic tongue, Anal. Chim. Acta 683 (2011) 192-197.

[14] A. Mimendia, J.M. Gutierrez, L. Leija, P.R. Hernandez, L. Favari, R. Muñoz, M. del Valle, A review of the use of the potentiometric electronic tongue in the monitoring of environmental systems, Environ. Modell. Softw. 25 (2010) 1023–1030.

[15] I. Campos, R. Masot, M. Alcañiz, L. Gil, J. Soto, J.L. Vivancos, E. García-Breijo, R.H. Labrador, J.M. Barat, R. Martínez-Máñez, Accurate concentration determination of anions nitrate, nitrite and chloride in minced meat using voltammetric electronic tongue, Sens. Actuators B: Chem. 149 (2010) 71-78.

[16] G. Sehra, M. Cole, J.W. Gardner, Miniature taste sensing system based on dual SH-SAW sensor device: an electronic tongue, Sens. Actuators B: Chem. 103 (2004) 233–239.

[17] Z. Li, M.J. Rosen, Two-phase mixed indicator titration method for determination of anionic surfactants, Anal. Chem. 53 (1981) 1516-1519.

[18] V. Gomez, L. Ferreres, E. Pocurull, F. Borrull, Determination of Non-Ionic and Anionic Surfactants in Environmental Water Matrices, Talanta 84 (2011) 859-866.

[19] P. Ivarsson, M. Johansson, N. Höjer, C. Krantz-Rülcker, F. Winquist, I. Lundström, Supervision of Rinses in a Washing Machine by a Voltammetric Electronic Tongue, Sens. Actuators B: Chem. 108 (2005) 851-857.

[20]   M. Sak-Bosnar, D. Madunic-Cacic, R. Matesic-Puac, Z. Grabaric, Nonionic Surfactant-Selective Electrode and its Application for Determination in Real Solutions, Anal. Chim. Acta 581 (2007) 355-363.

[21]   J. Kondoh, S. Shiokawa, Z. Georgiev, A Shear-Horizontal SAW Device as a pH Monitor, Sens. Actuators B: Chem. 13 (1993) 429-431.

[22]   T. Nomura, A. Saitoh, T. Miyazaki, Liquid Sensor Probe using Reflecting SH-SAW Delay Line, Sens. Actuators B: Chem. 91 (2003) 298-302.

[23]   T.E. Parker, G.K. Montress, Precision surface-acoustic-wave (SAW) oscillators, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 35 (1988) 342-364.

[24]   T. Nomura, T. Yasuda, Surface Acoustic Wave Liquid Sensors Based on One-Port Resonator, Jpn. J. Appl. Phys. 32 (1993) 2372-2375.

[25]   T. Nomura, A. Saito, Y. Horikoshi, Measurement of Acoustic Properties of Liquid using Liquid Flow SH-SAW Sensor System, Sens. Actuators B: Chem. 76 (2001) 69-73.

[26]   J. Kondoh, Y. Matsui, S. Shiokawa, Identification of Electrolyte Solutions using a Shear Horizontal Surface Acoustic Wave Sensor with a Liquid-Flow System, Sens. Actuators B: Chem. 91 (2003) 309-315.

[27]   H.J. Lee, K. Namkoong, E.C. Cho, C. Ko, J.C. Park, S.S. Lee, Surface Acoustic Wave Immunosensor for Real-Time Detection of Hepatitis B Surface Antibodies in Whole Blood Samples, Biosens. Bioelectron. 24 (2009) 3120-3125.

[28]   M. Bisoffi, B. Hjelle, D.C. Brown, D.W. Branch, T.L. Edwards, S.M. Brozik, V.S. Bondu-Hawkins, R.S. Larson, Detection of Viral Bioagents using a Shear Horizontal Surface Acoustic Wave Biosensor, Biosens. Bioelectron. 23 (2008) 1397-1403.

[29]   K. Länge, B.E. Rapp, M. Rapp, Surface Acoustic Wave Biosensors: A Review, Anal. Bioanal. Chem. 391 (2008) 1509-1519.

[30]   M. Tsai, J. Jeng, Development of a Generalized Model for Analyzing Phase Characteristics of SAW Devices Under Mass and Fluid Loading, IEEE Trans. Ultrason. Ferroelectr. Freq. Control 57 (2010) 2550-2563.

[31]   J. Kondoh, Y. Matsui, S. Shiokawa, Identification of Electrolyte Solutions using a Shear Horizontal Surface Acoustic Wave Sensor with a Liquid-Flow System, Sens. Actuators B: Chem. 91 (2003) 309-315.

[32]   C. Caliendo, A. D'Amico, P. Verardi, E. Verona, K+ detection using shear horizontal acoustic mode, Proceedings of the IEEE Ultrasonics Symposium (1990), pp. 383–387.

[33]   M. Cole, G. Sehra, J.W. Gardner, V.K. Varadan, Development of Smart Tongue Devices for Measurement of Liquid Properties, IEEE Sensors Journal, 4 (2004) 543-550.

[34]   S. Yao, K. Chen, F. Zhu, D. Shen, L. Nie, Surface Acoustic Wave Sensor System for the Determination of Total Salt Content in Serum, Anal. Chim. Acta 287 (1994) 65-73.

[35]   A.J. Müller, Y. Garcés, M. Torres, B. Scharifker, A.E. Sáez, Prog. Colloid Polym. Sci. 122 (2003) 73-81.

[36]   Kabir-ud-Din, S.L. David, S. Kumar, Viscosities of Sodium Dodecyl Sulfate Solutions in Aqueous Ammonium Salts, J. Chem. Eng. Data 42 (1997) 1224-1226.

[37]   J. Henaff, M. Feldmann, M. A. Kirov, Piezoelectric Crystals for Surface Acoustic Waves (Quartz, LiNbO$_3$, LiTaO$_3$, Tl$_3$VS$_4$, Tl$_3$TaSe$_4$, AlPO$_4$, GaAs), Ferroelectrics 42 (1982) 161-185.

[38]   R.F. Schmitt, J.W. Allen, R. Wright, Rapid Design of SAW Oscillator Electronics for Sensor Applications, Sens. Actuators B: Chem. 76 (2001) 80-85.

[39]   S.L. Tan, J.A. Covington, and J.W. Gardner, Velocity-optimised diffusion for ultra-fast polymer-based resistive gas sensors, IEE Proc. Sci. Meas. Technol. 153 (2006) 94-100.

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