The use of acoustoelectrochemistry to investigate rectified diffusion

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Abstract

This paper describes the approach to bubble related phenomena using a novel 'acoustoelectrochemical' technique designed to investigate the physical and chemical effects of the acoustically induced motion of the bubble wall. In particular it describes the behaviour of a suspended gas bubble irradiated with sound of an appropriate frequency and pressure to induce bubble wall oscillation.

The first electrochemical measurement of the growth of a bubble through rectified diffusion is demonstrated. The technique employed relies on the sensitivity of a scanning electrochemical microscope (SECM) deployed close to the gas/liquid interface of a bubble. The growth rate of the bubble (<0.1 $\mu m\,s^{-1}$) is reported. It will be also demonstrated that gas exchange across the phase boundary at the bubble wall, can be successfully probed when the bubble is stationary.
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1. Introduction

The application of sound to liquids can have a wide variety of different effects. Many of these are associated with bubble activity within the media under investigation. As an example, power ultrasound can be employed to generate cavitation in liquids. In turn cavitation can have a range of physical and chemical consequences, ranging from the erosion of solid surface [1,2] to the generation of highly reactive radicals [3,4]. Subsequently these effects can be usefully employed, for example, in the activation of catalysts or the destruction of organic waste materials [5–7] respectively. However, the pressure amplitude required to generate such 'transient' or 'inertial' cavitation is normally in excess of 10^5 Pa under standard conditions in water [8]. This can be compared to the excitation of non-inertial bubble oscillation, which can produce measurable electrochemical effects [9,10] (and potentially useful applications) with much smaller applied acoustic pressures (10–100 Pa). Since the acoustic intensity in a linear plane wave is proportional to the square of the acoustic pressure, this represents a 10^6 to 10^8 reduction in the energy requirements of the system. However, the mass transfer coefficient measured for bubble oscillation was only an order of magnitude smaller than those recorded in the presence of inertial cavitation. Such mass flux has recently been used in a novel technique to monitor the motion of the gas/liquid interface of a tethered bubble using a novel electrochemical approach [9–11]. In this experiment a microelectrode [12] (25 μm diameter platinum) was positioned, using a micrometer and stage, close (∼5–10 μm) to the gas/liquid interface of a large gas bubble (bubble equilibrium radius, $R_0 \sim 2$ mm). The position of the microelectrode with respect to the gas/liquid interface was determined by employing standard negative feedback SECM theory [13,14]. The motion of the gas/liquid interface could then be followed as additional current resulting from the ensuing enhanced mass transfer due to forced convection [10]. This forced convection was produced by bubble oscillation as the result of acoustic irradiation of the liquid. This acoustic excitation, at an appropriate frequency and pressure amplitude, generated either Faraday wave motion (a surface wave at $f_p/2$ where f_p represents the drive frequency [11]) or bubble pulsation [9] at f_p. These studies have shown that this electrochemical technique is able to

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monitor the motion of the gas/liquid interface with high sensitivity. Bubble wall motion on the μm scale could easily be detected by the microelectrode as enhancements in mass transfer [9].

The acoustoelectrochemical [15] approach to the study of bubble dynamics is clearly powerful. However, other bubble phenomena have yet to be investigated. One such process is termed rectified diffusion. Rectified diffusion, which has been reviewed elsewhere [8], is the growth or dissolution of a gas bubble driven into oscillation by an appropriate acoustic field. This process has been studied by a number of authors [16–18]. Experimental observations have shown that the bubbles grow/shrink at different rates depending on their size and exposure to sound [17,18]. Church produced a theory to describe the growth of gas bubbles due to mass transfer of material to the bubble wall and consideration of the dynamics of bubble oscillation [16]. These studies indicated that bubble growth/dissolution could be accelerated by microstreaming (the circulation of the fluid close to the bubble wall) as the result of oscillation of the gas/liquid interface. The mechanism of rectified diffusion relies on the transfer of gas across the gas/liquid interface. However, Fyrillas and Szeri in a later publication suggested that, even with a comprehensive model of the physical situation, the growth rates measured for bubbles [18] were higher than those predicted [19].

Clearly the sensitivities of the acoustoelectrochemical techniques reported earlier [9], and the interest in the growth of gas bubbles through the process of rectified diffusion, lead one to the interesting question as to whether the same technique can be applied to measure rectified diffusion to high precision and accuracy. This is the subject of this manuscript.

2. Experimental

Experiments employing a low resolution SECM were performed using the apparatus described previously [11]. However, the bubble was supported on a nickel wire loop insulated with a coat of nail varnish. In this communication an SECM with higher spatial resolution (4 nm) was also employed to monitor the current as a function of the distance between the bubble wall and microelectrode surface. In this set-up the microelectrode was mounted onto a three dimensional stage (two TS-100 and one TS-300) driven by three piezoelectric Inchworm motors (model IW-710) which were controlled by an X, Y, Z, Inchworm motor controller (model 6200); all from Burleigh Instruments, UK. This particular SECM is capable of moving the microelectrode within a cube of 25 mm with a nominal resolution of 4 nm. This instrument was completely controlled using a personal computer equipped with two interface cards. A digital I/O card (PCL-724, Integrated Measurement Systems) was used to control inchworm movement and a DAC (PCL-818L, Integrated Measurement Systems) was used to collect the electrochemical data. Approach curves were obtained by first adjusting the Y Inchworm to approximately 0.25 mm from the bubble wall. The equator of the bubble was then approached and the position of the X and Z Inchworm adjusted appropriately.

$K_3[Fe(CN)_6]$ (99.5% A.C.S. Reagent, Sigma), KCl BDH, AnalaR and $Sr(NO_3)_2$ (99% A.C.S. Reagent, Aldrich) were used as received. Purified water was obtained from an Vivendi (Elga) Purelab option E10. This water had a high resistivity (>15 MΩ cm) and a low organic content (<30 ppb [1] TOC). All experiments were performed under aerobic conditions at 18–22 °C.

3. Results and discussion

The inset in Fig. 1 shows the current (*i*) recorded as a function of time as the 25 μm diameter Pt microelectrode approached the gas/liquid interface of a tethered air bubble. In this case the solution consisted of aerobic 0.1 mol dm^{-3} KCl(aq). The microelectrode was held at −0.7 V vs. Ag. This potential was chosen to maintain mass transfer limited reduction of molecular oxygen at the microelectrode surface. The current recorded in the bulk solution was −10.5 nA. This corresponds to a ∼4 electron reduction of molecular oxygen at the platinum surface (assuming a diffusion coefficient [20] (*D*) of oxygen of 2.29×10^{-5} cm^2 s^{-1} and a bulk concentration of molecular oxygen (*c*) of 0.24 mmol dm^{-3}). However, the inset shows that as the microelectrode approaches the gas/liquid interface of the air bubble the current can be seen to increase in a cathodic manner. This is due to transfer of molecular oxygen across the gas/liquid interface induced by the depletion of molecular oxygen in the water phase as a result of the microelectrode tip. This oxygen transfer has been shown to occur on planar air/liquid interfaces by Unwin et al. [21]. However, this is the first time, to the knowledge of the authors, that such oxygen transfer has been observed for a submerged air bubble. In order to investigate this further a series of experiments were performed using a standard high resolution SECM. In this case the motion of the microelectrode with respect to the gas/liquid interface was controlled with a high degree of accuracy and precision (see experimental section). Fig. 1 shows an approach curve. It plots the normalised current, i_{tip}/i_{inf}, where i_{tip} represents the current passed at the microelectrode at all distances while i_{inf} is the current passed at the microelectrode in the bulk solution against normalised dis-
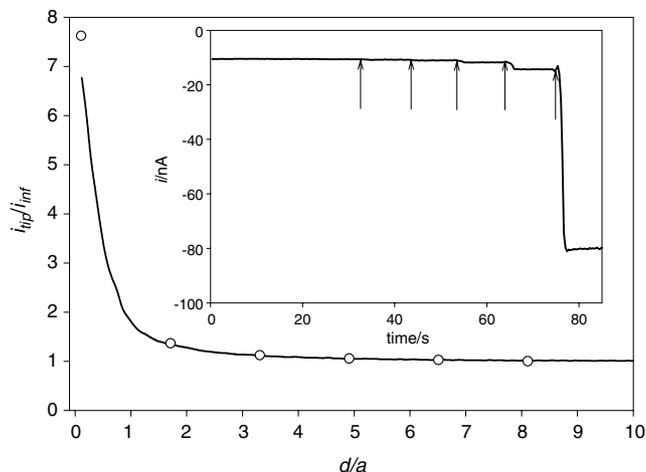
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[1] Manufacturer quoted figure.

Fig. 1. Plot showing the normalised current (i_{tip}/i_{inf}) as a function of the normalised distance for a 25 μm Pt microelectrode approaching an air bubble (—). This experiment was performed employing high resolution SECM equipment (see experimental section). (○) represents the data taken from the low-resolution experiment shown in the inset for comparison. The inset shows the current recorded as a function of time for a 25 μm diameter Pt microelectrode approaching the surface of an air bubble (∼2 mm radius) using a low-resolution SECM. The arrows indicate motion of the microelectrode of 20 μm towards the gas/liquid interface. In both experiments the microelectrode was held at −0.7 V vs. Ag in aerobic 0.1 mol dm^{-3} KCl.

tance, d/a. Here d is the distance between the air bubble wall and the microelectrode and a the electrode radius. It should be noted that in these experiments there was no surfactant material added (indeed great lengths were taken to avoid contact of the solution with possible contaminants including plastics, etc.). Fig. 1 also shows the data obtained from the low-resolution SECM (see Fig. 1 inset). Clearly the agreement between the two experiments is satisfactory validating the low-resolution technique employed to study bubble processes of this type.

In order to monitor and characterise the motion of a bubble wall ($R_0 \sim 2$ mm), a 25 μm diameter Pt microelectrode (in 'torpedoed' configuration [11]) was positioned close to the gas/liquid interface of a tethered gas bubble and the effects of sound irradiation on the current passed at the microelectrode recorded. In these experiments the gas/liquid interface acts as an inert substrate and the current in stagnant solution (e.g. when the bubble is not irradiated with sound) is less than that expected for the same microelectrode positioned in the bulk solution. Hence this corresponds to a classic 'negative feedback' situation in SECM [13] terminology. Fig. 2a illustrates the physical model of the microelectrode and gas/liquid interface of the bubble under the conditions stated. However, if the bubble is irradiated with sound of an appropriate frequency and pressure, then the oscillation of the bubble wall leads to enhanced mass transfer as the result of forced convection of the solu-
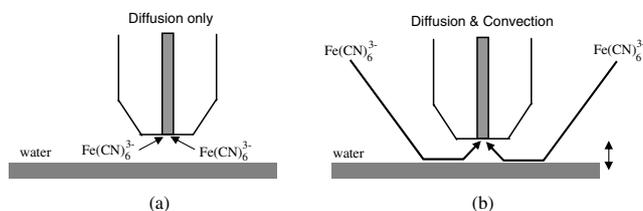

Fig. 2. (a) Illustration of the approach of a microelectrode to a gas/liquid interface of a gas bubble. As no Fe(CN)$_6^{3-}$ can enter the gas phase of the bubble hindered diffusion predominates in the absence of bubble wall oscillation and (b) illustration of an oscillating boundary inducing fluid flow and enhanced mass transfer to the microelectrode as a convective diffusion mechanism is initiated. Mass transfer to the microelectrode is enhanced as material is transported to the electrode from the bulk of the liquid.

tion. This is termed microstreaming [8]. Fig. 2b illustrates this situation.

The exchange of gas across the gas/liquid interface is extremely important for a number of industrial and global processes [8]. In bubbles this gas exchange effectively changes the size of the gas bubble and leads to growth or dissolution depending on their size. The effects of rectified diffusion on the size of a large gas bubble can be investigated using the acoustoelectrochemical experiments described here. It is possible using the acoustoelectrochemical approach to measure the threshold pressure for the onset of Faraday waves as a function of frequency around the pulsation resonant frequency of the gas bubble. While these experiments were being performed it was noted that the resonant frequency of the gas bubble fell over a period of time. Fig. 3 shows the pressure threshold for the onset of Faraday wave motion of a bubble wall (●) as a function
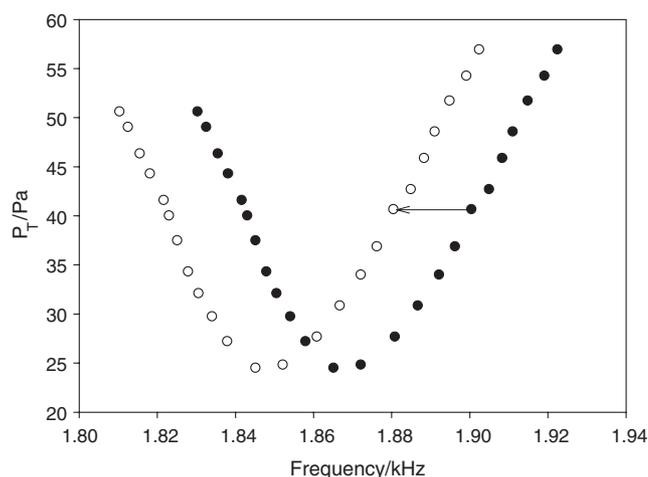

Fig. 3. Plot showing the threshold pressure (P_T) for the onset of Faraday wave motion of the bubble wall as a function of frequency (●). This threshold pressure was determined by the acoustoelectrochemical technique described previously. (○) represents the shifted pressure threshold caused by bubble growth calculated from measurements of the frequency shift of a point on the pressure threshold curve.

of frequency. However, after prolonged exposure to sound irradiation producing Faraday wave motion, the threshold was noted to fall by 20 Hz (shown as a predicted threshold data set ($\bigcirc$)). This corresponds to an increase in the bubble radius of $\sim$18 μm over the duration of the experiment. Although this is a relatively small change compared to the initial size of the bubble (1%, given that initially $R_0 \sim 1.707$ mm) it is clearly detectable with the acoustoelectrochemical technique employed.

Fig. 4 shows the results of an experiment performed specifically to investigate the growth of a large gas bubble through rectified diffusion. In this case a solution containing the redox couple $Fe(CN)_6^{3-}$ was employed. The potential of the microelectrode was held under mass transfer limiting conditions for the reduction of the $Fe(CN)_6^{3-}$ species at all times. Initially the microelectrode (25 μm diameter platinum) was positioned using a micrometer and stage to within $\sim$20 μm of the gas/liquid interface. Under these conditions and in the absence of sound irradiation (e.g. a stagnant solution) the microelectrode detects a current, which is less that that expected in the bulk solution (see Fig. 2a). This is due to negative feedback or blocking of mass transfer by diffusion alone to the microelectrode by the gas/liquid interface of the bubble. This is an ideal situation for the investigation of the growth or dissolution of a gas bubble as the current at the microelectrode is highly dependent on the distance between the microelectrode and the gas/liquid interface of the bubble wall [14]. If the bubble grows, the current will fall (in stagnant solution)
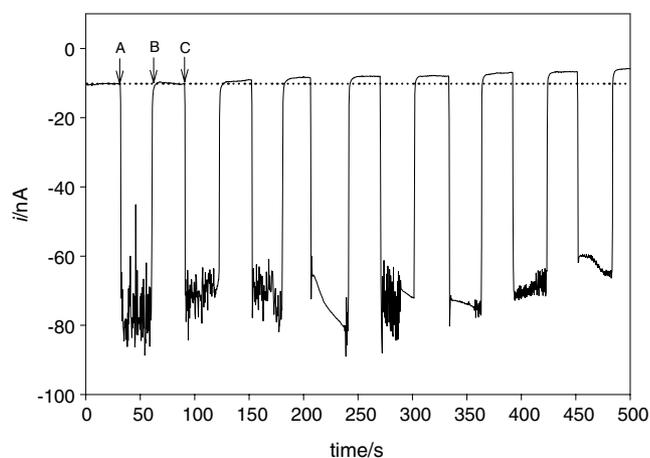
as the microelectrode to bubble wall distance decreases. Alternatively if the bubble shrinks through a dissolution mechanism then the current will approach that expected for the microelectrode in the bulk solution. Hence it is possible to detect the nature of the changes in bubble size as a function of time. A sound frequency and pressure were selected so as to ensure Faraday wave motion of the interface over a prolonged period of time. The bubble was then exposed to alternate 30 s periods of sound irradiation followed by silent conditions. This procedure ensured that the exposure of the bubble to sound was controlled and an accurate measurement of the growth or dissolution of the bubble (as determined by a reduction or increase in the microelectrode tip to bubble distance respectively) could be ascertained. This measurement was made possible by determining the current passed at the microelectrode under silent conditions, and comparing it to the predicted negative feedback curve from SECM theory under the appropriate physical conditions of the system [14]. Fig. 4 shows the current recorded as a function of time as the experiment was performed. The region denoted between 'A' and 'B' indicates a sound irradiation period while the region between 'B' and 'C' a silent period. Several points should be denoted from the figure. First, the current passed at the microelectrode in the presence of sound is enhanced by microstreaming caused by the motion of the bubble wall (see Fig. 4 region between 'A' and 'B'). Second, as the experiment continues the mass transfer enhancement in the presence of sound can be noted to tend to decrease with increased exposure time of the bubble (presumably due to the small microelectrode to bubble distance inhibiting fluid motion). Third, in the silent periods (see Fig. 4 region 'B' to 'C') the current passed at the microelectrode was observed to decrease as the exposure time of the bubble to sound was progressively increased. These observations are consistent with the bubble-to-microelectrode distance diminishing as the bubble was exposed to sound. This decrease in distance is attributed to growth of the bubble through rectified diffusion [22]. It is also possible from these experiments to estimate the rate of bubble growth under the conditions stated. In order to do this the currents in the silent periods where compared to the standard SECM theory for a negative feedback system and the absolute bubble to microelectrode tip distance calculated as a function of exposure time [11,14]. Fig. 5 shows the estimated growth in bubble radius as a function of time for two bubbles treated in the manner described above. The growth rates of the two bubbles were determined to be $3.72 \times 10^{-2} \pm 1.7 \times 10^{-3}$ and $3.04 \times 10^{-2} \pm 3.6 \times 10^{-3}$ μm s^{-1} under the conditions stated. A regression of the data in Fig. 5 shows that a linear description of the rate of increase of the radius as a function of time would fit with 95% confidence (see quoted errors). A linear description might, of course, fit less well over time periods greater

Fig. 4. Plot showing the current (i) as a function of time passed at a 25 μm Pt microelectrode positioned at $\sim$20 μm from the bubble wall. A sound field of 2.08 kHz at 51.74 Pa was applied to the system in 30 s periods (see text). The aerobic solution consisted of 5 mmol dm^{-3} $Fe(CN)_6^{3-}$ in 0.2 mol dm^{-3} $Sr(NO_3)_2$. The microelectrode was held at -0.2 V *vs.* Ag. 'A' indicates sound irradiation, 'B' termination of sound irradiation and 'C' initiation of sound irradiation for second period. The dotted horizontal line indicates the expected current under silent conditions if the bubble where not to change in size during the experiment.
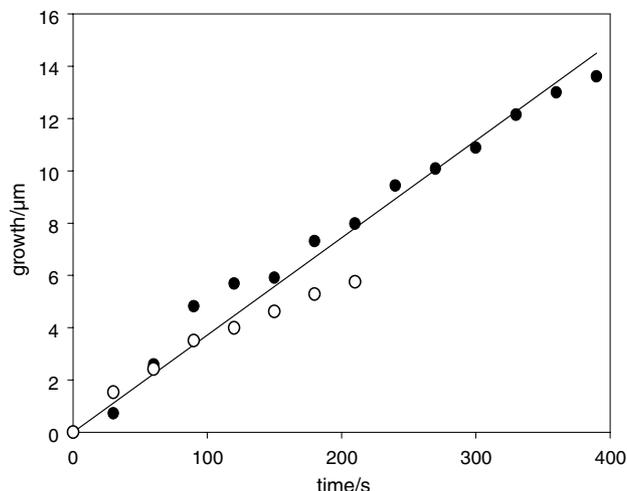
Fig. 5. Plot showing the estimated growth as a function of exposure time for two bubbles. A sound field of 2.08 kHz at 51.74 Pa (●) and 2.29 kHz at 79.6 Pa (○) was employed in each case. All other experimental parameters are reported in Fig. 4.

than that employed in the experiments reported here. The growth rates reported here can be compared to other experiments [17] where rates of $\sim$0.5 $\mu m\,s^{-1}$ were measured. However, this was for bubbles in a 26.6 kHz sound field of 0.2 bar. Considering these conditions it is unsurprising that the growth rate reported here is less than that reported by Eller. Clearly the acoustoelectrochemical technique is sensitive enough to measure slow growth rates. However, in the technique reported here, microstreaming, with any associated augmentation of bubble growth rates, was present.

4. Conclusions

The exchange of oxygen across a bubble interface has been demonstrated for the first time. The acoustoelectrochemical technique has been shown to be able to measure the rate of bubble growth due to rectified diffusion of gas from the liquid to gas phase. The bubble radius growth rate determined using this technique was of the order of $\sim$0.03 $\mu m\,s^{-1}$ under the conditions stated. This is considerably smaller than previously determined but at lower frequency and acoustic pressure amplitude.

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