Characterisation of cavitation using electrochemical, acoustic and luminescent techniques (GR/M24615/01)

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1. Background

There is an international need to understand the influence of cavitation on chemical and physical processes. While sonochemistry offers a variety of beneficial and appealing characteristics many limitations are apparent from the available literature. This is due in part to the diverse nature of sonochemistry, relying on aspects of chemistry, electrochemistry and acoustics. In general the understanding of the acoustic environment of a sonochemical cell is complex and relies on the characterisation of the transducer/cell/cavitation interaction that can be generated within the system as a whole. This fundamental problem often results in poor reproducibility between experiments and laboratories even though the same chemical environment and system is being employed (assuming no differences in the chemistry occur). In this context the proposed project set out to investigate cavitation using electrochemical sensors to characterise the chemical effects, while also employing luminescent and imaging technology to investigate the nature of the process termed 'sonoluminescence'. In order to achieve these goals, controlled and characterised acoustic cells with the ability to generate cavitation were employed. Within these a further series of experiments was proposed to investigate the chemical and physical effects of cavitation. This involved the study of multi bubble and single bubble systems, each of which is known to have differing characteristics. While the single bubble sonoluminescent systems (SBSL) may initially be regarded as 'simpler' with the possibility to investigate a single event at one time, the difference in the observations reported in the literature between MBSL and SBSL have clouded the issues further.

The project was successful in producing and characterising a set of sonochemical cells, which were then investigated using electrochemical, luminescent and imaging technology.[1-7] Further to this, a link between sonoluminescence and sonochemical activity was verified[4], a new series of experimental procedures for the electrochemical detection of radical reactions was developed and the first electrochemical evidence for radicals produced by SBSL was found. While some results have yet to be published, the authors (TGL & PRB) have produced a series of high quality publications outlining the major results of the project (including 14 peer reviewed papers in the process of or published, with more in preparation in high quality journals). This success has led to 3 further EPSRC grants including non-academic sponsors all of which rely on well-characterised experimental procedures. In addition to these achievements the grant supported a PhD student directly plus (at no extra cost to the grant) an additional PhD student and 2 undergraduate final year projects.

2. Key Advances

2.1. Summary: Key Aims

There were three key aims of the project. (1). To establish a well-characterised environment to study cavitation. (2). To investigate sonoluminescence in both the MBSL and SBSL format. (3). To develop electrochemical sensors for cavitation activity. These project aims were satisfied fully. Some key advances relating to these aims will now be summarised.

2.1.1 A Characterised Cell

The need to understand the acoustic environment of sonochemical cells is paramount before any conclusions of sonochemical processes can be drawn (see key aim 1). This was achieved by modelling the acoustic modes of a cylindrical reactor. This involved the understanding of the acoustic characteristics of the materials involved, the modelling of the sound field with respect to the geometry of the cell, the pioneering investigation of the boundary conditions at the cell walls, and experimental verification from acoustic and imaging experiments.[1]

2.1.2 Acoustoelectrochemical radical detection

A new method was developed to detect the presence of oxidising and reducing species within an environment subjected to cavitation (see key aim 3).[2,3] This method utilised an electrochemical flow cell to separate the electrochemical processes from the sonochemical and cavitation processes. This achieved a considerable and groundbreaking advance on previous studies. In each of the previous experiments reported in the literature, it was proposed that the electrochemistry was 'inserted' into the cavitation environment. While this leads to impressive rates of mass transfer, these are extremely inhomogeneous in space and time due to the nucleation and pressure dependence of cavitation itself. This imposes severe difficulty when attempting to measure coupled sonochemical reactions, as careful mass transfer calibration is required and this is reliant on high reproducibility from experiment to experiment. The separation of the electrochemistry from the sonochemical environment ensures not only that this problem is avoided, but also that the acoustic characteristics of the cell are not compromised by the electrochemical system employed.

2.1.3 Electrochemistry in a SBSL cell

The electrochemical investigation of SBSL was achieved for the first time[i] (see key aim 2). This involved the development of a cell capable of supporting SBSL and electrochemical equipment. This was achieved through the fabrication and employment of a needle microelectrode capable of penetrating the acoustic field within a SBSL cell without loss of the bubble. This also required the development of a positioning apparatus with the ability to control accurately the distance between the tip of the microelectrode and the bubble to a sub micron resolution but with a travel in excess of 5 cm.

This microelectrode and control apparatus was successful and the first electrochemical measurements of mass transfer enhancements as a result of the single cavitation bubble was achieved. In addition a measurement of radical products from SBSL was obtained. This represents the first electrochemical measurements of radical production from SBSL.

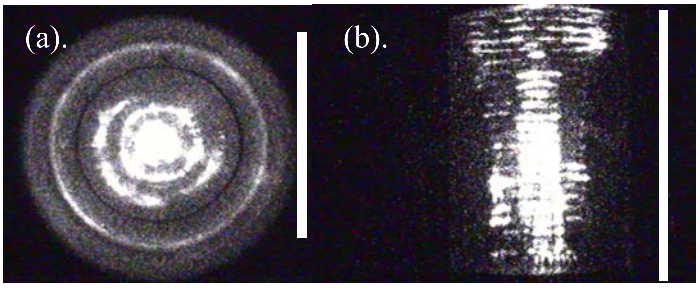

Figure 1. Images taken from above (a) and to the side (b) of a cylindrical cell. The scale bar in (a) represents 9.4 cm while in (b) 14 cm.

2.1.4 Luminescent and Imaging

A set of images and luminescent data was obtained from a set of cells.[1] These measurements showed where cavitation activity was located within each environment employed (see key aim 1 and 3). In the case of the MBSL cell (cylindrical) this enabled the confirmation of the modal structure of the sound field to be obtained. In addition to this confirmation an estimation of the speed of sound within this environment was determined and showed that considerable reduction in the speed of sound within the liquid was possible (to 863 m s^{-1}). This was the first measurement of this kind within a sonochemical cell. In addition a 'bubble population' feedback mechanism was proposed (this was singled out by a reviewer for praise). The luminescent measurements were compared to a range of other characterisation techniques and shown to be highly accurate at predicting high sonochemical activity (see key aim 2 and 3). This study demonstrated the need for precise control of the acoustic frequency employed and suggests that comparisons of results over a wide frequency band, without consideration of the changes in the sound field, are invalid.

2.2 SCIENCE AND TECHNOLOGY

The acoustic characterisation of the cylindrical cells employed in many of the experiments performed on multi bubble systems was shown to be vital in the understanding of the sonochemical effects observed within the system (see key aim 1). The

$$f_{m,n,q} = \frac{c}{2\pi}\sqrt{\left(\frac{j_{m,n}}{a}\right)^2 + \left(\frac{(2q+1)\pi}{2L}\right)^2} \quad (1).$$

acoustic model described a set of acoustic modes within the cylindrical environment with an associated natural frequency (equation 1).[1] Where c represents the speed of sound, a the cylinder inner radius, L the liquid height, $j_{m,n}$ the stationary point of the appropriate Bessel function and m,n,q integer values depicting the mode. Whilst the production of such a modal for an air filled cylindrical cavity would be simple (the boundary conditions all being rigid), for a liquid filled water-jacketed cell, pioneering work on the boundary conditions was required.[1]

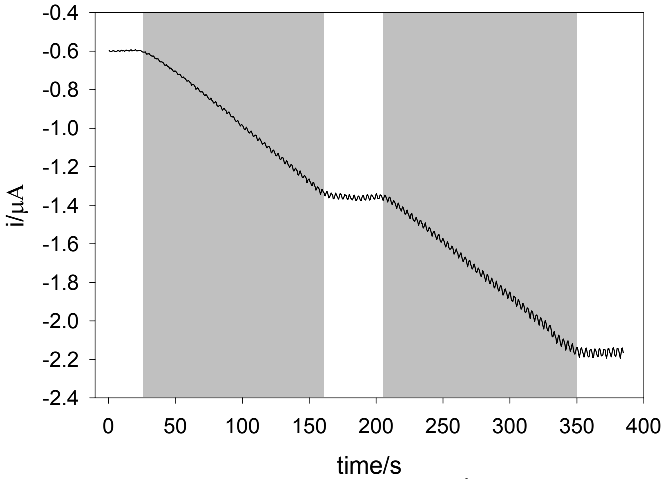

Figure 2. Plot showing the build up of Fe^{3+} generated from a sonochemical Fricke reaction. The grey regions indicate the 'exposure' of the solution to ultrasound.

The acoustic model predicted a series of rings of activity when viewed from above and bands when viewed from the side. This was found to be the case (see figure 1).

In order to measure the sonochemical yield of the sonochemical cells studied a novel electrochemical flow system was employed (see key aim 3).[2,3] This had the advantage of having a well-controlled mass transfer regime with a minimum delay in transfer of the sonochemical products of the reactions from the sonochemical cell to the electrochemical cell. Figure 2 shows an example response of this technology employed on the Fricke reaction. This was extended to a number of different systems including a novel copper based system targeted at producing electrochemical evidence for $H^{\bullet}$ production from acoustic cavitation. The electrochemical approach to the detection of radicals from cavitation was extended to SBSL[i] (see key aim 2). In this case a novel microelectrode housed in a needle was developed and tested successfully. Figure 3 shows the

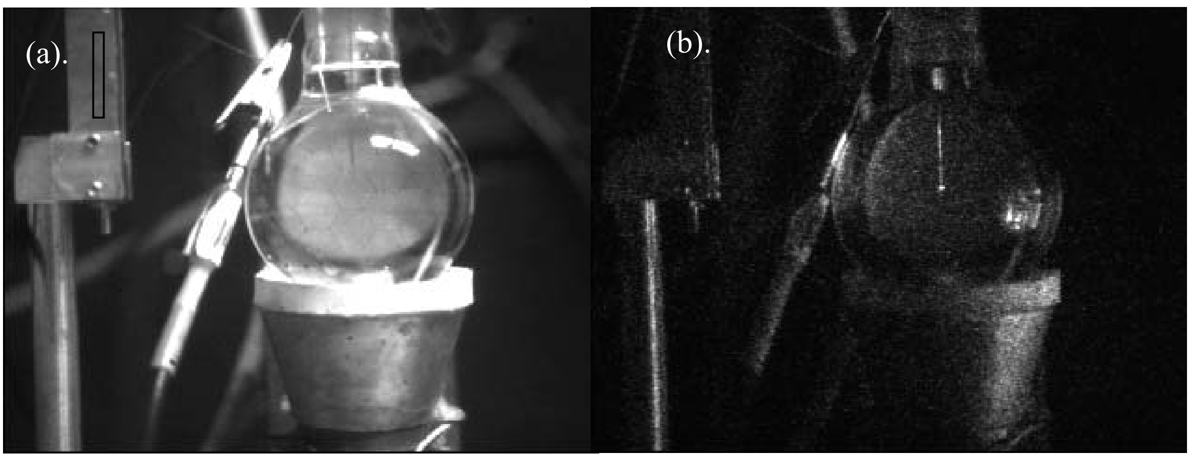

Figure 3. Images of the eSBSL cell. Frame (a) shows the illuminated cell while frame (b) shows an image of the cell with a luminescent single bubble in the centre. The needle microelectrode can be seen as a thin bar (due to scattered light) approaching the single bubble (seen as a dot of light). The scale bar represents 1.5 cm.

SBSL cell and needle microelectrode approaching a luminescent bubble. Control experiments were performed with a radical scavenger to demonstrate that the signal originated from radical oxidations of I^- and mass transfer calibrations showed that the response was not the result of convective flow changes due to bubble motion. The response of the microelectrode indicated that the luminescent bubble through reactions assumed to produce oxidising agents generates I_3^-. This is the first electrochemical evidence for radical production from SBSL. The magnitude of the microelectrode response (*ca.* 20 pA) can be used to estimate the effective concentration of I_3^- detected by the microelectrode of 0.2 μmol dm^{-3}. However, to equate this to a real radical yield relies on estimations of capture efficiency and the distance between the bubble and the tip of the microelectrode.

2.3 AUXILIARY FINDINGS

As well as the satisfaction of the main project aims, this grant (at no extra cost) helped support another PhD student (Yvonne Watson). This auxiliary project investigated the motion of gas bubbles driven by an acoustic field.[8-12] In particular surface waves (or Faraday waves) were detected as enhancements in mass transfer to a microelectrode positioned close to (~5-10μm) the gas/liquid interface of a tethered bubble. This project was extremely successful demonstrating that the motion of the gas/liquid interface of a gas bubble could be electrochemically investigated to ascertain the type of bubble oscillation (breathing[8] or surface wave), the extent of mass transfer enhancement[10] as a function of distance from the gas/liquid interface (see figure 5), the detection of surface waves on a moving gas bubble[ii], the measurement of gas transfer across the gas/liquid interface[iii], the measurement of surface wave ring-up and the measurement of rectified diffusion[iv]. This research has led to the possibility of 'green chemistry' by employing much lower acoustic pressures to achieve similar mass transfer enhancements.

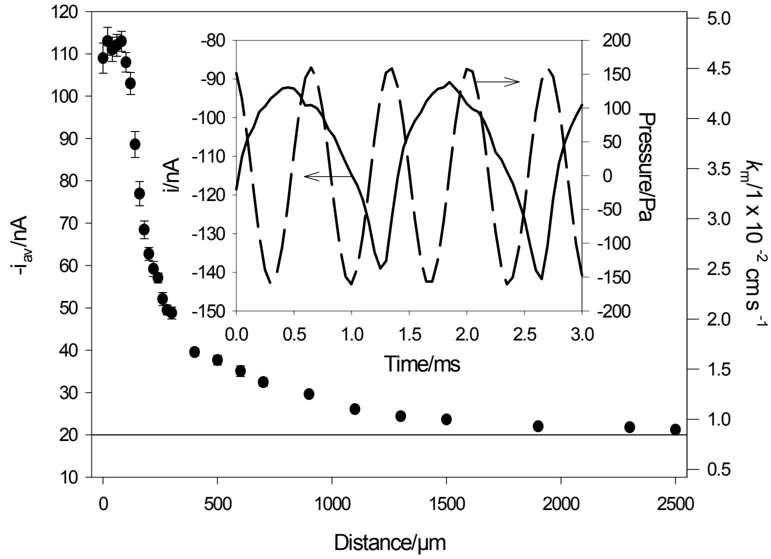

Figure 4. Plot showing the mass transfer enhancement as a function of distance caused by surface waves driven by an appropriate acoustic field. The insert shows the actual current time profile indicating the characteristic subharmonic signal associated with surface waves.

3. Personnel

The project provided funding to support a project student (John Power) and equipment money to develop the apparatus necessary to measure the rates of sonochemical processes and the imaging and luminescent data. However, at no extra cost, the project supported another PhD student (Yvonne Watson, who worked on items described in section 2.3) and a short-term postdoctoral researcher. In addition a number of undergraduate projects benefited from the project. The project has led to a number of publications either in the public domain, in press or in preparation. Also Y. Watson won the Russian Interdisciplinary Student Prize for an oral presentation at an international conference of the Institute of Acoustics, 'Acoustical Oceanography, 2001'.

Tim Leighton received the Inaugural award of the International Medwin Prize for Acoustical Oceanography (Acoustical Society of America), in large part because of this work. It also significantly contributed to his being awarded the 2002 Tyndall Medal of the UK Institute of Acoustics, and a Royal Society Leverhulme Trust Senior Research Fellowship. During the grant he received Fellowship of the Institute of Physics, and Fellowship of the Institute of Acoustics, and was appointed to 7 international committees on acoustics. He founded an interdisciplinary acoustics group, was Editor-in-Chief of a peer-reviewed conference proceedings, and gave 3 invited addresses, which included the material of this contract. His committee work included the Council, and (as a founding member) the Research Coordination Committee, of the Institute of

Acoustics; in this capacity he met on a number of occasions with EPSRC staff to assist with the EPSRC 2002 Acoustics Theme Day (and associated arrangements, such as gathering data on current UK Acoustics research via a questionnaire he helped to devise). In addition PRB (CI) was invited to speak at 2 UK Universities and gave 3 presentations publicising results obtained from the grant-funded project at international conferences in the UK and in Europe.

During this project the ISVR, along with the rest of the Faculty of Engineering and Applied Science at Southampton, achieved Grade 5* in the 2001 Research Assessment Exercise. The Chemistry Department achieved a Grade 5a in the 2001 Research Assessment exercise.

4. Project Plan Review

The original project plan was followed closely throughout the project. However, the second half of this grant was carried out in difficult personal circumstances for TGL. In 2001, as a result of the stress, associated with a close family bereavement and a serious illness to his wife, resulted in a vertebra, fractured in a mugging in 1992, to be stressed such that the increased level of pain and impediment caused TGL to be registered disabled in early 2002. He was unable to travel for 6 months and his contributions to the project had to be done from home, via telephone, email and meetings at home etc.

5. Research Impact

The research impact of this project has been substantial and diverse. A number (12) of papers in international journals have been published and a further 4+ publications are in preparation. A number of reports and conference proceedings have also been published.[14-17] In addition the results of the study have been publicised within international conferences by a number of the workers.

Beneficiaries of the research extend from the general scientific community where the need for accurate and characterised acoustics in sonochemical studies has been highlighted to the wider community where the virtues of son electrochemistry has been reported in a number of publications. One such publication was highlighted in the New Scientist were the general implications of the results reported in a scientific publication was flagged to the general public

6. Further Research and Dissemination Activities

The student is in the process of writing up his Ph.D. thesis (the first draft is complete and corrections are being made). It is expected that this thesis will be submitted in December 2002. In addition to the 14 peer-reviewed and 9 non-peer-reviewed items listed in the IGR, the intention is to publish a minimum of 4 journal papers based on the work funded by this grant.[i-iv]

7. Direct References

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8.1 Some of the Papers in Preparation

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ii. Birkin P R, Watson Y E, Leighton T G, *Measurement of surface waves on a rising gas bubble*. In preparation for JACS.
iii. Birkin P R, Watson Y E, Leighton T G, *The effect of surfactants on Surface waves*. In preparation for Langmuir
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