Sonochemistry - A Demonstration Lecture

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Abstract: The potential for the use of sonochemistry in the processing and chemical industries of the future has been established in the chemical laboratory. The majority of the dramatic effects which have been identified with sonochemical processes are known to be the result of the effects of cavitation bubble collapse in the supporting liquid systems. It is because the basis of sonochemistry lies in acoustic cavitation that such studies provide a focus for active discussion and a range of research projects for chemists, mathematicians and physicists. In the past interaction between these disciplines has been limited due to the different scientific circles in which they move however in recent years a few conferences such as this one, have sought to bring such disciplines together to promote cooperation. This presentation will incorporate a series of demonstrations which illustrate the types of physical and chemical effects of cavitation and ultrasound which are of particular interest to the chemist.

INTRODUCTION

For the practising chemist the importance of cavitation as a source of system activation is twofold. Firstly there is a true chemical effect associated with the production of high energy species such as radicals. This effect occurs within the bubble itself and at the bubble interface, regions which can be thought of in terms of chemical microreactors. The reactive species generated can then react either within these regions or as they enter the liquid immediately adjacent to the bubble. The second involves the mechanical and physical effects which are generated in the immediate vicinity of the bubble and generally associated with the shockwave produced on bubble collapse and a possible lesser effect associated with bubble oscillation. Whatever the origins of the sonochemical effects arising from acoustic cavitation the chemist will be concerned with the results generated in three systems, a homogeneous liquid, a heterogeneous liquid/solid and an immiscible liquid/liquid.

DEMONSTRATIONS OF THE EFFECTS OF ACOUSTIC CAVITATION

DEGASSING: A cavitation bubble generated in a homogeneous liquid system does not enclose a vacuum. Vapour is generally drawn in from the liquid itself or from any volatile material dissolved in it. However if a gas is dissolved in the liquid the bubbles will fill with the gas and such bubbles are not easily collapsed. Gas filled bubbles will continue to grow on further rarefaction cycles, taking in more gas and eventually floating to the surface. Since the rarefaction cycles are taking place extremely rapidly the bubbles grow so quickly that degassing appears to occur almost instantaneously.

Ultrasonic degassing has found applications in many areas. In its simplest form it is used to degas solvents for use in high performance liquid chromatography but it can also be used to improve electroplating and more generally in electrochemical processes by removing the unwanted gas build up on the electrodes. Industrially it affords efficient degassing from molten metal and glass.

RADICAL GENERATION: On collapse of an acoustic cavitation bubble the extremes of conditions generated can cause chemical break-down of any vapour within it. In the case of aqueous systems rupture of the O-H bond of water vapour causes the initial formation of radical species H and OH in the bubble and eventually leads to the formation of oxygen gas and hydrogen peroxide. This can be shown through the oxidation of any iodide ions present in solution to iodine by reaction with ultrasonically generated peroxide. The iodine produced can then be detected by its reaction with starch to produce a characteristic colour.
Several uses for the ultrasonic generation of free radicals are under active investigation including the oxidative removal of chemical contaminants from water and the enhancement of radical polymerisation processes.

**EFFECT OF CAVITATION ON A SOLID SURFACE:** The majority of sonochemical studies have involved heterogeneous reactions occurring at solid/liquid interfaces in which the solid component can be either a reagent or a catalyst. When the solid is in the form of a metal the result of sonication in a solvent is often surface damage in the form of pitting. This damage is caused by impacts from high power liquid jets produced by cavitation bubble collapse at or near the surface. This effect can be demonstrated through the perforation of aluminium foil immersed in an ultrasonic cleaning bath. If the foil is held reasonably steadily in the bath then the perforations will be clearly seen to be in horizontal rows corresponding to the areas of maximum cavitation effect at half wavelength distances vertically through the bath liquid.

The liquid jet can activate surfaces by removing passivating coatings and by keeping the surface clear of deposits. It will also improve mass and heat transfer and can be used to force the extraction or impregnation of materials into porous solids.

**EFFECT OF CAVITATION ON A SUSPENSION OF POWDER:** If the solid is in the form of a powder then the effects of sonication will be the destruction of agglomerates and/or the reduction in size of individual particles. The first of these can be demonstrated using blackboard chalk in water where sonication can be clearly seen to break up the surface into clouds of chalk particles and efficiently improve its dispersion in the medium. The reduction of particle size of a material will depend on its original particle size. For larger particles, defects on the exterior may cause surface cavitation and result in fragmentation. In the case of small particles the extremes of agitation generated as a result of cavitation lead to violent collisions and thereby erosion or even fusion. Thus sonication can lead to powder dispersion and activation via an increase in surface area accompanying any reduction in particle size together with the removal of surface coatings.

**EFFECT OF CAVITATION ON A HETEROGENEOUS LIQUID MIXTURE:** Sonication of immiscible liquids provides extremely fine and stable emulsions. This can be shown by placing some water and an organic liquid in a flask dipped into an ultrasonic bath. The clearly defined phase boundary between the two immiscible liquids is seen to become agitated and soon a cloudiness appears in the interfacial region and within 1 minute substantial emulsification has been caused.

Applications for such processes lie in emulsification and dispersion and in chemistry to improve reactions between reagents dissolved in different immiscible phases i.e. in situations where a phase transfer catalyst is normally used.

**PARTICLE AGGLOMERATION:** In a standing wave field small particles have a tendency to move to the nodes of the wave. This phenomenon is illustrated by immersing a measuring cylinder containing an aqueous suspension of copper bronze in an ultrasonic bath. In the presence of ultrasound the uniform suspension changes to a set of horizontal bright metallic lines at separated distances of the half wavelength of the ultrasound in water.

This demonstrates a potentially useful application of ultrasound as a method of manipulating small particles suspended in a liquid medium and also of conglutinating, and hence precipitating, airborne smokes.

**ENHANCED CHEMILUMINESCENCE:** Luminol is a chemical which emits light in the presence of hydrogen peroxide and highly oxidising species. For this reason a solution of this reagent is often used as an indicator of cavitation in water because the process generates peroxide, this is the basis of the experiment. Luminol can also be used as a dosimeter based on the intensity of the light emitted.

**CONCLUSIONS**

Current research in sonochemistry suggests that in order to exploit its tremendous potential of the subject in industry a fundamental understanding of cavitation will be required. Such an understanding will only come with the aid of cross-discipline discussion. It is to be hoped that this is what this conference may achieve.