Effects of Particle Size Morphology on Ultrasonic-induced Cavitational Mechanisms in Heterogeneous Systems

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Ultrasonic irradiation of copper and lead, separately, in hydrochloric acid shows that mechanistic effects would depend largely on the structural nature of the solid reactants: if the size of a solid reactant is substantially large, microject formation will be the predominant mechanism.

Cavitation near extended liquid–solid surfaces is very different from cavitation in pure liquids; the bubble collapse differs substantially from the spherically symmetric implosion observed in homogeneous liquids. There are two proposed mechanisms[1] for the effects of cavitation near surfaces: microjet impact and shock wave damage. The asymmetry of the environment near the interface induces a deformation of the cavity during its collapse. This generates a fast moving jet of liquid directed at the surface with velocities exceeding 100 m s^{-1}. The impingement of this jet can create localized surface damage and is responsible largely for cavitational erosion, surface pitting and ultrasonic cleaning. The second mechanism of cavitational-induced surface damage is the impact of shock waves created by bubble collapse.

Since the existence of both microjet impact and shock wave mechanisms is well established, the objective of this study is to investigate which mechanistic aspect of cavitation is predominantly prevalent in a solid–liquid system when size characteristics of the solid itself are structurally different. We subjected two structurally different forms of (*a*) copper and (*b*) lead in dilute hydrochloric acid to ultrasound; the amount of copper(II) chloride† formed, as determined by UV–VIS spectrophotometric methods, and the amount of lead ions by atomic absorption analyses, are then used as mechanistic probes for our investigations.

For the experiments with copper, four samples labelled C1, C2, C3 and C4 were prepared. C1 and C2 are the experimental samples and C3 and C4, the controls. Samples C1 and C3 were prepared using *ca.* 0.01 mol of copper powder (Merck AR grade < 63 micron size), whilst C2 and C4 contained approximately 0.01 mol of copper turnings (BDH) each. 10 ml of 1 mol dm^{-3} HCl were then added to all the four samples. Samples C1 and C2 were subjected to ultrasonic irradiation in an ultrasonic cleaning bath (Kerry Pulsatron #KS60, 38 kHz) for 30 min, whilst controls C3 and C4 were left to stand, with intermittent stirring, for the same duration. At the end of this time, the filtrates from all four samples were analysed with a UV–VIS spectrophotometer [Hewlett Packard Diode model 8452 (diode array detector)] in a scanning mode.

For the experiments with lead, four samples labelled P1, P2, P3 and P4 were prepared. P1 and P2 are the experimental samples and P3 and P4, the controls. Samples P1 and P3 were prepared using *ca.* 0.002 mol of lead powder (Hayashi Pure Chemical Industries Ltd., pure grade, 100 mesh), whilst P2 and P4 contained approximately 0.002 mol of lead foil (8 mm × 8 mm approximately) each. 10 ml of 0.1 mol dm^{-3} HCl were then added to all four samples. Samples P1 and P2 were subjected to ultrasonic irradiation in an ultrasonic cleaning bath (Kerry Pulsatron #KS60, 38 kHz) for 30 min, whilst controls P3 and P4 were left to stand, with intermittent stirring, for the same duration. At the end of this time, the filtrates from all the four samples were analysed with an atomic absorption spectrophotometer (Shimadzu Model A690).‡

In the case of copper, it is expected that the ultrasound-treated sample C1 should display a higher absorbance reading compared to control C3, but we observe that the extent of absorbance for C1 is 2.90 A.U. (A.U. = absorbance unit), whilst that for C3 is 2.87 A.U. The difference between these two values is very marginal and can be statistically discounted. Similarly with lead (P1, 1.724 A.U. and P3, 1.675 A.U.). We assume that microjet formation and impact are largely responsible for the depassivation of oxide coatings. In fact, it has been attributed that the erosive effects of ultrasound derive in large part from microjet impacts.[2] However, microjet distortions of bubble collapse depend on surfaces several times larger than the resonant bubble size.[1] At 20 kHz, for example, simple calculations have indicated that the collapsing bubble will have a diameter of about 150 microns,[3,4] particles smaller than this size cannot cause microjet formation.

When copper turnings and lead foils are used instead, we find that the difference in results is very obvious; in the comparison of ultrasonic-treated and control copper turnings, we see that the extent absorbance for C2 (3.05 A.U.) is *ca.* 22 times greater than that of C4 (0.14 A.U.). Similar results were obtained for lead; absorbance of P2 is approximately 1.6 times greater than that of P4. There is no doubt here that the considerable size of the copper turnings or lead foil (*cf.* cavitation bubble) must have played a role for this significant increment. In simple terms, a bullet can very well split an apple but NOT a molecule. If we consider Newton's First Law of Motion, this can be explained more easily. Accordingly, all objects with masses possess inertia. The bigger the body is, the greater its inertia. So, copper turnings and lead foil, being larger than their powder forms, are greatly depassivated by ultrasonically induced microject impacts.

In conclusion, cavitational mechanistic effects depend largely on the structural nature of the solid reactants. If the sizes of the solid reactants are substantially large (> 150 µm), microjet formation will be the predominant cavitational mechanism (over interparticle collision) in the system.

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Footnotes

† It is recognized that copper, located near the bottom of the reactivity series, would have negligible or no reaction at all with dilute acids; thus, it can be construed that the formation of copper(II) chloride in solution is not simply attributed to a direct reaction between copper and HCl. However, it is not the intention of this extract to discuss the possible reaction mechanism.

‡ Due to the nature of sonication effects, it is difficult to control experimental conditions absolutely. Hence, sonication experiments are always subject to some uncertainty, so that some results may show discrepancies. However, our results have shown clear and consistent trends.

References

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