Chem. Soc. Rev., 1987, **16**, 239—274

Sonochemistry
Part 1—The Physical Aspects *

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1 Introduction

Up to a few years ago the use of ultrasound in chemistry was something of a curiosity and the practising chemist could have been forgiven for not having met the term sonochemistry. And yet the use of ultrasound in chemistry is not a new topic; there were publications in primary chemical journals and industrial applications reported in the 1950s. After a period of neglect in the sixties and early seventies however, the subject is undergoing a renaissance which is generally considered to be due to the current wide availability of laboratory ultrasonic equipment in the form of cleaning baths and ultrasonic probes (often marketed as biological cell disruptors).

The Royal Society of Chemistry provided a focus for this rapidly increasing area of study by including the first international symposium on sonochemistry at its 1986 Annual Congress held over three days in April 1986 at the University of Warwick.[1] The meeting brought together research groups whose studies spanned a range of different aspects of sonochemistry and generated considerable academic and industrial interest, so much so that the R.S.C. has now formed a new Subject Group devoted to the topic. It is hoped that this review will serve as both an introduction to the topic and a survey of current trends in sonochemistry.

Ultrasound is the name given to sound waves having frequencies higher than those to which the human ear can respond (*i.e.* >16 kHz). The upper limit of ultrasonic frequency is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids.

Being a sound wave, ultrasound is transmitted through any substance, solid, liquid, or gas, which possesses elastic properties. The movement of a vibrating body (*i.e.* sound source) is communicated to the molecules of the medium, each of which transmits its motion to an adjoining particle before returning to approximately its original position. It is this continuous movement of molecules, producing areas where they are compressed together, followed by layers where there is a deficiency of molecules, which gives rise to the alternate compression and rarefaction portions of the wave. For liquids and gases, particle oscillation

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* Part II—Synthetic Applications by James Lindley and Timothy J. Mason will appear in *Chemical Society Reviews*. 1987. Issue No. 3 (September).

[1] Special edition covering the R.S.C. Sonochemistry Symposium, Warwick 1986. *Ultrasonics*, 1987, **25**. January.

takes place in the direction of propagation and produces longitudinal waves. Solids, however, since they possess shear elasticity can support tangential stresses, and hence tranverse waves in which particle movement takes place perpendicular to the direction of the wave.

The use of ultrasound may be divided broadly into two areas. First, low amplitude (high frequency) propagation, which is concerned with the effect of the medium on the wave. Typically, low amplitude waves are used to measure the velocity and absorption coefficient of the wave in the medium. Secondly, high energy (low frequency) propagation, which is concerned with the effect of the wave on the medium. Examples of high energy applications are ultrasonic cleaning, drilling, soldering, chemical processes, emulsification *etc.* These processes are the result of either the mechanical agitation caused by the wave or are a consequence of cavitation (tiny bubbles) produced in the liquid.

Although the field of ultrasound had been established in 1880 with the discovery of the piezoelectric effect by Curie and the ultrasonic whistle by Galton in 1893, the first commercial application of ultrasonics did not appear until 1917 with Langevin's echo-sounding technique. Langevin's discovery was the direct result of a competition organized in 1912 to find a method of detecting icebergs and so avoid any repetition of the disaster which befell the Titanic. Echo-sounding consists of sending a pulse of ultrasound from the keel of a boat to the bottom of the sea where the wave is reflected back to a detector which is also situated on the keel. The time interval between issuing and receiving the pulse allows the determination of depth, since $\textit{depth} = \frac{1}{2} \times \textit{time interval} \times \textit{velocity of sound in the water}$. Essentially all imaging, from medical ultrasound to non-destructive testing (flaw detection) relies upon the same pulse-echo type of approach but with considerably more advanced electronic hardware. High frequency (>1 MHz) ultrasound is employed for this work since the much shorter wavelengths involved are able to detect much smaller areas of phase-change *i.e.* differences in tissue structures in the body, or flaws in a metal.

It is only since 1945 with the increased understanding of the phenomenon of cavitation, together with significant developments made in electronic circuitry and transducer design that a rapid expansion in the application of ultrasound to chemical processes has occurred.

The last decade has seen sonochemistry come of age and it has become increasingly evident that sonochemistry may be as important a topic within chemistry as photochemistry, thermochemistry, or high pressure chemistry—possibly even more important because of its greater general applicability across the whole breadth of chemistry from polymer science to chemical physics. It has the distinct advantage that the methodology is straightforward with relatively simple apparatus requirements.

The aim of this review is to outline how important a tool ultrasound has become to the chemist in studying a range of topics from analysis and relaxation phenomenon (using low amplitude waves) to the acceleration of chemical processes, organic synthesis, and polymerization (high energy waves).

2 General Principles

The vast majority of chemical reactions are carried out in the liquid phase under either homogeneous or heterogeneous conditions. This is certainly true of those processes which have been studied in the presence of ultrasound *e.g.* chemical synthesis, structural determinations, kinetic studies, and polymer degradations. For this reason the following review of the physical effects of ultrasonic irradiation on chemical processes has been restricted to those occurring in the liquid phase. The mathematical treatment has also been kept to a minimum, consistent with the aim of introducing the topic to chemists. However the authors are well aware of the many rigorous mathematical treatises which relate to ultrasound and these can be found in the selection of books and reviews (written predominantly by physicists).[2–14] For some sections of the following qualitative discussions, where an awareness of the underlying mathematical concepts is considered advantageous, semi-quantitative descriptions have been provided.

A. Sound-induced Vibrations.—When an acoustic field is applied to a liquid the sonic vibrations create an acoustic pressure (P_a) which must be considered to be additional to the ambient hydrostatic pressure (P_h) already present in the medium. The acoustic pressure is time (t) dependent and is represented by equation 1

$$P_a = P_A \sin 2\pi f t \qquad (1)$$

where f is the frequency of the wave (>16 kHz for ultrasound) and P_A is the maximum pressure amplitude of the wave. By analogy with electrical vibrations[15] the intensity of the wave (I, the energy transmitted per second per cm^2 of fluid) is as described in equation 2

$$I = P_A^2(2\rho c)^{-1} \qquad (2)$$

where ρ is the density of the medium and c is the velocity of sound in that medium.

As the wave propagates through the medium the sound-induced oscillations of the molecules about their mean rest-position may be described mathematically in

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[2] H. G. Flynn, 'Physical Acoustics', Vol. 1B, ed. W. P. Mason, Academic Press, New York, 1964, pp. 57—172.

[3] R. E. Apfel, 'Ultrasonics', ed. P. D. Edmonds in 'Methods of Experimental physics', ed. E. Marton, Academic Press, New York, 1981, pp. 355—411.

[4] A. Basedow and K. H. Ebert, 'Advances in Polymer Science', Vol. 22, ed. H. J. Cantow, Springer Verlag, New York, 1978.

[5] B. Brown and J. E. Goodman, 'High Intensity Ultrasonics', D. Van Nostrand Co. Inc., Princeton, New Jersey.

[6] J. Blitz, 'Fundamentals of Ultrasonics', Butterworths, London, 1967.

[7] E. A. Neppiras, *Phys. Rep.*, 1980, **61**, 160.

[8] B. E. Noltingk and E. A. Neppiras, *Proc. Phys. Soc. B (London)*, 1950, **63B**, 674.

[9] E. A. Neppiras and B. E. Noltingk, *Proc. Phys. Soc. B (London)*, 1951, **64B**, 1032.

[10] K. S. Suslick, 'Modern Synthetic Methods', vol. 4, Springer Verlag (Berlin), 1986, pp. 1—60.

[11] P. Riesz, D. Berdahl, and C. L. Christman, *Environ. Health Persp.*, 1985, **64**, 233.

[12] A. Henglein, *Ultrasonics*, 1987, **25**, 6.

[13] L. D. Rosenberg, 'High Intensity Ultrasonic Fields', 1971, Plenum Press, New York, pp. 203—491.

[14] I. E. El'piner, 'Ultrasound', Consultants Bureau, New York, 1964.

[15] Ref. 5, p. 16.

terms of molecular displacement (x), velocity (v) and acceleration (a) (equations 3—5).

$$x = x_0 \sin 2\pi ft \tag{3}$$

$$v = (\mathrm{d}x/\mathrm{d}t) = 2\pi fx_0 \cos 2\pi ft \tag{4}$$

$$a = (\mathrm{d}v/\mathrm{d}t) = -4^2 f^2 x_0 \sin 2\pi ft \tag{5}$$

B. Attenuation of Sound in a Liquid Medium.—The intensity of sound is attenuated (*i.e.* decreases) as it progresses through a medium. As the molecules of a liquid vibrate under the action of the sound wave they experience viscous interactions which degrade the acoustic intensity and some energy is lost in the form of heat. Heating will occur at the sites of compression, and cooling at the sites of rarefaction, but, because of its low compressibility there will be little appreciable heating of the bulk medium from this source. The small bulk heating effect which does occur on passing high power ultrasound through a liquid medium is due to the absorption of degraded acoustic energy. The energy loss is represented in equation 6,

$$I = I_0 \exp(-2\alpha l) \tag{6}$$

where I is the intensity at some distance l from the radiation source and α is the absorption coefficient.

Kirchoff derived an equation (7) for the calculation of α based upon losses due to viscous forces and heat conduction,[16]

$$\alpha = \frac{2\pi^2 f^2}{\rho c^3}\left[\eta_b + \frac{4}{3}\eta_s + \frac{(\gamma - 1)\,k'}{C_p}\right] \tag{7}$$

where η_s and η_b are the shear and the bulk viscosities of the medium respectively, k' is thermal conductivity of the medium, C_p is the specific heat at constant pressure, and γ is the ratio of specific heats.

For any given medium, at a given temperature, the value of α/f^2 must be a constant and so any increase in sound frequency f must result in a compensatory increase in α and thus a more rapid attenuation of the sound intensity with distance. This effect is best explained with a specific example. Whereas sound at 20 kHz is reduced to $\frac{1}{2}$ of its intensity after passing through 30 km of water, the distance required to achieve the same reduction of intensity for 118 kHz sound is only 1 km. Calculations such as these demonstrate clearly that in order to achieve identical intensities at a given distance in a medium it will be necessary to use a higher initial power for the source with the higher sound frequency.

C. The Formation of Cavitation Bubbles.—Under the influence of a pressure wave the average distance between the molecules in a liquid will vary as the molecules

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[16] G. Kirchoff, *Ann. Phys. (Liepzig)*, 1868, **134**, 177.

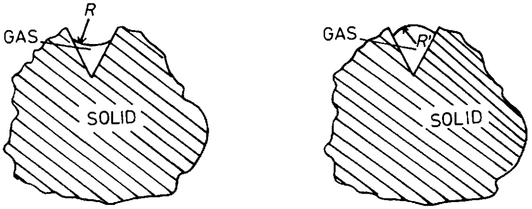

Figure 1 *Crevice model for stabilizing cavitation nuclei* (ref. 11). (a) *For external positive pressure.* (b) *For external negative pressure*

oscillate about their mean position. If a sufficiently large negative pressure (P_c) is applied to the liquid (here it is the acoustic pressure on rarefaction $P_c = P_a - P_h$) so that the distance between the molecules exceeds the critical molecular distance (R) necessary to hold the liquid intact, the liquid will break down and voids will be created *i.e.* cavitation bubbles will form. For water the critical distance is assumed to be 10^{-8} cm and the tensile stress, or pressure involved, can be calculated[17] to be of the order of 10 000 atmospheres ($P_c \approx 2\sigma/R$ where σ = surface tension). If the calculation is modified[18] so that allowance is made for the bubbles to be filled with vapour (from evaporation of the liquid) cavitation will still require negative pressures of about 1 000 atmospheres.

In practice cavitation occurs at considerably lower applied acoustic pressures due to the presence in the liquid of weak spots which lower the tensile strength. One possible source of weakspots is the presence of gas nuclei in the form of either dissolved gas, minute suspended gas bubbles, or gas bubbles produced as a result of heat fluctuations within the liquid. Evidence for this has been obtained from degassing the liquid[19–21] or raising the hydrostatic pressure,[22–25] both of which lead to an increase in the cavitation threshhold.

Ultrafiltration[26] is also known to raise the cavitation threshhold of liquids. This suggests that it is the presence of particulate matter, and more especially the occurrence of trapped vapour–gas nuclei in the crevices and recesses of these particles, which is responsible for lowering the cavitation threshhold.[27–29] Nucleation from these sites (and from similar sites on the vessel walls) is easy to visualize (Figure 1). During the rarefaction cycle of the acoustic wave, as the

[17] L. A. Crum, *IEEE Ultrasound Symp.*, 1982, **1**.
[18] Ya. B. Zel'dovich, *Zh. E'Ksp. Tevr. Fiz.*, 1942, **12**(11—12), 525.
[19] H. N. V. Temperley, *Proc. Phys. Soc.*, **59**, 199.
[20] W. J. Galloway, *J. Acoust. Soc. Am.*, 1954, **26**, 849.
[21] G. W. Willard, *J. Acoust. Soc. Am.*, 1953, **25**, 669.
[22] E. N. Harvey, *J. Colloid Comp. Physiol.*, 1944, **24**, 1.
[23] D. C. Pease and L. R. Blinks, *J. Phys. Cellular Chem.*, 1947, **51**, 556.
[24] M. Strasberg, *J. Acoust. Soc. Am.*, 1959, **31**, 163.
[25] H. J. Naake, K. Tamm, P. Damming, and H. W. Helberg, *Acustica*, 1958, **8**, 193.
[26] M. Greenspan and C. E. Tschiegg, *J. Res. Natl. Bur. Stand., Sect. C*, 1967, **71**, 229.
[27] L. A. Crum, *Nature*, 1979, **278**, 148.
[28] R. H. S. Winterton, *J. Phys. D: Appl. Phys.*, 1977, **10**, 2041.
[29] R. E. Apfel, *J. Acoust. Soc. Am.*, 1970, **48**, 1179.

pressure decreases ($P = P_a - P_h$), the liquid–gas interface becomes increasingly more convex, its angle of contact decreases, until, at sufficiently low pressure ($P_a = P_A \sin 2\pi ft$), it breaks away from the surface to produce a bubble of radius R.

It can be shown [8,9,13] that the critical (or Blake Threshold) pressure (P_K) (neglecting vapour pressure and inertial and viscous effects) which must be exceeded by the acoustic pressure (P_a) to provide a bubble of radius R is given by equation 8,

$$P_K = P_h + \frac{2}{3\sqrt{3}}\left[\frac{(2\sigma/R)^3}{(P_h + 2\sigma/R)}\right]^{\frac{1}{2}} \tag{8}$$

where σ is the surface tension of the liquid.

For large bubbles ($P_h \gg 2\,\sigma/R$) the equation may be approximated to equation 9,

$$P_K = P_h + \frac{8\sigma}{9}\left[\frac{3\sigma}{2P_hR^3}\right]^{\frac{1}{2}} \tag{9}$$

whereas for small bubbles ($2\,\sigma/R \gg P_h$) it takes the form of equation 10.

$$P_K = P_h + 0.77\,(\sigma/R) \tag{10}$$

Equation 10 can be used in another sense. For bubbles with radii less than 10^{-7} cm it provides a good estimate of the limiting tensile strength of water (*e.g.* for $\sigma = 7.25 \times 10^{-2}$ Nm^{-1}, $P_K \approx 720$ atm).

Thus, although cavitation in the strictest sense is the production of empty voids (or, more likely, vapour-filled voids), the inability to remove all gas nuclei from the liquid necessitates the inclusion of gas-filled bubbles in discussions of cavitation phenomena. It is the subsequent fate (see 2E below) of some of these bubbles, as they oscillate in the applied sinusoidal acoustic field, which is the origin of sonochemical effects. It is certain that sonochemical effects cannot be the result of direct coupling of the sound field with the chemical species on the molecular level since the frequencies employed (20 kHz—10 MHz) are too low even for the excitation of rotational motion.

There are two forms of cavitation—stable and transient. Stable cavities are those which oscillate, often non-linearly, about some equilibrium size (R_0); such bubbles have an existence of many cycles. Transient cavities generally exist for less than a single acoustic cycle during which time they expand to at least double their initial size before collapsing violently into smaller bubbles (for further treatment of this see E below). It was once thought that the spectacular effects such as erosion, emulsification, molecular degradation, sonoluminescence, and sonochemical enhancement of reactivity were entirely attributable to the collapse of transient cavities. This is no longer believed to be true since the majority of visible bubbles generated in an acoustic field will oscillate in a stable manner and, because they are long-lived, the overall integrated effects of stable cavitation must be significant.

Stable bubbles are also capable of being transformed into transient cavities. For these reasons the study of the fate of stable bubbles has become important.

(i) *Transient Cavitation.* Transient cavitation bubbles are voids, or vapour-filled bubbles, produced using ultrasonic intensities in excess of 10 Wcm^{-2}. They exist for one, or at most a few acoustic cycles, expanding to a radius of at least twice their initial size before collapsing violently on compression and often disintegrating into smaller bubbles. (These smaller bubbles may act as nuclei for further bubbles, or if of sufficiently small radius, R, can simply dissolve into the bulk of the solution because of the very large pressure due to surface tension, $2\,\sigma/R$). During the lifetime of the transient bubble it is assumed that there is no time for any mass flow, by diffusion of permanent gas, into or out of the bubble, whereas evaporation and condensation of liquid is assumed to take place freely. There being no permanent gas to act as a cushion, the implosion leads to a very violent collapse. Theoretical considerations by Noltingk and Neppiras[8] and later by Flynn,[2] and separately by Neppiras,[7] assuming adiabatic collapse of the bubbles, allow for a calculation of the temperature ($T_{\text{max.}}$) (equation 11) and pressures ($P_{\text{max.}}$) (equation 12) within the bubble at the moment of collapse,

$$T_{\text{max.}} = T_0\left[\frac{P_{\text{m}}\,(\gamma - 1)}{P}\right] \tag{11}$$

$$P_{\text{max.}} = P\left[\frac{P_{\text{m}}\,(\gamma - 1)}{P}\right]^{\gamma/(\gamma - 1)} \tag{12}$$

where T_0 is the ambient (experimental) temperature, γ is the ratio of specific heats of the gas (or gas vapour) mixture, P is the pressure in the bubble at its maximum size and is usually assumed to be equal to the vapour pressure (P_{v}) of the liquid. [This assumption is a direct consequence of the initial assumption that transient bubbles grow without the influx of gas into the cavity. If gas does enter the cavity the value of $P\,(=P_{\text{v}} + P_{\text{g}})$ will depend upon the value of P_{g} when the bubble is at its maximum size.] P_{m} is the pressure in the liquid at the moment of transient collapse $(=P_{\text{h}} + P_{\text{a}})$.

The collapse time T for an empty bubble (equation 13)[30] is normally not longer than one fifth of the period of vibration and therefore P_{m} can be regarded as constant during the collapse.

$$T = 0.915\ R_{\text{m}}(\rho/P_{\text{m}})^{\frac{1}{2}} \tag{13}$$

An estimate of the temperature and pressure (equations 11 and 12) involved in the final phase of the implosion of a bubble containing nitrogen ($\gamma = 1.33$) in water at ambient temperature (20 °C) and ambient pressure (1 bar), provides values of 4 200 K and 975 bar. It is the existence of these very high temperatures within the

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[30] Lord Rayleigh, *Philos. Mag.*, 1917, **34**, 94.

bubble that have formed the basis for the explanation of radical production and sonoluminescence, whilst the release of the pressure, as a shock wave, is a factor which has been used to account for both increased chemical reactivity (due to increased molecular collision) and polymer degradation.

(ii) *Stable Cavitation.* We now turn our attention to stable cavitation, a phenomenon which, at one time, was not thought to be of much significance in terms of chemical effects. Stable bubbles are believed to contain mainly gas and some vapour and are produced at fairly low intensities (1—3 Wcm^{-2}), oscillating, often non-linearly, about some equilibrium size, for many acoustic cycles. The time-scale over which they exist is sufficiently long that mass diffusion of gas, as well as thermal diffusion, with consequent evaporation and condensation of the vapour, can occur, resulting in significant long-term effects. If the rates of mass transfer, across the gas–liquid interface, are not equal, it may result in bubble growth. The mechanism by which small microbubbles in the liquid (which are normally instantly dissolvable due to surface tension) grow, is termed rectified diffusion. In the expansion phase of the acoustic cycle gas diffuses from the liquid into the bubble, whilst in the compression phase, gas diffuses out of the bubble into the liquid. Since the interface area is greater in the expanded phase, the inward diffusion is greater, leading to an overall growth of the bubble. As the bubble grows the acoustical and environmental conditions of the medium will change, the medium becoming acoustically lossier and more compressible. The stable bubble may be transformed into a transient bubble and undergo collapse (see 2E below). The violence of collapse, however, will be less than that for a vapour-filled transient since the gas will cushion the implosion. The cavity will reduce to a minimum size $R_{\mathrm{min.}}$ during compression, after which it will expand to $R_{\mathrm{max.}}$ and subsequently oscillate between these extremes. On the other hand the bubbles may continue to grow during subsequent cycles until they are sufficiently bouyant to float to the surface and be expelled—this is the process of ultrasonic degassing.

Not all bubbles are capable of producing significant cavitational effects. The greatest coupling of the ultrasonic energy will occur, according to Minneart (equation 14),[31] when the natural resonance frequency (f_r) of a bubble is equal to the applied ultrasonic frequency.

$$f_r = \frac{1}{2\pi R_r}\left[\frac{3\gamma}{\rho}(P_h + 2\sigma/R_r)\right]^{\frac{1}{2}} \tag{14}$$

(R_r is the resonance radius of the bubble). For applied frequencies greater than the bubble's natural resonant frequency, oscillations will be complex. However, for applied frequencies less than the bubble's resonance frequency, collapse can occur (Figure 2).

As with transient cavitation, estimates have been made of the temperatures and pressures produced in stable bubbles as they oscillate in resonance with the applied

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[31] M. Minneart, *Philos. Mag.*, 1933, **16**, 235.

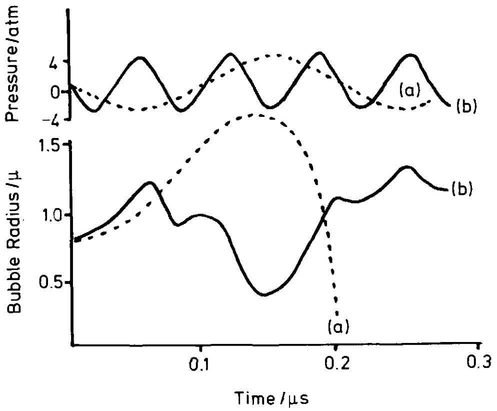

Figure 2 *Radius–time curves for air bubble in sonicated water at* (a) 5 MHz, (b) 15 MHz (ref. 7). $R_0 = 8 \times 10^{-5}$ cm; $P_A = 4$ bar; $P_h = 1$ bar; $f_r = 6.8$ MHz (ref. 31)

acoustic field. Griffing *et al.*[32] derived an expression (equation 15) for the ratio $T_0/T_{\text{max.}}$,

$$\frac{T_0}{T_{\text{max.}}} = \{1 + Q[(P_h/P_m)^{1/3\gamma} - 1] - 1\}^{3(\gamma-1)} \tag{15}$$

where Q is a damping factor equal to the ratio of the resonance amplitude to the static amplitude of vibration of the bubble and P_m ($= P_h + P_a$) is the peak pressure of the bubble. For a bubble containing a monatomic gas ($\gamma = 1.666$) and $P_m/P_h = 3.7$ (corresponding to an intensity of 2.3 Wcm^{-2}) and assuming a value of $Q = 2.5$, the $T_{\text{max.}}$ for the bubble is deduced to be 1 665 K.

Calculations[33] of the local pressures due to these resonance vibrations has resulted in values which exceed the hydrostatic pressure by a factor of 150 000. There is no doubt that the intense local strains in the vicinity of the resonating bubble are the cause of the many disruptive mechanical effects of sound.

D. Parameters Effecting Cavitation.—Given the differences in irradiation conditions (frequency, solvents, system vapour pressure, intensities, hydrostatic pressure) it is pertinent to discuss briefly how these parameters affect the distinct stages of acoustic cavitation: namely nucleation, bubble growth, and collapse. Since the dynamics of cavity growth and collapse are dependent upon local environment, one must also consider how cavitation in a homogeneous liquid is modified when it occurs at a liquid–solid interface, as for example in heterogeneous catalysis (see Part 2).

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[32] M. E. Fitzgerald, V. Griffing, and J. Sullivan, *J. Chem. Phys.*, 1956, **25**, 926.

[33] F. D. Smith, *Philos. Mag.*, 1935, **19**, 1147.

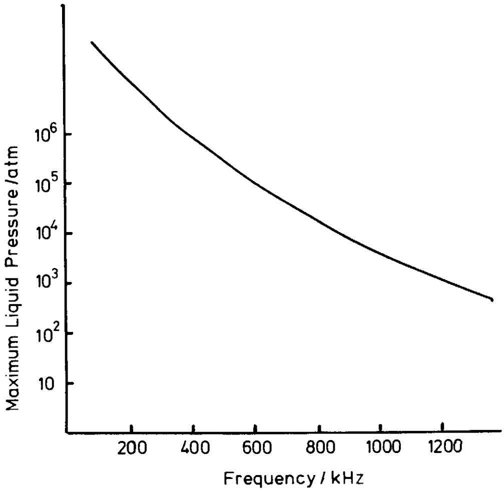

Figure 3 *Variation with frequency of maximum fluid pressure during collapse* (ref. 8). $R_0 = 3.2 \times 10^{-4}$ cm; $P_A = 4$ bar; *adiabatic conditions*

(i) *Frequency.* As the ultrasonic frequency is increased[8,34–36] the production of cavitation in liquids decreases. Various explanations[37] have been put forward to explain this observation. In qualitative terms it may be argued that at very high frequency, where the rarefaction (and compression) cycles are very short, the finite time required for the rarefaction cycle is too small to permit a bubble to grow to a size sufficient to cause disruption of the liquid.

On the other hand it can be argued that even if a bubble was produced during rarefaction, the time required to collapse that bubble may be longer than that available in the compression half-cycle. (Figure 3 shows the variation[8] of maximum fluid-pressure against frequency for constant pressure amplitude (P_A), and bubble radius).

Higher frequencies require more power for an equivalent amount of chemical work, since the higher rates of molecular motion at the higher frequencies result in greater power losses. Ten times more power is required to make water cavitate at 400 kHz than at 10 kHz, and it is for this reason that 20—50 kHz frequencies were generally chosen for cleaning purposes and have subsequently been found to be of value in sonochemistry.

(ii) *Solvent.* The formation of voids or vapour-filled microbubbles (cavities) in a

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[34] G. Muller and G. W. Willard, *J. Acoust. Soc. Am.*, 1948, **20**, 589.
[35] W. Gaertner, *J. Acoust. Soc. Am.*, 1954, **26**, 977.
[36] R. Esche, *Akust. Beih.*, 1952, **4**, 208.
[37] H. J. Eyring, *J. Chem. Phys.*, 1936, **4**, 283.

Table 1 *Sound pressure (P) producing cavitation in various liquids under a hydrostatic pressure of* 1 *atmosphere*

Liquid	η/Nsm^{-2} (25 °C)	P/atm
Castor oil	0.630	3.90
Olive oil	0.084	3.61
Corn oil	0.063	3.05
Linseed oil	0.038	2.36
CCl_4	0.001	1.75

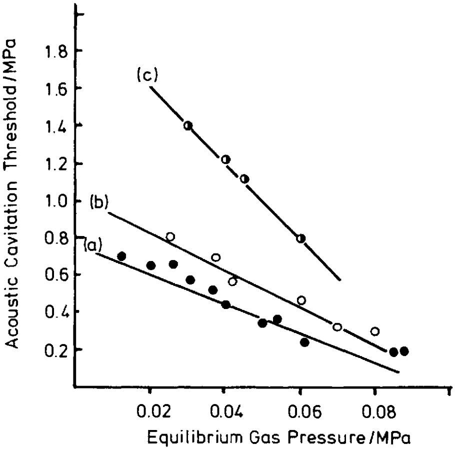

Figure 4 *Variation of acoustic cavitation threshold of water with dissolved gas content* (f = 38 kHz; T = 25 °C) (ref. 39). (a) *Distilled water;* (σ = 7.2 × 10^{-2} Nm^{-1}). (b) *Aqueous guar gum* (100 p.p.m.); σ = 6.2 × 10^{-2} Nm^{-1}. (c) *Aqueous photoflow* (80 p.p.m.); σ = 4.0 × 10^{-2} Nm^{-1}

liquid requires that the negative pressure in the rarefaction region must overcome the natural cohesive forces acting within the liquid and hence cavitation should be more difficult to produce in viscous liquids. Published data[38] indicate that such an effect, albeit small, does occur (Table 1).

Conversely, the use of solvents with low surface tensions should lead to a reduction in the cavitation threshold. However Crum,[39] using non-polar hydrophobic solids to vary the surface tension of distilled water, has observed, at constant gas content, that the cavitation threshold increases with a decrease in surface tension (Figure 4).

Solvents with high vapour pressure (P) undergo less intense cavitational effects. This is most easily demonstrated for the maximum temperature on implosion, (equation 12), since any increase in P leads to a decrease in $T_{\mathrm{max.}}$. The effect of $P_{\mathrm{max.}}$

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[38] L. Bergmann, 'Ultrasonics', G. Bell and Sons, 1938.
[39] L. A. Crum, *Appl. Sci. Res.*, 1982, **38**, 101.

is not so obvious at first glance. For ease of calulation, if it is assumed that γ remains constant (an incorrect assumption since γ will be lowered by the introduction of vapour into the bubble) and is equal to 1.33 (an air-filled bubble), then $P_{\max.} \propto P_m{}^4/P^2$. Thus as P (the solvent vapour pressure) increases, $P_{\max.}$ rapidly decreases and the bubble collapse is less violent.

(iii) *Temperature.* Increasing the ambient temperature[40–44] will raise the equilibrium vapour pressure of the medium and so lower both $T_{\max.}$ and $P_{\max.}$. However Rosenburg[45] observed that, in a number of liquids, the amount of aluminium eroded in a 8 kHz ultrasonic field increased as the temperature increased from −10 °C to 50 °C, and decreased (as expected) from 50 °C to 90 °C. The maximum (in erosion and hence cavitation intensity) is readily explained by assuming that as the temperature is increased the number of nuclei for cavitation is also increased. However, with continued increase in temperature, the decrease in surface tension and increase in vapour pressure (pressure within the cavity) results in a damping of the shock wave ($P_{\max.}$ decreases) when the cavity implodes.

A further factor which must be considered in cases where large numbers of cavitation bubbles are generated concurrently is the cushioning or dampening effect of these bubbles on the dissipation of ultrasonic energy from the source through the fluid.

(iv) *Gas Type and Content.* According to equations 11, 12, and 15, employing gases with large γ values will provide for larger sonochemical effects from gas-filled bubbles. For this reason monoatomic gases (He, Ar, Ne) are used in preference to diatomics (N_2, air, O_2). It must be remembered that this dependence on γ is a simplistic view, since the extent of the sonochemical effects will also depend upon the thermal conductivity of the gas:[46] the greater the thermal conduction of the gas, the more heat (formed in the bubble during collapse) will be dissipated to the

Table 2 *Rate of formation of free chlorine by irradiation of water containing* CCl_4 *in relation to the nature of the saturating gas*

Gas	*Reaction rate* (mM/min)	γ	*Thermal conductivity* (10^{-2} Wm^{-1} K^{-1})
Argon	0.074	1.66	1.73
Neon	0.058	1.66	4.72
Helium	0.049	1.66	14.30
Oxygen	0.047	1.39	1.64
Nitrogen	0.045	1.40	2.52
Carbon monoxide	0.028	1.43	2.72

[40] W. Connolly and F. E. Fox, *J. Acoust. Soc. Am.*, 1954, **26**, 843.
[41] F. G. Blake, *Phys. Rev.*, 1949, **75**, 1313.
[42] J. P. Horton, *J. Acoust. Soc. Am.*, 1953, **25**, 480.
[43] A. S. Bebchuk, *Akust. Zh.*, 1957, **3**, 90.
[44] W. C. Schumb, H. Peters, and L. H. Mulligan, *Metals and Alloys*, 1937, **5**, 126.
[45] L. Rosenberg, *Ultrasonics News*, 1960, **4**, 4.
[46] F. R. Young, *J. Acoust. Soc. Am.*, 1976, **60**, 100.

surrounding liquid, effectively decreasing $T_{max.}$. Unfortunately a strict correlation between conductivity and effect has not been observed (Table 2).

Increasing the gas content of a liquid leads to a lowering of both the cavitational threshold (Figure 4) and the intensity of the shock wave released on the collapse of the bubble. The threshold is lowered as a consequence of the increased number of gas nuclei (or weak spots) present in the liquid, whilst the cavitational intensity is decreased as a result of the greater 'cushioning' effect in the microbubble.

The latter point may be deduced semi-quantitatively from a consideration of equations 11 and 12. In the strictest sense, P should be replaced by P_{vg} ($= P_v + P_g$), and increasing the gas content of the liquid increases P_g, and hence P_{vg} increases, to provide for decreases in $P_{max.}$ and $T_{max.}$.

It might be anticipated that employing gases with increased solubility would also reduce both the threshold intensity (by virtue of providing a large number of nuclei in the solvent) and the intensity of cavitation. Indeed there is a definite correlation[47–49] between gas solubility and cavitational intensity. The greater the solubility of the gas, the greater the amount which penetrates into the cavitation bubble, and the smaller the intensity of the shock wave created on bubble collapse. A further factor affecting the intensity of collapse may be that the more soluble the gas the more likely it is to redissolve in the medium during the compression phase of the acoustic cycle.

(v) *External (Applied) Pressure.* Increasing the external pressure (P_h) leads to both an increase in the cavitation threshold and the intensity of cavity collapse.

Qualitatively it can be assumed that there will no longer be a resultant negative phase of the sound (since $P_h - P_a > 0$) and so cavitation cannot occur. Clearly a sufficiently large increase in the intensity I of the applied ultrasonic field can produce cavitation even at high overpressures since it will generate larger values of P_a ($I \propto P_A^2$; $P_a = P_A \sin 2\pi ft$) making $P_h - P_a < 0$.

In that P_m (the pressure in the bubble at the moment of collapse) is approximately $P_h + P_a$, increasing the value of P_h will, according to equations 11, 12, and 13, lead to a more rapid and violent collapse.

The increase in overpressure may even allow cavitation to occur at higher ultrasonic frequencies, since the time for collapse, T, is reduced under these conditions (equation 13).

The effect of increasing P_h is somewhat more difficult to visualize for stable bubbles, but strangely it leads to a decrease in $T_{max.}$.

(vi) *Intensity.* In general an increase in intensity (I) will provide for an increase in the sonochemical effects. Since $I \propto P_A^2$, the maximum pressures and temperatures within a transient collapse will increase according to equations 11 and 12 ($P_m \approx P_h + P_A$). However it must be realized that intensity cannot be increased indefinitely. With increase in the pressure amplitude (P_A) the bubble may grow so

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[47] H. W. W. Brett and H. H. Jellinek, *J. Polym. Sci.*, 1954, **13**, 441.

[48] R. O. Prudhomme and P. Graber, *J. Chim. Phys.*, 1949, **46**, 667.

[49] R. O. Prudhomme, *J. Chim. Phys.*, 1950, **47**, 795.

large on rarefaction ($R_{\max.}$) that the time available for collapse [$T = 0.915\, R_{\max.} (\rho/P_m)^{\frac{1}{2}}$] is insufficient (see 2E below).

For stable bubbles the quantitative effects of increasing I are not easily visualized. Increasing I leads to an increase in P_A (and hence P_m) such that there is a decrease in P_h/P_m. The quantity $Q(P_h/P_m) - 1$ becomes more negative and the right hand side of equation 15 smaller *i.e.* $T_{\max.}$ increases.

E. Cavitation Bubble Dynamics.—The fundamental dynamical problem of acoustic cavitation is the determination of the pressure and velocity fields in the two-fold medium (gas–liquid), together with the motion of the bubble wall, when under the influence of a time-dependent (acoustic) pressure.

By ignoring mass and heat-flow across the interface, Noltingk and Neppiras[8,9] were able to show that the motion of the cavity wall for a gas-filled bubble may be given by equation 16,

$$R\ddot{R} + \frac{3}{2}(\dot{R})^2 = \frac{1}{\rho_0}\left[(P_0 + 2\sigma/R_0)(R_0/R)^{3\gamma} - \frac{2\sigma}{R} - (P_0 - P_A \sin 2\pi f t)\right] \quad (16)$$

where R is the bubble radius at some time t, R_0 is the equilibrium bubble radius, P_0 is the ambient pressure, $\dot{R}$ is the bubble wall velocity, and $\ddot{R}$ is the bubble wall acceleration.

This equation adequately describes the motion of stable bubbles over several cycles but it fails for transient bubbles where the bubble wall velocity exceeds $\frac{1}{5}$ of the velocity of sound. Writing $R = R_0 + r$ and substituting in equation 16 yields equation 17.

$$\ddot{r} + \omega^2{}_r\, r = \frac{P_A}{\rho R_0} \sin \omega_r t \quad (17)$$

Where ω_r is the resonance frequency given by equation 18.

$$\omega_r{}^2 = \frac{1}{\rho R_0{}^2}\left[\,{}^3\gamma\,(P_h + 2\sigma/R_0 - P_v) - 2\sigma/R_0 - \frac{4\eta^2}{\rho R_0{}^2}\right] \quad (18)$$

Neglecting the effects of viscosity and solvent vapour pressure, equation 18 reduces to equation 19 (for large bubbles) and equation 20 (for small bubbles).

$$\omega_r{}^2 = \frac{3\gamma P_h}{\rho R_0{}^2} \quad (19)$$

$$\omega_r{}^2 = 2\,(3\gamma - 1)\sigma/\rho R_0{}^3 \quad (20)$$

It is possible to solve equation 17 (for which equation 21 is the general solution) and generate various $r - t$ curves for given P_A and R_0 values.

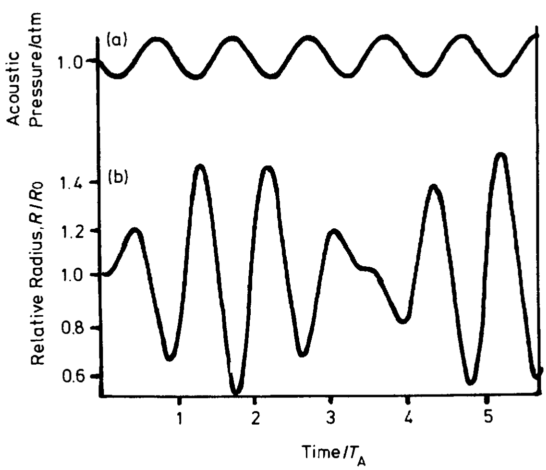

Figure 5 *Radius–time curve for a cavity insonated below resonance frequency.* $R_0 = 2.6 \times 10^{-3}$ cm; $P_A = 0.333$ bar; $P_h = 1$ bar. (a) *applied frequency* (83.4 kHz). (b) *Relative radius of bubble*

$$r = \frac{P_A}{\rho R_0(\omega_r^2 - \omega^2)}\left[\sin \omega t - \frac{\omega}{\omega_r} \sin \omega_r t\right] \tag{21}$$

For small P_A/P_h ratios, with $R_0 \simeq R_r$ (the resonant bubble radius), oscillations take place at approximately the excitation frequency (Figure 5). For $R_0 > R_r$ bubble oscillation has a strong component of its own natural resonant frequency (Figure 6). However, for very small bubbles, $R_0 \ll R_r$, transient conditions are attained as P_A increases beyond P_h (Figure 7, $P_A = 4$ and 10 atm). It may be that as P_A is further increased the bubble grows so large in the tension phase that it has insufficient time to collapse before the end of the pressure cycle and collapse occurs at the end of the second positive peak (Figure 7, $P_A = 25, 100, 200$ atm). Eventually if $P_A/P_h >>> 1$ the bubble may never undergo transient collapse.

3 Relaxation Phenomena

Whenever a sinusoidal sound wave propagates through a liquid it induces oscillation of the volume occupied by the molecules and thereby increases, momentarily, the mean translational energy of the molecules. Although, in principle, this translational energy can be transferred *in toto* to other molecules by elastic collisions, and so increase their translational energy, in reality energy losses will occur due to (*a*) viscosity effects (motion of one molecule relative to another in the liquid) and (*b*) thermal effects (heat transfer from regions of high to low translational energy). It is expected therefore that the energy of the wave (*I*) will be attenuated as it passes through the medium.[16] The extent of

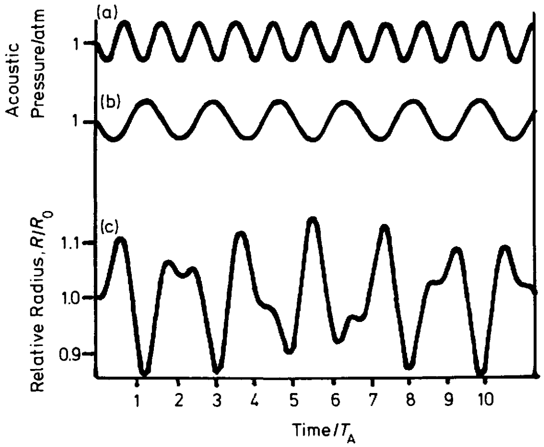

Figure 6 *Radius–time curve for bubble for a cavity insonated above resonance.* R_0 = 2.6 × 10^{-3} cm; P_A = 0.333 bar; P_h = 1 bar. (a) *Applied frequency* (83.4 kHz). (b) *Resonance frequency of bubble* (ref. 31). (c) *Relative radius of bubble*

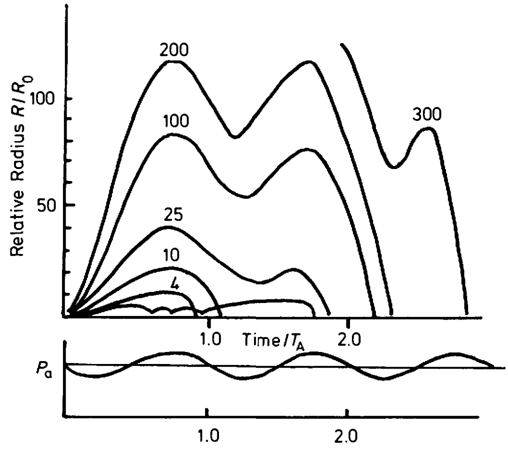

Figure 7 *Radius–time curves for an insonated air bubble in water* (ref. 7). R_0 = 10^{-4} cm; f = 500 kHz. *The numbers on the curves refer to the ratio* P_A/P_h. *Time is measured in units of the period* (T_A) *of the applied acoustic field*

attenuation has already been discussed in General Principles and is given by equations 6 and 7.

Since for any given liquid η_s, η_b, γ, k', and C_p are constant at constant temperature, the value, α/f^2 should be independent of the experimental frequency employed to determine α. Experimentally this is not the case for many liquid systems with α/f^2 decreasing with increase in frequency. This is due to the fact that the total energy content of a liquid is not restricted solely to translational energy, but is the sum of many components including rotational, vibrational, molecular conformational, and structural forms. It is the coupling of the translational energy with these other energy forms which leads to the absorption of sound in excess of that deduced from equation 7, and to the non-constancy of α/f^2 with increasing frequency. The occurrence of this excess absorption is most easily illustrated by considering the fate of a vibrationally excited molecule, produced as a result of the energy interchange between the translation and vibrational modes. Provided the vibrationally excited molecules can be deactivated (by inelastic collisions with other molecules) and returned to the ground state in a time period which is shorter than the period of sound oscillation, the energy will be returned to the system in phase with the sound wave, and no net loss will be observed in the sound energy per cycle. As the frequency of the sound wave increases (*i.e.* the time period decreases) the return of energy will become increasingly out of phase with the wave and will appear as an energy loss. Ultimately if the period of the wave is decreased sufficiently (*i.e.* very high frequency ultrasound is applied) a situation will be reached when the perturbation of translational energy occurs so fast that there is no time available for exchange with the other energy forms. Between these two extremes of high and low frequency there exists a condition when the frequency of the fluctuation induced by the sound wave is comparable with the time required for energy exchange. The time lag between the excitation and de-excitation processes is observed as an acoustic relaxation. Since detailed discussions of the theoretical basis of acoustic relaxation have been published elsewhere[50,51] it is sufficient to report here that any relaxation is observable[52] as either an increase in the velocity–frequency curve, a peak in the $\alpha\lambda$-frequency curve, or a decrease[53,54] in the α/f^2 *vs.* frequency curve. For the latter case the experimental data may be represented by equation 22,

$$\frac{\alpha}{f^2} = \frac{A}{[1 + (f/f_r)^2]} + B \tag{22}$$

where f_r is the relaxation frequency, A is the relaxation amplitude, and B is the high frequency residual absorption, which is frequency independent.

If more than one relaxation process (*i.e.* n processes) can occur, equation 22 is more accurately written as equation 23:

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[50] R. A. Pethrick, *J. Macromol. Sci. Revs. Macromol. Chem.*, 1973, **9**, 91.

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[54] R. A. Pethrick, *Sci. Prog.*, 1970, **58**, 563.

[54a] H. O. Kneser, *Ann. Phys.*, 1938, **32**, 277.

$$\frac{\alpha}{f^2} = \sum_{i=i}^{i=n} \frac{Ai}{(1 + (f/f_i)^2)} + B \qquad (23)$$

Absorption studies have proved important in the investigation of the structural aspects of liquids. Basically liquids may be classified into three groups according to their sound absorption properties.[53] The first in which absorption only slightly exceeds the classical value (equation 7); the second, containing the majority of organic liquids, show large excess absorptions ($\alpha/\alpha_{\text{class}}$ = 3—400).[55] These large absorptions have been attributed to thermal relaxation due to the slow interchange of the internal and external energies. The third group, containing associated liquids, have $\alpha/\alpha_{\text{class}}$ values of approximately 3. The excess sound absorption here is thought to be due to structural, rather than thermal relaxations, since the liquids have negative temperature coefficients of absorption.[56]

The excess sound absorption characteristics of various binary aqueous mixtures,[57–61] especially alcohol–water mixtures, have attracted a great deal of attention.[62–74] This excess absorption, for a given experimental frequency varies greatly from one alcohol to another,[56] depends strongly on the composition of the mixture, and decreases rapidly with rising temperature. With a change in the experimental frequency, the magnitude of the peak in the sound absorption concentration (PSAC) decreases and moves to a lower mole fraction of the non-aqueous component [75] (Figure 8). For all binary systems the existence of a PSAC is interpreted in terms of changes in the H-bonding (*i.e.* solute–solvent interaction), between like and unlike molecules (AA + WW = 2AW), the transfer equilibrium being displaced by the compression of the acoustic wave. Such displacement is opposed by potential energy barriers, and the molecular translations and reorientations called upon to occur within each half cycle introduce a relaxation which is the source of the excess absorption.

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[75] Y. Shindo and M. Nanbeutal. *Acustica*, 1981, **48**. 186.

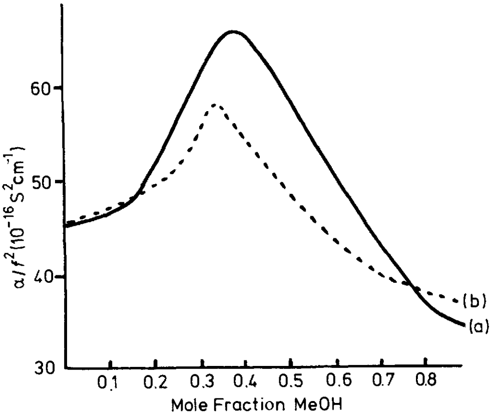

Figure 8 *Variation of absorption* (α/f^2) *in* MeOH–H$_2$O *mixtures at* 5 °C (ref. 70). (a) 10 MHz. (b) 200 MHz

Ultrasonic velocity measurements[76–79] have also been used to study molecular structure[80–82] and interaction.[82–84] At any temperature the ultrasonic relaxation, arising from the perturbation of the equilibrium:

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}$$

where A and B are the two conformers, is accompanied by a variation in velocity according to (equation 24), where C is the velocity at frequency f, C_0 is the velocity at low frequency ($f \ll f_r$), C_∞ is the velocity at high frequency ($f \gg f_r$) and f_r is the relaxation frequency.

$$\frac{C_\infty{}^2 - C^2}{C_\infty{}^2 - C_0{}^2} = \frac{1}{1 + (f/f_r)^2} \tag{24}$$

Together with ultrasonic absorption[63,85–88] they afford a means of calculating

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[88] J. Emery and S. Gasse, *Acustica*, 1979. **43**. 206.

both the kinetic[89,90] (k_f and k_b) and thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0, ΔV^0) for structural[90] and conformational[91] change.

Relaxation in polymers may be divided into processes involving segmental motion of the backbone or side groups (independent of RMM) and overall co-operative motion of the whole backbone (RMM-dependent). Prior to the use of acoustic relaxation techniques[52] the study of segmental (and side-chain) motion was restricted mainly to dielectric relaxation studies on polar molecules (dielectric studies are unable to provide information regarding motion of a non-polar molecule), with investigation of whole chain movements[92] restricted to a study of the frequency-dependence of the shear viscosity of the polymer solution.[93,94]

Most experimental investigations of polymers use frequencies in the range 100 kHz—500 MHz, with the attenuation determined as a function of temperature, frequency, polymer concentration, and relative molar mass. Equation 23[95,96] is fitted, reiteratively, by computer to the experimental data in the frequency range investigated and the best fit * values of A_1, f_{r1}, and B are obtained by assuming that single, double, or multiple relaxation phenomena were involved.

In general the dynamic spectrum of a polymer may be divided into two parts. The first is a low-frequency process, with a relaxation time ($T_r = \frac{1}{2}\pi f_r$) which is molecular weight-dependent[97–100] and an amplitude (A) which correlates with the viscosity of the solution. The second is a high-frequency process which is molecular weight-dependent for low molecular weights and independent for higher molecular weights.[101–102]

Single relaxation models[103] (*i.e.* one value of A and f_r) have been interpreted in terms of segmental motion of the backbone, whereas two relaxation models (A_1 and f_{r1}: A_2 and f_{r2}) have been interpreted in terms of motion of the backbone and the side-groups. For example, the data for several polyvinyl esters[104–107] have

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* Error of fit is given by $\sum\left(\frac{(\alpha/f^2)_{\text{obs.}} - (\alpha/f^2)_{\text{calc.}}}{(\alpha/f^2)_{\text{obs.}}}\right)$

[89] S. Kato, H. Nomura, R. Zielinski, and S. Ikeda, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 707.

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been found to fit a double relaxation model yielding two values of A and f_r. The low frequency f_r value (3—8 MHz), being almost independent of the length of the side chain, was interpreted as being due to motion of the backbone. The high frequency f_r value (60—150 MHz) decreased significantly with increase in the length of the side-chain and was associated with reorientational motion of the side-chain. A study of the dependence of the acoustic absorption coefficient (α) on polymer concentration (c) has in some cases yielded[99,101,108,109] breaks in the α *vs.* c curves. These break points have been ascribed[110] to the increased polymer–polymer interactions which occur with the onset of chain entanglement[111] in the solution.

As with pure liquids, studies of the dependence of attenuation with temperature has allowed a determination of the various thermodynamic parameters (ΔG^0, ΔH^0, ΔV^0, ΔS^0) associated with the various conformational changes,[112] for example, the activation energy for polystyrene in CCl_4[101] obtained by plotting the acoustic relaxation time against $1/T$ is in good agreement ($\sim$27.3 kJmol^{-1}) with the values obtained from dielectric studies[113] in poly(*p*-chlorostyrene) ($\sim$21 kJmol^{-1}) and n.m.r.[114] measurements in the same solvent.

The energies associated with the conformational change, however, depend not only on the nature of the group attached to the backbone, but also upon the configuration (*i.e.* tacticity[115]) of the polymer. Certain configurations will have conformations which require lower activation energies to achieve a particular spacial arrangement than do others. For example, the acoustic energy difference between the conformational states of poly(α-methylstyrene) (PMS), when predominantly syndiotactic, is greater than when the polymer is predominantly isotactic. This PMS value (8.3 kJ mol^{-1}) is also greater than that for the less-hindered polystyrene chain (5.4 kJ mol^{-1}). For polymethyl methacrylate,[116] the energy differences for syndiotactic, atactic, and isotactic are 6.3, 6.3, and 3.7 kJ mol^{-1} respectively. Interestingly, the chains with the lowest energy difference are also those for which the solid polymer has the lowest glass transition temperature (T_g). Indeed the Gibbs–Dimarzio energies calculated[117] from T_g values bear a close resemblance to the acoustic segmental conformational energies. Changes in the tacticity of the polymer also appear to have a marked influence on both the position and amplitude of the variation of the absorption coefficient (α) with frequency.[116] More recently[118] ultrasonic attenuation has been used to follow the progress of the emulsion polymerization of polyvinyl acetate.

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[113] W. H. Stockmayer, H. Yu, and J. E. Davis, *Polym. Preprints*, 1963, **4**, 132.

[114] D. W. McCall and F. A. Borey, *J. Polym. Sci.*, 1960, **45**, 530.

[115] J. H. Dunbar, A. M. North, R. A. Pethrick, and D. B. Steinhauer, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 1478.

[116] C. Tondre and R. Cerf, *J. Chem. Phys.*, 1968, **65**, 1105.

[117] R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, 1966, **44**, 3054.

[118] P. Hauptmann, F. Dinger, and R. Sauberlich, *Polymer*, 1985, **26**, 1741.

Polyelectrolytes, combining the properties of polymers (chain flexibility) with those of electrolytes (strong electrostatic interaction) have also been investigated using ultrasonic relaxation methods.[86,102] Because of the many processes which, theoretically, could give rise to excess ultrasonic absorption, *e.g.* segmental motion of backbone and side groups, solvation, proton transfer, and ion-pair formation, caution must be exercised in assigning the relaxations to a particular process.

4 Kinetics

For many chemical reactions the application of high power ultrasound has led to substantial improvements in both the reaction rate and product yield. The question as to the precise origin of these enhancements has not been fully resolved. The reactions must be the result of one or other (or possibly a combination) of the following:

(*a*) reaction in the actual cavitation bubble,[119–124] within which there are very high temperatures and pressures;
(*b*) reaction as a result of secondary reactions[125–127] taking place at the gas–liquid interface of the bubbles;
(*c*) reaction as a result of the enormous pressures released on bubble collapse.[128–130]

What is certain is that all the above are consequences of cavitation. Despite the many experimental studies[14,131] in which ultrasonic chemical reactions have been investigated, few[119–124,129,130,132–139] have received any detailed kinetic study of the effects of variations in irradiation frequency or intensity, the type of gas in the system or its concentration, or the solvent type and its solvent vapour pressure. Most have been investigations of the oxidation–reduction[125,127,140] reactions of

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[119] K. S. Suslick, P. F. Schubert, and J. W. Goodale, *IEEE Ultrasound Symp.*, 1981, 612.
[120] K. S. Suslick, J. J. Gawienowski, P. F. Schubert, and H. H. Wang, *J. Phys. Chem.*, 1983, **87**, 2299.
[121] K. S. Suslick, J. W. Goodale, and H. H. Wang, *J. Am. Chem. Soc.*, 1983, **105**, 5781.
[122] K. S. Suslick, J. J. Gawienowski, P. F. Schubert, and H. H. Wang, *Ultrasonics*, 1984, **22**, 33.
[123] D. J. Donaldson, M. D. Farrington, and P. Kruus, *J. Phys. Chem.*, 1979, **83**, 3130.
[124] P. Kruus and T. J. Patraboy, *J. Phys. Chem.*, 1985, **89**, 3379.
[125] A. Weissler, *J. Am. Chem. Soc.*, 1958, **81**, 1077.
[126] A. Henglein and C. Kormann, *Int. J. Rad. Biol.*, 1985, **48**, 251.
[127] E. J. Hart and A. Henglein, *J. Phys. Chem.*, 1986, **90**, 5992; 1986, **90**, 5989.
[128] M. S. Doulah, *Ind. Eng. Chem., Fundam.*, 1979, **18**, 76.
[129] E. C. Couppis and G. E. Klinzing, *AIChE J.*, 1974, **20**, 485.
[130] J. W. Chen and W. M. Kalback, *Ind. Eng. Chem., Fundam.*, 1967, **6**, 175.
[131] A. Weissler, *J. Acoust. Soc. Am.*, 1953, **25**, 651.
[132] S. Folger and D. Barnes, *Ind. Eng. Chem., Fundam.*, 1968, **7**, 222.
[133] T. J. Mason and J. P. Lorimer, *J. Chem. Soc., Chem. Commun.*, 1980, 1135.
[134] T. J. Mason, J. P. Lorimer, and B. P. Mistry, *Tetrahedron Lett.*, 1982, **23**, 5563; 1983, **24**, 4371.
[135] T. J. Mason, J. P. Lorimer, and B. P. Mistry, *Tetrahedron*, 1985, **26**, 5201.
[136] T. J. Mason, J. P. Lorimer, and B. P. Mistry, 'Ultrasonics International 85, Proceedings', Butterworth, U.K., 1985, 839.
[137] T. J. Mason, J. P. Lorimer, and B. P. Mistry, *J. Chem. Soc., Chem. Commun.*, 1986, 611.
[138] T. J. Mason and J. P. Lorimer, unpublished work.
[139] S. Witekowa, *Acta Chim. Acad. Sci. Hung.*, 1972, **17**, 97.

aqueous solution and have been concerned with mechanistic[32,125,126,141–145] rather than kinetic[146] aspects.

In 1950 Miller[140] studied the oxidation of air-saturated Fe^{2+} ions to Fe^{3+} ions using ultrasound of frequency 500 kHz. The Fe^{3+} yield was found to be dependent upon the length of insonation for up to 10 minutes duration, beyond this time non-linearity of yield was observed. Miller concluded that the oxidation reaction was an indirect process, due to the reactive HO• radical fragments produced from water (equation 25) and that the non-linearity of yield beyond 10 minutes was due to degassing of the solution.

$$H_2O \longrightarrow H\cdot + \cdot OH \qquad (25)$$

Weissler[125] using a frequency of 400 kHz ($I = 2.5\ \mathrm{W\,cm^{-2}}$) investigated the effect of volatile scavengers (allylthiourea, acrylamide, and formic acid) on the sonochemical yield of hydrogen peroxide in oxygen- and argon-saturated aqueous solutions. The observation that formic acid proved to be a less efficient scavenger than either acrylamide or allylthiourea was unexpected since, being more volatile, it ought to find it easier to enter the vapour in the microbubble. From these experiments it was inferred that radical recombination to yield H_2O_2 took place partly in the liquid phase. Although this view was supported by Henglein[125,126] it was in contrast to the findings of Pecht[141] who found that whereas the non-volatile HO• scavengers, thallous and formate ions, did not affect the yield of H_2O_2, a number of different volatile organic solutes lowered the yield of H_2O_2. The inference was that radical recombination took place in the bubble phase. The presence of HO• radical has been established by Parke and Taylor[147] who produced *ortho*, *meta*, and *para* ($o > p > m$) hydroxybenzoic acid on irradiating air-, oxygen-, or nitrogen-saturated solutions of benzoic acid at 500, 1 000, and 2 000 kHz ($I =$ 1.2 to 4.1 W $\mathrm{cm^{-2}}$). The authors also reported that hydroxylation took place for toluene, nitrobenzene, and phenol, though not for benzene itself.

Anbar and Pecht[148] also showed that when deuterated formate ions were sonolysed in aqueous solutions, HD was produced indicating that H• atoms were formed during the sonolysis process. Henglein studied the sonolysis of water in the presence of D_2 as a scavenger and observed that the proportion of HD increased with the amount of D_2 in the system, thereby indicating the presence of H• radicals. At low concentrations of D_2, HOD was observed as a consequence of the scavenging of HO• radicals.

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[140] N. Miller, *J. Chem. Soc., Faraday Trans.*, 1950, **46**, 546.
[141] M. Anbar and I. Pecht, *J. Phys. Chem.*, 1964, **68**, 352.
[142] C. H. Fischer, E. J. Hart, and A. Henglein, *J. Phys. Chem.*, 1986, **90**, 222.
[143] A. Henglein and C. H. Fischer, *Ber. Bunsenges Phys. Chem.*, 1984, **88**, 1196.
[144] A. Henglein and R. Schultz, *Z. Naturforsch.*, 1953, **8**, 277.
[145] A. Henglein, *Naturwissenschaften*, 1956, **43**, 277.
[145a] P. Riesz and S. Rustgi, *Radiat. Phys. Chem.*, 1979, **13**, 21.
[145b] H. S. Frank and D. G. J. Ives, *J. Chem. Soc., Quart. Rev.*, 1966, **20**, 1.
[146] M. A. Margulis, *Soviet Physics–Acoustics*, 1971, **16**, 361.
[147] A. V. Parke and D. Taylor, *J. Chem. Soc.*, 1956, 4442.
[148] M. Anbar and I. Pecht, *J. Phys. Chem.*, 1964, **68**, 1460.

Recently Henglein[126,127] has extended his earlier investigations on the effect of organic additives[144] and gas concentration and type[145] on the sonochemical yields of iodine and hydrogen peroxide from aqueous iodide solutions. Using an irradiation frequency of 300 kHz, Henglein[127] observed that the yield of H_2O_2 was at a maximum when the solution was saturated with a 30—70 mixture of O_2/Ar. The increase in peroxide concentration with increase in oxygen content was explained in terms of suppression of the combination reaction (26) by reaction (27), with subsequent reaction (28) to yield H_2O_2, in addition to that formed by (29).

$$H\cdot + \cdot OH \longrightarrow H_2O \tag{26}$$

$$H\cdot + O_2 \longrightarrow HO_2\cdot \tag{27}$$

$$HO_2\cdot + HO_2\cdot \longrightarrow H_2O_2 + O_2 \tag{28}$$

$$HO\cdot + \cdot OH \longrightarrow H_2O_2 \tag{29}$$

Henglein[126] has also been able to conclude, from scavenging experiments with a variety of organic solutes, that although a similarity exists between sonolysis and radiolysis, radiation studies do not explicitly predict the efficiency of a scavenger.

More recently Riesz *et al.*,[149] using spin-trap techniques in conjunction with e.s.r., have provided direct and conclusive evidence for the formation of H· and HO· radicals by the sonolysis of aqueous solutions.

Of the few groups who have addressed themselves to detailed kinetic studies, most have considered reactions in aqueous media. Several[128–130,132] have investigated the effect of ultrasound on the acid-catalysed hydrolysis of methyl ethanoate. The increased reaction rates (4—10%) have been attributed to different aspects of cavitation. Folger and Barnes[132] (using 27.5 kHz) considered that the increased reaction rates resulted from temperature effects associated with the microbubbles, whereas Couppis and Klinzing[129] (at 540 kHz and 780 kHz) and Chen and Kalback[130] (at 23 kHz) attributed them to increased molecular motion due to the presence of the pressure gradient associated with the bubble. More recently Doulah[128] has provided evidence to suggest that they are a result of increased diffusion within the reacting system. Working at several different experimental intensities Couppis and Klinzing,[129] and separately Folger and Barnes,[132] have also observed an optimum power (at a given temperature) at which a maximum rate constant was obtained. Similar dependencies have been observed by other workers from product studies.[150–153] Couppis and Klinzing[129] have also

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[149] K. Makino, M. M. Mossoba, and P. Riesz, *J. Am. Chem. Soc.*, 1982, **104**, 3537; *ibid.*, *J. Phys. Chem.*, 1983, **87**, 1369; *ibid.*, *Radiat. Res.*, 1983, **96**, 416.

[150] C. Bondy and K. Sollner, *J. Chem. Soc., Faraday Trans.*, 1936, **32**, 556.

[151] S. Kusano, *Tohoku J. Exp. Med.*, 1936, **30**, 175.

[152] O. Nomoto and S. Okui, *J. Phys. Soc. Jpn.*, 1948, **3**, 47.

[153] N. Sata and K. Nakasima, *Bull. Chem. Soc. Jpn.*, 1943, **18**, 220.

demonstrated that the reaction rate constant decreases with an increase in frequency. Both observations agree with the theoretical predictions outlined in General Principles above.

The effect of ultrasonic irradiation on the hydrolysis of 2-chloro-2-methylpropane in aqueous alcoholic media has been studied in detail by Lorimer and Mason.[133–137] Initial studies[133] of the reaction in aqueous ethanol as solvent at 25 °C using a cleaning bath revealed modest rate enhancements (up to twofold) with the larger values obtained in the more alcoholic media.[133,134] Using a cuphorn device (at 20 kHz), capable of operating at different powers, and by studying the reaction at a variety of different temperatures and solvent compositions, the authors observed that the ultrasonic rate enhancement (up to 20 fold) increased with increase in the alcohol content and a decrease in the reaction temperature,[135] that there existed a maximum[136] in rate enhancement at an ethanol–water composition closely coincident with that thought to be the structural maximum[64,141] for such systems, and that there existed an optimum power[136] at which a maximum rate enhancement occurred. The authors failed to obtain a simple relationship between rate enhancement and solvent vapour pressure.[136]

Witekowa[139] has studied the effects of frequency, acoustic intensity, temperature, and nature of the gas on a wide variety of aqueous redox reactions. Of the twelve reactions investigated eight were found to proceed, under irradiation, by zero order kinetics, an observation noted by Lorimer and Mason for the aqueous polymerization of *N*-vinyl pyrrolidinone.[138] Although the redox reaction rates were found to be independent of the frequency employed (15, 20, 25, 500, 800, 1 000, 2 100 kHz), maxima were observed when plotted as functions of temperature and intensity as predicted by theory (see General Principles). In the presence of various gases the authors observed the following sequence of rate constants: $k_{\mathrm{air}} > k_{\mathrm{oxygen}} > k_{\mathrm{argon}} > k_{\mathrm{nitrogen}}$. The larger rate constants in the presence of air and O_2 were explained in terms of the production of the oxidizing radical, $HO_2\cdot$ (equation 27). Several other investigations,[154–156] though not so detailed, have also been reported.

Kristol[154] has reported ultrasonically (20 kHz) induced rate enhancements for the hydrolysis of the 4-nitrophenyl esters of a number of aliphatic carboxylic acids. The rate enhancements at 35 °C were all in the range of 14—15% and were independent of the size of the alkyl substituent (R = Me, Et, Pr^{i}, Bu^{t}) on the carboxylic acid. The authors concluded that the rate enhancements could not be due simply to an increase in the bulk temperature of the system (due to ultrasonic heating effect). This was based on the large differences in the energy of activation for the hydrolysis of each of the substrates which would result in considerable variations in rate enhancements if a simple heating effect alone were responsible for the enhancement. The rate enhancements were thought to

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[154] D. S. Kristol, H. Klotz, and R. C. Parker, *Tetrahedron Lett.*, 1981, **22**, 907.
[155] V. Griffing, *J. Chem. Phys.*, 1952, **20**, 939.
[156] W. C. Schumb and E. S. Rittner, *J. Am. Chem. Soc.*. 1940, **62**, 3416.

be most probably due to the intense localized pressure increase as a result of bubble collapse.

Griffing *et al.*[155] studied the effect of high frequency ultrasound (2 MHz, $I = 6.5$ W cm^{-2}) on the acid-catalysed inversion of sucrose and observed no detectable rate enhancements, even though the solution visibly cavitated. The particular reaction was chosen since it proceeds at a reasonable rate at room temperature and has a high temperature coefficient—for this reaction a rise in temperature of 10 °C brings about a threefold increase in rate. Since sucrose has a negligible vapour pressure, hydrolysis must take place in the liquid phase so that the lack of enhancement with ultrasound was interpreted as indicating that there was no appreciable heating at the bubble–liquid interface.

Although the first example of sonolysis in a non-aqueous solvent, the decolorization of diphenylpicrylhydracyl (DPPH) radical in methanol, was reported in 1953,[157] it took some 20 years to realize that cavitation could successfully be supported in organic solvents.[158] The lack of progress in this area was the result of a combination of two factors (i) the failure to observe, in organic media, certain sonochemical reactions which occurred in water and (ii) the knowledge that the addition of organic solutes supressed sonochemically induced aqueous reactions. In hindsight it should have been argued that the lack of success was due to the higher vapour pressures of the organic liquids which, in turn, led to substantial lowering of the cavitational intensities in the organic media. In recent times, with the advent of more powerful instrumentation a resurgence of interest in non-aqueous studies has occurred, most notably in the field of synthetic organic chemistry, the subject of Part 2 of this review. Non-aqueous high intensity ultrasound can be broadly divided into three major areas. These are cavitation-induced decomposition of the solute or solvent, ultrasonically induced free-radical polymerization, and ultrasonic polymer degradation. The last two areas are dealt with in the section on Polymers.

Chloroform[143] has been subjected to ultrasonic irradiation of frequency 300 kHz ($I = 3.5$ W cm^{-2}) to yield a large number of products, the major proportion of which are unsaturated compounds. Decomposition was found only to occur in the presence of mono- or diatomic gases, free radicals being postulated as the intermediates based upon scavenging studies with O_2 or cyclohexene. Somewhat earlier, Weissler[159] had confirmed the free-radical nature of such reactions by irradiating CCl_4 in the presence of Ar, O_2, and 1-iodobutane. Recently, direct spectroscopic evidence for free-radical formation in the sonolysis of CCl_4 has been provided by Rosenthal.[160]

According to the theory outlined in General Principles, the maximum temperature reached inside a collapsing transient bubble may be taken to be inversely proportional to the solvent vapour pressure (P_v). If it can be assumed that the reaction mechanism in the bubble is governed by the Arrhenius equation, then

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[157] R. Schultz and A. Henglein. *Z. Naturforsch.*, 1953, **8**, 160.

[158] B. A. Niemczewski. *Ultrasonics*, 1980, **18**, 107.

[159] A. Weissler. I. Pecht, and A. Anbar, *Science*. 1965. **150**, 1288.

[160] I. Rosenthal. M. M. Mossoba. and P. Riesz. *J. Magn. Reson.*, 1981. **45**, 359.

it follows (from equation 11) that the reaction rate constant (k) decreases with increasing solvent vapour pressure (equation 30).

$$\ln k = \ln A - \frac{E\, P_v}{RT_0(\gamma - 1)} \tag{30}$$

By combining the use of two dosimeters, $Fe(CO)_5$ and DPPH, Suslick and co-workers[119–122,161] have evaluated the effectiveness of various solvents in producing cavitational sonochemistry and free-radical formation in particular. Although the authors neglected the effects of viscosity, surface tension, and bond dissociation energy, the correlation between experimental rate-constant and solvent vapour-pressure met with reasonable success.[120–122] The higher the vapour pressure of the solvent medium the lower the rate of decolorization of DPPH. Kruus[5] has also obtained a similar, though somewhat less successful correlation for the polymerization of nitrobenzene, at 20 kHz and 20 W cm^{-2}, in the presence of various gaseous and liquid solutes. The reaction rate was not only lowered by the presence of a liquid solute with high vapour-pressure, it was also lowered by the presence of a gaseous solute with a high solubility.

Finally, whenever kinetic investigations are undertaken into the effect of ultrasound, care must be exercised in deciding upon the method of monitoring the reaction progress. Previous studies[119,162–164] have shown that the ultrasonic intensity is dependent upon the irradiation depth of the liquid. In a recent investigation into the ultrasonic polymerization of methyl methacrylate, Kruus[124] developed kinetic equations to compensate for the reduction in volume on removing aliquots from a sonicated reaction. This volume compensation, though useful in most circumstances, may not be strictly correct in cases where a substantial lowering of liquid height occurs.

5 Sonoluminescence

Sonoluminescence is the name given to the light emitted when a liquid cavitates. The emitted light has been detected by a number of methods which include the naked eye,[165] exposure of photographic plates,[166] the use of photomultipliers,[166–169] and image intensification techniques.[170,171] Since its first observation[172] in 1933, many explanations have been offered for the origin of the effect. They fall into two broad categories, thermal and electrical.

[161] K. S. Suslick, P. F. Schubert, and J. W. Goodale, *J. Am. Chem. Soc.*, 1981, **103**, 7342.

[162] F. G. P. Aerstin, K. D. Timmerhaus, and H. S. Folger, *AIChE J.*, 1967, **13**, 453.

[163] S. Folger, *Ind. Eng. Chem., Fundam.*, 1968, **7**, 387.

[164] B. Pugin, *Ultrasonics*, 1987, **25**, 49.

[165] L. A. Chambers, *J. Chem. Phys.*, 1937, **5**, 290.

[166] R. D. Finch, *Ultrasonics*, 1964, **1**, 87.

[167] C. Seghal, R. P. Steer, R. G. Sutherland, and R. E. Verrall, *J. Chem. Phys.*, 1979, **70**, 2242.

[168] C. Seghal, R. G. Sutherland, and R. E. Verrall, *J. Phys. Chem.*, 1980, **84**, 396.

[169] C. Seghal, R. G. Sutherland, and R. E. Verrall, *J. Phys. Chem.*, 1980, **84**, 388.

[170] G. T. Reynolds, A. J. Walton, and S. Gruner, *Rev. Sci. Instrum.*, 1982, **53**, 1673.

[171] L. A. Crum and G. T. Reynolds, *J. Acoust. Soc. Am.*, 1985, **78**, 137.

[172] N. Marinesco and J. J. Trillat, *C. R. Seances Acad. Sci.*, 1933, **196**, 858.

A. Thermal Theories.—These include: the hot-spot theory,[8,173] in which the temperatures produced in the microbubbles produce incandescence; the thermochemical theory, according to which the heating of the vapour–gas mixture in a collapsing bubble results in thermal dissociation or ionization of the water molecules, the light originating from the recombination of radicals[174–176] or ions;[177] the mechanico-thermal theory, proposed by Jarman,[178] in which the collapse of a cavitation bubble is assumed to give rise to high temperatures, pressures, and light radiation, similar to the case of converging shock waves.

B. Electrical Theories.—These have been proposed by Nathanson,[179] Degrois and Baldo,[180] Harvey,[181] and Frenkel,[182] the last named suggested that on creation of the cavity (initially lens shaped) charges form on opposite sides of the cavity. Under certain conditions micro-discharges occur to produce light. Although, more recently, Margulis[183] has proposed a new electrical theory which more satisfactorily accounts for the experimental observations than previous theories,[180] the thermal theories appear more acceptable.[184]

There is now sufficient spectral evidence to show that sonoluminescence originates mainly from the recombination of radicals created within the high temperature and pressure environment of both transient and stable cavitation bubbles. A particular example is the emission observed by Verrall[167] from argon-saturated aqueous alkali-metal halide solutions during insonation at 460 kHz. The emission is ascribed to the de-excitation of excited alkali-metal atoms formed by free-radical reduction process.

Verrall *et al.*[167] have also used sonoluminescence to measure indirectly the intercavity temperature and pressure within a collapsing bubble. The values obtained (3 400 K and 310 atm) were substantially less than those predicted theoretically (9 500 K and 12 400 atm). They ascribed the differences to thermal conductivity of the gas.[46] Investigations have also been undertaken into the dependence of sonoluminescent intensity on the nature of the liquid,[185,186] the nature of the dissolved gas,[46,168,187] the liquid temperature,[168,185,188–190]

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[173] D. Srinivasan and L. V. Holroyde, *J. Appl. Phys.*, 1961, **32**, 446.
[174] V. Griffing and D. Sette, *J. Chem. Phys.*, 1955, **23**, 503.
[175] V. Griffing and D. Sette, *Phys. Rev.*, 1952, 234.
[176] C. Sehgal, R. P. Steer, R. G. Sutherland, and R. E. Verrall, *J. Phys. Chem.*, 1977, **81**, 2618.
[177] M. A. Margulis, *Russ. Acoustic J.*, 1969, **15**, 153.
[178] P. D. Jarman, *J. Acoust. Soc. Am.*, 1960, **32**, 1459.
[179] G. L. Nathanson, *Dokl. Akad. Nauk SSSR*, 1948, **59**, 83.
[180] M. Degrois and P. Baldo, *Ultrasonics*, 1974, **14**, 25.
[181] E. N. Harvey, *J. Am. Chem. Soc.*, 1939, **61**, 2392.
[182] Ya. I. Frenkel, *Russ. J. Phys. Chem.*, 1940, **14**, 305.
[183] M. A. Margulis, *Russ. J. Phys. Chem.*, 1985, **59**, 1497.
[184] T. K. Saksena and W. L. Nyborg, *J. Chem. Phys.*, 1970, **53**, 1722.
[185] P. Jarman, *Proc. R. Soc. Lond.*, 1959, **73**, 628.
[186] P. I. Golubinchii, V. D. Goncharov, and Kh. V. Protopopov, *Sov. Phys. Acoust.*, 1971, **16**, 323.
[187] R. O. Prudhomme, *Bull. Soc. Chim. Biol.*, 1957, **39**, 425.
[188] V. P. Gunther, W. Zeil, U. Grisar, and E. Heim, *Z. Electrochem.*, 1957, **61**, 188.
[189] G. Iernette, *Acustica*, 1972, **26**, 112.
[190] P. K. Chendke and H. S. Folger, *J. Phys. Chem.*, 1985, **89**, 1673.

the presence of impurities,[184,188,191] ultrasonic intensity,[174] and frequency.[169]

6 Polymers

A chemist has at his disposal two types of ultrasonic wave, high intensity (usually low frequency) and low intensity (usually high frequency), which are used for two different areas of investigation. The use of low intensity waves provides information on relaxation phenomena[81,192,193] such as segmental motion,[102,194] conformational change,[86] vibrational–translational energy interchange[51] and polymer–solvent interactions. High intensity waves have been used to effect such chemical changes as polymerization and depolymerization. Applications of the former type of irradiation have been dealt with elsewhere (see Relaxation Studies).

A. Degradation of Polymers.—It is now well established[47,195–208] that the prolonged exposure of solutions of macromolecules to high energy (>10 W cm^{-2}) ultrasonic waves produces permanent reductions in the solution viscosity. Even after the irradiated polymers are isolated and redissolved, their viscosities remain low in comparison to those of the initial non-irradiated solutions. Schmid[195,196,209] and Mark[210] did not invoke cavitation to explain these observations since degradation still occurred even when the systems were degassed or pressurized. They suggested that degradation occurred as a result of the increased frictional forces developed between the faster moving solvent molecules and the larger, less mobile, macromolecule. Although envisaging different modes of interaction between the solvent molecules and the macromolecule, both authors concluded that the increased frictional forces were sufficient to break an atomic C–C bond. Schmid[195] considered two ideal cases: the first in which the macromolecules were tightly held in solution and the solvent molecules were swept rapidly past them by the applied acoustic field, and a second which involved allowing the macromolecule

[191] V. L. Levshin and S. N. Rzhevkin, *Dokl. Akad. Nauk SSSR.*, 1937, **16**, 407.

[192] S. K. Hassun, S. H. F. Al-Madfai, and M. M. F. Al-Jarrah, *Br. Polym. J.*, 1985, **17**, 330.

[193] M. F. Haque, S. J. Fast, S. S. Yun, and F. B. Stumpf, *J. Acoust. Soc. Am.*, 1985, **77**, 2181.

[194] A. Juszkiewica, A. Janowski, and J. Ranachowski, *Acta Polym.*, 1985, **36**, 147.

[195] G. Schmid and O. Rommel, *Z. Phys. Chem.*, 1939, **A185**, 97.

[196] G. Schmid and O. Rommel, *Z. Elektrochem.*, 1939, **45**, 659.

[197] G. Schmid, *Phys. Z.*, 1940, **41**, 326.

[198] G. Schmid and E. Beutenmuller, *Z. Elektrochem.*, 1943, **49**, 325; 1944, **50**, 209.

[199] H. H. Jellinek and G. White. *J. Polym. Sci.*, 1951, **6**, 745; 1951. **6**, 757; 1951, **7**, 33.

[200] M. A. K. Mostafa, *J. Polym. Sci.*, 1956, **22**, 535; 1958, **27**, 473; 1958, **28**, 499; 1958, **28**, 519.

[201] A. Weissler, *J. Appl. Phys.*, 1950, **21**, 171.

[202] A. Weissler, *J. Chem. Phys.*, 1950, **18**, 1513.

[203] H. W. Melville and A. J. R. Murray, *J. Chem. Soc., Faraday Trans.*, 1950, **46**, 996.

[204] N. Sata, H. Okuyama, and K. Chujo, *Kolloidn. Zh.*, 1951, **121**, 46.

[205] P. E. M. Allen, G. M. Burnett, G. W. Hastings, H. W. Melville, and D. W. Ovenall, *J. Polym. Sci.*, 1958, **33**, 213.

[206] D. W. Ovenall, G. W. Hastings, and P. E. M. Allen, *J. Polym. Sci.*, 1958, **33**, 207.

[207] G. Gooberman, *J. Polym. Sci.*, 1960, **42**, 25.

[208] G. Gooberman and J. Lamb, *J. Polym. Sci.*, 1960, **42**, 35.

[209] G. Schmid, *Z. Phys. Chem.*, 1940, **186A**, 113.

to move with the solvent molecules under the action of the ultrasound. Mark[210] recognized that molecular configuration would influence the extent of the frictional forces, and so included micro-Brownian motion of the rotating polymer segments as well as the macro-Brownian motion of the whole polymer molecule.

Since the frictional forces depend upon the size of the macromolecule, then no matter which interpretation is adopted, both predict that the extent of degradation should decrease with chain size. Based upon experimental data, Schmid[195,196] was able to show this mathematically for dilute solutions ($<0.02\text{M}$) (equation 31) and

$$\mathrm{d}x/\mathrm{d}t = k\,(P_t - P_l) \tag{31}$$

for concentrated solutions (equation 32)

$$\mathrm{d}x/\mathrm{d}t = k \log P_t/P_0 \tag{32}$$

where dx is the number of chemical bonds broken in unit volume in an irradiation time dt, P_t is the degree of polymerization at time t, P_0 is the initial degree of polymerization and P_1 is the limit degree of polymerization.

Although this limit degree of polymerization has been observed by many workers,[204,211,212] different values have been quoted by different authors for a given polymer.[196,205,213,214] This discrepancy arises from the early investigators' use of viscosity measurements to determine molar mass ($[\eta] = KM^a$) and the difficulty[215] in deciding upon K and a values.

There is now a wealth[35,48,49,199,201,207,214,216–219] of experimental evidence to suggest that degradation is due to cavitation effects. What is debatable, however, is whether the degradation is caused by (i) the hydrodynamic[203,207,208,219] forces of cavitation (*i.e.* the shock-wave energies produced on bubble implosion), (ii) the shear stresses at the interface of pulsating bubbles,[211] or (iii) the associated thermal and chemical effects of both stable and transient cavitation, since all of the above are dependent upon the same factors *i.e.* intensity, frequency, gas content and type (see General Principles). For instance[48,49,199,201,216,217,220,221] diatomic gases (N_2, O_2, H_2) are found to enhance depolymerization, whereas polyatomic gases (NH_3, SO_2, CO_2), which also have increased solubility as well as decreased γ values, inhibit depolymerization. Degassed solutions have been found to exhibit no depolymerization effect.[48,49,210]

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[212] H. Okuyama, *Z. Elektrochem.*, 1951, **59**, 565.

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[216] A. Weissler, *J. Acoust. Soc. Am.*, 1951, **23**, 370.

[217] F. Gebert, *Angew. Chem.*, 1952, **64**, 625.

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[220] A. Botinov, P. Kubeko, and F. Marci, *Zh. Fiz. Khim.*, 1942, **16**, 106.

[221] A. Henglein and R. Schultz, *Z. Naturforsch.*, *B*, 1952, **7**, 484.

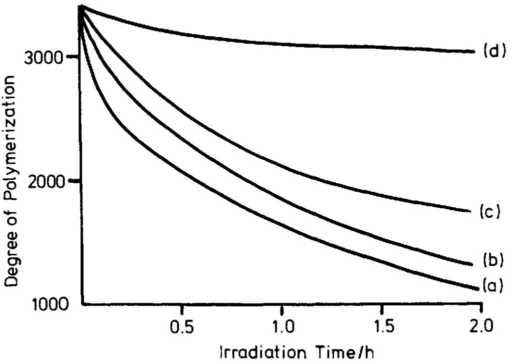

Figure 9 *Degradation of* 1% *poly*(*styrene*) *in benzene at different ultrasonic frequencies* (ref. 211). (a) 1 MHz. (b) 1.25 MHz. (c) 1.5 MHz. (d) 2 MHz

Most workers in the field[35,211,212,222] agree that increasing the frequency of the ultrasound leads to a decrease in the extent of depolymerization (Figure 9).

This, no doubt, is due in part to the need, at higher frequencies, to employ greater intensities to ensure cavitation. For instance, although Gaertner[35] has observed depolymerization at both 400 kHz and 2 500 kHz, the lower frequency only necessitated an intensity of 0.5 W cm^{-2} whereas the higher frequency required approximately 2 KW cm^{-2}. Higher frequencies also provide for shorter periods in which bubble growth and collapse can occur (see General Principles). It is likely that at the higher frequencies (at the same intensity) there is insufficient time available to produce cavitation. Although investigating a polymerization process, Henglein[222] confirms this view. He found that the polymerization rate (and degree of polymerization) of acrylamide (in water), at a given frequency, using pulsed ultrasound, depended upon the duration of the pulse. As the duration of the pulse was reduced, the rate of polymerization decreased.

In respect of ultrasonic intensity, Gebert[217] has shown that an increase in intensity leads to an increase in the extent of depolymerization.

Whatever the mechanism involved, depolymerization results in the breakage of an atomic bond in the macromolecule to produce long-chain radical species. The existence of these radical entities is easily established by investigating the depolymerization process[223–226] in the presence of a radical scavenger such as DPPH.[227] Spectroscopic analysis of the loss of DPPH ($\lambda_{max.}$ = 525 nm) allows both a determination of the depolymerization rate and the number of break points

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[222] A. Henglein, *Makromol. Chem.*, 1954, **14**, 15.
[223] A. Henglein, *Makromol. Chem.*, 1955, **15**, 188.
[224] I. E. El'piner, *Akust. Zh.*, 1959, **5**, 133.
[225] A. S. Berlin, *Dokl. Akad. Nauk SSSR.*, 1956, **110**, 401.
[226] J. R. Thomas, *J. Phys. Chem.*, 1959, **63**, 254.
[227] C. E. H. Bawn and S. F. Mellish, *J. Chem. Soc., Faraday Trans.*, 1951, **47**, 1216.

in the macromolecule. (To estimate the number of break points it must be assumed that two DPPH molecules are consumed per bond break.) In the absence of radical scavengers the molecular fragments are free to recombine by the usual termination mechanisms. Combination termination will produce macromolecules of the same, or differing lengths, as those existing just prior to bond breakage depending upon whether the combining molecular fragments are from the same or differing polymer chains. Disproportionation termination between fragments, no matter what their origin, must result in smaller macromolecules. Henglein has investigated the probability of the combination reactions for several polymers.[223,228,229]

Direct evidence for the formation of macroradicals in the degradation of poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) has been provided by Tabata[230,231] using spin trapping and e.s.r. techniques. From studies in which deuterium-labelled polymers were used it was concluded that degradation took place by main-chain homolysis as a result of ultrasonically induced hydrodynamic action on the polymer.

Perhaps one of the distinctive and remarkable effects of these competing degradation and recombination processes is the reduction in the polydispersity[203,204,211,213,232] of a polymer sample (*i.e.* reduction in the $\bar{M}_w : \bar{M}_n$ ratio). Although the absolute magnitude of a polymers relative molar mass ($\bar{M}_w$ or $\bar{M}_n$) is important, there is a whole series of physicochemical properties, such as film formation, chemical stability, solution flow *etc.* which depends upon the degree of polydispersion. According to several workers[204,213,233,234] there is a high probability of breakage of chemical bonds at any site in the molecular chain, on applying ultrasound, provided $P \gg P_1$. This random scission ought to result in a mixture of molecular fragments of various lengths, and an increase in the polydispersity, certainly in the initial periods of irradiation. With the passage of time, the smaller molecular fragments so produced are broken into equal halves[4,235,236] so that long exposure leads to the attainment of an almost monodisperse solution of the polymer. The present authors can confirm that, for certain macromolecules, degradation takes place with an initial increase in polydispersity.[138] Further, they have observed that the shape of the macromolecule, as determined by viscosity studies, changes with irradiation time.

Unlike chemical or photodegradation, ultrasonic degradation does not appear to take place predominantly at the points of inherent weakness within the polymer's backbone. For example, Melville[203] has shown that degradation of two

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[228] A. Henglein, *Z. Naturforsch., B*, 1955, **10**, 616.
[229] A. Henglein, *Makromol. Chem.*, 1956, **18**, 37.
[230] M. Tabata, T. Miyanawa, O. Kabayashi, and J. Sohma, *Chem. Phys. Lett.*, 1980, **73**, 178.
[231] M. Tabata and J. Sohma, *Eur. Polym. J.*, 1980, **16**, 589.
[232] K. Edelmann, *Fasserforsch. Textiltech.*, 1953, **10**, 407.
[233] P. A. R. Glynn, B. M. E. Van der Hoff, and P. M. Reilly, *J. Macromol. Sci., Chem.*, 1972, **A6**, 1653.
[234] P. A. R. Glynn and B. M. E. Van der Hoff, *J. Macromol. Sci., Chem.*, 1973, **A7**, 1695.
[235] A. Basedow and K. H. Ebert, *Makromol. Chem.*, 1975, **176**, 745.
[236] A. Basedow and K. H. Ebert, *Polymer Bulletin*, 1979, **1**, 299.

separate polymethylmethacrylate (A)–acrylonitrile (B) copolymers (molar ratios of A:B of 40:1 and 400:1 respectively) yielded almost identical molar masses after irradiation with ultrasound. If it is assumed that the A–B linkages are appreciably weaker than the corresponding A–A or B–B linkages, then, as in the case of thermal degradation, appreciably different molar masses ought to have been obtained.

Those readers wishing a more quantitative discussion of depolymerization are referred to articles by Jellinek[237] and Glynn.[233,234]

B. Polymerization.—It is well known that the structural, physical, and physicochemical characteristics of macromolecules depend not only on the nature of the monomer (homopolymer) or monomers (copolymer) from which they are synthesized, but also on the method of production (*e.g.* graft, block, or random copolymers). For instance, whereas random copolymerization of two monomers A and B produces a polymer with a property (*e.g.* solubility, polarity) which is the weighted average of the two constituent monomers, block (or graft) copolymers have properties which are the sum of the two homopolymers. Typically a graft copolymer consisting of water soluble (polyethylene oxide) and oil-soluble (polystyrene) components is capable of dissolving in both solvent types.

In the previous section it was shown that ultrasound was capable of producing radical entities. It is not surprising, therefore, that the application of ultrasound to polymer synthesis has attracted the attention of many investigators. Until recently, most of the work involved applying ultrasound to systems containing a mixture of homopolymers in the hope of producing graft or block copolymers, rather than in the initiation of polymerization from monomer. The latter study suffers from the complication that as the polymerization proceeds and the concentration of polymer increases, the competing depolymerization reaction will become increasingly more significant. It is also likely that the increase in viscosity accompanying the reaction will lead to a change in the acoustic environment within the system. (See General Principles).

Keqiang[238] has successfully produced block copolymers, based upon cellulose, while Henglein[223,228,229] has produced both graft and block copolymers using polystyrene and polymethyl methacrylate. Malhorta,[239] employing a variety of homopolymers (rigid and flexible), has met with limited success in the synthesis of block copolymers. In each of the above syntheses degradation of the homopolymers by ultrasound provides long-chain radicals of each component which terminate by combination. However both homopolymers must have degrees of polymerization greater than P_1 to ensure production of a radical entity.[239] The fact that irradiation by ultrasound leads to the breakage of only a limited number of bonds in the macromolecule, yet the yield of block copolymer may be as high as 90% in some cases, has prompted Berlin[240] to suggest that the macroradical is also capable of degrading a stable macromolecule. The suggestion that a radical could

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[237] J. J. G. Jellinek, 'Degradation of Vinyl Polymers', Academic Press, New York, 1955.

[238] C. Keqiang, S. Ye, L. Huilin, and X. Xi, *J. Macromol. Sci., Chem.*, 1985, **A22**, 455.

[239] S. L. Malhorta, *J. Macromol. Sci., Chem.*, 1981, **A18**, 1055.

[240] A. A. Berlin, *Usp. Khim.*, 1960, **29**, 1189.

itself cause degradation of a polymer chain has been supported by Ramsden and McKay[241] who reported that hydroxyl radicals were capable of inducing chemical degradation of polyacrylamide.

Block copolymers have also been produced by irradiating a solution containing a homopolymer (from monomer type A) and a monomer (type B).[242] In such cases polymerization of the monomer (B) is initiated by the macroradical produced by ultrasonic degradation of the homopolymer. In cases where polymer was absent, no polymerization occurred. Similar findings have been reported[240,243,244] by other workers when attempting to homopolymerize pure vinyl monomers in the presence of ultrasound. Such observations are in direct contrast to the findings of other workers[124,221,222,245,246] including the present authors. Ultrasonic waves ($I = 8$ W cm^{-2}) have been found to initiate the polymerization of acrylonitrile in aqueous media saturated with N_2.[245] The initiating species are presumably HO• radicals from the decomposition of water (equation 26). Berlin[247] confirms this opinion in his investigation of the polymerization of polystyrene in the presence of styrene monomer since addition of water to the solvent (benzene) greatly enhanced the yield of polymer. It could be argued, however, that the appearance of water decomposition products (*e.g.* H_2O_2) led to oxidation of the various impurities, which previously, may have acted as inhibitors.

Ultrasonic waves have also been found to increase the rates of emulsion[221,222,246,248–250] and suspension[251] polymerizations. Various explanations have been proposed to explain the increase in rate. These include (i) the oxidation of impurities (see above), (ii) the removal of oxygen (known to inhibit radical reactions) by ultrasonic degassing, (iii) ultrasonic degradation of the polymer to provide more active sites (*i.e.* autocatalysis), and (iv) prevention of agglomeration between droplets, or the sticking of the droplets to the walls of the reaction vessel, in suspension polymerization.

Few workers[130,242,252,253] have investigated the effects of varying such parameters as frequency, intensity, temperature, and the nature of the gas, on the polymerization process. Berlin[242] has shown that for the block copolymerization of polymethyl methacrylate with acrylonitrile, the time required to produce a given amount of polyacrylonitrile in the block decreased with increasing intensity. Kruus[124] has been able to show that there is a propagation rate (R_p) dependence, for the bulk polymerization of methyl methacrylate, on the square root of the

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[241] D. K. Ramsden and K. McKay, *Polym. Deg. Stab.*, 1986, **15**, 15.
[242] A. A. Berlin and A. M. Dubinskaya. *Bysokomole Kulyameje Soedin.*, 1960, **2**, 1426.
[243] K. F. Driscoll and A. U. Sridhari, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 1975, **26**, 135.
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[245] O. Lindstrom and O. Lamm, *J. Phys. Colloid Chem.*, 1951, **55**. 1139.
[246] P. Alexander and M. Fox. *J. Polym. Sci.*, 1954, **12**, 533.
[247] A. A. Berlin and B. S. El'tsefon. *Khim. Nauka Prom.*, 1957, **2**, 667.
[248] A. S. Ostroski and R. B. Stambaugh. *J. Appl. Phys.*, 1950, **21**, 478.
[249] N. Sata and Y. Harisaki. *Kolloidn. Zh.*, 1951, **124**, 36.
[250] R. Fox, E. Yaeger, and F. Hovorka, *J. Acoust. Soc. Am.*, 1960, **32**, 1499.
[251] Y. Hatate, T. Ikeura, M. Shinonome, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn.*, 1981, **14**, 38.
[252] T. Miyata and F. Nakashio, *J. Chem. Engl., Jpn.*, 1975, **8**, 463.
[253] J. R. McKee and C. J. Christman. *Biochemistry*. 1977, **16**. 4651.

intensity ($I^{\frac{1}{2}}$), as is the case for photopolymerization. The present authors have found that at a given temperature and irradiation frequency ($T = 60, f = 20$ kHz), there is a maximum in the R_p *vs* I curve for the solution polymerization of NVC.[138] At very high intensities (> 10 W cm^{-2}) the conversion is negligible. Henglein[222] has shown that the degree of polymerization decreases when the duration of pulsed ultrasound is decreased. The growth and collapse of cavitation bubbles require a finite time—they are not instantaneous. Henglein[221] has also shown that the rate (and degree of polymerization) depends upon the nature of the gas used to saturate the system. For the polymerization of methacrylic acid in aqueous solution, a 15 minute irradiation yielded 10.7% conversion in the presence of N_2, 1.8% conversion in the presence of O_2 (low presumably due to inhibition), and no polymerization in a degassed solution).

Kruus[123,124] is one of the few investigators who has attempted to interpret the results of ultrasonically induced polymerizations in terms of equation 11 (General Principles). For the polymerization of nitrobenzene[123] he has observed, as predicted by equation 30, that the polymerization rate (measured as solution darkening) decreases both in the presence of gases with high solubility (*e.g.* SO_2 and CO_2) and solutes with high vapour pressures. The model used, although containing serious oversimplifications, allows for a deduction of the minimum and maximum temperature, in the region of bubble collapse, of 600 K to 40 000 K. Using a similar model[124] he has been able to explain the conversion of methyl methacrylate (bulk polymerization) in terms of reaction time, reaction volume, and ultrasonic intensity. Polymer yields and molar masses ($Y = 3\%$ in 2 h; $T = 40$ °C; $I = 20$ W cm^{-2}; $M_w = 700\,000$) were somewhat lower than those found by the present authors for the solution polymerization of NVC ($Y = 30\%$, $T = 60$ °C, $I = 30$ W cm^{-2}; $M_w > 2 \times 10^6$). Kruus[124] has also determined activation energies for the bulk polymerization of methyl methacrylate in the presence of ultrasound. The value obtained (~ 19 kJ mol^{-1}) is similar to that observed for the bulk thermal polymerization reaction (17—20 kJ mol^{-1}), provided the contribution from the initiation step is excluded. This close correspondence in activation energies suggests that the effective activation-energy for the initiation step, in the presence of ultrasound, may be taken to be 0 kJ mol^{-1}, as is the case in photopolymerization. Kruus also studied the polymerization in the presence of the radical scavenger DPPH. Unfortunately the rates of initiation as deduced from both the overall polymerization rate and the rate of DPPH consumption, although of similar magnitude, showed inexplicable differences in temperature dependence.

Recently Toppare[254] has investigated the use of ultrasound (25 kHz) on the rate of polymerization, and copolymer composition, of the electroinitiated cationic polymerization of isoprene with α-methylstyrene. In the presence of ultrasound the total % conversion was found to increase with the polymerization potential (E). The authors attributed this to a 'sweeping clean' of the electrode surface due to the action of ultrasound. The proportion of isoprene incorporated in the copolymer, under sonication, was found to pass through a maximum value of 54% when the

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[254] U. Akbulut, L. Toppare, and B. Yurttas, *Polymer*, 1986, **27**, 803.

polymerization potential was 2.6 volts.

Little work has been performed on the effect of frequency on polymerization rate (and yield). Frequency is a factor which determines cavitation threshold, size of bubble, and the time scale of bubble growth and collapse. It is anticipated that changing frequency will alter the polymerization process.