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Influence of dissolved gases on sonochemistry and sonoluminescence in a flow reactor

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ABSTRACT

In the present work, the influence of gas addition is investigated on both sonoluminescence (SL) and radical formation at 47 and 248 kHz. The frequencies chosen in this study generate two distinct bubble types, allowing to generalize the conclusions for other ultrasonic reactors. In this case, 47 kHz provides transient bubbles, while stable ones dominate at 248 kHz. For both bubble types, the hydroxyl radical and SL yield under gas addition followed the sequence: Ar > Air > N_2 >> CO_2. A comprehensive interpretation is given for these results, based on a combination of thermal gas properties, chemical reactions occurring within the cavitation bubble, and the amount of bubbles. Furthermore, in the cases where argon, air and nitrogen were bubbled, a reasonable correlation existed between the OH-radical yield and the SL signal, being most pronounced under stable cavitation at 248 kHz. Presuming that SL and $OH^{\cdot}$ originate from different bubble populations, the results indicate that both populations respond similarly to a change in acoustic power and dissolved gas. Consequently, in the presence of non-volatile pollutants that do not quench SL, sonoluminescence can be used as an online tool to qualitatively monitor radical formation.

1. Introduction

Ultrasonic reactors show increasing potential for application in chemical and physical processes such as wafer cleaning, waste water treatment and crystallization [1–5]. The beneficial effect of ultrasound arises mostly from acoustic cavitation, involving the formation and implosion of micron-sized bubbles in less than a few microseconds. Depending on the operational conditions, the bubbles can either be stable, oscillating for hundreds of acoustic cycles around their equilibrium radius, or transient when they grow to twice their initial size and implode in a few cycles [6,7]. The implosion of both types of cavitation bubbles creates a local high energy density, giving rise to the formation of a hot spot. As a result, temperature and pressure reach levels of over 5000 K and 1000 atm in aqueous systems, respectively [8]. These extreme conditions promote the chemical activity of ultrasound, indicated as sonochemistry. The process is initiated by the thermal dissociation of water vapour, yielding reactive hydroxyl ($OH^{\cdot}$) and hydrogen radicals ($H^{\cdot}$), whose existence was demonstrated by using electron spin resonance measurements [4,9–11]. Alternatively, the presence of $OH^{\cdot}$ can be indicated by dosimeters such as the hydroxylation of terephthalic acid [4,12,13]. When other species are present in the bubble core, additional radicals and reactive molecules such as $HO_2^{\cdot}$, $O^{\cdot}$ and H_2O_2 may form. All of these products can recombine, react with other species present in the gas phase of the bubble, or diffuse towards the bulk medium where they can oxidize other compounds. Parallel to these radical reactions, pyrolysis of volatile solutes that evaporate into the bubble takes place [8,14]. In some cases, it was observed that the production of radicals can also promote chemical reactions [15]. In addition, some bubbles can emit light from their core, a phenomenon called sonoluminescence (SL). During the last stages of the adiabatic collapse, short flashes of light, lasting about 100 ps, are radiated from the bubble core [16]. In general, this light originates from plasma emissions generated by Bremsstrahlung, excited OH-radicals and other species [17,18]. This was confirmed by SL spectra recordings from multibubble fields, showing characteristic atomic and molecular emission lines from noble gases and active species, superimposed on a broad continuum [19–21]. If the bubbles exhibit a core temperature below 10,000 K, emission from electronically and vibrationally excited species mainly causes SL. Similarly, some authors suggest that a bubble cloud is composed of both colder and hotter bubbles, the latter of which generate the broad continuum [17,22]. Moreover, Yasui et al. claim that the exact mechanism of multibubble sonoluminescence (MBSL)

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depends on the acoustic pressure and frequency. Above 140 kHz, the light is mainly caused by plasma emissions other than those originating from excited OH-radicals due to the absence of water vapour in the bubble that normally acts as a source for hydroxyl radicals. The origin of SL at lower frequencies such as 20 kHz can be luminescence of OH· or other species, depending on the acoustic pressure. When the amplitude is below 2 bar, light emission of the former species is negligible. At higher amplitudes, the bubble contains mostly water vapour, and as a result excited OH-radicals dominate the light emission [17,23]. Pflieger et al. further elucidated the mechanism of sonoluminescence by recording SL spectra of water saturated with different noble gases such as Argon, Krypton and Xenon. By analysis of the OH-emission lines it was shown that a non-thermal plasma was formed in the presence of noble gases during multibubble cavitation [18,21,24].

Overall, sonoluminescence obtained by total light emission measurements or by spectral investigation, gives important information about the processes occurring inside a cavitation bubble [25]. Consequently, this technique is often used to probe the temperature inside the bubble upon collapse [26,27]. Therefore, some authors determine an average bubble temperature T_f [K] using a model that assumes adiabatic compression during the implosion.

$$T_f = T_i\left(\frac{R_i}{R_f}\right)^{3(\gamma-1)} \quad (1)$$

Herein, T_i [K] denotes the initial temperature, R_i [μm] and R_f [μm] the initial and final bubble radius, respectively, and γ [–] the polytropic index of the gas inside the bubble. This equation does not take bubble dynamics and temperature dependence of γ into account, and neglects thermal transport, solvent vapour pressure and chemical reactions. In spite of these simplifications, some experimental results can be reasonably fitted with this model [26]. In contrary, the work of Pflieger et al. questions the use of this average bubble temperature, since it was shown that a non-equilibrium plasma is formed. This type of plasma should be characterized by different temperatures such as the electron (T_e), vibrational (T_v), rotational (T_r) and translational temperature (T_0). Spectral analysis allows to quantify these temperatures, and these usually follow the order: $T_e > T_v > T_r \approx T_0$ [18,21,28].

Both sonochemical activity (production of radicals) and sonoluminescence are influenced by operational parameters such as frequency, power, pressure, temperature, addition of gaseous additives, etc. Among these parameters, the effect of frequency and gas addition were proven to be most significant [14].

The ultrasonic frequency determines the active bubble size, which decreases at increasing frequency. Generally, most authors report a more violent bubble collapse at low frequency, characterized by an increased average bubble temperature [14,29,30]. Kanthale et al. studied the effect of frequency on sonoluminescence and H_2O_2 production. They concluded that both MBSL and sonochemistry depend on the number of active bubbles. In addition, sonoluminescence is influenced by the maximum bubble temperature, while the radical yield is influenced by the average temperature and the amount of water vapour present in the bubbles. The authors reported that the maximum temperature is reduced at increased frequency, resulting in a significant decrease in SL intensity at higher frequency. H_2O_2 yield showed a similar response in the frequency range between 213 and 647 kHz, while a MHz frequency significantly reduced the production of radicals that form H_2O_2 [30]. Similar results were obtained by Zhou et al. while investigating sonoluminescence and sonochemiluminescence (SCL) at various frequencies. SL signals were also inversely proportional to the ultrasonic frequency, while SCL, a measure for OH-radicals, remained fairly constant from 213 to 647 kHz. Only at 1056 kHz, the sonochemical intensity dropped significantly [31]. In contrast, recordings of SL spectra at different frequencies between 200 kHz and 1.1 MHz showed an optimum profile, peaking at 358 kHz. Although these results do not show a reduction in SL over the entire frequency domain, as was reported before [30,31], the decline in SL with respect to frequency is again present above 358 kHz. The corresponding quantification of the radicals, by H_2O_2 measurements and degradation kinetics of 1,4-dioxane, showed the same optimum profile as sonoluminescence, with a clear reduction above 1 MHz [11]. As was mentioned before, evidence is provided that a non-thermal plasma is created in the bubbles which can be characterized by the electron, vibrational, rotational and translational temperature. Calculation of these plasma temperatures within the frequency range 20–1057 kHz showed the opposite effect of the average bubble temperature. Higher electron and vibrational temperatures were obtained at high frequency, meaning that more drastic conditions are created. Therefore, Ndiaye et al. attribute the decrease in total SL intensity at higher frequency that was reported in the previous studies to a lower bubble volume instead of to milder bubble conditions [18]. The lower frequency range from 20 kHz to 80 kHz was investigated by Hua et al., and it was observed that both H_2O_2 production and terephthalic acid dosimetry showed identical trends. Sonochemical yield was almost identical at 20 and 40 kHz, while a significant increase occurred at 80 kHz. The authors attribute this to variations in acoustic pressure, a larger active bubble population, and a reduced collapse time at higher frequency leading to more radical ejection from the bubble [4].

Addition of gas to the solution eases the initiation of cavitation and augments the bubble volume in the reactor [14,32]. The effect of dissolved gases on sonoluminescence and radical formation has been investigated by numerous authors. Young et al. measured SL of water saturated with different gases at a fixed frequency of 20 kHz and power density of 10 W cm^{-2}. The SL signal resulted in the following sequence of Ar > Air = O_2 > N_2 > H_2 = CO_2 [3]. The attenuation of the SL signal by carbon dioxide was also confirmed by Kumari et al. and Brems et al., both emphasizing the ability of CO_2 to control cavitation in order to obtain damage free wafer cleaning. The reduction in sonoluminescence yield was attributed to strong gas diffusion into the bubble, leading to a cushioning effect. In addition, the authors discussed the possibility that carbon dioxide dissolved in water can form carbonic acids that inhibit bubble coalescence and therefore alter the bubble size distribution. As a consequence, the number of collapsing bubbles is strongly reduced [2,33]. The same order for radical production, or at least partially, was obtained in several other studies at different frequencies in the range 300–1000 kHz [4,14,29,34–38]. In these different publications, the explanation for the gas sequence is usually based on the gas solubility, the chemical reactions occurring in the bubble, and the average bubble temperature. Using numerical simulations for example, Merouani et al. concluded that the gas solubility and the internal bubble chemistry determine the radical production processes of the bubbles [14,38]. Gas solubility controls the number of collapsing bubbles in the reactor, and a higher value will increase the amount of cavitational collapses. Gases such as O_2 and N_2 directly influence the radical production, since they participate in reactions that promote or scavenge radicals, respectively. In addition, the bubble temperature is an important factor, as it influences the production rate of OH-radicals. Gases affect the bubble temperature through two aspects. A gas with a higher polytropic index γ yields a higher average bubble temperature, as can be derived from Eq. (1). In turn, an elevated temperature enhances the thermolysis of water molecules, resulting in more radicals. Furthermore, when the gas has a low thermal conductivity, the increase in temperature and sequential radical yield is further facilitated. Although this suggests that radical yield is proportional to the bubble temperature, Merouani et al. claim that an optimum