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Experimental quantification of cavitation yield revisited: focus on high frequency ultrasound reactors

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Abstract

Acoustic cavitation plays an important role in enhancing the reaction rate of chemical processes in sonochemical systems. However, quantification of cavitation intensity in sonochemical systems is generally limited to low frequency systems. In this study, an empirical determination of cavitation yield in high frequency ultrasound systems was performed by measuring the amount of iodine liberated from the oxidation of potassium iodide (KI) solution at 1.7 and 2.4 MHz. Experiments for determining cavitation were carried out at various solute (KI) concentrations under constant temperature, obtained by direct cooling of the solution and variable temperature conditions, in the absence of external cooling. Cavitation yield measurements, reported in this work, extend previously reported results and lend credence to the two step reaction pathway in high frequency systems. Additionally, the concentration of KI and temperature affect the cavitation yield of a system such that the iodine production is proportional to both conditions. It is proposed that direct cooling of sonicated KI solution may be advantageous for optimization of cavitation intensity in high frequency sonochemical reactors.

Keywords: Cavitation intensity; Sonication; KI solution; High frequency

1. Introduction

Acoustic cavitation during sonication is well recognized to have an influence on reaction rate kinetics in low frequency sonochemical processes [1–4]. At higher frequencies, acoustic cavitation is produced in the liquid phase further away from the transducers, thus reducing mechanical wear of transducers due to imploding bubbles. However, sonochemical reactions performed at high frequencies have lower cavitation yield and are used in limited sonochemical applications. More recent sonochemical studies at very high frequencies (>500 kHz), such as aerosol based reactions [5], destruction of biological contaminants [6] and nano-particle formation by ultrasonic aero–sol–gel method [5] have demonstrated the need for developing an understanding of the effect of cavitation at higher frequencies. In order to understand sonochemical behavior in high frequency ultrasound systems, the effects of frequency, (solute) concentrations, temperature, and acoustic power intensity on cavitation must be realized.

Typically, cavitation yield measurements are conducted by determining the amount of iodine liberated when potassium iodide solutions are subjected to ultrasound (Weissler's reaction, [7]). When water is sonicated, cavitation activates the generation of hydrogen, hydroxide, and peroxy radicals [4]. The hydroxide and peroxy radicals act as oxidizing agents for the solute (KI) and iodine is then liberated. Cavitation yield is generally defined as the grams of iodine liberated per power

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density in the system [8]. Previous studies have concentrated on determining the cavitation yield at frequencies ranging from 20 to 900 kHz [1,2,9]. Entezari and Kruus [1] reported the amount of oxidation of iodide to iodine at 20 kHz and 900 kHz. They determined that the cavitation yield (μmol/(W/mL)) using a 900 kHz transducer was more than 20 times greater than that of the 20 kHz transducer [1]. Seymour et al. [2] reported that the cavitation yield at 900 kHz was 0.8 times the yield at 640 kHz. This can be attributed to the rapid attenuation of ultrasound at higher frequencies. Discrepancies have been observed in the literature regarding the role of solute (potassium iodide) concentration on cavitation yield. Gutierrez et al. [10] reported that at 1 MHz, the oxidation of KI was not dependent on the solute concentration, however experiments conducted by Naidu et al. [4] at 25 kHz and Seymour et al. [2] 640 kHz show that the amount of iodine produced was directly proportional to the initial KI concentration.

The objective of the present work is to determine the cavitation yield in water sonicated at 1.7 and 2.4 MHz and to investigate the effect of sonication frequency, power intensity, solute concentration and temperature on the yield.

2. Experimental setup

A schematic representation of the experimental arrangement used in this work is shown in Fig. 1. A series of experiments were conducted using 1%, 2%, and 3.5 wt.% KI aqueous solutions in the sonication vessel. Two ultrasonic transducers operating at 1.7 MHz or 2.4 MHz and 18 mm diameter, supplied by Honda Electronics, were installed in the bottom of a glass column 5 cm in diameter and 100 cm in height, with a stainless steel bottom. During sonication at high frequencies (in the MHz range), the ultrasonic energy imparted to the reactants results in the formation of a fountain jet at the surface of the liquid, releasing droplets from the surface of the jet. Image processing of photographs collected of the fountain jet were analyzed and show that the oscillating jet using 2.4 MHz transducer is typically 0.0075 m in diameter at the surface of the sonicated solution and 0.05 m in height above the surface of the liquid, while jet dimensions measured with the 1.7 MHz transducer are 0.015 m in diameter at the surface of the sonicated solution and 0.065 m in height. A glass coil, filled with coolant was also installed in the glass column to provide direct cooling during cavitation measurements. The cooling system was operated so as to maintain a constant temperature of 16 °C in the liquid during sonolysis with the 1.7 MHz transducer and at a temperature of 18 °C with the 2.4 MHz transducer. The input power to the transducers was fixed at 21 W and 18 W for the 1.7 and 2.4 MHz transducers respectively based on transducer manufacturer's recommendation for optimized operation. This work concentrated on obtaining information about the cavitational activity in the overall system similar to previous research on low frequency ultrasound reactors. Experiments were also conducted using 3.5 wt.% KI solution when the temperature of the sonicated liquid was not controlled. The amount of liberated iodine was measured using a UV/VIS spectrophotometer at 350 nm and quantified using a calibration curve ranging from 0 to 1.4×10^{-4} M of iodine for determining the cavitation yield at various intervals of time.

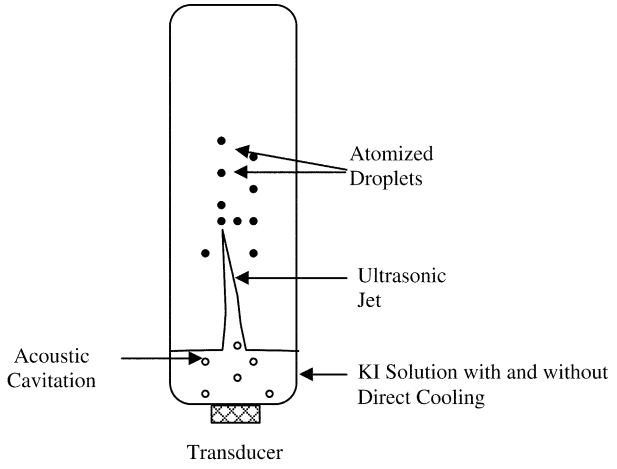

Fig. 1. Schematic representation of experimental arrangement for cavitation yield determination.

3. Results and discussion

3.1. Effect of sonication frequency

Fig. 2 summarizes the cavitation yield measurements for oxidation of KI solution during sonication. Cavitation yield measurements, obtained by oxidation of

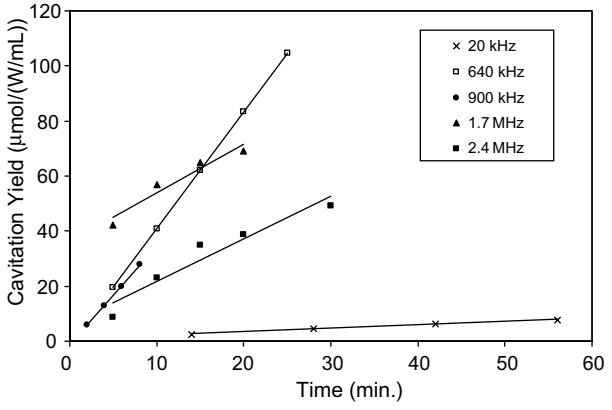

Fig. 2. Comparison of cavitation yield measurements over a range of frequencies for oxidation of 3.5 wt.% KI solution.

3.5 wt.% KI to produce iodine, for 1.7 and 2.4 MHz transducers at regular time intervals are shown in Fig. 2. Earlier measurements by Entezari and Kruus [1] performed at 20 kHz and 900 kHz and Seymour et al. [2] at 640 kHz are also included in Fig. 2. The presence of dissolved air in the solution reduces the threshold pressure during cavitation inception resulting in a significant rise in the number of cavities formed and consequent increase in reaction rates. Liberation of dissolved air by degassification becomes insignificant after 20 min of sonication using 1.7 MHz and 2.4 MHz transducers as shown by the asymptotic behavior of iodine liberation in Fig. 2. The linear relationship between cavitation yield and sonication time was applied for the determination of cavitation yield after 20 min of sonication and shown in Table 1.

A comparison of cavitation yield measurements for the two frequencies examined in this work along with previously reported data show that oxidation of iodide to iodine increases in the low frequency sonication range and generates maximum cavitation at an optimum frequency followed by a decrease in cavitation intensity in the high frequency range. This occurrence of an optimum frequency for sonication was also reported by Mason and Lorimer [11] and was explained by considering a two step reaction pathway during water sonolysis produced radicals within the bubble initially and in the second step, the radicals migrate to the bubble interface to form peroxide. It was suggested that lower frequencies were the most efficient for decomposition of molecules inside the radicals but radicals may recombine inside the bubble at high temperature to form water reducing the overall yield of the reaction [11]. The occurrence of an optimal frequency at 1 MHz approximately, shown in Fig. 3, can also be explained by the two step reaction pathway for iodine production by Weissler's reaction. We postulate that although lower frequencies may be efficient for the decomposition of molecules, the shorter rarefaction and compression cycles at higher frequencies (MHz range) reduce the occurrence of recombination of

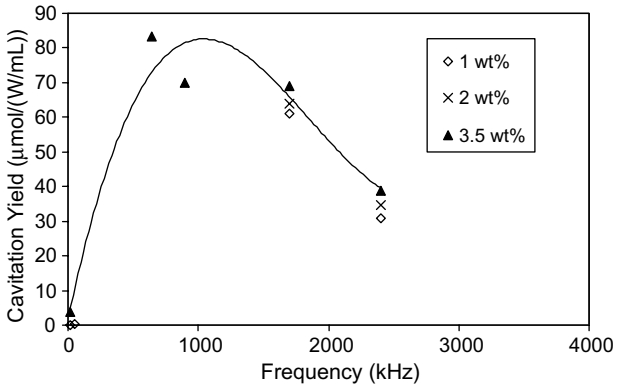

Fig. 3. Dependence of cavitation yield on frequency with respect to KI concentration.

radicals. As a result, with an increase in frequency above 1 MHz, the pulsation and collapse of bubbles occurs more rapidly and more radicals escape from the bubble. However, as frequency increases, the cavitation yield decreases as the cavitation bubbles tend to be smaller and less energetic, reducing the yield of radicals and thereby the number of radicals that reach the interface and bulk solution. Similar changes in cavitation behavior were observed while sonicating at 1.7 and 2.4 MHz without cooling as shown in Fig. 5. It is important to note that the fountain jet formed at the surface of the liquid during sonication at 2.4 MHz was smaller than at 1.7 MHz.

3.2. Effect of KI concentration

A great deal of work has been previously reported on the determination of the effect of KI concentration on the production of iodine in an ultrasonic system. Seymour et al. [2] reported that at 640 kHz, as the concentration of KI was increased by a factor of 8, the amount of iodine produced increases by a factor of 2. Naidu et al. [4] also noted an increase in iodine liberation when solutions with higher KI concentrations were sonicated at 25 kHz. On the other hand, Gutierrez et al.

Table 1
Summary of cavitation yield measurements after 20 min of sonication with different transducers

Frequency (kHz)	Temperature (°C)	Amount KI (%)	Power supplied (W)	Sonication time (min)	Cavitation yield (μmol/(W/mL))	Cavitation yield (μmol/(W/mL)) over 20 min	Reference
20		1	50	15	0.12	0.15	[6]
50		1	50	15	0.35	0.46	[6]
1700	25	1	21	20	61.14	61.14	Present work
2400	21	1	18	20	30.75	30.75	Present work
1700	25	2	21	20	63.97	63.97	Present work
2400	22	2	18	20	34.79	34.79	Present work
20	30	3.5	39	14	2.56	3.66	[1]
640		3.5	258	20	83.33	83.33	[2]
900	30	3.5	25	8	28	70	[1]
1700	16	3.5	21	20	69.08	69.08	Present work
2400	18	3.5	18	20	38.89	38.89	Present work

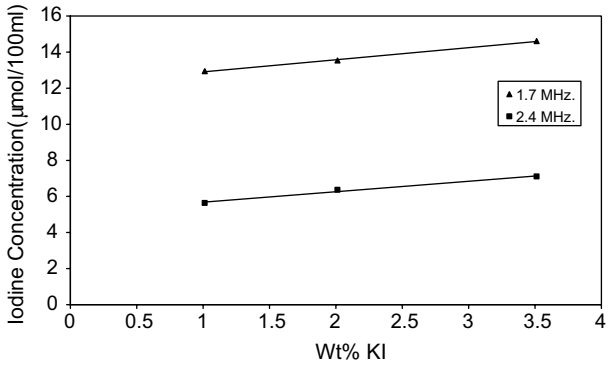

Fig. 4. Iodine concentration after 20 min of sonication with respect to KI concentration.

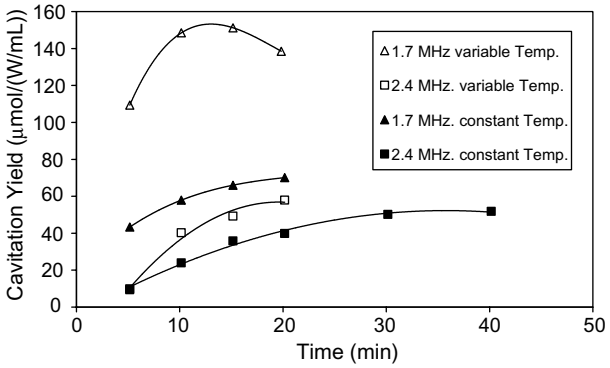

Fig. 5. Cavitation yield with and without direct cooling of KI solution at 1.7 and 2.4 MHz.

[10] determined that at 1 MHz, the iodine yield was not dependent on the solute concentration. Shirgaonkar and Pandit [9] explained this discrepancy between Naidu et al. and Gutierrez et al. by attributing it to the ultrasonic source used due to its impact on the life of a cavity. Shirgaonkar and Pandit [9] implied that cavitation yield was independent of KI concentration at higher sonication frequencies due to the shorter compression and rarefaction cycles. The effect of solute concentration at 1.7 MHz and 2.4 MHz is illustrated in Figs. 3 and 4, which show that cavitation yield is not independent of KI concentration. The dependence of cavitation yield on KI concentration during sonication at both frequencies confirms that even at high sonication frequencies, the concentration of KI affects the amount of iodine produced and thereby cavitation yield. Increase in cavitation yield at both frequencies can be attributed to the amount of hydroxyl radicals available due to rapid collapse of cavities lowering the probability of radical recombination to form peroxide and also the consumption of hydroxyl radicals by iodide ions that increases with an increase in KI concentration.

3.3. Effect of temperature

Increasing the reaction temperature is widely known to allow cavitation to be achieved at lower acoustic intensity due to the rise in vapor pressure associated with heating of the liquid. However, the effects of cavitational collapse are also reduced. At 20 kHz Entezari and Kruus [12] noted that rate of KI oxidation decreases linearly with increasing temperature. In contrast, at 900 kHz, they reported that iodine liberated increased with temperature until a maximum. A further increase in temperature resulted in a reduction in iodine production. Cavitation yield measurements at 1.7 MHz show that with temperature control of the sonicated liquid by direct cooling of KI solution, cavitation intensity increased uniformly towards a maximum. Without cooling, cavitation intensity increased rapidly and then decreased as shown in Fig. 5. In this case, the temperature of the solution increased from 14 °C to 45 °C over 20 min of sonication. At higher temperatures, there is less dissolved gas present which also increases the vapor pressure of the reactant solution. As a result, the ratio of partial pressures of p_{gas}/p_{liquid} inside the bubbles is lower and cavitation tends to be more unstable and vaporous in nature leading to a decrease in the cavitation rate. Also, as the solution is degassed, there may be a lack of cavitation nuclei. The unstable production of iodine without cooling may be due to the change from stable, gaseous cavitation to unstable, vaporous or transient cavitation since the increase in temperature reduces the effect of cavitation collapse as a result of increase in the vapor pressure of the liquid. At lower temperatures with direct cooling, cavitation tends to be more stable or gaseous in nature. Alternately, for 2.4 MHz and 18 W of power supplied to the transducer, a similar unstable behavior for cavitation yield without cooling was not reached during the experiments.

A comparison of cavitation yield measurements with and without cooling of the bulk solution is summarized in Table 2. Fig. 5 also shows that the cavitation yield

Table 2
Comparison of cavitation yield per unit power density with and without direct cooling of KI solution during sonication

Frequency (kHz)	Feed condition	Amount KI (%)	Power supplied (W)	Sonication time (min)	Cavitation yield (μmol/(W/mL))
1700	Direct cooling	3.5	21	20	69.08
2400	Direct cooling	3.5	18	20	38.89
1700	Without cooling	3.5	21	19.68	137.51
2400	Without cooling	3.5	18	20	56.87

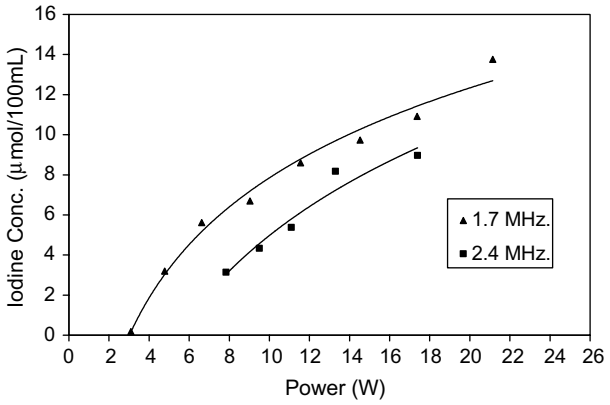

Fig. 6. Change in iodine concentration with respect to acoustic power supplied at 1.7 and 2.4 MHz.

increases logarithmically and tends to peak off after 30 min of sonication with cooling.

3.4. Effect of acoustic power supplied

The effect of power supplied on the oxidation of KI while sonicating between 20 kHz and 900 kHz has been studied previously [7,12,13]. Entezari and Kruus [1] observed that at 900 kHz, as the power supplied increases, the production of iodine increased linearly between 8 and 76 W with a clear cavitation threshold at 0.14 W cm^{-2}. In contrast, at 20 kHz, they found that the increase in iodine production was non-linear as the power supplied was increased from 8 to 130 W. To explain the non-linear behavior, they proposed that the iodine production rate slows at higher power due to the large number of visible bubbles that migrate out of solution. Both Weissler et al. [7] and Henglein and Gutierrez [13] studied the effect of power density on the oxidation of KI at 1 MHz and observed that the amount of iodine liberated increased with acoustic power supplied and then decreased sharply for small volumes (up to 50 mL) of KI solution under sonication. At 1 MHz, Weissler et al. [7] also observed that for large volumes (100 mL), iodine production increased linearly as power increased from 0 to 600 W. Henglein and Gutierrez [13] reported that at large volumes, the iodine production tends to show a non-linear increase with an increase in power, however the drop off was not observed in the experimental range (20–150 W). In this study, initial experiments determined the threshold power for iodine production, which coincides with the appearance of cavitation bubbles, was 1.17 W cm^{-2} and 3.14 W cm^{-2} for 100 mL of KI solution in the 1.7 MHz and 2.4 MHz systems respectively. In order to determine the relationship between acoustic power and the amount of iodine liberated, the power supplied to 1.7 MHz and 2.4 MHz transducers was varied from 3 to 21 W and 8 to 18 W respectively. As shown in Fig. 6, for 100 mL of KI solution, amount of iodine liberated increased with power supplied for both systems similar to earlier studies at lower frequencies [7,12,13].

4. Conclusion

Acoustic cavitation by Weissler's reaction for high frequency ultrasound systems operating at 1.7 MHz and 2.4 MHz has been studied. This study examines the effects of high frequency, solute concentration, and temperature conditions, and acoustic power intensity on cavitation yield. At frequencies in the MHz range, this study shows that cavitation yield decreases with an increase in frequency. Also, cavitation at 1.7 MHz is clearly higher than at 2.4 MHz. Also, operation in the MHz range generates a 20% increase in cavitation yield for a threefold increase in KI concentration. When the sonication was conducted with cooling of the KI solution at 1.7 MHz, the cavitation yield was distinctly lower than without cooling. However, the iodine release rate and hence yield were found to increase asymptotically and approach a maximum yield after 20 min of sonication approximately.

Without direct cooling of the KI solution, the cavitation yield is much higher but varies significantly over a short period of time altering the rate kinetics of the process. The unstable behavior has been postulated to be due to the change in cavitation from stable, gaseous cavitation to vaporous cavitation. This indicates that effective control of sonochemical processes in MHz range can be achieved by maintaining a constant temperature of the reactants subjected to irradiation.

References

[1] M.H. Entezari, P. Kruus, Ultrason. Sonochem. 1 (1994) S75–S79.
[2] J.D. Seymour, H.C. Wallace, R.B. Gupta, Ultrason. Sonochem. 4 (1997) 289–293.
[3] P.R. Gogate, S. Mujumdar, A.B. Pandit, J. Chem. Technol. Biotechnol. 78 (2003) 685–693.
[4] D.V. Prasad Naidu, R. Rajan, R. Kumar, K.S. Gandhi, V.H. Arakeri, S. Chandrasekaran, Chem. Eng. Sci. 49 (6) (1994) 877.
[5] A. Gedanken, Ultrason. Sonochem. 11 (2004) 47–55.
[6] P. Gogate, S. Mujumdar, A.B. Pandit, Adv. Env. Res. 7 (2003) 283–299.
[7] A. Weissler, H. Cooper, S. Snyder, J. Am. Chem. Soc. 72 (1950) 1769–1775.
[8] P. Gogate, I. Shirgaonkar, M. Sivakumar, P. Senthilkumar, N. Vichare, A.B. Pandit, AIChE J. 47 (2001) 2526–2538.
[9] I.Z. Shirgaokar, A.B. Pandit, Ultrason. Sonochem. 4 (1997) 245–253.
[10] M. Gutierrez, A. Henglein, F. Ibanez, J. Phys. Chem. 95 (1991) 6044.
[11] T.J. Mason, J.P. Lorimer, Applied Sonochemistry: the Uses of Power Ultrasound in Chemistry and Processing, Wiley-VCH Press, New York, 2001, pp. 140–141.
[12] M.H. Entezari, P. Kruus, Ultrason. Sonochem. 3 (1996) 19–24.
[13] A. Henglein, M. Gutierrez, J. Phys. Chem. 97 (1993) 158–162.