Ultrasonics Sonochemistry 23 (2015) 37–45

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

New interpretation of the effects of argon-saturating gas toward sonochemical reactions

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ARTICLE INFO

Article history:
Received 30 July 2014
Received in revised form 12 September 2014
Accepted 18 September 2014
Available online 28 September 2014

Keywords:
Sonochemical activity
Saturating gases
Single bubble
Computer simulations
·OH radical

ABSTRACT

A number of literature reports showed that argon provides a more sonochemical activity than polyatomic gases because of its higher polytropic ratio; whereas several recent studies showed that polyatomic gases, such as O_2, can compensate the lower bubble temperature by the self decomposition in the bubble. In this work, we show for the first time a numerical interpretation of these controversial reported effects. Computer simulations of chemical reactions inside a collapsing acoustic bubble in water saturated by different gases (Ar, O_2, air and N_2) have been performed for different frequencies (213–1100 kHz). In all cases, ·OH radical is the main powerful oxidant created in the bubble. Unexpectedly, the order of saturating gases toward the production rate of ·OH radical was strongly frequency dependent. The rate of production decreases in the order of Ar > O_2 > air > N_2 for frequencies above 515 kHz, and Ar starts to lose progressively its first order to the following gases with a gradually decreasing of frequency below 515 kHz up to a final order of O_2 > air ~ N_2 > Ar at 213 kHz. The analysis of chemical kinetic results showed a surprising aspect: in some cases, there exists an optimum bubble temperature during collapse at which the chemical yield is much higher than that of the maximum bubble temperature achieved in the bubble. On the basis of this, we have concluded that the lower sonochemical activity induced by Ar for frequencies below 515 kHz is mainly due to the forte consumption of radicals inside a bubble prior the complete collapse being reached.

1. Introduction

When a liquid containing dissolved gas is irradiated by an ultrasound wave, many tiny bubbles appear which is a phenomenon known as acoustic cavitation [1]. The bubbles repeat expansion and contraction according to the pressure oscillation of an ultrasonic wave [1]. Some bubbles collapse violently at the contraction phase and extreme temperature and pressures are developed therein (several thousands of Kelvin and several hundreds of atmospheres) [2]. Under such conditions molecules trapped in the bubble (water vapor, gases and vaporized solutes) can be brought to an excited-state and dissociate. As results, reactive species such as ·OH, HO_2, H·, O and H_2O_2 are created from H_2O and O_2 dissociation and their associate reactions in the bubble [3]. These chemical products may diffuse out of the bubble and dissolve in the surrounding liquid [4]. Reactions involving free radicals can occur within the collapsing bubble, at the liquid interface and in the surrounding liquid [4]. Solutes, i.e. aqueous pollutants, can easily oxidized by the oxidants such as ·OH, which is considered the primary oxidizing species during aqueous sonolysis. The chemistry using acoustic cavitation is called sonochemistry. Sonochemistry is one of the recent advanced oxidation processes for water and wastewater treatment. Cavitation bubbles due to the very high temperatures generated at the final stages of bubble collapse emit light, which is known as sonoluminescence [5].

The sonochemical activity (production of radicals) is influenced by a number of factors such as frequency of ultrasound, dissolved gas, acoustic power and liquid temperature [6–12]. Among these factors, the nature of the dissolved gases have shown controversial effects, particularly differences between argon and polyatomic gases. A number of experimental reports [13–16] showed that argon provides a more sonochemical activity than polyatomic gases because of its higher polytropic ratio, which yields higher bubble temperature at the collapse. Whereas several other studies [9,11,12,17–20] showed that polyatomic gases, such as O_2, can compensate the lower O_2-bubble temperature by the self-decomposition in the bubble and then yield more sonochemical

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http://dx.doi.org/10.1016/j.ultsonch.2014.09.009
1350-4177/

Nomenclature

c	speed of sound in the liquid medium, (m s^{-1})
f	frequency of ultrasonic wave, (Hz)
I_a	acoustic intensity of ultrasonic irradiation, (W m^{-2})
p	pressure inside a bubble, (Pa)
p_{max}	maximum pressure inside a bubble (Pa)
p_∞	ambient static pressure, (Pa)
P_A	amplitude of the acoustic pressure, (Pa)
P_v	vapor pressure of water, (Pa)
P_{g0}	initial gas pressure, (Pa)
R	radius of the bubble, (m)
R_{max}	maximum radius of the bubble, (m)
R_0	ambient bubble radius, (m)
t	time, (s)
T	temperature inside a bubble, (K)
T_{max}	maximum temperature inside a bubble, (K)
T_{opt}	optimum bubble temperature for the production of ·OH radical, (K)
T_∞	bulk liquid temperature, (K)
x_i	solubility (in mole fraction) of the gas i in water

Greek letters

γ	specific heat ratio (c_p/c_v) of the mixture
σ	surface tension of liquid water, (N m^{-1}).
ρ	density of liquid water, (kg m^{-3}).
λ	gas thermal conductivity, (W m^{-2} K).

activity than argon. Therefore, the mechanism of the argon-induced lower or higher sonochemical activity than polyatomic gases is until now not understood. The present work deals with studying the effects of some saturating gases in scale of single-bubble for a possible explanation of these controversial results reported in the literature. Computer simulations of chemical reactions occurring inside a collapsing acoustic bubble in water saturated by different gases (Ar, O_2, air and N_2) have been performed for different frequencies (213–1100 kHz). The employed model combines the dynamic of bubble collapse in acoustic field with the chemical kinetics occurring in the bubble during the strong collapse.

2. Model and computational methods

The theoretical model used in the present numerical simulations has been described in our previous works [21,22]. The following is a brief description of the model.

2.1. Bubble dynamics model

A gas and vapor filled spherical bubble isolated in water oscillates under the action of a sinusoidal sound wave. The temperature and pressure in the bubble are assumed spatially uniform and the gas content of the bubble behaves as an ideal gas [23]. The radial dynamics of the bubble is described by the Keller equation that includes first order terms in the Mach number $\dot{R}/c$ [24,25]:

$$\left(1-\frac{\dot{R}}{c}\right)R\ddot{R}+\frac{3}{2}\left(1-\frac{\dot{R}}{3c}\right)\dot{R}^2 = \frac{1}{\rho_L}\left(1+\frac{\dot{R}}{c}+\frac{R}{c}\frac{d}{dt}\right)\left[p-p_\infty-\frac{2\sigma}{R}-4\mu\frac{\dot{R}}{R}+P_A\sin(2\pi ft)\right] \quad (1)$$

in this equation dots denote time derivatives (d/dt), R is the radius of the bubble, c is the speed of sound in the liquid, ρ_L is the density of the liquid, σ is the surface tension, μ is the liquid viscosity, p is the pressure inside the bubble, p_∞ is the ambient static pressure, P_A is the acoustic amplitude and f is the sound frequency. The acoustic amplitude P_A is correlated with the acoustic intensity I_a, or power per unit area, as $P_A = (2I_a\rho_L c)^{1/2}$ [4].

The expansion of the bubble is assumed as isothermal and its total compression is considered as adiabatic [26]. These assumptions, which are widely accepted since the lifetime of an oscillation at high frequency is relatively short with a very rapidly occurring collapse event, were pointed out by Yasui et al. [27] using a more detailed model. We also assume that the vapor pressure in the bubble remains constant during the bubble expansion phase and there is no gas diffusion during expansion and no mass and heat transfer of any kind during collapse. We note here that Storey and Szeri [28] demonstrated that the inclusion of mass transfer (non-equilibrium condensation and evaporation and gas diffusion at the bubble wall) on the bubble dynamics has practically no effect on the maximum bubble temperature attained in the bubble at the collapse when the compression ratio of the bubble (R_{max}/R_{min}) is less than 20 (R_{max} is the maximum radius of the bubble and R_{min} is the minimum bubble radius at the collapse). This level of R_{max}/R_{min} was never attained in the present numerical study. Therefore, in order to reduce computational parameters, the current model takes, as input, initial bubble vapor content and neglects mass and heat transfer during bubble expansion and collapse.

Based on the above assumptions, the pressure and temperature inside the bubble at any instant during the collapse phase can be calculated from the bubble size as

$$p = \left[P_v + P_{g0}\left(\frac{R_0}{R_{max}}\right)^3\right]\left(\frac{R_{max}}{R}\right)^{3\gamma} \quad (2)$$

$$T = T_\infty\left(\frac{R_{max}}{R}\right)^{3(\gamma-1)} \quad (3)$$

where P_v is the vapor pressure, $P_{g0} = p_\infty + (2\sigma/R_0) - P_v$ is the gas pressure in the bubble at its ambient state ($R = R_0$), R_0 is the ambient bubble radius, T_∞ is the bulk liquid temperature and γ is the ratio of specific heats capacities (c_p/c_v) of the gas/vapor mixture. The maximum internal temperature (T_{max}) and pressure (p_{max}) in the bubble are reached at the end of the bubble collapse and they are approximated by:

$$T_{max} = T_\infty\left(\frac{R_{max}}{R_{min}}\right)^{3(\gamma-1)} \quad (4)$$

$$p_{max} = \left[P_v + P_{g0}\left(\frac{R_0}{R_{max}}\right)^3\right]\left(\frac{R_{max}}{R_{min}}\right)^{3\gamma} \quad (5)$$

It is important to notice here that the assumption of spatial uniform pressure and temperature inside the bubble is valid as long as inertia effects are negligible and the velocity of the bubble wall is below the speed of sound in the vapor/gas mixture. This assumption was justified in detail in the paper published by Kamath et al. [29]. In addition, several researchers [27,30–32] pointed out in their models which include heat transfer that the bubble temperature and pressure are roughly uniform except at a very thin layer, called thermal boundary, near the bubble wall.