Opinion Paper

An alternative technique for determining the number density of acoustic cavitation bubbles in sonochemical reactors

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ABSTRACT

The present paper introduces a novel semi-empirical technique for the determination of active bubbles’ number in sonochemical reactors. This method links the chemistry of a single bubble to that taking place over the whole sonochemical reactor (solution). The probe compound is CCl4, where its eliminated amount within a single bubble (though pyrolysis) is determined via a cavitation model which takes into account the non-equilibrium condensation/evaporation of water vapor and heat exchange across the bubble wall, reactions heats and liquid compressibility and viscosity, all along the bubble oscillation under the temporal perturbation of the ultrasonic wave. The CCl4 degradation data in aqueous solution (available in literature) are used to determine the number density through dividing the degradation yield of CCl4 to that predicted by a single bubble model (at the same experimental condition of the aqueous data). The impact of ultrasonic frequency on the number density of bubbles is shown and compared with data from the literature, where a high level of consistency is found.

1. Introduction

The irradiation of a solution with ultrasonic waves causes acoustic cavitation, a transitory phenomenon that increases chemical activity [1]. Through the growth of previously formed nuclei during the alternating expansion and compression cycles of ultrasonic waves, acoustic cavities are obtained [2]. As a result, at collapse, peculiar conditions are created, where a temperature as high as 5000 K and pressure exceeding 1000 atm are believed to exist within the acoustic bubble (hot spot) [3-7]. These tremendous conditions lead to the thermalization of water vapor and non-condensable gas present inside the hot spots, therefore, a variety of radicals (e.g. OH, HO2 and H) and reactive species (e. g.H2O2) are created [8]. These species are able to initiate other secondary chemical reactions and emit light [9-11]. The sonochemical process has found a variety of applications in different fields such as the synthesis of nanomaterials, polymers, degradation of organic pollutants, biomedical and food science applications, etc. [12-22]. On the other hand, several works have been oriented towards the enhancement of our understanding regarding the effect of the different operational conditions (i.e. frequency, acoustic intensity, liquid temperature and viscosity, irradiation mode…etc.) on the acoustic bubble activity as well as the efficacy of sonochemical reactors [23-30].

In the last two decades, a number of theoretical and experimental (and semi-empirical) works [26,31-34] have been focused on the different characteristics of bubbles population (i.e. distribution of acoustic bubbles and number density). To illustrate, Lee et al. [35] have used a pulsed sonoluminescence technique in order to determine the size distribution of SL bubbles (at 515 kHz) by using the total dissolution time of bubbles and Epstein-Plesset equation. The same method has been adopted by Brothie et al. [36] to correlate the ultrasound pulse separation with the ambient bubble radius in absence of ultrasound in a dual-frequency system (355 and 20 kHz). It has been demonstrated that the pulsed mechanism increases the bubble density, improving coalescence rates and increasing the bubble size, contrary to the continuous operation, which has the opposite effect. Furthermore, Brothie et al. [36] have indicated the strong correlation between the relative coalescence extent and the enhancement in sonochemical reaction rates in a dual-frequency system. On the other hand, Burdin et al. [37] have employed two laser techniques (Laser diffraction (LD) and phase Doppler (PD)) in order to

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evaluate the effect of acoustic power on the mean radii and the void fraction of bubbles population at 20 kHz. The determination of the number of active bubbles (number density) according to the experimental works of Labouret and Frohly [38,39] and Iida et al. [40] is based on the evaluation of void (total volume of bubbles) fraction. In the experimental study of Iida et al. [40] the void rate is determined via a capillary system, whereas, the size distribution of active bubbles is evaluated by a pulsed laser diffraction method. Labouret and Frohly [38,39] determined the void fraction through electromagnetic resonance; therefore, the size distribution of bubbles is obtained from the linkage between the single bubble chemistry (resulting from CCl$_4$ pyrolysis) and HOCl resulted from the pyrolysis of CCl$_4$ within a single acoustic bubble. According to the results of these works [60,61], CCl$_4$ degradation within the bubble not only produces RCS but also accelerates the generation of hydroxyl radical through its strong scavenging effect on H$^\bullet$ radical (CCl$_4$+H$^\bullet$→HCl+CCl$_3$).

In the present work, a new technique is proposed for evaluating the active bubble number generated within a sonochemical reactor per unit volume and unit time (i.e. number density). This method is based on the linkage between the single bubble chemistry (resulting from CCl$_4$ pyrolysis) to that developed inside the sonoreactor (in solution). The single bubble sonochemistry model developed early for CCl$_4$ has been used for the prediction of the single bubble degradation of CCl$_4$, under some experimental data revealing the degradation of CCl$_4$ in aqueous solutions (principally the works of Petit and Francyron [62] and of Hung and Hoffmann [48] which provided the effect of frequency on the sonochemical degradation of carbon tetrachloride). A qualitative and quantitative comparison has been made between our results and those found in the literature.

2. Theoretical package
2.1. The single bubble system

For the simulation of the bubble dynamics and the internal bubble chemistry, the mathematical model developed early by our research group [60,61] for studying the CCl$_4$ sonochemistry is used. A detailed discussion about these reaction schemes is available in [60,61]. The model is based on a set of ordinary differential equations that account for non-equilibrium evaporation and condensation of water vapor at the bubble wall, heat transfer between the bubble interior and the surrounding liquid, chemical reactions heat, and CCl$_4$ pyrolytic reactions. Table 1 summarizes the equations that govern the model. All numerical simulations were carried out for a single bubble oscillating in argon or oxygen-saturated water containing varying concentrations of carbon tetrachloride. The bubble–bubble interactions are ignored. This assumption has been made due to the complicated nature of multibubble systems (clusters) which makes the process modeling more and more complex. The bubbles interaction in sonication medium may increase the coalescence of bubbles or reducing their intensity of implosion, ultrasound frequency [45-49]. In fact, the reactivity of CCl$_4$ toward hydroxyl radical is negligible [49,59]. Recently, our research group has published two interesting computation works on CCl$_4$ degradation by ultrasound [60,61], where a new reaction scheme for CCl$_4$ has been used to identify the main reactive chlorine species (RCS: Cl$^\bullet$Cl, Cl$^\bullet$Cl$^\bullet$ and Cl and HOCl) resulted from the pyrolysis of CCl$_4$ within a single acoustic bubble. According to the results of these works [60,61], CCl$_4$ degradation within the bubble not only produces RCS but also accelerates the generation of hydroxyl radical through its strong scavenging effect on H$^\bullet$ radical (CCl$_4$+H$^\bullet$→HCl+CCl$_3$).

| Nomenclature | Definition |
|--------------|------------|
| $A_f$ ($A_v$) | Pre-exponential factor of the forward (reverse) reaction, ([cm$^3$ mol$^{-1}$ s$^{-1}$] for two body reaction and (cm$^6$ mol$^{-2}$ s$^{-1}$) for three body reaction), |
| $b_f$ ($b_v$) | Temperature exponent of the forward (reverse) reaction. |
| $c$ | Speed of sound in the liquid medium, (m s$^{-1}$). |
| $E_{af}$ ($E_{av}$) | Activation energy of the forward (reverse) reaction, (cal mol$^{-1}$). |
| $f$ | Frequency of ultrasonic wave, (Hz). |
| $I_a$ | Acoustic intensity of ultrasonic irradiation, (W m$^{-2}$). |
| $k_f$ ($k_v$) | Forward (reverse) reaction constant, ([cm$^3$ mol$^{-1}$ s$^{-1}$] for two body reaction and (cm$^6$ mol$^{-2}$ s$^{-1}$) for three body reaction). |
| $p$ | Pressure inside a bubble, (Pa). |
| $p_{max}$ | Maximum pressure inside a bubble (Pa). |
| $p_{ao}$ | Ambient static pressure, (Pa). |
| $P_v$ | Amplitude of the acoustic pressure, (Pa). |
| $P_o$ | Vapor pressure of water, (Pa). |
| $R$ | Radius of the bubble, (m). |
| $R_{max}$ | Maximum radius of the bubble, (m). |
| $R_o$ | Ambient bubble radius, (m). |
| $t$ | Time, (s). |
| $T$ | Temperature inside a bubble, (K). |
| $T_{max}$ | Maximum temperature inside a bubble, (K). |
| $T_{aw}$ | Bulk liquid temperature, (K). |
| $x_i$ | Solubility (in mole fraction) of the gas i in water. |
| $y_{H2O}$ | Mole fraction of water vapor trapped at the collapse. |

Greek letters

| Symbol | Definition |
|--------|------------|
| $\gamma$ | Specific heat ratio ($c_p/c_v$) of the gas mixture. |
| $\sigma$ | Surface tension of liquid water, (N m$^{-1}$). |
| $\rho$ | Density of liquid water, (kg m$^{-3}$). |
| $\lambda$ | Gas thermal conductivity (W m$^{-2}$ K). |
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Table 1
Principal equations of the model (see detail in Refs. [60,61])

| Equation | Description |
|----------|-------------|
| $P_0(t) = P(t) - 2 \frac{4\rho R}{R}$ | Pressure at the external bubble wall. |
| $P(t) = \frac{n_b \lambda}{am} \left( T - \frac{E}{\lambda} \right)$ | Bubble pressure and Temperature. |
| $T = \frac{T_0}{\lambda}$ | (Eq. 4) |
| $m = \alpha \frac{(P_{am}R - P(t))}{M_{H_2O}} \left( \sqrt{R} \right)$ | Heat transfer (thermal conduction): |
| $n_{H_2O}(T + \Delta t) + n_{H_2O}(T) = 4\pi R^2 \Delta \xi \left( \frac{T_1 - T}{\lambda} \right) + \frac{4 \pi R^2 \Delta \xi}{\lambda} \sum_{i=1}^{4} \Delta \xi \delta_i$ | Internal bubble energy: |

*aVariables description: dots denoted here time derivative (d/dt), R is the bubble radius, C is the sound speed in the medium (water), $\rho_0$ is the liquid density, m is the net rate of evaporation per unit area and unit time and $P_{am}$ is the ambient static pressure, $P_0$ is the acoustic amplitude (linked to the acoustic intensity $I_0$ by: $P_0 = (2\alpha I_0 \rho_0 \xi)^{1/2}$), $P(t)$ is the liquid pressure at the liquid side of the bubble, $P_0(t)$ is the pressure inside the bubble, $\sigma$ is the surface tension, $\mu$ is the liquid viscosity, $s$ is the sound speed, $P_s$ is the vapor pressure within the bubble, $a$ and $b$ (in Eqs. (3) and (4)) are the Van der Waals constants (given in [95]), $R$ is the universal gas constant, $V$ is the volume of the bubble [$V = 4/3(2\pi R^3)$], $T$ is the temperature inside the bubble. E is the internal bubble energy, $P_{am}[R]$ is the saturated vapor pressure (calculated by using Antoine’s equation) at the interface temperature $T_{int} = T_{h_2o}$. $M_{H_2O}$ is the molecular weight of water vapor and ‘$a$’ is the accommodation coefficient (given in [69]). $\lambda_{water}$ and $\lambda_{air}$ are the heat conductivity, thermal diffusivity of the gas mixture and the thickness of the thermal boundary layer, respectively. (Individual $\lambda$ of gases [95,96]; $\lambda_{H_2O}(T) = 9.967213 \times 10^{-2} - 1.1705 \times 10^{-7}$, $\lambda_{H_2O}(T) = 3.5887 \times 10^{-7}$ + 6.81277 $\times 10^{-2}$ + 2.22 $\times 10^{-7}$ + 6.4478 $\times 10^{2}T + 7.2211 \times 10^{-3}T^2$ + $\lambda_{Ar}(T) = \lambda_{H_2O}(T)$). $C_p$ is the heat capacity concentration (J m⁻³ K⁻¹) for H₂O, Cl₂, Ar, or O₂ mixture (given in [75]), $C_m$ is the molar heat of gases and vapor in the bubble [$C_m = (3/2)R$] for monoatomic gases (Ar, H₂, …), (5/2)R for diatomic gases (O₂, Cl₂, …) and (6/2)R for triatomic gases. $\Delta H_i$ and $\gamma_i$ are the enthalpy change and the rate of the ith reaction, respectively, and $\epsilon_{H_2O}$ is the energy transported by 1 mol of an evaporating or condensing water vapor [$\epsilon_{H_2O} = C_{H_2O}T$]. $U_{h_2o}$ and $U_{l_2o}$ are the production rate of H₂O and Cl₂ species within the bubble. |

which make the sonochemical process less efficient. The involvement of this phenomenon in computation will be studied in future project. However, many leading research groups in sonochemistry have adopted the single bubble approach (without bubbles interaction) for understanding the overall observed sonochemical effects (sonoluminescence and sonochemistry) in aqueous solutions, with relation to influencing factors [42,63-79]. Tables 2 and 3 show the reaction mechanism used to study the internal bubble chemistry for an Ar-Cl₂Cl₂-bubble (Table 2, 31 reversible reactions) and an O₂-CCl₄-bubble (Table 3, 29 reversible reactions). A detailed discussion about these reaction schemes is available in [60,61]. Table 1 contains the following main equations:

1. Eq. (1) (the modified Keller-Miksis equation [80]) describes the radial dynamics, $R(t)$, of the bubble during its oscillation in compressible medium (water) saturated with Ar or O₂ in presence of a determined concentration of Cl₂Cl₂. |

2. Eqs. (3) and (4) provide the internal bubble pressure and temperature during oscillation.

3. Eq. (5) (the Hertz-Knudsen formula [81]) describes the mass flux, $dm/dt$, of water evaporation and condensation at the bubble-solution interface.

4. Eqs. ((6)–(8)) (heat dissipation by conduction [75]) describe the heat exchange $dQ/dt$ inside and outside the bubble during oscillation. According to Eq. 6, the heat exchange is given as a function of the interior bubble temperature and the bubble surface temperature, which is assumed constant ($T_s = T_{h_2o}$). This approach has been adopted from the work of Toegel et al. [75] (i.e. which is one of the pioneers in sonoluminescence and sonochemistry fields) and it is largely used in several theoretical studies giving interesting results in
sonoechemistry [60,65,67,75,79,82,83]. This assumption is supported by the short lifetime of the bubble and the very short collapsing time especially at higher ultrasound frequencies, which is the case of our study (200–1078 kHz). For example at 205 kHz (I_b = 1.48 W/cm²), the collapse time is 1.24 μs, representing 24.8% of the whole bubble lifetime (5 μs). At 1078 kHz (I_b = 1.48 W/cm²), the
In the present study, the initial rate of CCl₄ degradation (mol L⁻¹ s⁻¹) is determined based on the experimental work of Hung and Hoffmann [48] and Pétier and Francony [62], who investigated the degradation of CCl₄ over a wide range of frequency of ultrasound. The initial rates of CCl₄ degradation (mol L⁻¹ s⁻¹) inferred from these studies are regrouped in Tables 4 and 5(a) and (b). The experimental work of Pétier and Francony [62] is conducted under an atmosphere of oxygen, whereas, the type of saturating gas was not specified in the work of Hung and Hoffmann [48]. Nevertheless, the predominance of C₂Cl₂ and C₄Cl₄ upon the sonolysis of carbon tetrachloride indicates the possibility of using argon (during CCl₄ sonolysis) as a dissolved gas in our study in the purpose to simulate the experimental findings obtained by Hung and Hoffmann [48]. This choice is supported by the experimental results obtained by Hua and Hoffmann [56] for the decomposition of CCl₄ in presence of argon, where the main species resulting from CCl₄ decomposition are chloride ion, Hypochlorous acid and the low concentrations of hexachloroethane and tetrachloroethylene. In contrast, for example, the sonolysis of CCl₄ under an atmosphere of oxygen generates preferably CO₂, CO, Cl⁻ [46,56]. Consequently, in order to simulate the decomposition of CCl₄ in presence of O₂ under the experimental conditions of Pétier and Francony [62], the chemical reactions occurring within a bubble initially composed of oxygen and CCl₄ is followed according to the scheme given in Table 3. On the other hand, the decomposition of CCl₄ under an Ar atmosphere under the experimental conditions of Hung and Hoffmann [48], is simulated according to the chemical kinetics shown in Table 2.

3. Results and discussions

The obtained results of the present developed technique (i.e. based on CCl₄ pyrolysis) are compared to those obtained semi-empirically by Merouani et al. [42] for air and oxygen bubbles and theoretically by Kerboua et al. [44] for oxygen bubbles. The obtained findings of Merouani et al. [42] are based on the determination of the molar yield of H₂O₂, O²⁺ and HO• of a single bubble in addition to the production rate of H₂O₂ measured experimentally. On the other hand, Kerboua and Hamdadou’s [43] work is built on an energetic analysis of the macroscopic (control volume) and microscopic (acoustic bubble) systems under the action of ultrasonic perturbation. It should be noted that the discussed results in this paper are confronted on a range of ultrasound frequencies from ~20 to 1000 kHz, Tables 4-7.

### Table 4

| [a] Number of active bubbles under the experimental conditions of Hung and Hoffmann [48] (conditions: [CCl₄]₀ = 0.2 mM, P₀ = 2.05 atm for the range of ultrasound frequency from 205 to 1078 kHz, with the exception of 500 kHz where P₀ = 2.31 atm, Tᵢₕ = 13 °C). [b] Maximal bubble radius (R_max, µm) achieved during oscillation, bubble lifetime and the acoustic period (µs), under the same conditions of [a]. |
|---|
| f (kHz) | CCl₄ removal by a single bubble (mol) | Initial rate of CCl₄ removal in solution (mol L⁻¹ s⁻¹) | Production rate of bubbles (L⁻¹ s⁻¹) |
|---|---|---|---|
| 205 | 3.12 × 10⁻¹⁶ | 1.31654 × 10⁻⁰⁷ | 4.22 × 10⁻¹⁰ |
| 358 | 2.00 × 10⁻¹⁷ | 1.44684 × 10⁻⁰⁷ | 7.25 × 10⁻¹⁰ |
| 500 | 1.65 × 10⁻¹⁷ | 1.26277 × 10⁻⁰⁷ | 7.67 × 10⁻¹⁰ |
| 618 | 1.46 × 10⁻¹⁷ | 1.60285 × 10⁻⁰⁷ | 1.10 × 10⁻¹⁰ |
| 1078 | 5.19 × 10⁻²⁰ | 1.1811 × 10⁻⁰⁷ | 2.28 × 10⁻¹² |
| [b] | Maximum bubble radius (R_max, µm) | Bubble lifetime (µs) | Acoustic cycle (µs) |
|---|---|---|---|
| 205 | 22.81 | 4.25 | 4.87 |
| 358 | 11.01 | 2.25 | 2.79 |
| 500 | 9.39 | 1.71 | 2.0 |
| 618 | 7.37 | 1.37 | 1.61 |
| 1078 | 4.38 | 0.79 | 0.92 |
3.1. The single bubble degradation of $CCl_4$

It is initially critical to demonstrate how to determine the single bubble conversion of $CCl_4$ using the model described in Section 2. Even though we have done this in detail in our earlier works [61,82] for many simulation circumstances (frequency, acoustic intensity, and liquid temperature), it is best to describe briefly the topic here to provide the reader a quick grasp of the established approach. The evolution of the bubble dynamics, the bubble temperature and pressure, and the interior bubble chemistry are illustrated in Fig. 1 (for one acoustic cycle in Fig. 1 (a) and (b) and around the end of the bubble collapse in Fig. 1 (c)). The numerical simulations of Fig. 1 are for a bubble of $R_0 = 3 \mu$m oscillating in argon-saturated water containing 0.2 mM of $CCl_4$, under the following sonication conditions: frequency: 500 kHz, acoustic amplitude $P_a$ = 2.31 atm, liquid temperature 13 °C, and ambient static pressure $P_{atm}$ = 1 atm. These acoustical conditions are a part of those applied by Hung and Hoffmann [48] for degrading $CCl_4$ in argon-saturated solution. The Henry law for $CCl_4$ is given as $P_{CCl_4,0} = K_{CCl_4}C_{CCl_4,0}$, where $K_{CCl_4} = 1733.06$ Pa m$^2$ mol$^{-1}$ [88], 13 °C and $C_{CCl_4,0}$ is the $CCl_4$ concentration in the azeotropic phase, 0.2 mM. By applying this rule, the initial pressure of $CCl_4$ within the bubble (at $t = 0$ μs or $R = R_0$) could be 0.346 kPa. Given that the initial bubble pressure is $P_0 = P_a + 2\pi R_0/R = 150.515$ kPa, the initial fraction of $CCl_4$ with the bubble is $P_{CCl_4}/P_0 = 2.3028 \times 10^{-3}$ (so 0.23%). Similarly, the initial bubble content on water vapor is 9.79 × 10$^{-3}$. This is calculated as $P_a/\sigma$, where $P_a$ is the water vapor (saturated) calculated through Antoine’s equation. The remnant of the initial bubble content [1 - $P_{w,v}/P_a P_{CCl_4}/P_0$] is occupied by the saturating gas (i.e. argon in this case).

The bubble oscillation in Fig. 1(a) represents the temporal behavior of the bubble radius, which has been extensively discovered experimentally [89,90] and numerically by a number of sonochemists, including Yasui [91], Merouani et al. [68], Kerboua et al. [69], and others [79,92]. During the negative rarefaction cycle of the sound wave, the bubble grows from $R_0$ to $R_{max}$ in 1.219 μs and then abruptly collapses in 0.49 μs, producing the occurrence of a peak temperature around the end of the bubble collapse (around $t = 1.71$ μs), as shown in Fig. 1(b). A maximum temperature of 5155.53 K is attained within the bubble at $R_{min}$. This intense temperature enables reaction chemistry to occur within the bubble; this latter is considered as a micro-reactor within which high-energy chemical reactions occur during the final instant of collapse (about $R_{min}$), as seen in Fig. 1(c). According to this figure, a part of $CCl_4$ and $H_2O$ molecules trapped at the collapse are pyrolyzed, yielding a variety of chemicals (argon is unreactive species; its amount could be then unchanged). Refs. [60,61] provide a thorough description of the reaction findings that led to Fig. 1(c). This could not be supplied here since the study is aimed primarily to determine the bubbles’ number, which needs knowledge of the quantity of $CCl_4$ removed (degraded) by one bubble in one acoustic cycle (i.e. from one implosion). This latter is obtained by subtracting the amount of $CCl_4$ at the end of the bubble collapse (at $R = R_{min}$ 9.46 × 10$^{-22}$ mol) from the initial quantity of $CCl_4$ within the bubble (at $t = 0$ μs, 1.647 × 10$^{-17}$ mol), which yields 1.6466 × 10$^{-17}$ mol (99.85% of $CCl_4$ is eliminated).

3.2. Production rate of active bubbles “the number density”

In Tables 4 and 5(a), the predicted removal of $CCl_4$ for a single bubble, the initial rate of $CCl_4$ removal in the sonoreactors (solution) and the calculated production rates of active bubbles (i.e. number density) are given under the experimental conditions of Hung and Hoffmann [48] and Pétier and Françon [62], respectively. The obtained results in Table 4(a) and Table 5(a) are compared to those obtained semi-empirically by Merouani et al. [42] under: (i) their experimental conditions [air-bubble, Table 6(a)] and (ii) under the Pétier and Françon’s [62] and Jiang et al.’s [93] conditions [O$_2$-bubble, Table 6(b)]. Additionally, the obtained results in Table 4(a) and Table 5(a) are confronted with those obtained theoretically by Kerboua et al. [44] for an oxygen bubble (Table 7). The obtained results in Tables 4-7 are depicted in Fig. 2.

In general, it is observed that the number of active bubbles is substantially increased with the rise of ultrasound frequency either according to our study (Table 4(a) and Table 5(a)) or as it is obtained by Merouani et al. [42] and Kerboua et al. [44] (Fig. 2). For example, under the experimental conditions of Hung and Hoffmann [48] (Table 4(a), Fig. 2), the production rate of active bubbles goes up from 4.22 × 10$^8$ to 2.28 × 10$^9$ L$^{-1}$ s$^{-1}$, when ultrasound frequency increased from 205 to 1078 kHz. This trend (i.e. increase of number density with wave frequency) is in good agreement with those reported qualitatively by

### Table 5

| Frequency (kHz) | CCl4 removal by a single bubble (mol) | Initial rate of CCl4 removal in solution (mol L$^{-1}$ s$^{-1}$) | Production rate of bubbles (L$^{-1}$ s$^{-1}$) |
|----------------|--------------------------------------|----------------------------------------------------------|---------------------------------|
| 200            | 7.70 × 10$^{-10}$                    | 5.50 × 10$^{-9}$                                         | 7.14 × 10$^{-8}$               |
| 500            | 1.93 × 10$^{-9}$                     | 6.17 × 10$^{-8}$                                         | 3.20 × 10$^{-7}$               |
| 800            | 1.03 × 10$^{-9}$                     | 8.33 × 10$^{-8}$                                         | 8.10 × 10$^{-7}$               |

| Frequency (kHz) | Maximum bubble radius (µm) | Bubble lifetime (µs) | Acoustic cycle (µs) |
|----------------|---------------------------|---------------------|---------------------|
| 200            | 21.91                      | 4.28                | 5                   |
| 500            | 8.04                       | 1.63                | 2                   |
| 800            | 5.83                       | 1.08                | 1.25                |

### Table 6

Production rate of active bubbles “N (L$^{-1}$ s$^{-1}$)” according to the semi-empirical model of Merouani et al. [42].

| Frequency (kHz) | N (L$^{-1}$ s$^{-1}$) (Merouani et al. conditions) | N (L$^{-1}$ s$^{-1}$) (Jiang et al. et al. conditions) |
|----------------|---------------------------------------------------|-----------------------------------------------------|
| 300            | 2.84 × 10$^{-6}$                                  |                                                     |
| 585            | 3.94 × 10$^{-6}$                                  |                                                     |
| 860            | 3.04 × 10$^{-6}$                                  |                                                     |
| 1140           | 3.08 × 10$^{-6}$                                  |                                                     |

### Table 7

Production rate of active bubbles “N (L$^{-1}$ s$^{-1}$)” according to the theoretical work of Kerboua et al. [44] (P$_a$ = 1.5 atm, T$_{liq}$ = 20 °C and oxygen-saturation gas).

| Frequency (kHz) | N (L$^{-1}$ s$^{-1}$) |
|----------------|-----------------------|
| 200            | 5.2249 × 10$^{-10}$   |
| 500            | 3.7399 × 10$^{-7}$    |
| 800            | 6.3968 × 10$^{-7}$    |

| Frequency (kHz) | N (L$^{-1}$ s$^{-1}$) |
|----------------|-----------------------|
| 200            | 1.60 × 10$^{-12}$     |
| 300            | 1.20 × 10$^{-13}$     |
| 360            | 1.80 × 10$^{-12}$     |
| 443            | 2.58 × 10$^{-13}$     |
| 500            | 5.00 × 10$^{-13}$     |
| 600            | 2.40 × 10$^{-14}$     |
| 800            | 4.00 × 10$^{-15}$     |
Kanthale et al. [94] and Brotchie et al. [36]. The increase of the production rate of active bubbles proportionally with the rise of ultrasound frequency can be explained according to the effect of incident ultrasonic waves on the dynamics of bubbles. The increase of ultrasound frequency causes the lifetime of bubbles to be reduced as well as the maximum radii of oscillating cavities, where this is ascribed to the decrease of acoustic period monotonically with the rise of frequency, as seen in Table 4 (b) and Table 5 (b). Consequently, the number of active bubbles created per unit time is remarkably increased at higher acoustic frequencies compared to the lower ones. The confrontation of our findings (Table 4(a) and Table 5(a)) to those obtained by Merouani et al. (Table 6 (a) and (b)) and Kerboua et al. (Table 7) indicates the good concordance between these results concerning the improvement of the production rate of bubbles as a result to the rise of frequency. However, it is clearly observed that our results (production rate of bubbles) are quantitatively situated between those of Merouani et al. (lower values of N) and Kerboua
4. Conclusion

et al. (higher values of N). This is probably ascribed to the adopted techniques for determining the number density of bubbles [42,44] as it was indicated previously. It should be noted that the improvement of the number density of bubbles is also obtained by the increase of acoustic intensity, use of the pulsed mode of sono-irradiation, increase of the irradiation time and the application of dual-frequency field [26,36,38]. Indeed, as it can be observed in Fig. 2, the number density obtained in our study under the experimental conditions of Pétier and Francony [62] is greater than that retrieved under the experimental conditions of Hung and Hoffmann [48] for the range of acoustic frequency in common. This behavior is observed especially for wave frequencies greater than \( \sim 358 \text{ kHz} \). According to the operational conditions of Pétier and Francony, the number of active bubbles increases from \( 8.399 \times 10^3 \) at 20 kHz to \( 8.1 \times 10^{14} \text{ L}^{-1} \text{ s}^{-1} \) at 800 kHz [Table 5(a)]. Whereas under the experimental conditions of Hung and Hoffmann, the number of active bubbles goes up from \( 4.22 \times 10^3 \) at 205 kHz to \( 2.28 \times 10^{12} \) at 1078 kHz [Table 4(a)]. This trend is owing to the relatively higher acoustic amplitude used by Pétier and Francony (\( P_a = 2.62 \text{ atm} \) for 200–800 kHz) [62] compared to that of Hung and Hoffmann (\( P_a = 2.05 \text{ atm} \) for 205–1078 kHz, and 2.31 atm for 500 kHz) [48]. Furthermore, the higher number density obtained in our study under the experimental conditions of Pétier and Francony compared to that of Hung and Hoffmann is probably promoted by the relatively higher CCl4 concentration and liquid temperature used by Pétier and Francony [62] (0.43 mM and 20 °C) compared to those of Hung and Hoffmann [48] (0.2 mM and 13 °C). In fact, the increase of CCl4 concentration and the liquid temperature is expected to induce the activation of more bubbles (increases the number density) even when the maximal bubble temperature is reduced [82].

4. Conclusion

In the present paper, a simple technique is proposed for the determination of the number density of acoustic bubbles in sonicated aqueous solution. This method relies on the combination of single bubble chemistry to that of the whole volume of the solution in the reactor. The obtained results (under the experimental conditions of Pétier and Francony and those of Hung and Hoffmann) have demonstrated the good concordance between our findings and those found in literature especially that obtained semi-empirically under the operational conditions of Merouani et al. (Table 6(a)). It is found that the number of active bubbles is proportionally increased by the rise of ultrasound frequency for all adopted experimental conditions. Additionally, the positive effect of acoustic intensity on the number of active bubbles has been revealed, where the number density is improved monotonically with the increase of acoustic amplitude. This positive impact is clearly observed for higher frequencies (>358 kHz). On the other hand, this technique shows the probable dependence of number density to the CCl4 concentration and liquid temperature, which means that more investigations are needed (in future works) to determine the impact of these crucial parameters (i.e. CCl4 dosage and liquid temperature) in addition to the acoustic intensity on the number of active bubbles. Moreover, the present work indicates the possibility of using other volatile compounds in order to determine the number of active bubbles and investigate the efficacy of these species compared to that of carbon tetrachloride.

CRediT authorship contribution statement

Aissa Dehane: Conceptualization, Methodology, Software, Formal analysis, Writing – original draft, Writing – review & editing. Slimane Merouani: Project administration, Conceptualization, Supervision, Visualization, Writing – review & editing, Methodology, Formal analysis, Writing – review & editing. Oualid Hamdaoui: Visualization, Validation, Writing – review & editing. Muthupandian Ashokkumar: Visualization, Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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