Pressure Variations in Closed Sonochemical Reactors

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The pressure inside a closed sonochemical reactor evolves during sonication of a gas-saturated solution. The pressure evolution is dependent on the nature of the dissolved gas: after a common increase during the first 30 minutes, the pressure keeps increasing under argon, stays constant under dinitrogen and decreases under dioxygen and air. The reasons for these observed pressure variations and their implications on physico-sonochemical experiments are discussed in terms of gas solubility and gas reactivity of solutions submitted to intense pressure waves.

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Introduction

Acoustic cavitation is the phenomenon by which intense ultrasonic waves induce the formation, oscillation, and implosion of gas bubbles in liquids. Chemical reactions (sonochemistry) and the emission of light (sonoluminescence) often accompany this process.[1] The light emission mechanism is due to the bubble interior achieving high temperatures and pressures during its quasi-adiabatic collapse.[2] These conditions also cause chemical reactions. For instance, in water, the bubble collapse leads to the homolysis of the water molecules into OH and H radicals and to the re-formation of water but also of H_2O_2 and H_2 after recombination of these radicals.[3]

Several studies on the influence of the hydrostatic pressure on sonochemistry and/or sonoluminescence have been published[3−7] and have shown the importance of this parameter. On the one hand, an increase of the pressure affects the bubble's dynamics, increasing, for instance, the cavitation threshold and the velocity of the bubble wall during the implosion.[6,7] On the other hand, a pressure increase affects indirectly the cavitation through a change of the acoustic impedance of the liquid, which itself induces changes in the transducer characteristics, including its resonance frequency.[4] Obviously, the concentration of the dissolved gas, which is known to have an effect on the chemical yields[8−10] of sonochemical reactions (whether they involve the dissolved gas or not) and which differs under sonication[11] from that predicted by Henry's law, is also a function of the gas partial pressure. Considering the broad range of parameters that depends on variations of the hydrostatic pressure above the sonicated solution, it was of interest to investigate the pressure evolution in a closed sonochemical reactor under sonication.

Results and Discussion

The typical evolution of the pressure in the closed sonochemical reactor during sonication of water saturated with air, argon, dinitrogen and dioxygen is represented in Figure 1. For each saturating gas, at least three experiments have been conducted and all show qualitatively the same evolution, although small differences of less than 5 mbar can be observed between two sets of data. Starting with an initial pressure equal to the atmospheric pressure, the same evolution is observed for the four gases during the first 30 minutes: a pressure increase of 10 to 15 mbar is observed. After this first phase (phase 1), and depending upon the gas, three different kinds of evolution are observed (phase

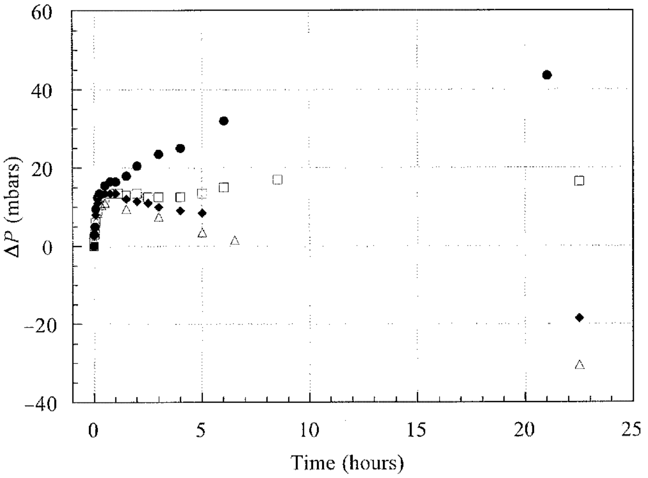

Figure 1. Evolution of the pressure in a closed reactor during sonication of water saturated with (●) argon, (□) N_2, (◆) O_2 and (△) air

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2). Under argon, the pressure increases slowly during phase 2 (<1 mbar/hour) and experiments conducted over very long sonication times (> 70 hours) have not shown any plateau. When the experiment is conducted under dinitrogen, the pressure remains constant during phase 2. The evolution of the pressure under air is similar to that observed under dioxygen: phase 2 is characterized by a linear pressure decrease, at a rate of about 2 mbar/hour, leading to a reduction in pressure in the reactor.

Fluctuations in the temperature are insufficient to explain the observed pressure evolutions. Indeed, the experimental set-up (see Exp. Sect.) allows for a control of the temperature to within ±1 °C, in the liquid phase as well as in the gas phase, leading to pressure fluctuations in the reactor of a maximum of ±3.5 mbar, i.e. much smaller than the observed variations. Furthermore, the consistency observed between repeated experiments is incompatible with random temperature fluctuations.

The pressure increase during phase 1 is likely to be due to the well-known degassing effect of ultrasound: cavitation bubbles grow by rectified diffusion, pumping gas out of the liquid, and are pushed out of the liquid by buoyancy, leading to a lowering of the gas concentration in the solution.[11−15] In the case of open reactors, the resulting stationary gas concentration in the liquid is lower than that predicted by Henry's law. In our case, with a closed reactor, the decrease of the gas concentration in the solution will inevitably lead to an increase of the pressure in the gas phase.

In order to explain the differences that are observed during phase 2, it is necessary to resort to the chemical effects of ultrasound on water solutions of argon, dioxygen, dinitrogen and air. As the experimental set-up does not allow a continuous monitoring of the concentration of the different reaction products in the reactor, and as it is not possible to withdraw samples from it either, the discussion of the experimental results is based on the analysis of the final reaction products and also on what is known concerning the reactivity of water and water solutions when they are insonified.

In the case of dioxygen, the pressure decreases linearly during phase 2. This is due to the reactivity of dioxygen.[16] In addition to the sonochemical reactions that occur in cavitation bubbles filled with water vapour and an inert gas like argon (reactions 1−7), dioxygen-consuming reactions also take place (reaction 8−9).[3] This explains the linear pressure decrease that is observed as soon as a stationary concentration of dissolved dioxygen is reached, i.e. at the end of phase 1.

$$H_2O \rightarrow OH^{\cdot} + H^{\cdot} \qquad (1)$$

$$H_2O \rightarrow H_2 + O \qquad (2)$$

$$O + H_2O \rightarrow OH^{\cdot} + OH^{\cdot} \qquad (3)$$

$$H^{\cdot} + H_2O \rightarrow H_2 + OH^{\cdot} \qquad (4)$$

$$OH^{\cdot} + H^{\cdot} \rightarrow H_2O \qquad (5)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \qquad (6)$$

$$H^{\cdot} + H^{\cdot} \rightarrow H_2 \qquad (7)$$

$$O_2 \rightarrow O + O \qquad (8)$$

$$H^{\cdot} + O_2 \rightarrow OH^{\cdot} + O \qquad (9)$$

In the case of argon, phase 2 is characterized by a weak pressure increase. As argon is inert, this increase probably reflects the production of H_2 (reactions 2 and 7) and, perhaps, the production of a small amount of dioxygen (reactions 10−12, or via another mechanism involving the dissociation of $HO_2^{\cdot}$ but leading to the same net result).[3]

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \qquad (10)$$

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \qquad (11)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (12)$$

Dinitrogen is also usually considered as an inert gas, although this is usually not true in sonochemical reactions. As the dissociation energy of N_2 ($\Delta H_{D,N_2}$ = 944 kJ/mol) is much higher than that of O_2 ($\Delta H_{D,O_2}$ = 496 kJ/mol), thermal dissociation in the cavitation bubbles is not expected to be important. However, N_2 is reactive towards the products of the sonolysis of water, O and $OH^{\cdot}$. Indeed, dinitrogen is oxidised through a series of reactions to form eventually NO_2^- and NO_3^-.[17−19] The presence of nitrogen oxides in the solution at the end of the sonication was confirmed by the observation of strong absorption bands in the UV spectrum. The reactivity of N_2 towards O also explains why the pressure evolution under air, although composed of 80% N_2, is similar to the evolution under O_2. The increase of the concentration of the oxygen atoms, from thermal dissociation of the dioxygen present in air, will strongly favour the consumption of N_2, compared to a situation where the only oxygen atoms come from water sonolysis.

As pointed out earlier, the degassing effect of ultrasound leads to a gas stationary concentration lower than that predicted by Henry's law. The value of this stationary concentration is gas- and solvent-dependant and is generally situated between 60% and 90% of the saturation concentration.[11−15] Using Henry's law ($k_{H,Ar}$ = 714 atm/M) and the perfect gas law, it is easy to calculate the total amount of argon in the reactor and then to estimate its stationary concentration in the solution under sonication. The result of this calculation shows that the concentration of argon decreases to about 30% of the concentration predicted by Henry's law. In the case of air, the measure of $[O_2]$ in water has shown that the concentration drops from 8.5 mg/L to 3.5 mg/L while the pressure drops from 1015 to 987 mbar (corresponding to an O_2 consumption of approximately 1 μmol/h, which is typical for a sonochemical reaction rate). Similar calculations, with the hypothesis that the ratio N_2/O_2 remains constant throughout sonication, lead to the conclusion that the stationary concentration of O_2 in sonicated water is only 40% of the equilibrium concentration, in the absence of sonication. In both cases, the stationary concentration under sonication is therefore significantly lower than what has been measured previously.

Conclusion

We have shown that the pressure inside a closed sonochemical reactor evolves during sonication and that the evolution is gas dependant. The differences that have been observed result from phenomena already described in the literature, namely the degassing effect of ultrasound and the reactivity of any gas other than the rare gases inside the cavitation bubbles.

These pressure variations, although relatively weak, might have a non-negligible impact on some sonochemical studies performed in closed reactors. For instance, in the case of studies in the literature concerning gas effects, it is common to find differences which are fairly small and which, generally, are never explained by pressure effects.[20,21] In this work we have shown that, starting from the same initial pressure, differences of 70 mbar can exist between a sonochemical experiment conducted under argon and the same sonochemical experiment conducted under air. In a similar manner, von Sonntag has shown that a pressure change above a water solution can modify the sonochemical yields of H_2O_2 production by up to 20%.[3] Under these conditions, if the pressure inside the reactor has not been carefully measured as a function of time, how can one assess what are, and in which proportions, the real causes for a gas effect: the gas itself, the hydrostatic pressure or, for instance, the gas concentration?

Experimental Section

General Remarks: The experiments were conducted in an Undatim Ultrasonics D-Reactor operating at 518 kHz, at a power, estimated by calorimetry, of 17 Watts. The hermetically closed reactor had a gas inlet and a gas outlet (equipped with a precision valve) and was connected to an Eirelec manometer (model MP 340A), allowing precise measurement (±1 mbar) of the reactor's internal pressure. The reactor was also equipped with a cooling jacket in order to keep the temperature constant at 23 ± 1 °C. All experiments were performed in a thermostatted room at 23 ± 1 °C, assuring the control of the gas phase temperature above the solution. The hermeticity of the reactor was tested by checking that a pressure of 1200 mbar could be maintained for 48 hours.

The experiments were conducted under air, argon (Air Liquide, N57), dinitrogen (Messer, 4.0) and dioxygen (Air Liquide, N48). The "Milli-Q" water was saturated with gas by bubbling the gas through it for 2 hours. It was then transferred into the reactor (under gas flux) and a second bubbling of 30 minutes was performed. Closing the reactor resulted in an overpressure that was adjusted, with the precision valve, to 1015 mbar. The water volume was 100 mL while the gas-phase volume was 165 mL. The concentration of dioxygen was measured with an Oxi 323-A/Set WTW Oxymeter.

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[1] K. S. Suslick, Y. T. Didenko, M. M. Fang, T. Hyeon, K. J. Kolbeck, W. B. McNamara III, M. M. Mdleleni, M. Wong, *Philos. Trans. R. Soc. London, Ser. A* **1999**, *357*, 335−353.
[2] Y. T. Didenko, W. B. McNamara III, K. S. Suslick, *J. Phys. Chem. A* **1999**, *103*, 10783−10788.
[3] C. von Sonntag, G. Mark, A. Tauber, H. P. Schuchmann, *Adv. Sonochem.* **1999**, *5*, 109−145.
[4] R. D. Finch, *Brit. J. Appl. Phys.* **1965**, *16*, 1543−1553.
[5] B. T. Balica, E. Whalley, *Can. J. Chem.* **1970**, *48*, 528−536.
[6] A. Henglein, M. Gutierrez, *J. Phys. Chem.* **1993**, *97*, 158−162.
[7] L. Kondic, C. Yuan, C. K. Chan, *Phys. Rev. E* **1998**, *57*, R32−R35.
[8] M. H. Entezari, P. Kruus, R. Otson, *Ultrason. Sonochemistry* **1997**, *4*, 49−54.
[9] N. Segebarth, O. Eulaerts, Y. Kegelaers, J. Vandercammen, J. Reisse, *Ultrason. Sonochemistry* **2002**, *9*, 113−119.
[10] Y. Nagata, H. Okuno, Y. Mizukoshi, Y. Maeda, *Chem. Lett.* **2001**, *2*, 142−143.
[11] O. A. Kapustina, *Sov. Phys. -Acoust.* **1969**, *15*, 54−59.
[12] O. A. Kapustina, *Sov. Phys. -Acoust.* **1970**, *15*, 328−331.
[13] A. N. Kotyusov, *Sov. Phys. -Acoust.* **1992**, *38*, 94−96.
[14] L. Broeckaert, T. Caulier, O. Fabre, C. Maerschalk, J. Reisse, J. Vandercammen, D. H. Yang, T. Lepoint, F. Mullie, in *Current Trends in Sonochemistry* (Ed.: G. J. Price), Royal Soc. *Chem.* Cambridge, **1992**, p. 8−25.
[15] T. G. Leighton, *The Acoustic Bubble*, Academic Press INC, London, **1994**.
[16] C.-H. Fischer, E. J. Hart, A. Henglein, *J. Phys. Chem.* **1986**, *90*, 1954−1956.
[17] E. J. Hart, C.-H. Fischer, A. Henglein, *J. Phys. Chem.* **1986**, *90*, 5989−5991.
[18] E. J. Hart, C.-H. Fischer, A. Henglein, *J. Phys. Chem.* **1986**, *90*, 5992−5995.
[19] C. A. Wakeford, R. Blackburn, P. D. Lickiss, *Ultrason. Sonochemistry* **1999**, *6*, 141−148.
[20] M. E. Fitzgerald, V. Griffing, J. Sullivan, *J. Phys. Chem.* **1956**, *25*, 926−933.
[21] E. L. Mead, R. G. Sutherland, R. E. Verrall, *Can. J. Chem.* **1976**, *54*, 1114−1120.

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