

# ULTRASOUND-INDUCED POLYMERISATIONS IN HIGH-PRESSURE FLUIDS

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Ultrasound-induced cavitation is known to enhance chemical reactions as well as mass transfer at ambient pressures. Ultrasound is rarely studied at higher pressures, since a high static pressure hampers the growth of cavities. However, in the case of compressed gases such as liquid carbon dioxide, propane and ammonia, the static pressure is counteracted by the higher vapour pressure, which enables cavitation. With the use of a dynamic bubble model, the possibility of cavitation and the resulting hot-spot formation upon bubble collapse have been predicted. These simulations show that the implosions of cavities in high-pressure fluids generate temperatures ( $\pm 585$  K) at which radicals can be formed. To validate this, radical formation and polymerisation experiments have been performed in CO<sub>2</sub>-expanded methyl methacrylate systems. The radical formation rate in this fluid is approximately  $1.5 \cdot 10^{14} \text{ s}^{-1}$ . Cavitation-induced polymerisations in these systems have resulted in high-molecular weight polymers.

## INTRODUCTION

Sonochemistry comprises all chemical and physical effects that are induced by ultrasound. Most of these effects are caused by cavitations, i.e. the collapse of microscopic bubbles in a liquid. The chemical effects of ultrasound include the formation of radicals and the enhancement of reaction rates at ambient pressures [1]. The enhanced dissolution of a solid reactant or catalyst caused by renewal of the liquid at the solid-liquid interface illustrates a mechanical effect induced by ultrasound. In ordinary solvents, cavitation does not occur at elevated pressures [2]. As a result, sonochemical studies have been limited to atmospheric conditions. In the case of high-pressure fluids such as liquid carbon dioxide, ethylene and propane, the static pressure is counteracted by the higher vapour pressure, resulting in cavitation and radical formation [3]. Especially the application of liquid carbon dioxide is interesting since it is regarded as an environmentally friendly compound. Additionally, carbon dioxide is non-toxic, non-flammable and naturally abundant.

In this work cavitation effects have been studied at elevated pressure in liquid carbon dioxide and CO<sub>2</sub>-expanded methyl methacrylate (MMA). The maximum temperature and bubble wall velocity during collapse have been calculated using a dynamic bubble model for liquid CO<sub>2</sub>. To validate these calculations, high-pressure cavitation experiments have been performed in these fluids. In addition, radical formation experiments and polymerisation experiments have been performed to prove the hot-spot formation in CO<sub>2</sub>-expanded MMA.

## CAVITATION BUBBLE DYNAMICS

Cavities, i.e. microscopic bubbles in the liquid, are generated when the negative pressure during the rarefaction phase of the sound wave is sufficiently large to disrupt the liquid. In water, the implosions of these cavities generate temperatures and pressures of approximately 5000 K and 200 bar, respectively, due to compression of the gas-phase inside the cavity [4,5].

To initiate the growth of a cavitation bubble a minimum acoustic pressure has to be applied. This critical pressure is described by the Blake threshold pressure [6]:

$$P_B = P_0 - P_v + \frac{4}{3} \cdot \sigma \cdot \sqrt{\frac{2}{3} \cdot \frac{\sigma}{\left(P_0 + 2 \cdot \frac{\sigma}{R_0} - P_v\right) \cdot R_0^3}} \quad (1)$$

Equation 1 assumes that the external pressure ( $P_0$ ), the vapour pressure ( $P_v$ ), the surface tension ( $\sigma$ ) and the equilibrium radius of the bubble ( $R_0$ ) determine the required negative pressure in the liquid to produce an explosive growth of a cavity. During pressurisation of a liquid the Blake threshold pressure increases, which implies that higher acoustic pressures are needed to produce cavitations. Obviously, no cavitation occurs when the Blake pressure exceeds the maximum acoustic pressure that can be produced. Depending on the ultrasound equipment, cavitation in water stops at a hydrostatic pressure in the order of 30 bar. Since cavitation requires a phase boundary, no cavitation is possible at temperatures higher than the critical temperature, due to the absence of the liquid-gas interface.

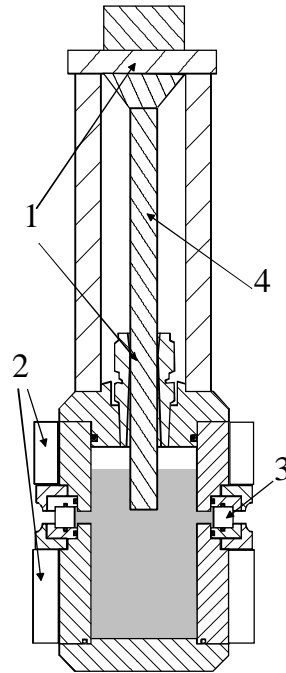
$$R \cdot \frac{d}{dt} R^2 + \frac{3}{2} \cdot \frac{d}{dt} R = \frac{1}{r} \cdot \left( \left( P_0 + \frac{2 \cdot \sigma}{R_0} - P_v \right) \cdot \left( \frac{R_0}{R} \right)^{3 \cdot \kappa} + P_v - \frac{2 \cdot \sigma}{R} - \frac{4 \cdot \eta \cdot \frac{d}{dt} R}{R} - P_0 - P_{ac}(t) \right) \quad (2)$$

The Blake threshold describes the onset of growth of the cavitation bubble, as it is based on a static equilibrium between the bubble and the liquid. After the explosive growth the bubble is no longer static, which requires a dynamic model in order to calculate the motion of the bubble radius ( $R$ ). In this study, the Kyuchi-Yasui model [7] is used to describe the dynamic movement of the bubble. The model is based on the Rayleigh-Plesset equation (Equation 2), which includes the surface tension, the vapour pressure, the liquid viscosity ( $\eta$ ), the polytropic index of the gas phase ( $\kappa$ ) and the acoustic pressure ( $P_{ac}$ ). The temperature, vapour and gas pressure inside the bubble are derived from the Rayleigh-Plesset equation in combination with a mass and energy balance over the bubble.

## EXPERIMENTAL

Cavitation in liquid-carbon dioxide and the radical formation experiments were studied in a jacketed 175 mL high-pressure vessel, equipped with quartz windows. A schematic drawing of this vessel is given in Figure 1. Sonification of the liquid was performed using 20 kHz ultrasound, which was produced by a Sonics and Materials VC-750 ultrasonic generator. A titanium ½ inch full wave probe was used to couple the piezoelectric transducer to the liquid. The probe was connected to the vessel at its nodes. The temperature inside the vessel was controlled by a heating/cooling bath. A camera in front of the quartz windows was used to observe cavitation events in the high-pressure vessel. Moreover, the concentration of the radical scavenger was measured by UV-vis spectroscopy through these windows. The absorption decrease of the active radical scavenger (1,1-diphenyl-2-picrylhydrazyl, DPPH) was used to determine the radical formation rate [8] in CO<sub>2</sub>-expanded MMA. The absorption coefficients for the active and inactive radical-scavenger are 8\*10<sup>3</sup> and 2\*10<sup>3</sup> L/(mol cm), respectively. The CO<sub>2</sub>-MMA system with a high molar fraction of CO<sub>2</sub>, required an additional argon head pressure to avoid boiling and to allow for cavitation. The composition and density of the MMA-CO<sub>2</sub> system is modelled with the Peng-Robinson equation of state and the Panagiotopoulos and Reid mixing rule [9]. The polymerisation experiments were performed in a 1.8 L high-pressure reaction calorimeter RC1e (Mettler-Toledo GmbH, HP60 reactor,

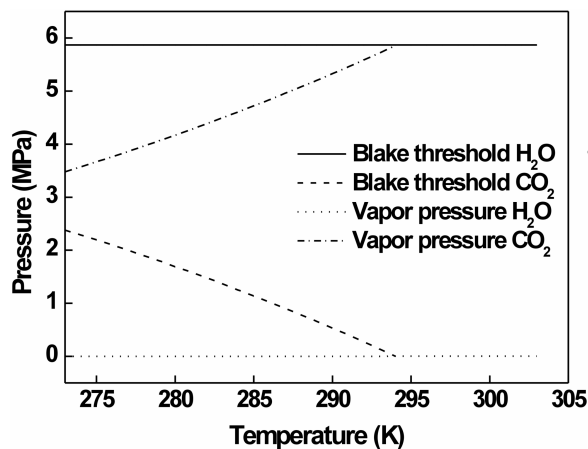
Switzerland). A detailed description of this equipment is given by Varela de la Rosa et al. [10].



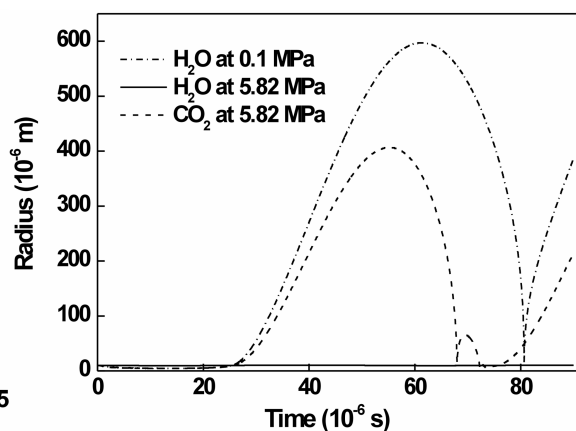
**Figure 1.** Schematic drawing of the high-pressure vessel (1) attachment points for ultrasound horn (2) cooling/heating jacket, (3) quartz windows, (4) ultrasound horn.

### BUBBLE DYNAMICS

The possibility of ultrasound-induced cavitation and in situ radical formation in liquid carbon dioxide has been studied. To assign the determining physical properties of high-pressure fluids, the growth and the implosion of a cavity in water and in liquid carbon dioxide have been compared. Since the Blake threshold pressure of liquid carbon dioxide at 58.2 bar equals the threshold pressure of water at 1 bar and 20 °C, 58.2 bar has been used in the calculations. In Figure 2 the calculated Blake threshold pressure of carbon dioxide and water at 58.2 bar is given as a function of temperature. The threshold curves are calculated using Equation 1, in which the vapour pressure is a determining parameter, next to the hydrostatic pressure and the surface tension. For water the Blake threshold is only determined by the static pressure and



**Figure 2.** Calculated Blake threshold pressure and vapour pressure for water and CO<sub>2</sub> at 58.2 bar as a function of temperature.



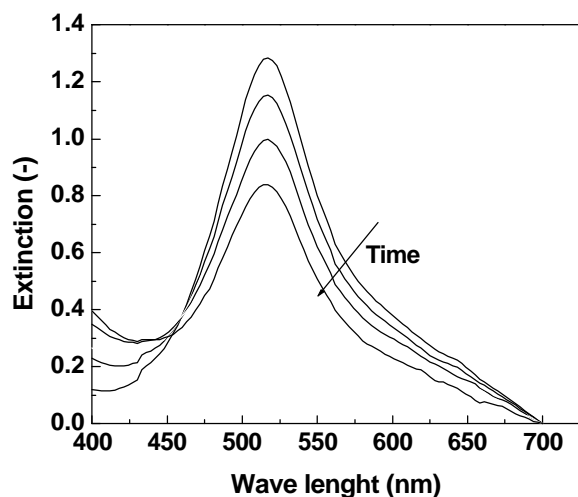
**Figure 3.** Calculated radius of a cavitation bubble as a function of time in water and carbon dioxide.

the surface tension of the liquid. As the vapour pressure of water is low does not change significantly with increasing temperature, the threshold pressure of water is virtually constant. In most liquids a high static pressure hampers the growth of nuclei as a result of the minor influence of the vapour pressure. In the case of carbon dioxide, which condenses at a substantially higher pressure, the vapour pressure does have a significant influence as can be seen in Figure 2. As a result of this, the Blake threshold is reduced, which enables cavitations in liquid carbon dioxide at higher pressures.

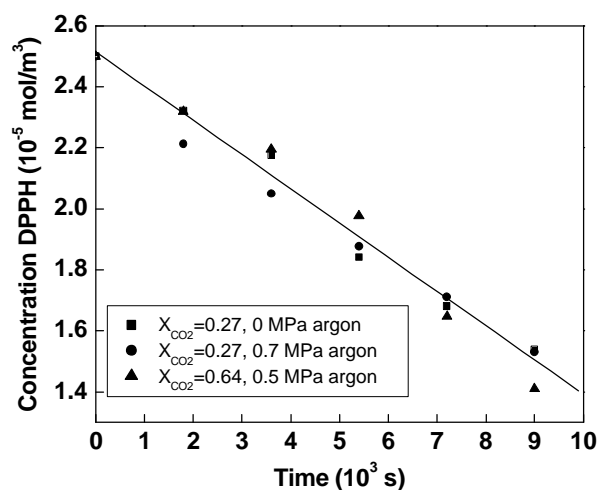
The dynamic movement of the bubble wall has been calculated using the Kyuchi-Yasui model. Initially, a small cavity with a radius of  $10^{-5}$  m is present, which consists of argon and the corresponding vapour of the liquid phase. In the simulations, an ultrasound wave with an acoustic pressure of 10 bar and a frequency of 20 kHz is imposed on this bubble. The variation of the radius of the bubble is shown in Figure 3. As the acoustic pressure for water at 58.2 bar is lower than the Blake threshold pressure almost no bubble movement is observed and no cavitation can occur. In contrast to the situation in water, carbon dioxide at 58.2 bar allows for cavitation and the bubble exhibits a similar movement compared to water at 1 bar. Moreover, the maximum temperatures (585 K) and maximum bubble wall velocities (777 m/s) reached during collapse in liquid CO<sub>2</sub> are in the same order of magnitude as compared to water at ambient pressure (722 K and 840 m/s).

### CAVITATION AND RADICAL FORMATION

Experiments in the high-pressure vessel showed that the required threshold pressure could easily be exceeded at a relatively low acoustic pressure for liquid CO<sub>2</sub> (10°C, 75 bar), proving the influence of the vapour pressure in the Blake Threshold calculations and the dynamic simulations. The occurrence of cavitation has been visually observed.



**Figure 4.** UV-Vis Spectra of DPPH in time for CO<sub>2</sub>-MMA (0.27-0.73) under sonification, at 20°C.



**Figure 5.** Concentration of DPPH in time as determined by UV-Vis analysis at 520 nm, for three different systems at 20°C.

To show that bubble collapse in liquid CO<sub>2</sub> is sufficiently strong to induce radical formation, measurements were done in CO<sub>2</sub>-methyl methacrylate (MMA) systems at high pressure. These UV-vis measurements show a decrease in the absorption of the radical scavenger during sonification (Figure 4), meaning that radicals are produced. The radical formation rate is

approximately  $1.5 \cdot 10^{14} \text{ s}^{-1}$ , for which no noticeable differences between the three systems have been observed (Figure 5).

## **POLYMERISATION**

In ultrasound-induced bulk polymerisations at ambient pressures a strong viscosity increase occurs which hinders cavitation, and hence radical formation. This limits the conversion to low values [11]. Since high-pressure carbon dioxide acts as an anti-solvent for polymers, the viscosity will not increase. The gyration radius of a polymer is smaller when an anti-solvent is present. Additionally, a low solvent viscosity will be maintained even at high conversions, as the polymer will precipitate from the solution. In polymerisation reactions, high-pressure  $\text{CO}_2$  acts as an anti-solvent, thus enabling a viscosity reduction that leads to high conversion.

The polymerisations performed in  $\text{CO}_2$ -expanded MMA at 293K and 6 bar showed a minor viscosity increase up to a conversion of 5%. A similar experiment performed in pure MMA showed a decrease of the overall heat-transfer coefficient (U), which is a measure of the liquid viscosity. A lower U implies a higher liquid viscosity. The polymerisations resulted in polymethyl methacrylate with a molecular weight of approximately  $10^5 \text{ g/mol}$  (no  $\text{CO}_2$ ) and  $10^7 \text{ g/mol}$  (6 bar  $\text{CO}_2$ ).

## **CONCLUSION**

Ultrasound has been applied to create cavitation in high-pressure liquid carbon dioxide ( $10^\circ\text{C}$ , 75 bar) in which the threshold pressure for cavitation can be exceeded at a relatively low acoustic intensity. The hydrostatic pressure is counteracted by the high vapor pressure of carbon dioxide, as explained by the Blake Threshold model. Using a dynamic bubble model, the formation of hot spots upon bubble collapse is predicted. This hot-spot formation has been experimentally confirmed by radical formation and polymerization experiments. The radical formation rate is approximately  $1.5 \cdot 10^{14} \text{ s}^{-1}$  in  $\text{CO}_2$ -expanded MMA at  $20^\circ\text{C}$ . The ultrasound-induced precipitation polymerisations resulted in polymethyl methacrylate with a molecular weight of approximately  $10^5$ - $10^7 \text{ g/mol}$ . Due to the anti-solvent behavior of  $\text{CO}_2$  only a slight viscosity increase is found during polymerization up to 5%.

## **REFERENCES**

- [1] THOMPSON, L.H., DORAISWAMY, L.K., *Ind. Eng. Chem. Res.*, Vol. 38, **1999**, p. 1215
- [2] BERLAN, J., TRABELSI, F., DELMAS, H., WILHELM, A.M., PETRIGNANI, J.F., *Ultrason. Sonochem.*, Vol. 1, **1994**, p. S97
- [3] KUIJPERS, M.W.A., VAN ECK, D., KEMMERE, M.F., KEURENTJES, J.T.F., *Science*, Vol. 298, **2002**, p. 1969
- [4] SUSLICK, K.S., *Sci. Am.*, Vol. 260, **1989**, p. 80
- [5] LUCHE, J.-L., *Synthetic Organic Sonochemistry*, Plenum, New York, **1998**
- [6] LEIGHTON, T.J., *The Acoustic Bubble*, Academic Press, London, **1998**
- [7] YASUI, K., *J. Acoust. Soc. Am.*, Vol. 98, **1995**, p. 2772
- [8] KUIJPERS, M.W.A., KEMMERE, M.F., KEURENTJES, J.T.F., *Ultrasonics*, Vol. 40, **2002**, p. 675
- [9] KEMMERE, M.F., CLEVEN, M.H.W., VAN SCHILT, M.A., KEURENTJES, J.T.F., *Chem. Eng. Sci.*, Vol. 57, **2002**, 3929
- [10] VARELA DE LA ROSA, L., SUDOL, E.D., EL-AASSER, M.S., KLEIN, A., *J. Polym. Sci.*, Vol. 34, **1996**, p. 461
- [11] PRICE, G.J., *Ultrason. Sonochem.*, Vol. 3, **1996**, p. S229