Ultrasonic cavitation in CO₂-expanded N, N-dimethylformamide (DMF)

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1. Introduction

Gas expansion liquid (GXL) is a mixed solvent generated by dissolving a compressible gas (such as carbon dioxide or ethane) in an organic solvent [1,2]. Because of the safety, sustainability and economic advantages of carbon dioxide (CO₂), CO₂-expanded liquid (CXL) becomes the most commonly used class of GXL [1]. By varying the CO₂ composition ratio, a continuum of liquid media ranging from neat organic solvent to supercritical CO₂ is generated, and the properties of the media can be adjusted by tuning the operating pressure. Due to the tunability in mass transfer, solvation and solubility, CXL shows advantages over traditional organic solvents in many characteristics [3].

CXLs have been exploited in a variety of applications such as particle formation [4], polymer processing [5], and homogeneous and heterogeneous catalysis [6]. CXL system was reported effective at separating large volumes of concentrated nanoparticle solutions. Large quantities of iron oxide nanoparticles were successfully fractionated in CXL media based upon particle size [7]. By adjusting the parameters of CO₂ expanded hexane, colloidal nanoparticles of controlled size can be embedded in ordered mesoporous silica for high-load recyclable catalysis [8]. It was reported that owing to the decrease in liquid viscosity caused by the addition of CO₂, liquid–liquid extraction efficiency in CO₂-expanded n-octanol is significantly improved [9]. The activities of bio-catalysts were found to be significantly higher in CXLs than in the corresponding neat liquids without expansion with CO₂ [10].

If enough power is applied to overcome the cavitation threshold, cavitation can occur in almost all organic solvents [11]. Acoustic cavitation and its intense sonoluminescence from numerous polar, aprotic organic solvents were discovered by Didenko et al. [12] It is well known that cavitation caused by ultrasound can enhance chemical reactions and the transfer of heat and mass in liquids. Ultrasonic cavitation is a series of dynamic processes involving the formation, growth, oscillation, and collapse of bubbles in a liquid under ultrasonic radiation [13]. The collapse of ultrasonic cavitation bubbles is accompanied by a series of physical and chemical effects, such as micro-jetting, turbulence, acoustic streaming, and free radical production. Cavitation effects induced by ultrasound are the main reason for the increase of chemical reactions degree as well as heat and mass transfer in liquids [14]. The coupling of ultrasound and GXLs has brought many new discoveries. In the reported studies, ultrasound-induced free radical polymerization of methyl methacrylate (MMA) was successfully carried out in CO₂ expanded MMA [15]. Ultrasound was also introduced into the supercritical CO₂...
anti-solvent (SAS) process to produce curcumin particles. Ultrasound accelerated the mixing speed between the solution and CO₂, and therefore reduced the gradient between the gaseous region and the local saturation region [16,17]. In that study, ultrasound was proved to be effective for adjusting the shape and size of crystal materials in SAS [18]. The introduction of ultrasound in the high-pressure CO₂-ethanol system was proved to enhance the efficiency of extraction. Compared with mechanical stirring, ultrasonic radiation increased the extraction rate by about two times. The intensity of ultrasonic irradiation and the implosion of cavitation bubbles were beneficial to the mass transfer and extraction efficiency [19]. The addition of direct ultrasonic treatment to CO₂-expanded ethanol aqueous solution (80%) proved to be the most influential factor in the extraction of polar compounds [20]. Expanded gases also produced new cavitation bubbles to enhance the ultrasound extraction efficiency [21].

Although there are new discoveries in the study of the application of combination of ultrasonication and GXLs, as far as we know, the experimental studies focusing on the occurrence of cavitation in GXLs and its influencing factors are rare. We believe a better understanding of ultrasonic cavitation mechanism in GXL will promote the coupling effectiveness and its application. In the current study, to our knowledge for the first time, the development of cavitation bubble cloud (CBC) structure in CO₂-expanded N, N-Dimethylformamide (CO₂-expanded DMF) under different pressures and input powers was observed by a high-speed camera, and cavitation intensity was recorded using a spherical hydrophone.

2. Experimental

2.1. Materials

DMF with a purity of > 99.9% was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. DMF used in the experiments is air-saturated without degassing. Carbon dioxide (CO₂) with a purity of > 99.99% is supplied by Shanghai Keju Chemical Co., Ltd.

2.2. Experimental setup

The experimental apparatus for the measurement of ultrasonic cavitation effect in CO₂-expanded DMF liquid is shown in Fig. 1. Similar to our previous studies [22,23], the reaction vessel is a self-made stainless steel autoclave assembled with a horn-based piezoelectric transducer (ultrasonic probe), a hydrophone, a heating/cooling jacket, a pressure indicator, a temperature indicator, and a back-pressure valve.

Two inline quartz windows (I.D. = 2.4 cm) are fitted in the reactor to visualize the cavitation phenomenon. The capacity of autoclave is 720 ml.

The horn-based piezoelectric transducer (FS-900 N, Shanghai Shengxi Ultrasonic Instrument Co., Ltd., China) with 63 mm in overall length, 13 mm diameter tip, and operating frequency of 20 kHz is used to induce ultrasonic oscillations in CO₂-expanded-DMF liquid. The ultrasonic power can be regulated from 900 W to 0 kW according to the experimental requirements.

A spherical hydrophone (RHS-20, Hangzhou Institute of Applied Acoustics, China). The hydrophone is fixed at the bottom of the container 10 mm directly below the ultrasonic horn for acoustic pressure measurements (Fig. 1). The receiving sensitivity of the hydrophone is ~193 dB re 1 V/μPa. Pressure signal in frequency domain is obtained by Fast Fourier Transform (FFT).

The reaction process is recorded by a high-speed digital video camera (Miro311, PHANTOM) equipped with a 105 mm focal length lens through the quartz window. An adjustable microscope ring light is used for backlighting. The image resolution is 640*480, and the capture speed is 10,000 frames per second.

Acoustic pressure signal of the hydrophone is recorded by a digital oscilloscope (InfiniiVision DSOX2014A, KEYSIGHT TECHNOLOGIES) with Keysight BenchVue software. System static pressure is monitored by pressure gauge (WIKA, Germany) and pressure sensor (PTI-E-MG40, Swagelok Company, Germany), and collected by a data acquisition card (MCC USB-231, NI). Each experiment was repeated five times with good reproducibility of the observed effects.

2.3. Experimental method

According to the experimental design, DMF with different volumes was added to the container. The heating/cooling jacket of device was then turned on to maintain the temperature at 20 °C. After the device was sealed, CO₂ was pumped into the container to a desired pressure (0.8 MPa or 2.0 MPa). The ultrasonic generator was then turned on, and its power was adjusted from 0% to 100% with a gradient of 5%. An oscilloscope was used to collect the data when the signal is stable after sonication for 1 min at each power. The oscilloscope’s FFT bandwidth is 1 MHz, the frequency resolution is 191 Hz, the center frequency is 500 kHz, the sampling mode is the average mode, and the average number in the time domain is 256. The sampling frequency of the data acquisition card is 1000 Hz, and the acquisition time is 4 s. After each set of experiments, wait until the pressure was stable before carrying out the next group of experiments.
2.4. Calculation of cavitation energy

The ultrasound spectrum is mainly composed of two parts including sharp and unique peaks in the low-frequency domain (kHz) and a broadband component. The sharp peaks are generated at integer frequency of the fundamental driving frequency [24,25]. Non-cavitation energy can be estimated by the intensity of fundamental wave pressure (FWP) [26].

The broadband noise is mainly associated with transient cavitation (i.e., inertial cavitation) which mainly originated from strong chaotic oscillations of bubbles [25], shock wave emissions during bubble collapse [24,26]. Cavitation energy can be estimated based on broadband integrated pressure (BIP), which is calculated using the following equation:

\[
\text{BIP} = \int_{f_s}^{f_e} [P_s(f) - P_N(f)] \, df
\]

where \(P_s(f)\) represents the broadband sound pressures excluding all the fundamental, harmonic, subharmonic, and ultraharmonic components, and \(P_N(f)\) represents the sound pressures of the background noise. The start frequency \(f_s\) and the end frequency \(f_e\) of the integration region are 20 kHz and 1 MHz, respectively.

When the ultrasonic probe operates, acoustic signals at integer frequencies of the fundamental frequencies are obtained using a hydrophone. The background noise is recorded by hydrophone under the same experimental conditions with the ultrasonic probe switched off.

3. Results and discussion

3.1. Observations of cavitation bubble cloud by high-speed video camera

Under normal temperature and high pressure, \(\text{CO}_2\) has high solubility in many organic solvents. The amount of \(\text{CO}_2\) dissolved in organic...
solvents will significantly change the properties (such as viscosity, surface tension, density, etc.) of liquids [27]. Due to these changes, when ultrasound is applied to a CXL system, the physics and chemistry of non-linearly oscillating acoustic cavitation bubbles are strongly influenced by the dissolved CO$_2$ [28], and gas oversaturation is a crucial parameter in determining the population of bubbles [29]. During the rarefaction of ultrasonication, the local pressure is lower than the saturation pressure of the CO$_2$-expanded DMF, resulting in a decrease in the gas solubility of the corresponding local liquid. Owing to this local supersaturation, CO$_2$ is rapidly released from the liquid and bubbles are generated. The bubbles are than expanded in the rarefied liquid (local pressure lower than the static pressure of saturated GXL), and continue to grow under the initial incremental pressure due to the inertia of the liquid. Then, forced by the rapid incremental-pressure phase of the acoustic wave and high static pressure, some bubbles may collapse or quickly dissolve into the liquid again in the subsequent compression stage [30], and some may exist for a long time due to the reduction of the ultrasonic force caused by migration.

The generated bubbles assemble themselves into various cluster structures in the liquid [31]. The formation of CBC structure and dimension is crucial for horn-type ultrasonic system since it defines the boundary of strong cavitation zone [32]. However, little information about the formation and development of CBC in CO$_2$-expended DMF liquid can be found in reported experimental studies. In the current research, the evolution process of CBC in CO$_2$-expended DMF liquid at different system pressure and power were recorded by a high-speed camera (Fig. 2, Movie S1, 2).

**3.1.1. Cavitation at 0.8 MPa**

At 25% ultrasonic power (Video S1), hemispherical bubble clusters are formed on the surface of the ultrasonic probe within ~ 20 ms. The diameter of the hemisphere is between 2 and 3 mm. The cluster is stable at the beginning and slightly swings as the bubble cloud volume increases. After ~ 300 ms, it slides away from the surface center along the surface at high speed, escaping to the upper right of the probe and disintegrating eventually. A new bubble cluster with similar size is soon regenerated in the center of the surface and evolves periodically followed the above steps.
When ultrasonic power is increased to 50% (Video S2), although the shape and size of the formed bubble cluster are similar to the 25% power, each stage of evolution is significantly accelerated. Multiple clusters begin to appear on probe surface. The entire cycle time drops sharply from ~320 ms to ~20 ms. When ultrasonic power is 75% (Video S3), the population of bubbles continually increases. A thin layer of bubbles can be observed being attached to the horn surface. The cluster structure changed from hemispheres to a superimposition of hemispheres and a thin layer. At 100% ultrasonic power (Video S4), the thickness of this bubble layer grows with the rise in bubble amount. Acoustic streaming and turbulence effects of fluid are significantly enhanced and distort the CBC structure. A constantly fluctuating and swaying bubble layer becomes the dominant cluster structure. The formed CBC no longer slides along the surface of the probe, but is thrown to the bottom of the device by turbulence and acoustic streaming. The residual microbubbles from the collapsed CBC can function as nuclei in the subsequent cavitation events. This phenomenon is called the cavitation memory effect [33,34]. It can be found from the video that this memory effect becomes more significant as the power increases. At 100% power, not only the residual microbubbles but also the smaller clusters remaining after the disintegration of the large CBC become new cavitation nuclei.

In general, attributing to the stronger translational forces at higher amplitudes, bubble population increases as the ultrasonic power increase [32]. A strong correlation between ultrasonic power and CBC structure development can be observed. With the rise of ultrasonic power, the increased acoustic streaming and turbulence effects of liquid distort the CBC structure and formation. The CBC structure is transformed from a single hemisphere centered on the probe surface to multiple hemispheres, and then into a fluctuating bubble layer covering the whole probe surface. When the ultrasonic power is small, the CBC has a small influence range. As the power increases, its influence range expands to the entire field of view of the observation window. The cavitation memory effect also becomes more significant with the increase of input power.

3.1.2. Cavitation at 2.0 MPa

For 2.0 MPa system pressure, at 25% ultrasonic power (Video S5), the cluster structure is similar to the case of 0.8 MPa at 50% power: the clusters are dominated by a single hemispherical structure and tend to form multiple hemispheres. It can be seen from the movie that after the cluster disintegrates, driving by the acoustic radiation force, the ejected bubbles drift backward and regroup in the center of the probe to form a new hemisphere. The time from cluster hemisphere formation to slide and disintegration is ~75 ms, significantly faster than the time of 0.8 MPa under the same power (320 ms). The number of bubbles is also higher than that under the same power of 0.8 MPa.

At 50% power (Video S6), the cluster structure is still dominated by
single hemisphere, but the time from bubble formation to slide drops to ~ 15 ms. At 75% power (Video S7), liquid system is further agitated by enhanced liquid acoustic streaming and turbulence effects. The time of cluster formation-to-disintegration is further reduced to 5 ms and the hemispherical bubble clusters slide and disintegrate right after they are formed. At 100% power (Video S8), the formation and decomposition of the hemisphere have been continuous. Fluctuating bubble layer combined with constantly moving hemispheres constitutes the main structure of the cluster.

3.1.3. Comparison and analysis
To 2.0 MPa, the formation time and collapse time of the CBC are much shorter, and the number of bubbles is > 0.8 MPa at the same input power. That is to say, under higher pressure, the structure of CBC is looser and much easier to form and collapse. When CO₂ dissolves into the liquid, the polarity and hydrogen-bonding ability of the expanded liquid decrease [2,35–39], and its surface tension will decrease accordingly [2,40–43]. The greater the amount of dissolved gas, the greater the drop in surface tension, and the higher the number of bubbles and the nucleation rate [44]. In our case, since the initial amount of DMF is the same, the dissolved CO₂ content at 2.0 MPa is significantly increased than 0.8 MPa, making the evolution rate of CBC speed up and the instability increase.

3.2. Spectrum analysis of the CO₂-expanded DMF liquids under different pressures

No sub-harmonics (fundamental frequency divided by integer) and ultra-harmonics (integer multiples of sub-harmonics excepting the fundamental and harmonics), but only 1th to 12th order harmonics (integer multiples of fundamental) appear in all the acoustic spectra obtained in our experiments (Figs. 3 and 4 and Fig. S1-2). Ultra-harmonics originate from the oscillating motion of bubbles and increase significantly at high intensity. The higher the amplitude of the sound wave, the more ultra-harmonic oscillation will occur [24]. The lack of high-order harmonics, sub-harmonics, and ultra-harmonics should be caused by the relatively low ultrasonic amplitude when the sound intensity is insufficient under high pressure, and the wave attenuation by the compressibility of GXL during the transmission process.

Fig. 3a-d and 4a-d (see Fig. S1-2 for the spectra at other ultrasonication power) show the frequency spectra of cavitation obtained by hydrophone at different ultrasonication power in CO₂-expanded DMF liquid. The 100% ultrasonication power is 900 W. Fig. 3e, 4e and 3f, 4f show the spectra of BIP (represents transient cavitation strength) and FWP (the pressure at f₁) against the square root of the ultrasonication power at 0.8 MPa and 2.0 MPa, respectively.
At both 0.8 MPa and 2.0 MPa, the transient cavitation strengths increase basically with the growth of input power. However, the growth of BIP is not steady: at 0.8 MPa, it starts to grow slowly and significantly enhanced at 23 W\(^1/2\) (540 W, 60% full ultrasonication power); While for 2.0 MPa, the BIP is almost stable before 26 W\(^1/2\) (676 W, 75% full power), and shows a slowly increasing trend after this point.

At 0.8 MPa, FWP tends to increase at low power and drop down after the inflection point of 60%. It can also be seen from Fig. 3e, 2rd to 6th order of harmonics increase to a quasi-saturation value at around 23 W\(^1/2\) (60% full power). This quasi-saturation point is consistent with the acceleration point of BIP and close to the inflection point of FWP. These findings indicate that most of the input energy above 540 W is converted into transient cavitation energy rather than non-cavitation energy.

For 2.0 MPa, FWP values enhance significantly before 450 W (50% full power) but the corresponding BIP values increase very slowly (Fig. 4e, f), indicating that most of the input energy presents in form of non-cavitation energy rather than transient cavitation energy at low ultrasonic power. Movie S2 tells us that the generation and decomposition rate of CBC under low power and high pressure is much higher than 0.8 MPa; the structure of CBC is also much looser than at 0.8 MPa. The generation of a large number of bubbles not only consumes energy but also absorbs, scatters and hinders the energy transfer of the ultrasonic probe. When the input power is increased to 675 W, the transient cavitation energy’s contribution enhances. However, they are still much lower than their counterparts at 0.8 MPa.

Generally speaking, high input power is conducive to the occurrence of transient cavitation at both 0.8 MPa and 2.0 MPa. The accelerated increase of transient cavitation corresponds to the decrease of non-cavitation energy. However, the promotion effect of input power on transient cavitation is more pronounced at low power. At full power, the transient cavitation energy released at 0.8 MPa is about half of that at 2.0 MPa (see the BIP line in Fig. 3e and 4e). According to the Rayleigh-Plesset equation, cavitation activity in a liquid strongly depends on other properties of the liquid, such as viscosity, surface tension and density [45-48]. The growth of transient nano-sized bubbles is greatly affected by the viscosity of the liquid [45]. At 2.0 MPa, the decrease in surface tension promotes the instability of bubble growth and collapse [28], which makes the bubbles decompose into nano-sized bubbles with less or less transient cavitation energy, resulting in a decrease in the total transient cavitation energy [49]; Loose structure of CBC means more vibration energy consumption; The jet velocity of transient cavitation also decreases with the reduction of surface tension [50]; The shielding effect caused by the increasing population of bubbles also hinders the propagation of the cavitation jet [51]; The compressible feature of GXLs also becomes a negative factor for transient jet propagation. All the above factors make the transient cavitation decrease with the increase of gas content.

4. Conclusion

The cavitation in the GXL system is greatly affected by the gas content, and the simple way of increasing the static pressure and increasing the cavitation intensity cannot be used to treat the cavitation problem in the GXL system. When the amount of organic solvent is the same, higher the decrease of surface tension and the shielding effect caused by the increase in the number of bubbles have also become negative factors for the propagation of the transient cavitation jet. From the other point of view, the rapid alternation of rarefaction and compression phase of ultrasonic makes the content of carbon dioxide in the liquid change rapidly due to the rapid change of saturation, which greatly promotes the mass transfer speed in GXL; The rapid formation and collapse of CBC and its violent oscillation also intensified the speed of mass transfer; GXL itself can reduce the viscosity of organic solvents and has the property of promoting mass transfer. All of the above indicates that the combination of ultrasonication with GXL can create an excellent platform for efficient mass transfer. This is especially useful for the manufacture of ultra-fine powders.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105713.

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