The influence of pressure on the acoustic cavitation in saturated CO$_2$-expanded N, N-dimethylformamide

Hanyang Gao$^a$$^*, $ Kunkun Pei$^a$, Guoxin Hu$^b$, Wenxing Liu$^a$, Aihua Meng$^a$, Hongcheng Wang$^a$, Huifeng Shao$^a$, Wenxin Li$^a$$^b$

$^a$ School of Mechanical Engineering, Hangzhou Dianzi University, Xiasha Higher Education Zone, 310018 Hangzhou, Zhejiang Province, China
$^b$ School of Mechanical and Power Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, 200240 Shanghai, China

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**A B S T R A C T**

CO$_2$-expanded organic solvent is a kind of important fluid medium and has broad applications in chemical industry, environmental protection and other fields. Ultrasonic cavitation in gas expanded liquids (GXLs) is conducive to enhancing mass transfer and producing many exciting phenomena. In this paper, the ultrasonic cavitations and streaming in the saturated CO$_2$-expanded liquid N, N-dimethylformamide (DMF) at 4.2 MPa and 5.2 MPa are observed by a high-speed camera. The cavitation intensity and time trace of pressure pulses are recorded using a PZT hydrophone. The influences of gas–liquid equilibrium pressure and ultrasonic power on the cluster dynamics of transient and stable cavitation are examined. The excess molar enthalpies required for CO$_2$ dissociation from DMF are calculated by Peng-Robinson equations of state and the change of surface free energy of CO$_2$-expanded DMF is predicted. The results show that the excess enthalpy of the mixture is one of the key factors to control ultrasonic cavitation at high pressurized conditions, while the surface tension is the key factor for low pressure. As the increase of applied ultrasonic power, the formation and collapsing frequency of bubble clusters increases, and the amplitude and cyclic frequency of pressure pulse are enhanced. The transient cavitation intensity increases as it reaches a maximum value at a certain ultrasonic power and then decreases. The change trends of stable cavitation intensity under different pressures are basically same. It can be concluded from the evidence that ultrasonic cavitation in CO$_2$-expanded DMF is affected by the combined effect of compression and substitution: compression depresses the nucleation and growth of bubbles, while the high solubility of CO$_2$ in DMF is conducive to the generation of bubbles in cavitation.

**1. Introduction**

CO$_2$-expanded liquid (CXL) consists of pressurized gaseous CO$_2$ dissolved in organic solvents [1]. When compressed CO$_2$ dissolves in an organic solvent, the solvent expands in volume and decreases in polarity, reducing the amount of organic solvent needed and using much lower pressures than those required for supercritical CO$_2$. By changing the composition ratio of CO$_2$, a continuous liquid medium from pure organic solvent to supercritical CO$_2$ is produced, and the characteristics of the medium can be adjusted by adjusting the operating pressure. CXLs combine the excellent permeability and diffusivity of CO$_2$ with the high solubility of organic solvents to solid and liquid solutes in an optimal manner for a given application [2]. Since CXL shows advantages over traditional organic solvents in many characteristics, it has been exploited in a variety of applications such as biofuels [3], particle formation [4], polymer processing [5], catalyst synthesis [6], nanoparticle separation [7] and deposition, etc. in recent years.

When a sound wave propagates in the liquid, the local pressure changes due to mechanical tension stretching. If the local pressure is lower than its saturated vapor pressure, the nucleation of vapor phase bubbles occurs. This process is called cavitation. Cavitation is closely related to physical phenomena such as light emission, shock wave emission, and free radical formation [8]. Once generated, acoustic cavitation bubbles may experience two completely different radial oscillations. It may oscillate non-linearly over many periods of sound wave cycles (stable cavitation) or may grow rapidly and collapse violently (transient cavitation) [9].

In recent years, the use of organic solvents to adsorb CO$_2$ and ultrasonic-assisted desorption process have attracted much attention in the field of CO$_2$ purification and utilization [10–12]. The ultrasound can
promote the desorption of CO₂ in organic solution, accelerate mass transfer and reduce energy consumption [13,14]. N, N-dimethylformamide (DMF) is a powerful organic solvent that may be used in combination with CO₂ in a variety of processes. When CO₂ is dissolved into DMF liquid, no reaction takes place, but the mixing enthalpy will be generated [15]. The contribution of excess enthalpy to the CO₂ desorption enthalpy was generally less than 5% at pressures up to 1 MPa [16]. For CO₂-expanded DMF at the gas–liquid equilibrium, the higher the mole fraction of CO₂ dissolved in the liquid, the higher the mixtures pressure. The excess molar enthalpies at high pressurized conditions were shown to be quite high [17] and must be considered in order to understand and optimize the process application. Meanwhile, the surface tension of the mixture changes greatly with the amount of CO₂ dissolved, which plays an important role in the cavitation bubble dynamics. In this paper, ultrasonic cavitations and streaming of the saturated CO₂-expanded DMF are observed by a high-speed camera at 4.2 MPa and 5.2 MPa. The cavitation intensity and time trace of pressure pulses are recorded using a PZT hydrophone. The influences of gas–liquid equilibrium pressure and ultrasonic power on the cluster dynamics of transient and stable cavitations are examined. The excess molar enthalpies required for CO₂ dissociation from DMF are calculated by Peng–Robinson equations of state. The change of specific surface free energy as a function of the molar fraction of CO₂ dissolved in DMF is predicted.

2. Experimental

2.1. Experimental apparatus

The inside of the reaction device has a cylindrical structure with an inner diameter of 80 mm and a volume of 720 ml. During the experiment, ultrasonic generator (FS-900N, Shanghai Shengxi Ultrasonic Instrument Co., Ltd., China) with a maximum power of 900 W generates 20 kHz ultrasonic signals. The solution inside the reaction device is continuously oscillated by an ultrasonic vibrating horn. The ultrasonic horn is embedded in the upper part of the reactor, and its upper end diameter is 13 mm. A hydrophone (RHS-20, Hangzhou Institute of Applied Acoustics, China) is installed at the bottom of the container for sound pressure signal measurement. The distance between the hydrophone and the end of ultrasonic horn is 10 mm. Pressure gauge (WIKA, Germany) and pressure sensor (PTI-E-MG40, Swagelok Company, Germany) are used to measure the static pressure in the vessel, and K-type thermocouple (WRNK-191-2PBO, Shanghai Songdao Heating Sensor Co., Ltd. Company, China) is equipped for temperature monitoring. Two inline quartz observation window (I.D. = 2.4 cm) are installed on the front and back walls of the reactor to monitor the inside cavitation phenomenon (Fig. 1).

2.2. Experimental method

After adding 275 ml N, N-Dimethylformamide (DMF, >99.9% (GC), Shanghai Aladdin Biochemical Technology Co., Ltd., China) to the container, CO₂ (>99.9%, Shanghai Keju Chemical Co., Ltd., China) is pumped into the reactor. A plunger pump (2J-XZ-HL-2L/50 MPa, HuaiLi Pump Industry, China) pressurizes the device intermittently until the pressure is stable. Experiment is divided into two groups according to the system pressure: 4.2 MPa or 5.2 MPa. Under each pressure, in range of 5% to 100% ultrasonic power, 20 sets of ultrasonic tests are carried out with a gradient of 5%. The ultrasonic time of each group is 30 s and the signal is collected after the system is stable. Temperature is kept at 300.15 ± 1 K throughout the entire process.

2.3. Data and image collection

Voltage type acquisition card (MCC USB-231, NI) is used to collect the static pressure and temperature signal at 1000 Hz sampling rate, and oscilloscope (InfiniiVision DSOX2014A, KEYSIGHT TECHNOLOGIES) is used for real-time monitoring of hydrophone voltage signal with 1 M acquisition bandwidth. Blackman window is applied to the original voltage signal, and the signal is converted to frequency domain using Fast Fourier Transform (FFT). Each acquisition corresponds to 5 ms FFT of the signal, and the resolution is 95.4 Hz. Images are recorded with a high-speed camera (Miro310, PHANTOM) equipped with a 105-mm camera lens. The image resolution is 640*480 and the camera’s capture speed is 10,000 fps.

2.4. Acoustic spectrum analysis

In this study, fundamental wave pressure (FWP) and broadband integrated pressure (BIP) are used to estimate the non-cavitation (vibration) energy and cavitation energy, respectively [17,18]. FWP and BIP are calculated using the following equation:

\[ FWP = \int_{f_1}^{f_2} P_s(f) \, df \]  
\[ BIP = \int_{f_1}^{f_2} P_N(f) \, df \]  

where \( P_s(f) \) represents the fundamental wave pressure, \( P_N(f) \) 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 (\( f_1 \)) and end (\( f_2 \)) frequencies of the fundamental wave region are at \( f_1 = 2.5 \, \text{kHz} \) and \( f_2 = 2.5 \, \text{kHz} \), respectively. The start frequency \( f_1 \) and the end frequency \( f_2 \) of the integration region are 20 kHz and 1 MHz, respectively.

3. Results and discussion

3.1. Modelling of the excess enthalpies of dissociation for CO₂ release from DMF

For ultrasonic cavitations in the CO₂-expanded DMF, energy must be provided to desorb the dissolved CO₂ from the liquid. The same amount of energy that is being released in the absorption must be provided to drive out the CO₂. The excess molar enthalpies at high pressurized conditions are shown to be quite high [17] and must be considered in order to understand and optimize the process application. As the mole fraction of CO₂ increases, the dissolution of CO₂ in the DMF liquid is predicted.
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conditions were shown to be quite high and must be considered to understand and optimize the process application [19,20]. Pando et al. used the Peng-Robinson equation to simulate gas–liquid equilibrium data and the excess enthalpies for CO2 + DMF mixtures, and compared them with the experimental data of mixing enthalpies. The two results are in good agreement [21]. Therefore, this model method is used to calculate the excess enthalpy required for CO2 release from DMF. The binary gas–liquid equilibria are done with the Peng-Robinson equation of state:

\[ P = \frac{R \times T \times \rho}{1 - b \times \rho} - \frac{a \times \rho^2}{(1 + b \times \rho) (1 - b \times \rho) (1 - \rho \times (1 - b \times \rho))} \]  (3)

The equation of state parameters a and b are evaluated for the mixtures using the classical mixing rules given by the equations [22]:

\[ a_n = x^2 a_i + (1 - x)^2 a_2 + 2x(1 - x) \sqrt{a_i \times a_2} \times (1 - \delta_{12}) \]  (4)

\[ b_n = x^2 b_i + (1 - x)^2 b_2 + x(1 - x) \times (b_1 + b_2) \times (1 - \delta_{12}) \]  (5)

where subscripts 1, 2 and m represent CO2, DMF and CO2-expanded DMF, respectively. The binary interaction parameters \(k_{12} = 0.047\) and \(\delta_{12} = 0.0025\) in reference [21] are used in the calculation.

The excess molar enthalpy for CO2 dissociation from DMF is given by

\[ H^E = \left[ xH^E_1 + (1 - x)H^E_2 \right] - H^E_m \]  (6)

where \(H^E_m\) is the residual molar enthalpy of the mixture and \(H^E_n\) is that of pure components. The residual molar enthalpy is given by [22]

\[ H^0_m = RT(Z_1 - 1) + M_m \times \frac{T \frac{dP}{dT}}{2v_h} \times \ln(\frac{Z_1 + 2.44b_i}{Z_1 - 0.414R_i}) \]  (7)

\[ M_m = xM_1 + (1 - x)M_2 \]  (8)

where \(\varepsilon\) is the compressibility factor and \(M\) is the molecular weight.

The CO2 dissolution enthalpy is related to the CO2 absorption enthalpy and excess enthalpy. The numerical results show that the excess molar enthalpy at 1 MPa pressure is nearly 850 J/mol for the condition of constant temperature (Fig. 2(a)). With the increase of CO2 dissolved in DMF, the higher the saturation pressure of the mixture, the higher the specific excess enthalpy. The excess molar enthalpies at 4.2 MPa and 5.2 MPa are about 5500 J/mol and 6400 J/mol, respectively, nearly 6~8 times higher than at 1 MPa. Therefore, the contribution of excess enthalpy at high pressures cannot be ignored and is one of the main energy consumption of ultrasonic cavitations. With the increase of CO2 dissolution, the specific excess enthalpy has a maximum. Beyond the critical molar fraction of CO2 dissolved in DMF, the specific excess enthalpy decreases with the increase of gas–liquid equilibrium pressure. Fig. 2(b) compares the specific excess enthalpy under the gas–liquid equilibrium temperature at 293.15 K, 298.15 K, 303.15 K, indicating that the temperature has a more complicated effect on the specific excess enthalpy of CO2 expansion DMF. The effect of pressure and temperature on the excess molar enthalpy is related to the changes of the state and density of pure components and their mixtures, which is essentially the result of the molecular interaction contribution to \(H^E_m\) [20,21]. For a constant temperature of 293.15 K, the density of pure DMF changes little with pressure while the density of carbon dioxide increases obviously when the pressure increases from 0.1 MPa to 5.2 MPa. With the increase of \(x\), the state of CO2 changes from gas-like fluid to liquid mixture component, so the excess molar enthalpy increases significantly and will reach a maximum value. After that it will decrease with the increase of the molar fraction of CO2 as the solvent structure of DMF is destroyed in the CO2-rich region.

3.2. Modelling of the change of specific surface free energy

Ultrasonic cavitation bubbles in CXLs generate a large number of new gas–liquid interfaces, which is one of the main energy consumption. Specific surface free energy refers to the increment of the free energy per unit surface area of the new phase, which is essentially the surface excess Gibbs free energy and is an important characteristic of the mixtures. The specific surface free energy (\(\gamma\)) of organic solvents can be calculated according to the Eötvös equation [23,24]:

\[ \gamma \eta^\frac{\sigma}{\pi} = D^\gamma(T_c - T) \]  (9)

where \(V\) is molar volume, \(T_c\) is critical temperature, and \(\eta_g\) is an Eötvös parameter related to the polarity of the liquid \(\pi\). Therefore, the specific surface free energy (which is numerically identical with the surface tension) at a constant temperature of CXLs can be calculated by the following formula:

\[ \gamma \eta = \left( \frac{V_0}{V} \right)^{\pi^*} \frac{\pi^*}{\pi_0} \]  (10)

where \(V_0\), \(\pi_0\), and \(\gamma_0\) represent molar volume, polarity, and specific surface free energy of DMF at ambient conditions, respectively. \(V/V_0\) is the volumetric expansion rate of CXLs.

For CO2-expanded DMF, the polarity of the mixture is related to the molar fraction in bulk [25]:

\[ \pi^* = x^*\pi_1^* + (1 - x)\pi_2^* \]  (11)

where \(x^*_1\) and \(x^*_2\) represent the polarity of CO2 and DMF at high pressures, respectively. The CO2 pressure has little effect on the polarity of the CO2-DMF mixture, \(\pi^* = 0.88\) for static pressure of 0.1MPa, and \(\pi^* = 0.841\) for

![Fig. 2. The excess molar enthalpies of dissociation for CO2 release from DMF.](image-url)
5 MPa [25].

The numerical results of the change of surface free energy can be seen from Fig. 3 that the specific surface free energy decreases rapidly as the increase of CO\(_2\) dissolved in DMF. The molar surface free energy at pressures of 5.2 MPa is more than 0.26 times lower than that at 1 MPa. The dissolved amount of CO\(_2\) in DMF has an important influence on surface free energy. The decrease of specific surface free energy will reduce the energy consumption of ultrasonic cavitations and be beneficial to the generation of cavitation bubbles.

### 3.3. Observations of cavitation and streaming by high-speed video camera

#### 3.3.1. Cavitation and streaming at 4.2 MPa

It can be seen from Video S1 and Fig. 4 that under 25% full power, many bubbles gather on the horn surface to form a hemisphere-shaped large cavitation bubble cluster (CBC). When reaching a maximum volume, the large CBC becomes unstable and quickly separates from the horn surface and breaks up, forming a converging-collapsing CBC cycle. Fig. 4 shows two cycles of CBC in ~180 ms.

When the ultrasonic power is greater than 35% full power, a large number of cavitation bubbles are formed immediately once the ultrasonication is turned on (Video S2). More bubble clusters converge and collapse quickly, resulting in a violent flow in the medium, and the medium observed by the observation window is almost completely opaque.

#### 3.3.2. Cavitation and streaming at 5.2 MPa

Under 25% full power at 5.2 MPa (Fig. 5 and Video S3), the cavitation bubbles can be seen to gather on the horn surface, forming a single CBC. When reaching a maximum volume, it escapes from the horn surface and breaks up. The average lifetime of a bubble cluster from formation to break up is about 270 ms. When the ultrasonic power is increased to 50% full power at 5.2 MPa (Video S4), the lifetime of CBC is shortened to about 45 ms, and the spatial extent of streaming produced by CBC collapses increases. For cavitation under the same power (50% full power, Video S2) at 4.2 MPa, the mixture in the observation window is entirely opaque due to too many bubbles. In contrast, the number of bubbles at 5.2 MPa is significantly reduced, and the periodic evolution of CBC can still be seen from the observation window. This finding shows that the nucleation and growth of bubbles are inhibited under high pressure.

When ultrasonic power increases to 75% full power at 5.2 MPa (Video S5), the CBC changes from a single hemisphere to a larger hemisphere superimposed on a thin bubble cloud layer. Although the thin bubble layer is stable, the cluster superimposed on it still follows periodic changes, and the cluster lifetime is further shortened to about 13.5 ms. When the ultrasonic power reaches 100% (Video S6), the lifetime of CBC is further shortened to about 8 ms. It can be seen from Fig. 5 that the large bubble cluster underneath the horn periodically collapses but not completely breaks up, and the streaming zone of bubble clusters expands to almost the whole observation window at 100% power.

#### 3.4. Time trace of pressure pulses under different pressures

Fig. 6 and Fig. 7 show the time trace of pressure pulses detected by the PZT hydrophone at static pressures of 4.2 MPa and 5.2 MPa, respectively. The pressure wave shows periodic changes and its amplitude and frequency increase with the increase of applied ultrasonic power. Since pressure fluctuations are caused by the collapse of CBC [26], the pressure pulse period should be related to the periodicity of the bubble event in CO\(_2\)-expansion DMF.

As shown in Fig. 6, for ultrasonic cavitation at 4.2 MPa, it can be found that the average cycle period (ACP) of pressure pulse under 25% full power is ~85 ms, which is consistent with the lifetime of CBC shown in Fig. 4 and Video S1. The cyclic frequency of pressure pulse is ~12 Hz, which is similar to the collapse frequency of CBC. For 50% full power, the ACP is reduced to ~57 ms and its cyclic frequency is ~60 Hz. While for 75% full power, the corresponding ACP is further reduced to ~7 ms, and the cyclic frequency is increased to ~140 Hz. For 100% full power, the ACP is ~5.5 ms, and cyclic frequency is increased to ~180 Hz. Although Video S2 show that the observation window is entirely opaque when ultrasonic power is >35%, the piezoelectric signal collected by hydrophone recorded the lifetime and breakup frequency of the CBC. As ultrasonic power increases, the ACP of pressure pulses decreases, while the cyclic frequency of pressure pulse increases.

As shown in Fig. 7, for cavitation at 5.2 MPa, ACP of the pressure pulse and the cyclic frequency are ~270 ms and 3.7 Hz for 25% full power, 45 ms and 22.2 Hz for 50% power, 13.5 ms and 74 Hz for 75% power, and 8 ms and 125 Hz for 100% power. These results are consistent with the bubble cluster lifetime and collapse frequency recorded in Fig. 7 and Video S3-6. As the ultrasonic power increases, the ACP of pressure pulse decreases, and the cyclic frequency increases. In addition, the cyclic troughs of pressure pulses for 75% and 100% power are getting bigger and bigger. This can be explained by the phenomenon observed in Fig. 5 (or Video S3-6): a thin layer of cavitation bubbles on the horn surface is streaming slowly, and the bubble clusters periodically collapse but will not completely break up.

Fig. 8(b) shows the maximum amplitude of pressure pulse recorded by PZT hydrophone in CO\(_2\)-expanded DMF under different ultrasonic power. It can be found that the largest amplitude of pressure pulse increases with the increase of ultrasonic power and static pressure. For 4.2 MPa, the maximum pressure pulse amplitude increases slowly when the power is less than 75%, and increases sharply when the power is greater than 75%. For 5.2 MPa, the maximum amplitude increases significantly when the power is less than 75%, but decreases when power exceeds 75%. This phenomenon further explains the observation recorded by high-speed camera that the large CBC periodically collapses but not completely breaks up when the ultrasonic power is greater than 75% at 5.2 MPa.

#### 3.5. Spectrum analysis of transient and stable cavitation under different pressures

Fig. 9 shows that, as the ultrasonic power increases, the BIP value (representing the transient cavitation intensity) and the FWP value (representing the stable cavitation intensity) both increase. The transient cavitation intensity reaches a maximum value at a certain ultrasonic power and then decreases. The critical power required to get the extreme BIP value at 4.2 MPa is lower than that needed at 5.2 MPa, but...
Fig. 4. Images of CBC structure development (two cycles of CBC in ~180 ms) underneath the ultrasonic horn under 25% full power at 4.2 MPa and 293.15 K in CO₂-expanded DMF, recorded by a high-speed camera. The 100% ultrasonication power is 900 W.

Fig. 5. Images of the development of CBC structure underneath the ultrasonic horn at various ultrasonic power at 5.2 MPa and 293.15 K in CO₂-expanded DMF, recorded by a high-speed camera. The 100% ultrasonication power is 900 W. The length of the red line in the first pictures represents 3 mm.
the extreme value of BIP at 5.2 MPa is greater than that at 4.2 MPa. When ultrasonic power is small, the FWP value of cavitation at 4.2 MPa is greater than that at 5.2 MPa. These findings are consistent with video observations. For cavitation at 4.2 MPa static pressure, only entire black can be observed through the window when the power is greater than 35%; while for 5.2 MPa, it will not turn black even at the power of 100%. For 5.2 MPa, when the ultrasonic power is small, the intensities of transient and stable cavitations are both small; while when ultrasonic power is high enough (>75% full power), the transient cavitation intensity generated at 5.2 MPa is higher than that at 4.2 MPa, and the amplitude of the pressure pulses collected by the hydrophone is also larger. These findings indicate that as long as the acting ultrasonic power is large enough, the transient cavitation intensity produced by ultrasonic will be higher, and the resulting streaming will also be more intense.

Compared with the results found in our previous research at lower pressure (0.8 MPa and 2.0 MPa) [27] (Fig. 10), both cavitation bubble amount and the transient cavitation intensity increase greatly at higher pressure (this study, 4.2 MPa and 5.2 MPa): (a) the BIP value is more than 3 times higher than the former; (b) the number of bubbles observed in video at higher pressure is much higher, especially for 4.2 MPa.

3.6. Discussion

(1) Ultrasonic cavitations in high x-CO$_2$ saturated DMF

As CO$_2$ dissolves into DMF liquid, the system pressure increases with the increase of the molar fraction of CO$_2$ in the mixtures. Thus, high x-CO$_2$ condition means high pressure of the mixtures. By analyzing the numerical simulation results of excess molar enthalpy and molar surface free energy (Figs. 2 and 3), it can be found that for high x-CO$_2$ mixtures (4.2 MPa ~ 5.2 MPa), the excess molar enthalpy required for CO$_2$ dissociation from DMF is as high as 5500 ~ 6400 J/mol, nearly 6 ~ 8 times higher than that of low x-CO$_2$ mixtures (0.8 MPa); while the molar surface free energy is about 0.26 times lower than that of pure DMF. According to the phenomena detected by high-speed photography and hydrophone, in the case of high x-CO$_2$ mixtures at pressure of 4.2 MPa and 5.2 MPa, many bubbles are generated under the action of ultrasound. The transient cavitation intensity is sensitive to the response of ultrasonic energy, but the stable cavitation intensity changes little (Fig. 10). In terms of energy consumption and conversion, the energy required for the formation of cavitation bubbles must be greater than the excess enthalpy required for CO$_2$ dissociation from DMF and the surface excess enthalpy of new gas–liquid interface between bubble and liquid phase. In the high x-CO$_2$ regions (4.2 MPa ~ 5.2 MPa), the excess enthalpy becomes larger and the surface excess Gibbs free energy becomes much smaller. Therefore, compared with low-pressure cavitation (0.8 MPa), the main energy consumption of bubble formation comes from high excess enthalpy used to dissociate carbon dioxide from DMF bulk phase, because at this time, the excess enthalpy increases by 6 ~ 8 times, the surface free energy becomes much smaller and small difference between the specific Gibbs free energy of CO$_2$ molecules in the bulk liquid and the specific Gibbs free energy of it in the interface phase. Thus, as long as the energy supply meets the excess enthalpy required for
CO₂ dissociation from DMF liquid, it is easy to accumulate into bubbles. However, due to the large static pressure at this time as well as the influence of energy fluctuation, the bubbles are also easy to collapse, and the CO₂ molecules are recompressed back into the mixtures. So, the transient cavitation intensity detected by hydrophone is large and sensitive to the change of sound energy. Therefore, according to the above experimental facts and theoretical analysis, we suggest that the high excess enthalpy is one of the key factor affecting the formation of

![Fig. 7. Time trace of pressure pulses at 5.2 MPa and 293.15 K. Pressure pulse measured by hydrophone submerged in the CO₂-expanded DMF liquid under (a) 25%, (b) 50%, (c) 75%, and (d) 100% full power. The 100% ultrasonication power is 900 W. The sampling frequency of the acoustic signal by hydrophone is 100 M Hz.](image)

![Fig. 8. (a) Cyclic frequency of pressure pulse; (b) Amplitude of pressure pulses measured by a PZT hydrophone in the CO₂-expanded DMF under different ultrasonic power.](image)
Ultrasonic cavitation bubbles in the CO$_2$-rich region.

(2) Ultrasonic cavitations in low x-CO$_2$ saturated DMF

For the low x-CO$_2$ mixtures, the surface free energy (the surface tension) is much larger than that of high x-CO$_2$ mixtures. The excess enthalpy required for CO$_2$ molecules dissociated from DMF liquid is low but the surface excess enthalpy of gas–liquid interface phase is large. From the phenomena detected by high-speed photography and hydrophone, there are fewer bubbles generated in CO$_2$-poor regions under the action of ultrasound, the transient cavitation intensity is also small while the stable cavitation intensity changes little (Fig. 10). Therefore, from the view of acoustic energy conversion and consumption, we suggest that the excess free energy required for the formation of cavitation bubbles is one of the main energy consumption for ultrasonic cavitations at low pressure of CXLs, it is one of the key factors affecting the formation of ultrasonic cavitation bubbles in the low x-CO$_2$ mixtures. The above results indicate that the ultrasonic cavitation in CO$_2$-expanded DMF is affected by the combined influence of compression and substitution. Compression depresses the nucleation and growth of bubbles, while high solubility of CO$_2$ in DMF (substitution) is in favor to the generation of cavitation bubbles.

4. Conclusion

In this paper, the ultrasonic cavitations and streaming are observed by a high-speed camera for the saturated CO$_2$-expanded DMF at 4.2 MPa and 5.2 MPa. The cavitation intensity and time trace of pressure pulses are recorded using a PZT hydrophone. The influences of gas–liquid equilibrium pressure and ultrasonic power on the cluster dynamics of transient and stable cavitations are examined. The excess molar enthalpies required for CO$_2$ dissociation from DMF are calculated by Peng-Robinson equations of state. The change of specific surface free energy as a function of the molar fraction of CO$_2$ dissolved in DMF is predicted. Under the experimental conditions, the following conclusions are obtained:

(1) With more dissolved CO$_2$ in DMF, the excess enthalpy increases to an extreme value and then decreases. However, the surface tension decreases sharply with the amount of CO$_2$ dissolved. The high excess enthalpy is one of the key factors to control ultrasonic cavitation in high x-CO$_2$ saturated DMF at high pressure, while the surface tension is one of the key factors in low x-CO$_2$ mixtures at low pressure.

(2) The number of cavitation bubbles and bubble clusters as well as the cavitation intensity increase greatly at high-pressure conditions (at 4.2 MPa and 5.2 MPa in this study) compared with the results at low pressure (0.8 MPa and 2.0 MPa in our previous study [27]).

(3) As the ultrasonic power increases, the formation and collapsing frequency of bubble clusters increases, and the amplitude and cyclic frequency of pressure pulses are enhanced.

(4) As the ultrasonic power increases, the transient cavitation intensities increase to a maximum value and then decreases, the
stable cavitation intensities increase significantly at 5.2 MPa but increase slightly at 4.2 MPa.

(5) The higher the mixture pressure, the greater the maximum value of transient cavitation intensity, and the higher the critical ultrasonic power required. The change trends of FWP value under different pressures are basically the same.

(6) The ultrasonic cavitation in CO\textsubscript{2}-expanded DMF is affected by the combined effect of compression and substitution. Compression depresses the nucleation and growth of bubbles, while high solubility of CO\textsubscript{2} in DMF (substitution) favors the generation of cavitation bubbles.

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

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