Generating Bulk Nanobubbles in Alcohol Systems

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ABSTRACT: Bulk nanobubbles (NBs) have attracted wide attention due to their peculiar physicochemical properties and great potential in applications in various fields. However, so far there are no reports on bulk NBs generated in pure organic systems, which we think is very important as NBs would largely improve the efficiency of gas–liquid mass transfer and facilitate chemical reactions to take place. In this paper, we verified that air and N₂ NBs could be generated in a series of alcohol solutions by using various methods including acoustical cavitation, pressurization−depressurization, and vibration. The experiments proved that NBs existed in alcohol solutions, with a highest density of 5.8 × 10⁷ bubble/mL in propanol. Our results also indicated that bulk NBs could stably exist for at least hours in alcohol systems. The parameters in generating NBs in alcohols were optimized. Our findings open up an opportunity for improving gas–liquid mass transfer efficiency in the field of the chemical industry.

1. INTRODUCTION

Nanobubbles (NBs) are a new class of nanoscale systems that exist in solutions. NBs have strong affinity for hydrophobic surfaces, extra-large wetting angle, high water−gas interface area per unit of liquid volume, and long-term stability for several days even weeks. Although many fundamental scientific questions in the NB field still remain unanswered, e.g., the amazing longevity of NBs in experimental observations in sharp contrast to ultrashort lifetimes predicted from the classical theories and commented in recent publications, NBs have shown great potential in applications for nanoscopic cleaning, control of boundary slip in microfluidics, wastewater treatment, medical applications, and so on.

Various methods for producing NBs have been recently developed, and evidences of the existence of NBs have been provided in a number of studies. For instance, NBs were generated via chemical reactions and by ultrasonic irradiation. It was found that NBs could be produced through alcohol−water exchange, which was well characterized by the nanoparticle tracking analysis (NTA), Fourier transform infrared spectroscopy (FTIR), gas chromatography−mass spectrometry (GC−MS), and inductively coupled plasma−mass spectrometry (ICP-MS). It was also reported that a procedure containing pressurization−depressurization steps would controllably generate NBs in different solutions, which was confirmed by the X-ray fluorescence intensity of the element of the gas in solutions and by NTA. Although these independent studies provide strong evidence for the existence of NBs, they focus on aqueous solutions as liquid carriers. There is still debate on the existence of bulk NBs in a mixture of an organic solvent and water. A few papers reported the formation of NBs in mixed systems.

Due to the increasing contact surface area and long residence time of small-sized bubbles dispersed in liquid mediums, it is recognized that NBs would largely improve the efficiency of gas−liquid mass transfer. If we could generate NBs in an organic liquid, the reaction between the gas and the organic liquid is expected to be largely promoted. Therefore, it is of great value to develop NBs in organic systems. At present, there are only few reports on whether NBs can be generated in pure organic systems. In 2004, Simonsen et al. observed surface NBs at the interface of pure alcohol and water, which was called the electrostatic repulsion model. They pointed out that there were no ions on the surface of organic molecules, and NBs could not be formed in such a pure organic system. Nirmalkar prepared NBs in different water−organic solvent systems by an acoustical cavitation method and suggested that hydroxide ions on the surface of aqueous solvents stabilized the NBs, which was also reported by different research groups. Recent studies carried out by Barigou et al. also indicated that NBs were formed during water−organic solvent mixing, but no NBs were detected in pure organic systems. However, it...
seems that the electrostatic repulsion model does not work for bulk NBs in pure water (without surfactant) as the calculation showed that the repulsive pressure associated with electrostatic force caused by surface charge was one order of magnitude smaller than the Laplace pressure inside the bubble; thus, the electrostatic repulsive pressure could not balance with the Laplace pressure at all.45,46 In 2015, Craig et al. observed the formation of surface NBs on highly oriented pyrolitic graphite (HOPG) covered by some pure organic solvents and believed the existence of a three-dimensional hydrogen bond network that promoted the formation of the surface NBs.39 However, so far bulk NBs have not been produced in pure organic liquids.

Complicated interactions between the molecules of the gas phase and the organic solvent may be involved in a NB, especially at the gas−liquid interface. Therefore, properly selecting a suitable organic carrier for NB generation is very important for forming and stabilizing a NB in an organic solvent. Even though some scientists have explored the generation of NBs in organic solvent−water mixing systems, the types of organic solvents they studied and the methods they employed were very limited. In this paper, we systematically explored the possibility of generating bulk NBs in alcohol systems and demonstrated that either air or N₂ NBs could be indeed generated in these organic solvents via different preparation methods. Results indicated that air NBs in propanol could reach a number density of 5.8 × 10⁷ bubble/mL, which is the largest one among the alcohol systems that we studied. Our results also indicated that bulk NBs could stably exist for at least hours in alcohol systems.

2. RESULTS AND DISCUSSION

2.1. Bulk Air NBs Prepared in Propanol by Acoustical Cavitation. Acoustical cavitation has been employed to prepare NBs in aqueous solutions.16−18,31 Under ultrasonic irradiation, the generation and reduction of NBs in liquids occurred simultaneously, and the bubble core grows into cavitation bubbles through the expansion and compression of NBs. Cavitation bubbles break into tiny bubbles of various sizes, such as bubble nuclei and NBs.22 In order to verify whether NBs can be generated in the alcohol systems, propanol solution and ultrapure water were sonicated and their results were compared. Ultrapure water was frozen at −20 °C for 8 h, whereafter it was degassed with melting at 0.1 atm and room temperature for 12 h, followed by cycling three times to obtain degassed water. Degassed water and untreated propanol were taken as controls.

Figure 1. Characterization of bulk air NBs in propanol. (a) Size distributions of the ultrasonic cavitation-generated NBs in water and propanol; (b) histogram indicating the number density of NBs; (c) evolution of the number density of the ultrasonic cavitation-generated NBs in propanol and water during resting; (d) the change of zeta potential of the cavitation-generated air NBs in propanol and water over time.
zero after 5 h, which indicated that the NBs have remarkable long-term stability in the alcohol system.

Zeta potential is a common method to measure surface charges of NB suspension in aqueous systems. Many scholars believe that negative charges on the NB’s surface are one of the main factors stabilizing NBs by creating repulsive forces to prevent the coalescence of bubbles.\textsuperscript{28,53,54} In order to explore the properties of the surface of the NBs formed in alcohol solutions, we measured the change of zeta potential in the air NB suspensions in propanol. As shown in Figure 1d, the zeta potential of NBs in propanol was stable around 0 mV over time in contrast to about $-30$ mV in water. Zero zeta potential on the air NBs in propanol may be due to that the propanol molecules are normally not ionized and cannot form negative charges on the surface of the NBs. Our results indicated that NBs could also be generated in propanol, which was hard to be ionized. Here, the zeta potential may refer to the potential at the interface of the gas phase and liquid propanol, in contrast to the potential at the electrical double-layer of the NBs in the water systems.\textsuperscript{49}

The factors that stabilize the NBs in propanol still remain unclear. We think hydrogen bonds between the propanol molecules around the NBs may play a role. As propyl is hydrophobic and hydroxyl is hydrophilic, propanol molecules will be redistributed with propyl facing the gas phase and hydroxyl facing the liquid phase when the bulk NBs are formed.\textsuperscript{55–57} In addition to weak C$\cdots$H$\cdots$O hydrogen bonds at the gas–liquid interface, the hydroxyl will form strong O$\cdots$H$\cdots$O hydrogen bonds with the adjacent propanol liquid.\textsuperscript{58,59} Therefore, hydrogen bond strength in propanol containing bulk NBs will be higher than that in liquid propanol.

2.2. Verification of the Air NBs Generated in Propanol. 2.2.1. Heating. Here, we indirectly verified that the nanoparticles detected by the NTA were NBs but not other nanoimpurities by means of heating. According to Henry’s law, when the temperature goes up, the solubility of gas goes down. On the other hand, since organic solution is partially volatilized during the heating process, assuming the presence of other nanoscale impurities, heating will increase the density of detected nanoparticles rather than decreasing. In our experiments, when propanol solutions were treated by ultrasound under varied temperatures, it was found that the generated particles became less at the elevated temperatures (Figure 2a). The result ruled out the possibility that the particles produced by the ultrasonic method were contaminations. Rather, the decreased particle number upon heating complied with the characteristics of NBs.
In our experiment, 20 mL glass bottles were filled with propanol solution and sealed with a lid to exclude the existence of a gas–liquid interface. Therefore, there would be no air NBs formed during ultrasonic treatment without a gas–liquid interface. As shown in Figure 2e, the bubble number density remained basically unchanged in such a case. It seems that, although propanol solution without a gas–liquid interface may be acoustically cavitated, no stabilized NBs were generated.

2.2.5. Tyndall Effect. The Tyndall effect is a direct way to distinguish colloids from solutions.\textsuperscript{18,61,62} Ultrasonic cavitation-treated propanol was observed with the illumination of a red laser in a dark room. As shown in Figure 2f, a bright light revealing the scattering of the laser in the treated propanol was observed, a strong Tyndall effect that was not found in the untreated propanol solution. According to previous verification experiments, the colloidal particles that scattered the light were mostly NBs.

2.3. Optimization of Acoustical Ultrasonic Conditions. We think that the increase of ultrasonic intensity and sonicating time would benefit the formation of NBs. However, an ultrasonic treatment with very high intensity and long treating time would lead to fusion of small NBs into larger bubbles, resulting in the escape of gas from the solution. Next, optimal conditions including sonication time and ultrasonic power for generating air NBs in propanol with the acoustical cavitation method were explored. The results showed that a treatment time of 10 min would generate the highest NB density in propanol (Figure 3a) in the time range (5–20 min) that we studied. The mean diameter of the generated NBs fluctuated in the range of 230–320 nm and gradually decreased with the increase of sonicating time (Figure 3b). When the output power of the ultrasonic unit was set to 60% of its rated power (300 W), the density of the bubble number reached to a maximum value of $\sim 5.8 \times 10^7$ bubble/mL (Figure 3c). The bubble diameter did not fluctuate significantly along with the change of the output power and reached its maximum at an output power of 70% rated power (Figure 3d).

2.4. Generating NBs in Propanol by Different Preparation Methods.\textsuperscript{30,63} NBs in propanol were also generated by using the pressurization–depressurization method and vibration method. During the pressurization–

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Figure 3. Optimization of conditions in an acoustical cavitation method. (a) Bubble number density plotted against the sonicating time; (b) mean diameter of the NBs plotted against the sonicating time; (c) bubble number density plotted against the sonicating power; (d) mean bubble diameter of the NBs plotted against the sonicating power.
depressurization process, the pressurization of the solvent increases the concentration of the dissolved gas, providing additional centers for gas nucleation, and the subsequent depressurization promotes uniform bubble nucleation. Meanwhile, in the vibration method, it mainly introduces more gases into organic solvents by speeding up the gas exchange at the gas−liquid interface. In this process, the formation of NBs has a complex relationship with the vibration time and frequency. Figure 4 showed typical differences in bubble size distribution and bubble number density between NBs produced with different methods. The bubble number density in the pressurization−depressurization method reached a value of $\sim 3.7 \times 10^7$ bubble/mL, in contrast to $\sim 5.8 \times 10^7$ bubble/mL in the acoustical cavitation method and $\sim 1 \times 10^7$ bubble/mL in the vibration method. The experimental results indicated that the generation of NBs in propanol could be routinely achieved with various methods.

2.5. Bulk Air NBs Produced in Alcohols with Different Carbon Chain Lengths. Bulk air NBs were generated in alcohols with different carbon chain lengths by the acoustical cavitation method. Figure 5 showed typical NB size distributions varied with the length of the alcohol carbon chains. The result indicated that NBs in pentanol were the largest in size (Figure 5b), while the NBs in propanol had the largest bubble number density. The trends in mean bubble diameter and bubble number density of the NBs in alcohols with different carbon chain lengths obtained by pressurization−depressurization ($\sim 3.7 \times 10^7$ bubble/mL) and vibration methods ($\sim 1 \times 10^7$ bubble/mL) were similar to those obtained by the acoustical cavitation method, as shown in Figure 6.

3. CONCLUSIONS

In summary, bulk NBs in alcohol systems have been successfully generated by using various methods. Our results indicated that bulk NBs could stably exist for at least hours in alcohol systems. Although trace impurities presented in alcohols might affect the light scattering measurements, our control experiments suggested that the colloidal particles that scattered the light were most likely bulk NBs. The highest number density of NBs varied in different alcohols that we studied, with a maximum value for the Propanol. The factors that stabilize the NBs in propanol still remain unclear. We think that hydrogen bonds between the propanol molecules...
around the NBs may play a role. Our studies provided a possibility for increasing gas/liquid mass transfer efficiency through a NB formation route, which should have a great potential in increasing the reaction efficiency in a gas/liquid reaction.

4. MATERIALS AND METHODS

4.1. Materials. Alcohols including methanol, ethanol, propanol, butanol, pentanol, and hexanol (all in analytical grade, 99.9%) and sodium hydroxide (in analytical grade, ≥96.0%) were purchased from Sinopec Group Co., Ltd. Glassware was used in order to avoid contamination from plastic products. Ultrapure water from an ELGA LabWater (ELGA Classic-PURELAB) was used in all experiments. All solvents were examined by the NTA before use to insure that no nanoscale impurities within the measurable range of NTA could be detected.

4.2. Generating Air NBs in Alcohols by the Acoustical Cavitation Method. The basic principle of NB generation is to create a local oversaturated state for gas and induce the nucleation of gas molecules. Here we used ultrasonic cavitation to nucleate air bubbles. When the ultrasonic intensity was higher than the cavitation threshold, a small nucleus would be formed inside, and the dissolved gas could be precipitated out of the dissolved gas in the alcohol solutions. Experiments were performed under room temperature in a custom-made stainless chamber that controlled the pressure inside. First, a 20 mL glass bottle containing 5 mL of alcohol solution was placed in a pressurized chamber (2 MPa) for 30 min. Then, a depressurization process containing 5 mL of alcohol solution was placed in a pressurized chamber (2 MPa) for 30 min. Then, a depressurization process with a speed of 0.33 MPa/h was executed to decrease the pressure inside the chamber to the normal atmosphere (~0.1 MPa). Detailed description of the experimental setup and procedures are available in a paper published previously.

4.3. Generating N2 NBs in Alcohols by the Pressurization–Depressurization Method. Alcohol solution (5 mL) in a 20 mL glass bottle was placed in a Talboys standard vortex mixer (Scientific Industries, Inc.), which was circularly oscillated at a range of 0–5400 rpm (r/min) for 3 min. In order to avoid contamination, the bottle was sealed with a parafilm. After the vibration, the NB suspension was left standing for 2 min so that larger bubbles visible to the naked eyes would burst and disappear.

4.4. NTA. The number density and size distribution of NBs were characterized by an NTA instrument (Nanosight, NS 300, Malvern), which is suitable for the real-time analysis of polydisperse particles ranging from 10 to 2000 nm in size and 10 to 100 particles/mL in number density. The NTA instrument was equipped with a 20-fold magnification microscope, a high-speed camera, and a 65 mW laser light source (405 nm). Each data was averaged from 10 individual measurements, and the film lasted 60 s, capturing at 25 frames/s. The camera level was usually set to 10, the threshold was set to 13, and the solution viscosity was 0.4–5 cP (mPa·s). During measurement, the optical field was fixed to about 80 μm, and the depth of the light beam was about 10 μm. The particle concentration could be obtained by dividing the volume of the field by the number of nanoparticles. The camera subsequently captured a video of the particles moving under Brownian motion within a field of view of approximately 100 μm × 80 μm × 10 μm. The size of nanoparticles was determined using the Stokes–Einstein equation:

Figure 6. NBs produced in alcohols with different carbon chain lengths by different methods (pressurization–depressurization method: treated at a pressure of 2 MPa for 30 min and release of pressure at a rate of 0.33 MPa/h; vibration method: 3 min, 1800 r/min). (a) Mean bubble diameter of vibration-generated NBs; (b) Bubble number density of vibration-generated NBs; (c) mean bubble diameter of pressurization–depressurization-generated NBs; (d) bubble number density of pressurization–depressurization-generated NBs.
\[ D_t = \frac{T k_B}{3 \eta d} \]

where \( k_B \), \( T \), and \( \eta \) are the Boltzmann constant, the temperature, and the liquid viscosity, respectively, and \( D_t \) is the diffusion coefficient, which is an experimentally measured value based on the Brownian motion of the particle.\(^62\)

4.6. Zeta Potential. Zeta potential, also known as electric potential at the slip plane in the case of colloids, is an important indicator of the stability of colloidal dispersion systems. Zeta potential can be derived using a theoretical model and experimentally determined electrophoretic mobility of charged entities under an applied electric field. The electrophoretic mobility, \( \mu_e \), is defined as

\[ \mu_e = \frac{\mu}{e} \]

where \( \mu \) is the drift velocity of the dispersed particle, and \( e \) is the strength of the applied electric field. Thus, the zeta potential, \( \zeta \), can be calculated from

\[ \zeta = \frac{2 \pi \epsilon \mu_e \eta f(x)}{3 \eta} \]

where \( \epsilon \), \( \mu_e \), \( \eta \), and \( f(x) \) are the relative permittivity or dielectric constant of the dispersion medium, the permittivity of vacuum, the dynamic viscosity of the dispersion medium at the experimental temperature, and Henry’s function, respectively. Here, the zeta potential of the NB suspensions was measured by a Zetasizer Nano ZS 90 (Malvern Instruments, U.K.).\(^64,65\)

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Author Contributions

Y.J. contributed to the conceptualization, methodology, and investigation of the study and writing the original draft. Z.G. performed the formal analysis and investigation and contributed to reviewing & editing the paper. T.T. and Y.W. contributed to the methodology and investigation. L.Z. participated in the investigation and supervision and in reviewing & editing the paper. J.H. contributed to the conceptualization and in reviewing & editing the paper. Y.Z. contributed in reviewing & editing he paper and in conceptualization, methodology, supervision, and funding acquisition.

Notes

The authors declare no competing financial interest.

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