A Microfluidic Method for Investigating Ion-Specific Bubble Coalescence in Salt Solutions

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ABSTRACT: This paper reports the direct and precise measurement of bubble coalescence in salt solutions using microfluidics. We directly visualized the bubble coalescence process in a microchannel using high-speed imaging and evaluated the shortest coalescence time to determine the transition concentration of sodium halide solutions. We found the transition concentration is ion-specific, and the capacity of sodium halide salts to inhibit bubble coalescence follows the order of NaF > NaCl > NaBr > NaI. The microfluidic method overcomes the inherent uncertainties in conventional large-scale devices and methods.

INTRODUCTION

Bubble coalescence in different salt solutions governs many interesting but unexpected phenomena. These phenomena are found in nature and industrial applications. Examples include the formation of white foam as waves break in seawater.1 Industrially, purification of mined coal from clays using air bubbles is possible in seawater and other saline waters.2 Fine bubbles were often generated in saline waters without the use of conventional surfactants. Unlike surfactants, salts are supposed to promote bubble coalescence by increasing the surface tension. Ironically, both surface-active compound (surfactants) and surface-inactive compound (inorganic salts) inhibit bubble coalescence. More interestingly, these compounds can only fully or partially inhibit bubble coalescence above a critical concentration referred to as the critical coalescence concentration (CCC) or increase the bubble coalescence time above a transition concentration (TC).3–12

Despite the inconsistent definitions of CCC and TC in the literature, different techniques have been developed to determine these values.3 Briefly, the techniques can be categorized into (i) bubble swarm experiments, (ii) bubble pair method, and (iii) film balance technique. All these techniques have not been satisfactory due to their inherent shortcomings and uncertainties. Values of CCC or TC obtained via different techniques have shown significant discrepancy.3

Bubble swarm experiment studies the population of a swarm of bubbles. The CCC in this experiment is defined either as the concentration corresponding to 50% bubble coalescence13 or as the concentration above which a constant bubble size is reached.7,14 The bubble swarm experiment is useful for studying the effects of flow conditions on bubble coalescence. However, the measurements of CCC are significantly influenced by hydrodynamic conditions, such as turbulence.15

Therefore, the uncertainties of these measurements are significant by nature. For example, the CCC of NaCl varies from 0.31 to 0.778 M in different measurements of bubble size distribution in a bubble column.15 Obtaining the average bubble size by measuring the whole bubble population is also time-consuming.

In the bubble pair method, two bubbles are generated from adjacent capillaries placed either side by side or facing each other. The CCC is now defined as the concentration at which 50% of the contacted bubbles coalesce. Compared with bubble swarm experiments, the relative uncertainties decrease due to the relatively stable environment. However, the bubble pairs are only labeled as “coalescence” or “noncoalescence”. Therefore, important information representing the efficiency of inhabitation, such as bubble coalescence time or lifetime of liquid film between bubbles, is missing.

The film balance technique, unlike the previous techniques, can provide important information to understand the bubble coalescence process. For example, both the drainage time and the thickness of liquid film can be measured. However, the exposure of the liquid film to the air results in many uncertainties, such as the contamination, evaporation, and thermal or mechanical fluctuations from the environment. Since no real bubble is generated, the film balance technique still cannot provide key information such as bubble deformation and postcoalescence oscillation.16

The present paper demonstrates that microfluidics is a powerful tool to understand the complex bubble dynamics. The design of the experiments in a microchannel eliminates the
effects of long-range inertial forces, therefore allowing for the investigation of only short-range effects (e.g., colloidal forces) on the bubble coalescence process. This tool also circumvents many limitations mentioned above. For example, the laminar flow behavior allows the generation of extremely well-controlled bubble size.\textsuperscript{17,18} Furthermore, the confinement of a microchannel guarantees the well-controlled transport of microbubbles. Therefore, microfluidic devices have been utilized to study bubble coalescence behaviors.\textsuperscript{19,20} However, past studies on bubble coalescence in microfluidic devices were limited mainly to the effect of hydrodynamics. We aim to report a different perspective where the transition concentration of salt solutions is determined in a microfluidic flow-focusing device. The well-controlled bubble dynamics in the microfluidic device allows for a more reliable and precise determination of the transition concentration as compared to existing conventional techniques.

\section*{EXPERIMENTS}

Air bubbles were generated in four sodium halide solutions (NaF, NaCl, NaBr, and NaI) using the flow-focusing geometry (Figure 1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Schematic diagram of the flow-focusing microfluidic device. (b) Image of the bubble generation and (c) coalescence in 0.5 M NaCl solution with a total NaCl solution flow rate of 500 $\mu$L/h and an air flow rate 100 $\mu$L/h. The depth of the channel is about 30 $\mu$m. The scale bar represents 100 $\mu$m.}
\end{figure}

The flow rates of salt solution and air were 500 and 100 $\mu$L/h, respectively. The frequency of bubble generation was about 52 ± 5 Hz. Coalescence of air bubbles was observed at the expansion of the micorfluidic channels (Figure 1a). It should be noted that only coalescence events between two bubbles with the same initial bubble size were chosen to calculate the coalescence time. Coalescence events between a bubble with initial bubble size and a relatively large bubble size were chosen to calculate the coalescence time. Coalescence events between two bubbles with the same initial bubble size were taken to obtain the average coalescence time for each solution. Some measurements were repeated on another day (four, three, and six measurements each for 0.05 and 0.1 M NaBr solutions) to ensure the repeatability of the results.

Sequential layer-by-layer deposition of polyelectrolytes (polyallylamine hydrochloride), i.e., PAH (98%, Sigma-Aldrich, USA), and poly(sodium 4-styrenesulfonate), i.e., PSS (98%, Sigma-Aldrich, USA), was used to yield stable hydrophilic surface in the PDMS microfluidic devices.\textsuperscript{22} Briefly, the PAH and PSS solutions (both 0.1% w/v in 0.5 M aqueous NaCl solution) and NaCl washing solution (0.1 M) were alternately injected to fill the microchannel. The first positively charged PAH layer was deposited onto the negatively charged PDMS surface treated by air plasma. Then the negatively charged PSS layer was deposited onto the PAH layer. After eight deposition cycles, a (PAH/PSS)\textsuperscript{8} polyelectrolyte multilayer was coated on the channel wall. Sufficiently long adsorption time of approximately 5 min was taken for the deposition of each layer.\textsuperscript{23} The structure of the PAH/PSS multilayer is very compact due to the high degree of complexation between the polyelectrolytes as well as hydrogen bonds between the amines in PAH and oxygen in PSS.\textsuperscript{24–26} The stability of the polyelectrolyte multilayer is independent of the salt type that we used because there is no interaction between the outermost PSS layer (negatively charged) and the anions, and the only cation is Na\textsuperscript{+}. The water content of the PAH/PSS multilayer remained unchanged with a high concentration of NaCl in the external solution up to 1.2 M.\textsuperscript{25} Considering the range of salt concentration in our study of 0–0.5 M, we can safely eliminate the influence of salt concentration on the stability of the polyelectrolyte multilayer. The final washing step was performed with deionized water to remove traces of contaminations in the microchannels. Because the channel volume in a microfluidic device is extremely small, applying a relatively large amount of deionized water (∼20 mL, about 50 000 times of the space in the microfluidic device) can thoroughly wash away the trace contaminants in the microchannels. Subsequently, the equilibrium surface tension of the water–air interface for the last 5 mL washing water was measured to check the cleanliness of the microchannel. The value of the equilibrium surface tension was measured as 72.35 ± 0.14 mN/m (standard deviation of the mean) at 23 °C using the Wilhelmy plate method and matches the reported value of 72.3 mN/m.\textsuperscript{27} It should be noted that the oxidation of the PDMS surface by plasma cleaning only leads to a temporarily hydrophilic surface. The PDMS surface regains its original hydrophobicity after exposing to a low-surface-energy medium such as air as used in our experiments to generate the bubbles.\textsuperscript{22,28,29}

Deionized (DI) water was utilized to make the salt solutions, i.e., solutions of NaF (99%, Sigma-Aldrich, USA), NaCl (99.5%, Sigma-Aldrich, USA), NaBr (99%, Sigma-Aldrich, Israel), and NaI (99%, Merck, Germany). Air and salt solutions were loaded in gastight glass syringes and delivered into the microfluidic device by a syringe pump (SPM 100 S-FLUIDPUMP, Singapore). Videos of bubble coalescence were recorded at a frame rate of 13 000 frames per second (fps) and subsequently processed with ImageJ (V1.48, NIH, USA). The coalescence time was calculated as the time interval from the contact of two air bubble interfaces to the first frame of bubble coalescence. The uncertainty for the measurement of coalescence time is the interval between two frames, i.e., 76.92 $\mu$s. Four to ten measurements were taken to obtain the average coalescence time for each solution. Some measurements were repeated on another day (four, three, and four measurements for 0.01, 0.05, and 0.075 M NaCl solutions and six measurements each for 0.05 and 0.1 M NaBr solutions) to ensure the repeatability of the results. Figure 2 shows image sequences of the coalescence process of two bubbles in a 0.75 M NaF solution. We identified four consecutive stages of the coalescence process: approaching (Figure 2a), contact (Figure 2b), liquid film draining (Figure 2c), and coalescence (Figure 2d). The average diameter and the collision speed of the bubbles were 255 ± 4 $\mu$m and 0.022 ± 0.004 m/s, respectively. The bubble size in this study is at least 1 order of magnitude smaller than the one measured in all existing conventional
techniques. The bubble approaching speed in this study is in the “instant coalescence” regime (0.0012–0.14 m/s); i.e., the bubble coalescence time is smaller than 0.01 s. Our measured bubble coalescence times of smaller than 0.001 s validate the existence of this regime.

**RESULTS AND DISCUSSION**

Figure 3a shows the coalescence time of a colliding bubble pairs in sodium halide solutions for different concentrations up to 0.5 M. The transition salt concentration (TC) was found at the shortest bubble coalescence time. At TC, the bubble dynamics moves from coalescence to inhibition, and the bubbles can merge most efficiently. The TCs are found at 0.070 ± 0.010, 0.0850 ± 0.010, 0.175 ± 0.025, and 0.325 ± 0.025 M for NaF, NaCl, NaBr, and NaI solutions, respectively. It is important to note that our measured results of TC are within the range of previously published results that were determined via the film balance technique, i.e., 0.080, 0.115, 0.195, and 0.345 M for NaF, NaCl, NaBr, and NaI solutions, respectively.31,32 However, the uncertainty of bubble coalescence time using our microfluidic method (<6%) is much smaller than that of the film balance technique (as high as 20%).32 Despite the consistency of our TC measurements, the measured bubble coalescence times ranging from 100 to 500 μs are much shorter than the reported values of 0.1 to 30 s using liquid film balance technique.32 The difference in the interface approaching speeds may lead to this discrepancy. The approaching speed of 22 mm/s in this study is much greater than the one that drives film drainage in the film balance technique (10–300 μm/s). A critical approach speed of approximately 35 μm/s was reported previously. Above this critical speed, the bubbles coalesce almost instantly within less than 0.1 s, and the transition concentration of salts is independent of the approaching speed.32 Our microfluidic method with the high-speed camera makes the observation of that instant coalescence possible. Furthermore, the time scale of the bubble coalescence process in our study of few hundreds of microseconds is more relevant to the practical systems such as bubble columns and flotation separation where the bubble contact time in solutions is shorter than 1 s, as compared with the time scale (as long as 20 s) of the film balance experiments.32 The laminar flow in a microchannel also eliminates the uncertainties of bubble coalescence due to the turbulence in the bubble swarm experiment. Finally, the microfluidic method provides a reliable and precise bubble coalescence time rather than qualitative description as “coalescence” or “noncoalescence” in the bubble pair method.

Figure 3a shows that the measured TCs for the monovalent anions increase with the anion size. The ion-specific effect on bubble coalescence in sodium halide salt solutions follows the order of inhibition capability: NaF > NaCl > NaBr > NaI. At concentrations lower than TC, the curves for bubble coalescence time almost overlap. However, at concentrations higher than TC, the curves deviate from each another significantly. In the regimes of low salt concentration, the bubble coalescence is controlled by the repulsion between the electric double layers at the bubble surfaces, which becomes weak with increasing salt concentration due to the compression of the double layers. The inhibition of bubble coalescence at high salt concentration is still not well understood.35,36 Gibbs elasticity of the liquid film caused by the surface tension gradient and hydrophobic forces between bubble interfaces due to dissolved gases in salt solutions are believed to be related to the ion-specific effect on bubble coalescence inhibition at high salt concentration.3

We also plot the coalescence time against Ohnesorge number (Oh = μ/(ρσD))1/2 where μ, ρ, σ, and D are viscosity, density, surface tension, and bubble diameter, respectively, which relates the viscous forces to inertial and surface tension forces, in Figure 3b. The coalescence of bubbles and drops in an outer fluid is related to this dimensionless number, and a phase diagram has been created to identify different regimes of the coalescence process.37 However, Figure 3b shows that the change of Ohnesorge number in current study is very small (0.0065–0.0068). Therefore, we can safely neglect the effects.
of physical properties of salt solutions on the bubble coalescence process.

Nearly 130 years on since the ion-specific effect on protein precipitation had been found by Hofmeister, its satisfactory explanation is still a challenge to classic theories, including the Debye–Hückel and DLVO theories. Only phenomenological set of rules such as the law of matching water affinities and combining rules of ions to inhibit bubble coalescence could successfully explain the effect. Nevertheless, microfluidic technology proves here to be a useful tool for investigating the ion-specific effect on bubble coalescence.

## CONCLUSIONS

In summary, we report a microfluidic method to investigate the ion-specific effect on bubble coalescence. We directly visualized the bubble coalescence in a microchannel using high-speed imaging and evaluated the bubble coalescence time to determine the transition concentrations of sodium halide solutions. We found the capacity of sodium halide salts to inhibit bubble coalescence follows the order of NaF > NaCl > NaBr > NaI. Compared with conventional techniques, the microfluidic method overcomes their inherent uncertainties and provides a promising tool for the future studies on ion-specific effect.

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The authors declare no competing financial interest.

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