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GASEOUS BUBBLE NUCLEATION UNDER SHEAR FLOW

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ABSTRACT

A decompression experiment of a water solution, saturated with methane gas at about 68 atm at room temperature, was done to investigate gas bubble nucleation under shear flow. A pressure reduction from 68 atm to atmospheric pressure is well below the decompression pressure required for spontaneous bubble nucleation of the methane gas, about 120 atm. The application of a shear flow from 5 minutes before to 1 minute after the decompression induced active bubble formation and the final gas content in the solution was reduced substantially, even with the application of low shear rate of 25/s.

INTRODUCTION

Understanding the degassing process from supersaturated liquid-gas solution is very important in many engineering applications. For example, industrial applications include degassing from molten metals [1] and the manufacture of foamed materials [2,3]. In the field of physiology, nitrogen bubble formation in blood vessels and tissue, as a result of an

excessive rate of decompression, causes caisson disease [4]. Degassing from a supersaturated solution, the gaseous bubble is formed by an aggregation process involving the dissolved gas molecules, and is quite different from boiling or cavitation phenomena, a typical phase change process [5].

Systematic experiments on gas bubble formation from a highly supersaturated liquid-gas solution have been done by Hemmingsen [6,7]. He investigated bubble formation in a capillary tube (diameter of 0.15 to 2.5 mm) from a water-gas solution which was decompressed to atmospheric pressure from an initial saturated state at high pressure. After a series of such decompression experiments with different values for the initial saturation pressure, quite different threshold pressures for bubble nucleation were obtained for different dissolved gas species. These findings are quite contradictory to the predicted values from the classical nucleation theory. A condition of "massive bubble formation" was obtained when the initial saturation pressure was 20-30 atm higher than the threshold value. Also, it was observed that the capillary diameter affected the threshold value for bubble nucleation. For nitrogen, the threshold pressure dropped to 100 atm using a 2.5 mm diameter capillary tube, while the threshold value obtained was 170 atm for a 1.1 mm capillary. In these

experiments, the pressure reduction time was reported as 2-3 s; however the bubble formation time was not given.

The effect of shear on nucleation of bubbles, droplets, and of crystals has drawn some attention recently and is still a debated subject [10]. A theoretical study by Reguera and Rubi [11] revealed that shear flow may enhance the diffusivity of molecules and, correspondingly, the nucleation rate. Particularly, the shear promotes a drastic change in the crystallization process of polymers having high viscosity. However, the effect is expected to be unimportant in condensation. Indeed, a factor of 10 in nucleation of isoactic polypropylene was observed at a rate of shear 14/s compared with the stationary case [12]. Another computational study for a van der Waals fluid has revealed that shear affects the bubble growth rate due to enhanced molecular transport, but has little effect on the bubble nucleation process [13]. The nucleation and growth of a bubble in a Newtonian liquid having very high viscosity were studied under simple shear and creeping flow using a Couette apparatus by Favelukis et al. [14]. They found that the growth rate of a slender bubble increases as the shear rate increases in the shear rate ranges between 2.0/s and 14.0/s.

In this study, decompression of a water solution saturated with methane gas at about 68 atm (1000 psi) at room temperature was done under shear flow. A shear stress by a Couette flow apparatus was imposed during the decompression process to investigate the shear effect on the bubble nucleation. This pressure reduction from 68 atm to atmospheric pressure is far below that required for spontaneous bubble formation for the methane gas, about 120 atm [5,15]. A shear flow was applied 5 minutes before to 1 minute after the decompression and the final gas content in the solution was measured and it was found to be reduced substantially, even with application of a low shear rate of 25/s.

EXPERIMENTAL APPARATUS AND PROCEDURES

A schematic diagram of the test equipment for the decompression experiment is shown in Fig.1. The test chamber is made of carbon steel. Two flat glass window

17.7 mm thick allow viewing of the sample during the decompression experiment. To receive the sample solution, a test tube cleaned with acetone and dried was inserted into the test chamber from the bottom.

The saturated water-gas solution was prepared in a separate mixing cylinder (500 cc), made of stainless steel. The cylinder was filled with deionized water. A magnetic stirrer was used to mix the water and methane gas. Mixing was started by opening valve (5) slowly. The typical mixing time was 6 hours. Next, the test chamber was purged and pressurized with methane gas by opening valve (2). After mixing was accomplished, the valve (2) is closed and the test section pressure was decreased slightly by opening valve (3). Then the mixture flows into the test tube by opening valve (1) and (4). About 6 cc of the water-methane gas solution was used in each experiment. After filling the test tube with the solution, valve (1) and (2) were closed to isolate the test chamber.

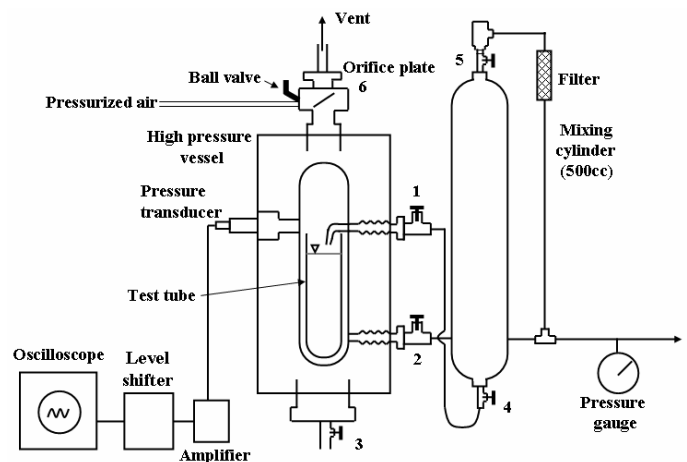


Fig.1. Schematic diagram of decompression experiment

A Couette flow apparatus imposes a shear stress in a fluid without changing the pressure in the fluid, as shown in Fig.2. The apparatus consists of an annulus formed by inserting a mirror finished aluminum rod with diameter of 7.94 mm into the center of the test tube. The shear flow is set up by rotating the rod by a small electric motor. The motor located at the top of the test chamber was attached to a gear box, and the speed was controlled by a variable DC voltage. The rotating rod was connected to a gear box with a 22:1 gear ratio. To eliminate the friction of the rotating rod, the end of

the test tube was made of aluminum and fitted with a bearing.

The speed of the rotating rod was measured with a digital strobe, and found to be 240 rpm to 1200 rpm. Speed below 240 rpm could not be operated. The corresponding shear rates are 20/s to 100/s and Taylor numbers are 37120 to 928000. The rotating speed of the rod was found to be linearly dependent on the input voltage to the motor. It is known that a secondary flow called a Taylor vortex occurs if the rotation speed is above a critical value of the Taylor number, 33000 in this case. The Taylor number for this particular case of rotating of inner cylinder only is defined as

$$T_a = \frac{4\Omega_1^2 R_1^4}{\nu^2 (1-\eta^2)^2} \quad (1)$$

where $\eta = R_1 / R_2$, ν is dynamic viscosity of liquid and the radius of aluminum rod, R_1 is 3.97 mm and the radius of the test tube, R_2 is 6.75 mm. The Taylor vortices were observed at all rotation speeds tested and at a speed of 600 rpm, the wiggly pattern of the Taylor vortex was seen in another test visualizing the flow pattern by using aluminum powder. This secondary flow is superimposed upon the main shear flow but is very weak in most instances. The time we imposed the shear flow field was 5 minutes before to 1 minute after the decompression.

The decompression process was started by opening a ball valve (6) equipped with a fast-action, automatic, compressed air operator, located above the top of the test chamber. A high speed camera (Fairchild, Model HS 401) was started just before the decompression process. The film speed employed was about 200-400 frames/s. A timing light with 100 cycles per second was used to indicate the time at the edge of the film. The rate at which the pressure in the test section dropped was controlled by the size of the orifice on the outlet side of the ball valve. In this experiment an 0.81 mm diameter orifice was used. A piezoelectric pressure transducer installed at the wall of the test chamber measured the pressure reduction rate in the test section. A typical decompression rate in the test section is shown in Fig.3.

After the decompression experiment finished, an attempt was made to measure the final concentration of the dissolved

gas using gas chromatography (Beckman) with some external modifications. This modification consisted of some equipment to separate the water from the gas before it entered the diffusion column in the gas chromatography setup. Reliable results with repetitive measurements were usually obtained if the concentration was less than about 10 times the saturated concentration equilibrated at atmospheric pressure. The mole fraction of methane gas in water solution was estimated by Henry's law, $P=Hx$, where P is equilibrium pressure in atm unit. The value of Henry's constant for water-methane solution at 25 °C is about 4.13×10^4 atm [16].

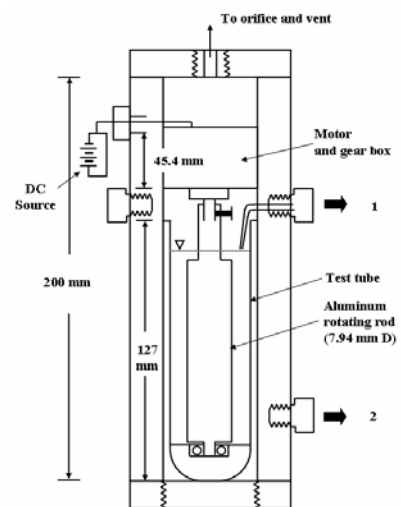


Fig. 2 A schematic for shear flow experiment

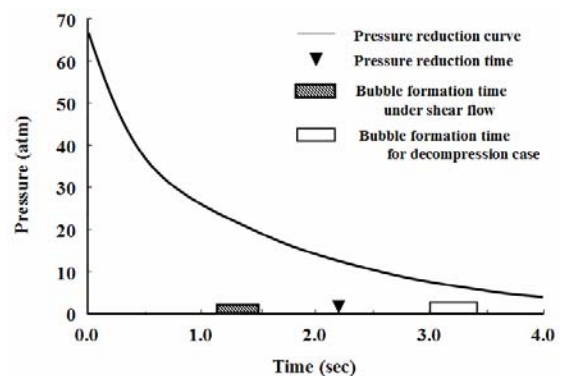


Fig. 3 Time dependent gas pressure inside the test chamber with an orifice diameter of 0.81 mm

EXPERIMENTAL RESULTS AND DISCUSSION

A. DECOMPRESSION EXPERIMENT

As shown in Fig.3, the pressure-time decay curve in the

test chamber was of an exponential type from which an exponential time constant (t_e) can be obtained. The pressure reduction time (t_p) is defined as twice as the exponential time, or $t_p=2t_e$. A bubble formation time (t_b) is defined as the time required to detecting a group of bubble in the solution after initiation of the decompression. Bubble nucleation in the supersaturated solution developed from the solution with the equilibrium pressure of 68 atm scarcely occurred by decompression only so that the final concentration of the dissolved gas was hardly measured. In this case the bubble formation time is about 2.97 s. As shown in Fig. 4(a), a countable number of bubbles might be formed from the cavities on the surface of the test tube heterogeneously [17]. As is well known, gas cavities on the surface provide sites for bubble nucleation with lower energy barrier than that for homogeneous nucleation. In all these decompression tests, heterogeneous bubble formation occurred only a short period of time and the solution remained highly supersaturated.

b. Gaseous bubble nucleation under shear flow

The shear flow effect on bubble formation was found to be very effective. Bubble formation under the shear flow occurred earlier than the decompression time, as shown in Fig.3. Also the bubble formation time decreased as the rotation speed was increased as noted in Table 1. Active bubble formation always occurred and the final gas concentration in the solution reduced substantially even at the lowest speed of 300 rpm. A picture of the bubble formation at this speed is shown in Fig.5. Many tiny bubbles move around the tube. A couple of large bubbles due to coalescence are also seen. The final supersaturation values decrease as the rotation speed increases from 300 rpm to 1200 rpm, as confirmed in Table 1. The test results for the bubble formation in a shear flow field accompanying the decompression process are summarized in Table 1. The local heating due to the shearing action is certainly negligible for the speed ranges tested.

The decompression amount for massive bubble

formation from a water-methane gas solution at 25 °C, calculated with a nucleation rate $J_{nc}=10^6/cm^3s$, is about 120 atm [5]. This value is the exactly same as the observed value by Gerth and Hemmingsen [17]. The number of molecules inside a critical cluster is about 560 in this case. A molecular dynamics study yielded that the shearing action changed the liquid structure to stratify along the line of shear [18] so that the molecules are reordered to be staggered in the normal to the velocity gradient, as shown in Fig.6. Such a structure rearrangement enhances the self-diffusion coefficient of the dissolved molecules and increases the dissolved gas volume occupied in the solution so that the decompression amount for bubble formation reduces correspondingly.

Table 1. Shear flow experiments; initial saturation gas pressure is 68 atm where mole fraction of methane gas saturated with atmospheric pressure in water solution at 25 °C, x_0 is 2.42×10^{-5} .

Test Description	Rotation speed (RPM)	Bubble formation time, t_b (s)	$X_f \times 10^5$ final mole fraction	Level of concentration $\delta = x/x_0$	Remarks
Shear Flow $t_p=2.64$ sec Pure water	No rotation	2.97	50.4	20.8	Bubbles form on metal rotor surface only. One can hardly measure the residual concentration in this case.
	300	1.46	12.6	5.21	Homogeneous bubble formation; bubbles can be seen inside tube.
	600	1.30	7.8	3.22	
	900	1.19	7.2	2.98	
	1200	1.13	5.2	2.15	

With a 20% increase in the effective diameter of the dissolved molecules, the decompression amount for massive bubble formation in the water-methane gas solution reduces to 70 atm from 120 atm, as verified in this experiment. In Table 2, given amount of decompression of 68 atm, the number of molecules constituting the critical cluster and the corresponding nucleation rate dependent on the applied shear rate are listed. The volume changes at given shear rate were chosen to correctly predict the measured number of degassed molecules, which can be calculated by the RHS in Eq.(2). A proper nucleation rate, J_{nc} , may be determined by the following equation

$$J_{nc} n_b t_{nu} = (x_i - x_f) N_w \quad (2)$$

where N_w is the number density of water, n_b is the number of molecules inside a 120 micron radius bubble developed from a critical cluster and t_{nu} is nucleation duration of 6 s. It is postulated that once a cluster reaches the critical size, it grows by kinetics to the critical size bubble and further growth of the bubble proceeds due to concentration defects at the interface by the diffusion process [19,20]. In the above equation x_i and x_f are the mole fractions of dissolved methane molecules at initial state saturated with 68 atm and at final state after the nucleation process, respectively.

Table 2. Possible fractions of volume changes and the corresponding number of molecules inside the critical clusters and their nucleation rates which are matched to the measured number of degassed methane molecules dependent on shear rates.

Shear Rate (/s)	Fraction of volume change of liquid	Number of molecules inside the critical cluster, n_c	Nucleation rate of the critical cluster, J_{nc}	Number of molecules degassed per unit volume calculated from Eq. (2)
25	0.21475	951.7	5.07×10^4	5.08×10^{19}
50	0.21490	951.0	5.19×10^4	5.24×10^{19}
75	0.21499	950.6	5.27×10^4	5.26×10^{19}
100	0.21505	950.3	5.31×10^4	5.29×10^{19}

Even though the final mole fraction of methane gas is discernable depending on the amount of shear rate, the nucleation events are almost similar as confirmed in Table 2. This is because only a few percent difference in the number of degassed molecules exists between the low and high shear rates. Furthermore, the calculation results shown in Table 2 indicate that homogeneous nucleation might occur under shear flow because degassing of large amount of molecules from the solution can not be possible through countable number of bubble formation on surface, or heterogeneous bubble nucleation. Homogeneous nucleation of gaseous bubble under shear may be explained by the structural change of the liquid state, which enables for the dissolved gases to have more larger occupied volume in liquid. Certainly, the homogeneous bubble nucleation under shear flow cannot be explained by the classical nucleation theory because the interfacial tension remains constant under the flow. Usually it is known that the heterogeneous nucleation on cavity is not active under flow

condition.

CONCLUSION

A decompression experiment of water-methane gas solution was done to investigate gas bubble formation under shear flow. The shearing action which changes the liquid structure stratifying along the line of shear promotes the bubble nucleation process quite a bit. It is understood that the dissolved gas molecules can occupy more volume in the shear layer where the interaction of solvent molecules is loosened.

A shear flow apparatus may be used for degassing process.



Fig. 4 Initial bubble formation stage for pure water at $t = 2.40$ s after decompression and for water mixed with a surfactant at $t = 3.60$ s after decompression. The bubble formation time in this case is $t_b = 1.83$ s.

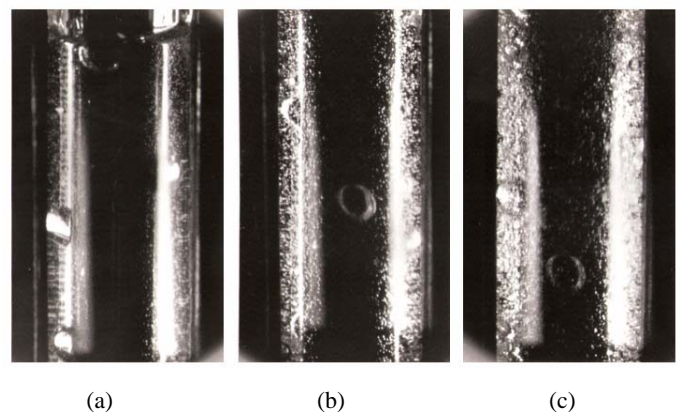


Fig. 5 Bubble nucleation and growing stage under shear flow at time (a) 2.16 s (b) 3.16 s and (c) 4.66 s after decompression. In this case, the bubble formation time is $t_b = 1.46$ s.

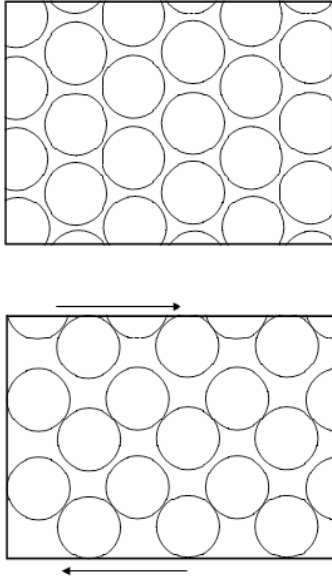


Fig. 6 A pictorial representation of the structural change of liquid molecules under shear flow by Heyes et al. (Reference 18).

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