

Dynamics of Bubbles in Conditions of Gas Hydrate Formation

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ABSTRACT

The objective of the present paper is to develop fundamentals of theory describing dynamics of gas bubbles in hydrate formation conditions. For this purpose our own experimental observations of methane bubble dynamics are analyzed and mechanisms of diffusion and heat transfer controlling bubble collapse are evaluated.

KEY WORDS: Gas hydrate, bubble dynamics, heat and mass transfer.

INTRODUCTION

Gas hydrates form at high pressures and low temperatures at some gas-liquid interfaces (Byk et al, 1980; Sloan, 1990; Makogon, 1997). Bubbles of hydrate forming gases at such pressures and temperatures can appear in deep-ocean environment (Maini and Bishnoi, 1981; Topham, 1984) and can be used in laboratory and industrial processes for efficient gas hydrate production. Properties of bubbles with gas hydrates can significantly differ from the properties of usual gas bubbles. The bubbles can be used for diagnostic and other applications. However, there exist few publications on bubble dynamics with gas hydrates. Existing experimental studies of bubble dynamics during hydrate formation reported qualitative behavior of the bubbles. In some experiments hydrates formed inside the bubbles (Saitëev and Lobkov, 1965), while in others hydrate formation was observed only on the bubble surface followed by shedding of hydrate particles, formation of rigid hydrate shells, and fast bubble collapse (Maini and Bishnoi, 1981). Different mathematical models for the dynamics of bubbles at conditions of hydrate formation were suggested by Topham (1984), Nigmatulin et al (1991), and Gumerov (1991). Generally, the rate of hydrate formation on the gas/liquid interface depends on kinetics of crystallization (Vysniauskas and Bisnoi, 1983; Makogon, 1985; Englezos et al, 1987), binary diffusion of hydrate forming agent and water in the gaseous, liquid, and solid hydrate phases (Gumerov, 1992), heat transfer (Gumerov, 1991, 1992), and the state of the hydrate layer such as 'mobile' (Topham, 1984), or 'snow-like' (Gumerov, 1991), and 'ice-like' (Nigmatulin et al, 1991). It was noticed that also stresses acting on the interface (Gumerov, 1991) and hydrodynamics of rising bubble (Topham, 1984) can drastically change the state of the hydrate layer coating the bubble

and define the regime and controlling mechanisms of hydrate formation.

In the present study we describe typical regimes of hydrate formation on methane bubbles observed in experiments and we make some theoretical estimations. The objective of the investigation is to build a base for mathematical theory of gas bubble behavior in hydrate formation conditions.

ORGANIZATION OF EXPERIMENTS

A photo of the high pressure cell used for visualization of the hydrate formation is shown in Fig. 1. The cell was fabricated from a thick-wall (5 cm) plexiglass cylinder of 21 cm height and 10 cm internal diameter that was tightly compressed between two stainless steel plates by steel bolts and sealed by neoprene o-rings. The bottom plate has an inlet and the top plate has an outlet. A steel needle of external diameter 1.65 mm and internal diameter 1.17 mm was used to inject compressed gas into the cell. The temperature and pressure in the cell were monitored by digital thermometer and pressure gauge. Commercial grade methane gas was supplied from a high pressure container through a pressure regulator to the cell nearly 95% filled by water obtained from molten ice. After bubbling, the gas can get out of the cell through a gas/liquid separator and a pressure valve. The cell was submerged into an ice/water mixture to operate at temperatures near the water freezing point.

In a typical experiment we started bubbling at the temperatures of the order of 4-5°C and maintained the pressures at 55-60 bars. Due to continuous cooling the temperature would slowly drop to 1.5-3°C. The size of the injected bubbles was 2-4 mm in diameter. Depending on the rate of bubbling, type of water, and degree of presaturation the time required to start forming hydrate in the systems varied from 25-30 minutes to several hours. Following this induction time required for saturation and creation of the first hydrate nuclei intensive hydrate formation was observed. First, on the free gas liquid interface growing spots of a thin non-transparent hydrate film appeared. After this bubbles rising under the influence of gravity did not disintegrate once they reached the free surface. Instead, they remained in an spherical shape 'glued' together without coalescing many hours and formed a large cell solid foam. Bubbles in the foam did not change their shape and sizes during the experiment and the foam disintegrated (melted like snow in warm water) only when the cell was depressurized.