

Kinetics of ethylene hydrate formation in water-in-oil emulsion



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ABSTRACT

The hydrate formation kinetics of ethylene in water-in-oil (w/o) emulsion were measured with the pressure–volume–temperature (PVT) method during isochoric processes in an agitated reactor. Effects of operating conditions on ethylene hydrate formation are investigated systematically, including bath temperature, pressure, water content and standard volume ratio. A kinetic controlled model is proposed which employs the difference between equilibrium temperature and system temperature as the driving force. The kinetic parameters are regressed using some of the experimental data. Then the kinetic model is used to predict rest of the experimental results. The predictions and experimental data have shown good agreement. Nevertheless, there are two issues that deserve attention. First, it is found water is not completely transformed into hydrate, even though the temperature is below equilibrium. Second, when pressure is raised, for example over 15 bar, the pressure curve begins to drop slower than expectation. Acceleration in impeller agitation could alleviate the slowdown. The phenomenon is explained by the control step switch between inter-phase mass transfer and intrinsic kinetics.

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1. Introduction

1.1. Background

Hydrates are non-stoichiometric, cage like compounds that are composed of water and gas. Recently, research on hydrate mainly focus on four aspects. First, efforts were made to prevent hydrate formation in pipelines [1,2]. Second, recently hydrate is studied for gas storage purposes, including natural gas storage and carbon dioxide capture [3–6]. Third, methods to exploit under-sea clathrate hydrate is also investigated [5]. The fourth aspect is gas separation. As advocated by Eslamimanesh et al. [7], hydrate is also a promising tool for the separation of gas mixtures. For instance, hydrate has been proved efficient in the separation of hydrogen and methane [8].

The bright future of hydrate cannot separate from the fundamental research of hydrate formation thermodynamics and kinetics. Work on hydrate thermodynamics began about a century ago and large quantity of data was obtained [9]. Theories that can predict hydrate formation conditions are proposed, including the famous Van-der-Waals and Plateeuw equations [10] as well as

Chen–Guo equations [11]. However, the research on hydrate kinetics only started in late 1980s.

1.2. Literature review on hydration kinetics

Englezos et al. [12] and Vysniauskas et al. [13] systematically studied hydration kinetics in pure water. Their investigation covers hydration kinetics of methane, ethane as well as their mixtures. The effect of additives such as SDS and THF on both hydrate formation and decomposition are investigated [14–17]. It is reported that the additives have influenced on both hydration thermodynamics as well as kinetics. Later on, researchers also performed experiments on other gas or gas mixtures, for example carbon dioxide and its mixtures [18].

Recently, it is found for industrial purposes such as gas storage, hydrate formation from pure water is unviable, because hydrate formed would float on top of water and further hydration is thus impeded [19,20]. To solve this problem, Liu et al. [21] proposed water-in-oil emulsion (w/o emulsion) as the new choice. Their observation shows that since hydrate are dispersed as tiny particles, the agglomeration can be prevented. Meanwhile, due to the large contact area between oil and water, growth rate of hydrates has been accelerated [22].

1.3. Theories on hydration kinetics

Three types of models exist in the realm of hydrate formation from pure water. Englezos et al. [12] proposed a kinetic controlled

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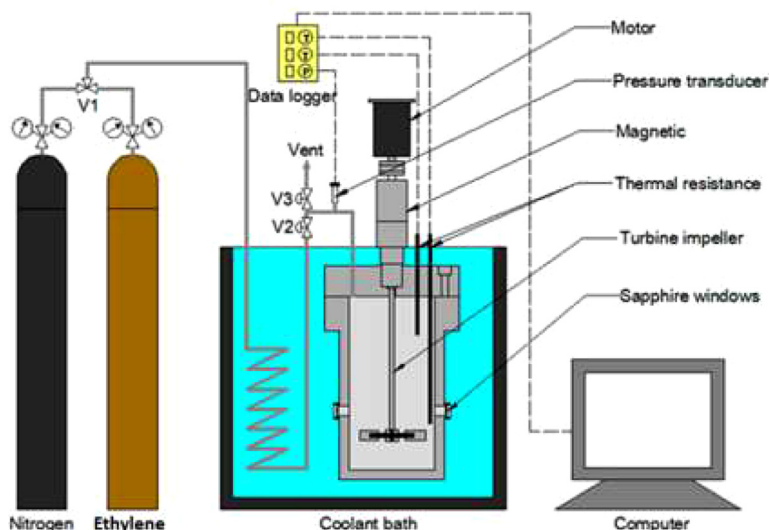


Fig. 1. Experimental apparatus for ethylene hydrate formation kinetics.

model. Fugacity difference is used as the driving force. Skovborg et al. [23] proposed a mass transfer controlled model, which is based on the assumption that the transportation of gas molecules across the gas-liquid interface is the rate-determining step in the overall hydrate formation process. Later, a heat transfer controlled model is proposed by Mori et al. [24].

Several models are also proposed for the formation of hydrate in w/o emulsion. Turner *et al.* proposed a shell growth model [25]. The assumption is that gas will diffuse across a hydrate film before forming new hydrate. Mu et al. [26] studied methane hydrate formation kinetics and propose when water droplets in w/o emulsion decrease to less than several microns, the mechanism become different from the shell growth model. They employed the heat transfer controlled model with the difference of contemporary and equilibrium temperature as the driving force.

1.4. Contribution of this work

Though a lot of work has been performed regarding hydrate kinetics, research focused on ethylene hydrate growth kinetics is scarce. For this reason and because recently much attention has been paid to ethylene storage and separation, we investigated ethylene hydrate formation kinetics in water-in-oil emulsion. Factors that influence ethylene hydrate formation are systematically studied.

2. Experiment

2.1. Apparatus

As shown in Fig. 1, the apparatus employed in this study consists of a stainless steel vessel, a coolant bath, a pressure control system, and a data logger. The vessel has a diameter of 50 mm with an effective volume of 200 mL (Beijing, Century SenLong experimental apparatus Co., Ltd., China). A pressure transducer (Model CYB-20S), Beijing, WESTZH Science and Technology Co., Ltd., China) and thermal resistance detectors (Pt100) were installed on the top detachable cover of the vessel. Accuracy of pressure transducer is ± 0.01 MPa and the Pt100 thermal resistance detector has a precision of ± 0.1 K. The vessel temperature was controlled by immersing the vessel in a circulating coolant bath (Model W-503B, Tianjin, BiLon Lab Equipment Co., Ltd., China). The coolant bath

temperature was maintained from 253.15 K to 368.15 K with an accuracy of ± 0.1 K. In addition, a vent was used to release the inert gases, unreacted gas or the gas from the decomposing hydrates. Two pressure gauges with a precision of ± 0.1 MPa were used to measure the pressure of gas supply. The pressure and temperature data were recorded every 30s, using a data acquisition system (KingView 6.53, Beijing, Wellintech Co., Ltd., China).

2.2. Experimental materials

Ethylene (99.99%) was purchased from Tianjin Liufang Gas Industry Corporation, and decane (98%), Span 80 (pharmaceutical grade), and Tween 80 (pharmaceutical grade) were obtained from Aladdin Industrial, Inc. Double-distilled water was used for all emulsions.

2.3. Emulsion preparation

The mixture of Tween 80/Span 80 with a mass ratio of 0.783 were used for the emulsion. Mass fraction of Span 80 in water is controlled at 2wt%. The quantities of water and decane were measured using a graduated cylinder. The emulsion was prepared by stirring a mixture of decane, water, and surfactant for 10 min with an IKA homogenizer (T 25 Digital) at 10,000 rpm. The average sizes of the water droplets in the emulsion were measured using a Zetasizer Nano-ZS laser nanoparticle size analyzer that was manufactured by Britain Malvern Instruments.

2.4. Experiment procedure

Before the experiment, the vessel was cleaned with distilled water and ethanol before drying. Then, w/o emulsion was added to the vessel. The vessel was sealed with the detachable top cover and immersed in the coolant bath. Nitrogen was added to the vessel until the pressure of the system reached 68.0 bar. Next, nitrogen injection was stopped by turning off valve V2. If the system pressure decreased < 0.1 bar over 30 min, the system was considered to be gas-tight. Potential errors that can be caused by the leak in the apparatus is calculated to be less than 0.5% on final ethylene consumption. Details for error estimation evaluation can be found in Supporting Information. Next, nitrogen was vented slowly through valve V3 until the system reached atmospheric pressure. Then the system is purged three times using nitrogen to ensure the absence

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