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Experimental and modeling investigation of kinetics of methane gas hydrate formation in water-in-oil emulsion

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ABSTRACT

Experimental data on hydrate formation kinetics for methane in water-in-oil emulsions are presented using a stirred batch reactor in the pressure range of 6.48–8.76 MPa and temperature range of 274.2–278.2 K. The influences of system temperature, initial pressure, and water cut of water-in-oil emulsion on the induction time of hydrate formation and hydrate growth rate were investigated, respectively. Experimental results show that the induction time varies inversely with initial pressure, and directly with temperature. The hydrate growth rate increases with increase of initial pressure and decrease of temperature. In the water-in-oil dispersed systems, the increase of water cut increases the hydrate growth rate. A mathematical model was developed for describing the formation kinetic behavior of methane hydrates in the dispersed system. The parameters of the model were determined by correlating the formation rate data, and the activation energies were further determined. The model was found to be able to calculate the formation kinetic behavior of methane hydrate in the dispersed system.

1. Introduction

Gas hydrates are crystalline compounds which occur when water forms a cage-like structure (lattice) around smaller molecules. The water molecules forming the lattice are known as host molecules and the smaller molecules are known as guest molecules. The guest molecules can be light hydrocarbons including methane, ethane, and propane or some other non-hydrocarbon gases including nitrogen and carbon dioxide, which are the components in the crude oil and natural gas. Gas hydrates have become of interest to the oil and gas industry since 1930's, because of their ability to plug the multiphase petroleum transport pipelines especially when operating under the deep sea. The most used solution to the problem of hydrate plug formation is adding some additives. These additives can be of three different types: thermodynamic, kinetic or anti-agglomerant types [1,2]. With respect to the traditional thermodynamic method, the hydrate formation conditions can be changed by injecting thermodynamic inhibitors such as methanol and glycol. However, to achieve remarkable effect, the concentration of methanol and glycol sometimes need reach 50% (by mass) on the free water basis, which will impose a critical burden on oil and gas companies [3] due to high cost and environmental problem. Therefore, kinetic inhibitors (KIs) and anti-agglomerates (AAs) are now being widely utilized in the oil and gas industry, with a concentration below 1.0% (by mass) typically. Unlike thermodynamic inhibitors, the KIs and AAs do not change the hydrate formation conditions. The KIs interfere with the nucleation and the growth of hydrate crystals, most of which are polymers or copolymers. In contrast, the AAs do not retard the formation of hydrate particles, but prevent them from agglomerating and accumulating into large masses.

Most of minimally processed well fluids transported to a central processing facility are water-in-oil emulsions. AAs can be used to disperse hydrate particles into the water-in-oil emulsion to form a kind of low-viscous and flowable hydrate slurry [4]. The pelletized natural gas hydrate is also expected to be able to improve the transportation and storage efficiency because of its high store capacity of natural gas. Therefore, the study of the kinetics of formation of gas hydrates in water-in-oil emulsion is of particular interest. Hydrate formation is closely related to crystallization processes [5–7] and as such it can be divided into the "nucleation" and "growth" phases [8]. Many studies on hydrate formation kinetics have been published in the literature, which can be divided into two categories: the primary nucleation process and the crystal growth process. Most researches are focused on the hydrate growth and the diameter distribution of hydrate pellets [5,6,9–14], and relatively less on the nucleation rate [8,15,16], where hydrate formed on the free surface of gas–water contact. For the kinetics of hydrate formation

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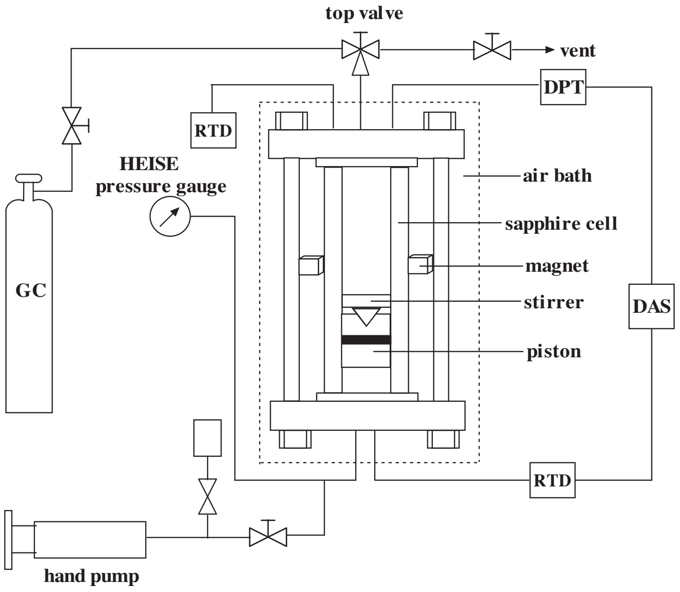

Fig. 1. Schematic diagram of the experimental apparatus: RTD, resistance thermocouple detector; DPT, differential pressure transducer; GC, gas cylinder; DAS, data acquisition system.

in water-in-oil emulsions, many investigations have reported on the differences between bulk solutions and emulsions, and some hydrate formation mechanisms have been proposed [17–22].

In this work, methane hydrate formation in water-in-oil emulsions was measured in the presence of anti-agglomerant. The influences of temperature, initial pressure, and water cut on the hydrate growth were surveyed. The experimental research has provided the basic data for the establishment of kinetic model of hydrate growth in the dispersed aqueous phase contained in oil. A mathematical model was developed to calculate the formation kinetics of methane hydrate in the dispersed system.

2. Experimental apparatus and procedure

2.1. Apparatus and material

A schematic of the experimental apparatus is shown in Fig. 1. The critical part of the apparatus is a transparent sapphire cell with a diameter of 2.54 cm, through which the formation process of the hydrate can be observed directly. The effect work-space of the cell is 60 cm^3, and the designed maximum working pressure is 20 MPa. The volume of the system can be altered by moving the piston up or down with a hand pump. The change of volume can be read from the scale of the pump with the precision of 0.002 mL. To observe the experimental phenomena occurring in the cell clearly, a luminescence source of type LG100H is fixed on the outside of the cell. The system temperature is controlled by an air bath with a precision of 0.1 K. The temperature sensor used is a secondary platinum resistance thermometer (type pt100). A calibrated Heise pressure gauge and differential pressure transducers are used to measure the system pressure with a precision of ±0.01 MPa. The changes of the system temperature and pressure with time are recorded and displayed by a computer.

Analytical grade methane (99.99%) was obtained from Beifen Gas Industry Corporation. Double-distilled water was used to prepare all the solutions. The freezing point of the diesel oil used is 273.2 K. Water, diesel oil, and reagents were weighed by an analytical balance with a precision of 0.1 mg when preparing the emulsion. The anti-agglomerant was developed in this laboratory and the mass concentration of which in water basis was 3.0%.

2.2. Experimental procedure

Before the experiment, the sapphire cell was washed with distilled water and dried, and then loaded with 10 mL of prepared water-in-oil emulsion, which were weighed using the balance. Afterwards, the cell was installed in the air bath, and the system was evacuated for about half an hour and the gas space of the system was then purged with methane 4 or 5 times to ensure the absence of air.

The air-bath temperature was adjusted to a given value. Once the temperature of the system was kept constant, methane was charged into the cell until the system pressure reached the specified value recorded as P_0. The stirrer was turned on with a stirring speed of 70 rpm to speed up the hydrate formation. Then the system pressure dropped rapidly to a stable value recorded as P_1, which means methane dissolved in the oil and reached saturation rapidly. The pressure remained constant (at P_1) in the cell until the hydrate formation started. This stable period is the time it takes for the initial hydrate nuclei to form, also called the induction time. The pressure in the cell then dropped continuously due to the consumption of gas during the hydrate growth period, and the hydrate growth in the transparent sapphire cell could be observed clearly with the naked eye. The pressure in the cell as a function of time was recorded by the computer. When the drop in system pressure was less than 0.01 MPa over 3 h, the formation of hydrate sample was assumed to be complete, and the pressure was recorded as P_E. The volume of the gas space in the cell was kept constant during the whole experimental period.

2.3. Experimental data analysis

It was reported [23] that the solubility of methane in pure water is 1.585×10^{-3} (mole concentration) at $T = 283.2$ K and $P = 6.05$ MPa, very less than that in the oil by several orders of magnitude. Therefore, the solubility of methane in water was overlooked in this work. The methane solubility in the oil, S, is defined as

$$S = \frac{n_G}{n_G + n_L} \times 100\% \tag{1}$$

where n_G represents the mole number of methane dissolved in the oil, and n_L is the mole number of diesel oil in the water-in-oil emulsion. The value of S can be obtained from gas–liquid equilibrium calculation by the equation of state. The value of n_L is calculated by

$$n_L = \frac{W_L}{M_L} \tag{2}$$

where M_L denotes the molecular weight of the oil, and W_L denotes the mass of the oil measured in the experiment. Eq. (1) can be rearranged to yield the mole number of methane dissolved in the oil

$$n_G = \frac{Sn_L}{1 - S} \tag{3}$$

During the induction time (at P_1), the total mole number of methane in the cell comprises that in the residual gas phase and dissolved in the oil, formulated as

$$n_1 = \frac{P_1 V_g}{Z_1 RT} + \frac{S_1 n_L}{1 - S_1} \tag{4}$$

where P_1, T, V_g, R, and Z_1 represent the initial pressure of hydrate crystallization, system temperature, volume of the gas space in the cell, universal gas constant, and compressibility factor at P_1 and T, respectively. The compressibility factor is calculated by the Peng–Robinson equation of state (PR EOS) [24]. S_1 in Eq. (4) is the solubility of methane in the oil at P_1 and T.

After the absorption process reaches equilibrium, the gas in the cell will be consumed resulting from the hydrate formation where