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Kinetic study of amino acids inhibition potential of Glycine and L-leucine on the ethane hydrate formation

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ABSTRACT

The experimental and theoretical investigations on ethane hydrate formation were performed for both pure water and amino acid aqueous solutions containing Glycine and L-leucine inhibitors. Herein, a kinetics model based on the thermodynamic natural path was proposed to describe the hydrate crystal growth in a stirred batch reactor at the constant volume. To explore the relationship between the kind and concentration of inhibitors and the rate of hydrate formation, the experiments were conducted at temperature of 277 K under the selective pressure as a driving force in different concentrations of Glycine and L-leucine (range: 0.05, 0.1, 0.5, 1, 2 and 3 weight percentage). The results measured based on the induction times and the kinetic trends of hydrate formation indicate that amino acids with lower hydrophobicity are better than others to delay the nucleation stage and reduce the growth rate. So that Glycine is introduced as a stronger inhibitor than L-leucine due to lower hydrophobicity. Moreover, the parameters of kinetic model, Ar/RT and tK, were obtained for each experiment in the presence of amino acids. The good agreement between predicted results and the experimental data indicated that this model is able to predict the ethane hydrate formation.

1. Introduction

The clathrate hydrates are crystalline solid compounds composed of hydrogen-bonded water molecules (host molecules), and some other gas species (guest molecules). Water molecules can form a cage-like structure at high pressure and low temperature conditions; then the guest molecules such as methane and ethane are trapped in the lattice and stabilize the structure. Crystals are divided into three distinct structures, (I, II, and H), that differ in cavity size and shape (Sloan and Koh, 2008; Sun et al., 2011).

Although hydrate formation processes can be considered in several applications such as the energy storage materials, air conditioning systems and water desalination (Akiya et al., 1999; Karamoddin and Varaminian, 2013); they are a main reason of pipeline occlusion in oil and gas industry. Thus the effects of various chemicals inhibitors have been investigated on the rate of formation and dissociation in gas hydrate process by several researchers (Kelland, 2011; Kelland et al., 2012; Niang et al., 2010; Tang et al., 2010; Valberg, 2006). Actually one of the promising technologies to overcome occlusion problem is the injection of hydrate inhibitors into the pipelines (Sa et al., 2011). Dou to using an appropriate quantity of the inhibitors, the resistance of mass transfer between gas and liquid phases can be increased. Therefore the rate of gas hydrate formation decreases. The inhibitors are classified as thermodynamic hydrate inhibitors (TIs) and low-dosage hydrate inhibitors (LDHIs) as kinetic inhibitors (KIs) and anti-agglomerates (AAs). The thermodynamic inhibitors such as methanol or glycols may be as high as 30–50% on the free water basis, to shift the hydrate three-phase equilibrium conditions and control the hydrate formation (Valberg, 2006; Sa et al., 2011). Nowadays, the kinetic inhibitors (KIs) are a great deal of attention due to economic and environmental concerns. KIs such as polymers, antifreeze proteins, some of ionic liquids and amino acids can delay the nucleation stage and decline the growth rate of hydrate crystals at low dose (concentrations below 1 wt%) (Kelland et al., 2012; Sa et al., 2011).

Although the kinetic of hydrate formation for natural gas components such as ethane have been comprehensively measured by many researchers in both pure water and in the presence of promoters (Ballard and Sloan, 2001; Cho and Beak, 2005; Erfan-Niya and Modarress, 2011; Han et al., 2002; Karamoddin et al., 2011,

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2013; Zhong and Rogers, 2000), but only a few investigations have been reported about the effect of inhibitors on kinetic behavior of ethane hydrate. In this work, the effect of Glycine and L-leucine amino acids was investigated as kinetic inhibitors on ethane hydrate formation.

The hydrate formation is introduced as nucleation and growth processes. Different models were studied based on mass and heat transfer problem (Clarke and Bishnoi, 2005; Varaminian, 2002; Zarenezhad and Varaminian, 2012) in isothermal and isobaric conditions. However, because of complex nature involved (Zarenezhad and Mottahedin, 2012), the initial and final conditions of the process are necessary to model the formation rate. A macroscopic kinetic model based on the reaction chemical potential was previously used by several researchers (Karamoddin et al., 2013; Zarenezhad and Varaminian, 2012; Zarenezhad and Mottahedin, 2012; Mottahedin et al., 2011; Karamoddin et al., 2014; Karamoddin and Varaminian, 2014) for description of gas hydrate formation in isothermal systems. Also the effect of different factors such as driving forces, additives concentration and operating conditions was validated on the model accuracy.

Our goal in this research is to investigate the kinetics of ethane hydrate formation in the presence of kinetic inhibitors. The kinetics modeling based on chemical affinity is used to predict the pressure of system versus reaction time during the formation and growth processes of hydrate crystal. In this work, all performed experiments were used to validate the new correlation for systems containing inhibitors. Generally, the acceptable agreement is found between the experimental and the predicted data.

2. Experimental procedure

2.1. Materials

Glycine and L-leucine with 99% purity and ethane gas with 99.95% purity were purchased from Merck and Technical Gas companies, respectively. Also De-ionized water was used in all experiments.

2.2. Apparatus

The experiments were performed in a setup consist of a reactor, a jacket for heat transfer and a data acquisition system. This apparatus is shown in Fig. 1.

Hydrate formation was conducted in a stirred batch reactor (AISI 304L) that was capable of operating pressures between 0 and 200 bar and the volume of reactor about to 500 cm^3. A jacket was used for heating and cooling in the system, and the temperature of reactor was controlled by flowing ethylene glycol through an external circulating temperature bath in the jacket. The cell pressure was measured by using a Druck PTX1400 pressure transmitter (0–200 bar) with accuracy of ±0.1 bar. The temperature was measured by using PT100 thermometers with accuracy of ±0.1 K. The pressure and temperature measured were acquired by a data acquisition system driven by a personal computer. For mixing, the experimental cell included a magnetically coupled stirrer shaft and a stirring motor speed controller. The maximum of stirring speed is 1000 rpm.

2.3. Hydrate formation

The first time, the experimental cell was rinsed with de-ionized water. The amount of solution injected into the reactor was 300 cm^3 for every experiment. The prerequisite amount of Glycine and L-leucine was weighed on an electronic balance and dissolved in de-ionized water. Then the prepared aqueous solution or pure water was poured into the cell. Air was removed from the cell by using a vacuum pump. The pressure of reactor was reached about −0.8 psig after using the vacuum pump. After the temperature was fixed in operating conditions (three phase equilibrium temperature), the ethane gas was injected into the cell at a driving force of approximately 5.5 bar. The magnetic stirrer was then turned on at a particular speed. When the pressure of reactor reached a constant value, the gas hydrate formation was completed. The pressure was recorded versus time during hydrate formation. Since the repeatability of the experimental kinetic data is very

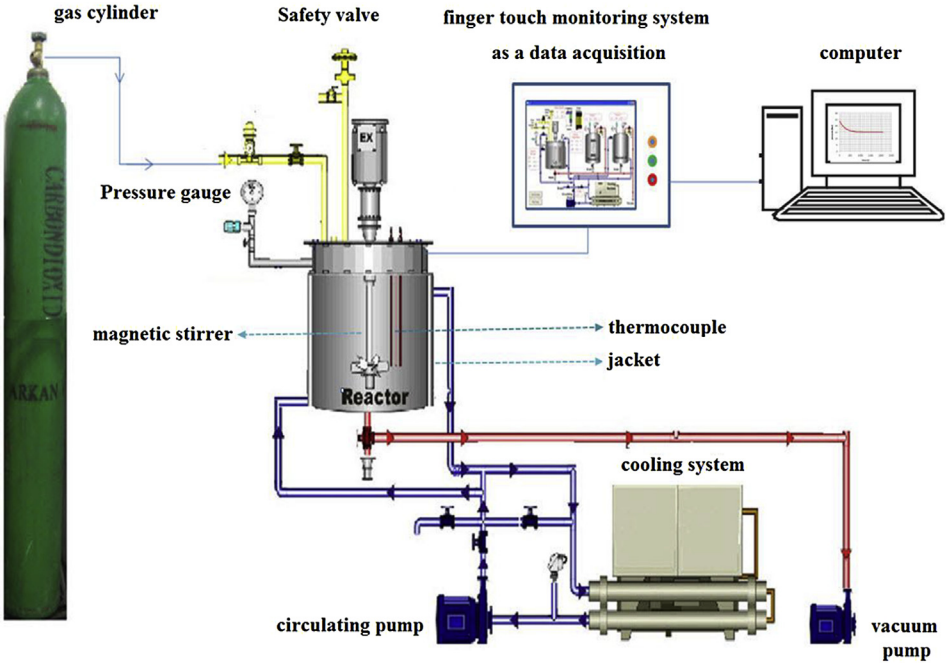

Fig. 1. Experimental setup, hydrate formation apparatus.