Fuel 212 (2018) 151–161

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The dual effect of amino acids on the nucleation and growth rate of gas hydrate in ethane + water, methane + propane + water and methane + THF + water systems

Hadi Roosta[a], Ali Dashti[a,*], S. Hossein Mazloumi[a], Farshad Varaminian[b]

[a] Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran
[b] Department of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

ARTICLE INFO

Keywords:
Gas hydrate
Growth rate
Induction time
Amino acid
Hydrophobic
Hydrophilic

ABSTRACT

In this work, new interesting results were obtained in relation to the dual effects of amino acids on the nucleation and growth rate of hydrate in different systems. Interestingly, some amino acids acted as promoter, while they are known as kinetic hydrate inhibitors. It considers that the hydrophobic and hydrophilic properties of amino acids play a significant role in the inhibition and promotion of hydrate formation when hydrophobic gas molecules (such as ethane, methane and propane) are only present in the system. In this regard, glycine and L-serine (as hydrophobic amino acids) showed a weak inhibitory effect on the growth rate of hydrate in ethane + water and methane + propane + water systems, while L-histidine and L-glutamine (as hydrophilic amino acids) acted as promoters in these systems. On the other hand, a different behavior was observed in the presence of THF (as a hydrophilic hydrate former), such that all the amino acids behaved as inhibitors. The induction time measurements also showed that all the amino acids (except L-glutamine) retard the nucleation, such that the nucleation was more retarded with increasing amino acid hydrophobicity. The performance of amino acids was also compared with SDS and PVP for evaluation of their potential as promoters and inhibitors. Also, the results showed that glycine and L-serine can be useful in the development of new synergists for kinetic hydrate inhibitors.

1. Introduction

Natural gas hydrates are an interesting class of ice-like crystalline compounds that are formed by water and certain gas molecules into three main structures (structures I, II and H) [1–3]. Recently, they are viewed as one of the promising energy sources for the future. They can be applied as premium fuel energy due to their high purity, environmental friendliness, and their large amounts in hydrate reserves [4]. Also, the other applications of gas hydrates such as the storage and transportation of natural gas [5,6], cooling application [7,8], gas separation [9–12], and desalination of seawater [13,14] has resulted in more studies on the kinetic promotion of hydrate formation. On the other hand, sometimes, the inhibition of hydrate formation can be a challenge. For example, gas hydrates cause blockages in gas and petroleum pipelines [1]. Therefore, the prevention and promotion of nucleation and hydrate growth is of importance in the aforementioned fields. The usage of additives is the most common method of reducing and increasing the hydrate formation rate. In this way, kinetic hydrate inhibitors (KHIs) such as PVP, PVCap, poly(N-isopropylmethacrylamide) and Gaffix VC-713 are the most important additives used to delay nucleation and reduce the hydrate growth rate [15–17]. Also, surfactants (especially anionic surfactants) are used as well-known additives for the enhancement of nucleation and hydrate growth rate [18–21]. Moreover, it is necessary to discover new green inhibitors and promoters with good biodegradability and special abilities. Recently, amino acids were introduced as green additives with abnormal effects [22].

Amino acids are biodegradable compounds comprised of amino and carboxyl groups with a specific side chain. They can be classified by the chemical nature of their side chains into hydrophobic, hydrophilic and charged amino acids [23]. Some recent studies have focused on the kinetic effects of amino acids as green inhibitors. For example, Sa et al. [24] introduced hydrophobic amino acids as a new class of KHIs. They showed that glycine, L-alanine, L-valine, L-leucine, and L-isoleucine can retard nucleation and slow down the growth rate of CO_2 hydrate. Also Naeiji et al. [25] tested the effects of hydrophobic amino acids such as glycine and L-leucine on tetrahydrofuran hydrate formation. They found that the inhibition performance of glycine is better than that of L-

* Corresponding author.
E-mail address: dashti@um.ac.ir (A. Dashti).

http://dx.doi.org/10.1016/j.fuel.2017.10.027
Received 25 August 2016; Received in revised form 2 July 2017; Accepted 5 October 2017
0016-2361/

leucine. On the other hand, some literatures have described the inhibitory effects of AFPs and AFGPs based on the role of amino acids [26–29]. In this way, Bagherzadeh et al. [26] confirmed that the amino acid sequences of AFPs and AFGPs can be adsorbed onto the crystal surface to prevent hydrate formation. In addition, the unusual behavior of amino acids in some hydrates such as CO_2 hydrates has prompted researchers to engage in further investigations [22].

An earlier study showed the inhibitory effects of amino acids on the growth rate of hydrate, in carbon dioxide + water system [30]. Although, it is better to perform hydrate kinetic test with fuel gas such as methane, propane, or a mixture of them, it must be demonstrated that the effects of some additives on hydrate formation kinetics may be dual in carbon dioxide + water and fuel gas + water systems. In fact, the effects of additives depend on the guest gas and the system [31–35]. For example, Zhang et al. [33] showed that sodium dodecyl sulfate (SDS) is not effective in enhancing the rate of CO_2 hydrate formation, while it has a significant effect on the kinetics of ethane, methane and propane hydrate formation. Also, Veluswamy et al. [31] reported the dual effects of some surfactants on hydrate formation kinetics. Therefore, an understanding of the different behaviors of amino acids in various systems can be useful for their suitable usage in specific applications. There is a gap in the literature about the effects of the hydrophobic and hydrophilic properties of amino acids on the inhibition and promotion of hydrate formation; especially in the presence of hydrophobic gases such as ethane, methane and propane. The potential of amino acids to act as synergists for kinetic hydrate inhibitors can also be investigated due to their good biodegradability and special abilities, although there is no study on the effects of amino acids in this regard.

In this work, the hydrate formation kinetics (in ethane + water, methane + propane + water and methane + THF + water systems) was investigated in the presence of hydrophobic, hydrophilic, and charged amino acids. The effects of amino acids as inhibitor and promoter were analyzed. Also, the dual effects of amino acids in different systems were investigated based on their hydrophobic and hydrophilic properties. In this regard, a possible mechanism was also described. In addition, the effect of hydrophobic amino acids as synergists for the kinetic hydrate inhibitor (PVP) was investigated.

2. Experimental

2.1. Materials

The gas hydrate formers, including ethane (99.95 vol% purity), methane (99.99 vol% purity), and propane (99.995 vol% purity) were supplied by Technical Gas Services. Also, the methane/propane gas mixtures were prepared from pure gases volumetrically. They were utilized for hydrate formation with de-ionized or aqueous solution of additives. The applied amino acids in this work were: two hydrophobic amino acids (glycine, L-serine) a hydrophilic amino acid (L-glutamine), and a hydrophilic and charged amino acid (L-histidine). They were supplied by Merck. Also, PVP (MW ≈ 10,000 g/gmol) as inhibitor and SDS as promoter were provided from Sigma Aldrich and Merck, respectively. Information on the chemical compounds are listed in Table 1.

2.2. Apparatus

The experimental setup is shown in Fig. 1. All experiments were performed in a high-pressure stainless steel cell with a total volume of 200 cm^3 (having an uncertainty of ± 1 cm^3). The cell was equipped with a mixer, which could be adjusted at different speeds (in the range of 0–1500 rpm) with the help of a high-speed stirrer and a speed controller. In addition, a vacuum pump was used to evacuate air from the cell, vent lines and connections. The cell could be operated with a maximum operating pressure of 60 bar. The cell temperature was adjusted and maintained by circulation of the coolant (a 50/50 vol mixture of water and ethylene glycol) through the jacket. A cooling thermostat (Lauda Alpha RA 8, Germany) with a working temperature range of 248.15–358.15 K, was used for cooling and circulating the mixture of water and ethylene glycol. The temperature and pressure of the cell were measured using a PT100 thermometer (with an accuracy of ± 0.1 K) and pressure transmitter (with an uncertainty of ± 0.1 bar), respectively. Also, the data were recorded using a data acquisition system, which was connected to a computer.

Table 1
The test chemicals used for the experiments.

Component	Chemical formula	Purity	supplier
Methane	CH_4	99.99%	Technical Gas Services
Ethane	C_2H_6	99.95%	Technical Gas Services
Propane	C_3H_8	99.995%	Technical Gas Services
Glycine[1]	$C_2H_5NO_2$	≥ 99.7%	Merck, Germany
L-serine[1]	$C_3H_7NO_3$	≥ 99%	Merck, Germany
L-glutamine[2]	$C_5H_{10}N_2O_3$	≥ 99%	Merck, Germany
L-histidine[2]	$C_6H_9N_3O_2$	≥ 99%	Merck, Germany
SDS	$C_{12}H_{25}NaO_4S$	≥ 98%	Merck, Germany
PVP	$(C_6H_9NO)_n$	≥ 98%	Sigma-Aldrich
Water	H_2O	deionized-distilled	–

1. Hydrophobic amino acid [36]
2. Hydrophilic amino acid [36]

2.3. Experimental procedure

Prior to experiment, the cell was carefully washed with de-ionized water. Then, it was evacuated for 5 min at a gauge pressure of −90 kPa by a vacuum pump. Subsequently, 55 cm^3 of water or aqueous solution of additives was charged in the cell. Then, the cell was pressurized to reach the desired pressure and the system temperature was adjusted to 275.15 K. Agitation was started at 600 rpm when the cell temperature reached the desired temperature. The induction time was determined based on a sudden drop in the pressure (a sudden increase in the temperature). The decrease in pressure was due to hydrate formation and the enclathration of gas molecules into the cages of the hydrate. The pressure changes in the cell were recorded during hydrate formation and the moles of gas consumed were calculated using the following equation:

$$n_{ci} = n_0 - n_i = \left(\frac{PV}{ZRT}\right)_0 - \left(\frac{PV}{ZRT}\right)_i \tag{1}$$

In Eq. (1), n_{ci}, n_o, n_i, P, V, Z, R and T are moles of gas consumed up to time t_i, initial moles of gas in the cell, moles of gas at time t_i in the cell, pressure, volume of gas in the cell, compressibility factor, universal gas constant and temperature, respectively. Also, the Peng–Robinson equation of state was used to calculate the compressibility factor.

3. Results and discussion

3.1. The effects of hydrophobic, hydrophilic, and charged amino acids on ethane hydrate formation

In the present study, gas hydrate nucleation in the presence of amino acids was determined by induction time measurements. In this regard, the experiments were repeated three times and finally, an average induction time was reported. Also, the hydrate growth rate was investigated based on the rate of gas consumption during hydrate formation. All experiments were performed at a temperature of 275.15 K and stirring rate of 600 rpm. Fig. 2(a–d) shows the gas consumption during ethane hydrate formation. The effects of amino acids and the growth rate of gas hydrate can be evaluated based on the slope of the gas consumption curve. First, the effects of glycine and L-serine (as hydrophobic amino acids) on ethane hydrate growth rate were