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

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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-

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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

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:

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

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

No	Description
1	Gas Cylinder
2	Regulator
3	Reactor
4	Speed Stirrer
5	Speed Controller
6	Cooling System
7	Pressure Transmitter
8	PT100 Thermometer
9	Data Acquisition System

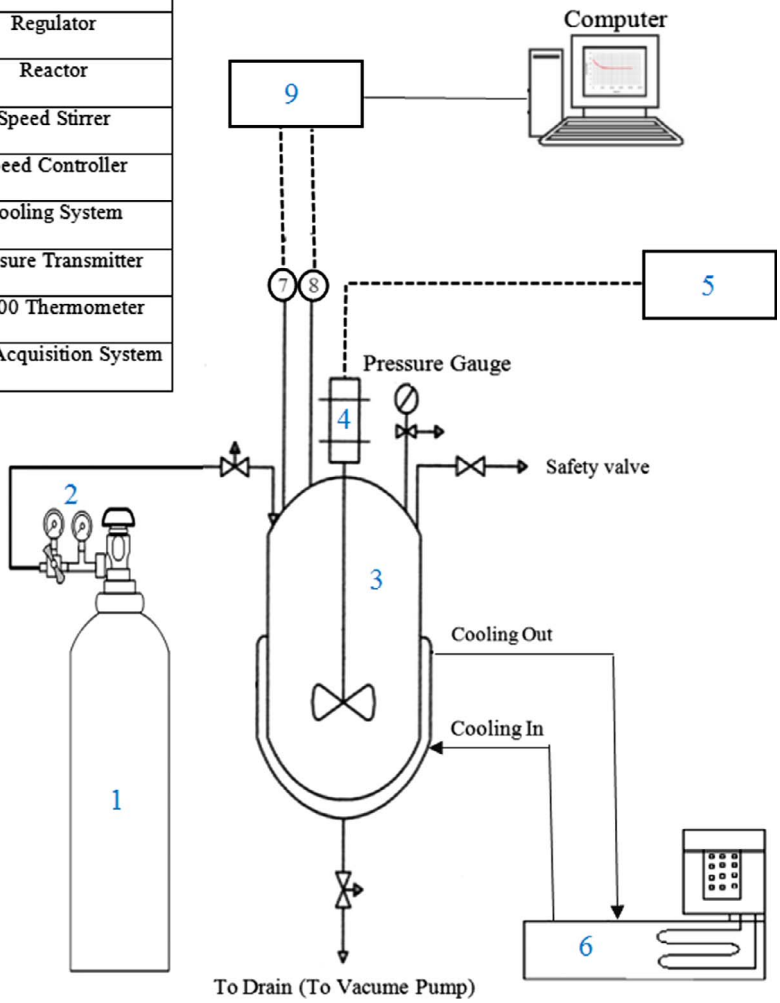

Fig. 1. Hydrate formation apparatus.

investigated. An evaluation of the results in Fig. 2(a) shows that the hydrate formation rate, in the presence of L-serine, decreased in comparison with pure water. Also, glycine reduced the hydrate formation rate, although it was more effective than L-serine. However, the decreases are insignificant and show a weak inhibitory effect of glycine and L-serine at a concentration of 0.5 wt%.

The effect of hydrophilic amino acids on ethane hydrate formation was also studied, and different interesting results were obtained in comparison with the hydrophobic amino acids. Fig. 2(b) shows that L-glutamine and L-histidine (as hydrophilic amino acids) increase hydrate growth rate at a concentration of 0.5 wt%, although the effect of L-histidine, which has a charged side chain, is more than that of L-glutamine. Also, the experimental results show that glycine and L-serine (in concentration of 1.5 wt%) have an inhibitory effect and L-glutamine and L-histidine have a promotion effect on hydrate growth. In fact, hydrophobic amino acids decrease while hydrophilic amino acids increase hydrate formation rate, and their effects increase with increase in concentration.

The effects of amino acids on hydrate nucleation were also examined. Fig. 3 shows the effects of hydrophobic and hydrophilic amino acids on the average induction time. The results indicate that glycine and L-serine increase the average induction time and can retard ethane hydrate nucleation (the average induction time is 1.22–2.67 times greater than that of hydrate formation with pure water). It was also observed that the effect of glycine is more than that of L-serine and the average induction time increased at higher concentrations. By comparing of the measured values of the average induction time and the hydrate growth rate, the dual effect of L-histidine was observed. L-histidine as a hydrophilic and charged amino acid increased ethane hydrate growth rate, while the obtained results of the average induction time, show that it has an inhibitory effect on ethane hydrate nucleation, even more than the hydrophobic amino acids (glycine and L-serine). The average induction time values for hydrate formation in the presence of 0.5 and 1.5 wt% L-histidine are 2.89–4.17 times greater than that of hydrate formation with pure water. These results show that L-histidine is more effective in retarding nucleation. On the other hand, L-glutamine decreases the average induction time insignificantly. So, it can be concluded that glycine and L-serine show inhibitory effects on the nucleation and growth of ethane hydrate, L-glutamine promotes the hydrate nucleation and growth, and L-histidine has an inhibition and promotion effect on nucleation and ethane hydrate growth, respectively.

For a better understanding of these differences, the effects of amino acids on nucleation and growth rate of gas hydrate should be investigated in other systems. As demonstrated previously, the effects of additives may be dependent on the guest gas and the system. Therefore, the hydrate formation experiments were also performed in methane + propane + water and methane + THF + water systems.

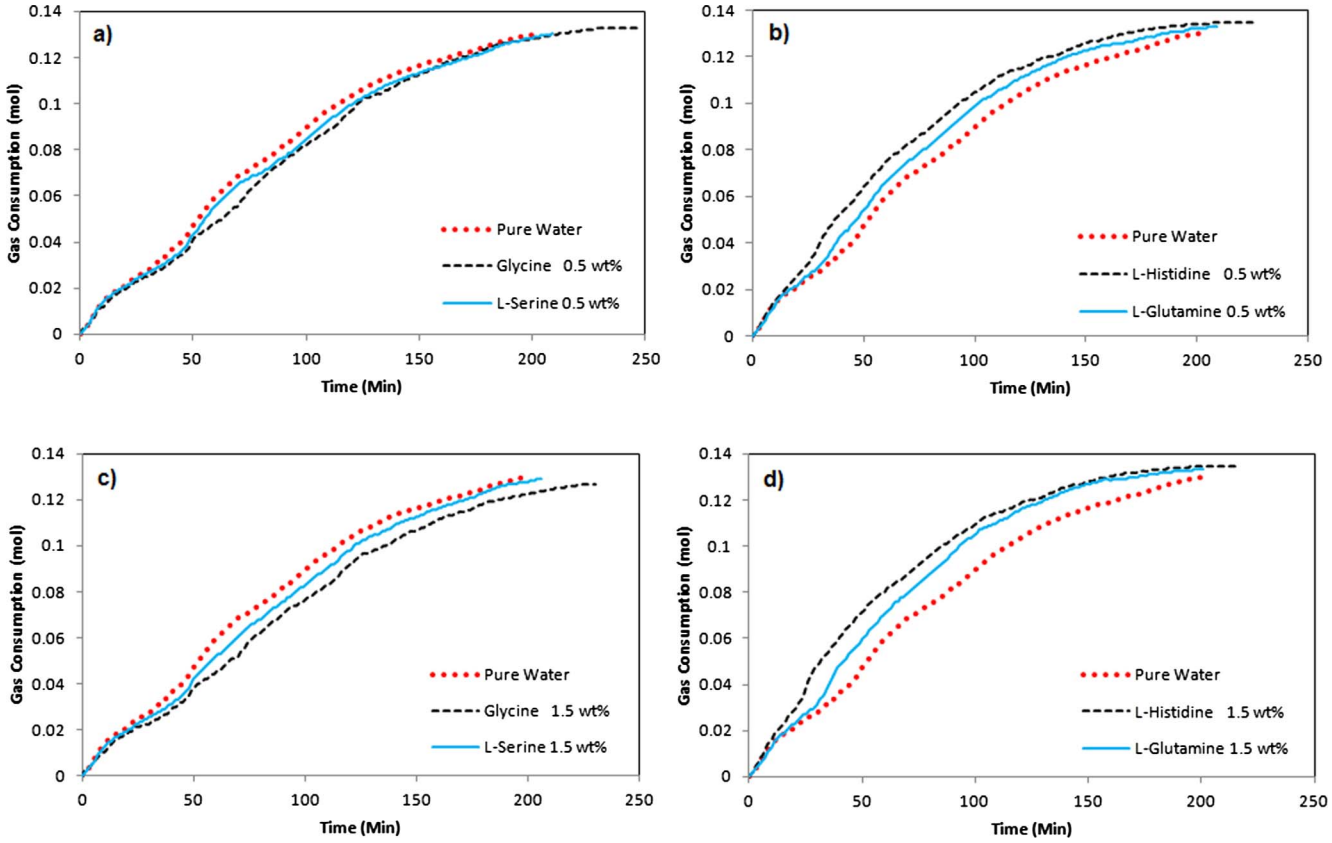

Fig. 2. The effects of hydrophobic (glycine and L-serine) and hydrophilic amino acids (L-glutamine and L-histidine) on ethane hydrate formation.

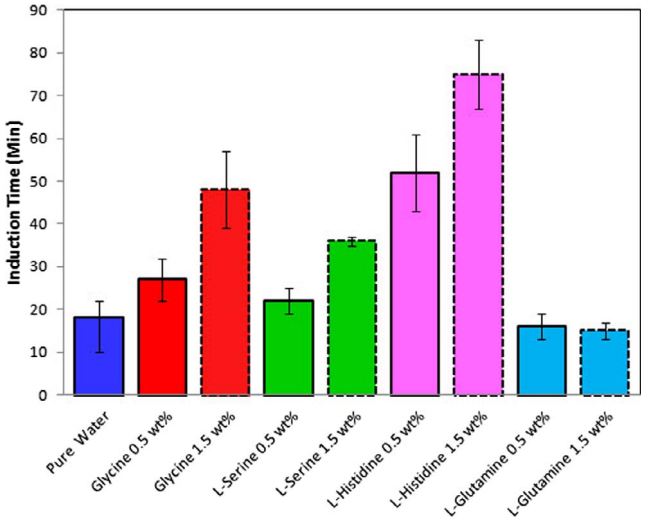

Fig. 3. The average induction time values for ethane hydrate formation in the presence of hydrophobic and hydrophilic amino acids.

3.2. The effects of hydrophobic, hydrophilic and charged amino acids on nucleation and growth rate of gas hydrate in methane + propane + water system

The effects of amino acids on methane/propane hydrate formation were also investigated. In this regard, a gas mixture containing 85 mol% methane and 15 mol% propane (mixture A), and also a gas mixture containing 90 mol% methane and 10 mol% propane (mixture B) were used for hydrate formation. The experiments were first performed with the mixture A. Fig. 4(a–f) shows the gas consumption during methane/propane hydrate formation in the presence of amino acids. The results indicate that L-serine is almost ineffective and glycine has a weak inhibitory effect at a concentration of 0.5 wt%, while the growth of methane/propane hydrate is largely enhanced by L-histidine and L-glutamine at this concentration. The results also show that by increasing the concentration from 0.5 to 1.5 wt%, the inhibitory effects of hydrophobic amino acids and promotion effects of hydrophilic amino acids increased. In fact, the results show that glycine and L-serine (hydrophobic amino acids) are weak inhibitors while L-histidine and L-glutamine hydrophilic amino acids) are highly effective promoters for methane/propane hydrate growth. These results also indicate that the promotion effects of hydrophilic amino acids on methane/propane hydrate formation rate are much more significant than their effects on ethane hydrate formation.

The induction time was also measured for methane/propane hydrate formation in the presence of hydrophobic and hydrophilic amino acids. Fig. 5 shows the average induction time values at different concentrations of amino acids. As shown in this figure, glycine, L-serine and L-histidine, increase the average induction time in comparison with pure water. The average induction time of methane/propane hydrate formation in the presence of L-histidine (in a concentration range of 0.5–1.5 wt%) is 2.7–3.6 times greater than the hydrate formation with pure water. Also, in the presence of glycine and L-serine, it is 1.8–2.3 and 1.7–2.2 times greater, respectively. On the other hand, the nucleation of hydrate is promoted by L-glutamine, although the decrease in the average induction time is not significant. In fact, the ranking of amino acids to retard hydrate nucleation is as follows: L-histidine > glycine > L-serine > pure water > L-glutamine. It should be noted that the inhibitory effect of L-histidine on nucleation is much significant, while the results showed that it can act as a highly effective promoter for the growth of the methane/propane hydrate. The dual effect was also observed in ethane hydrate formation. For further investigation, hydrate formation experiments in the presence of L-histidine were also performed with a gas mixture containing 90 mol%

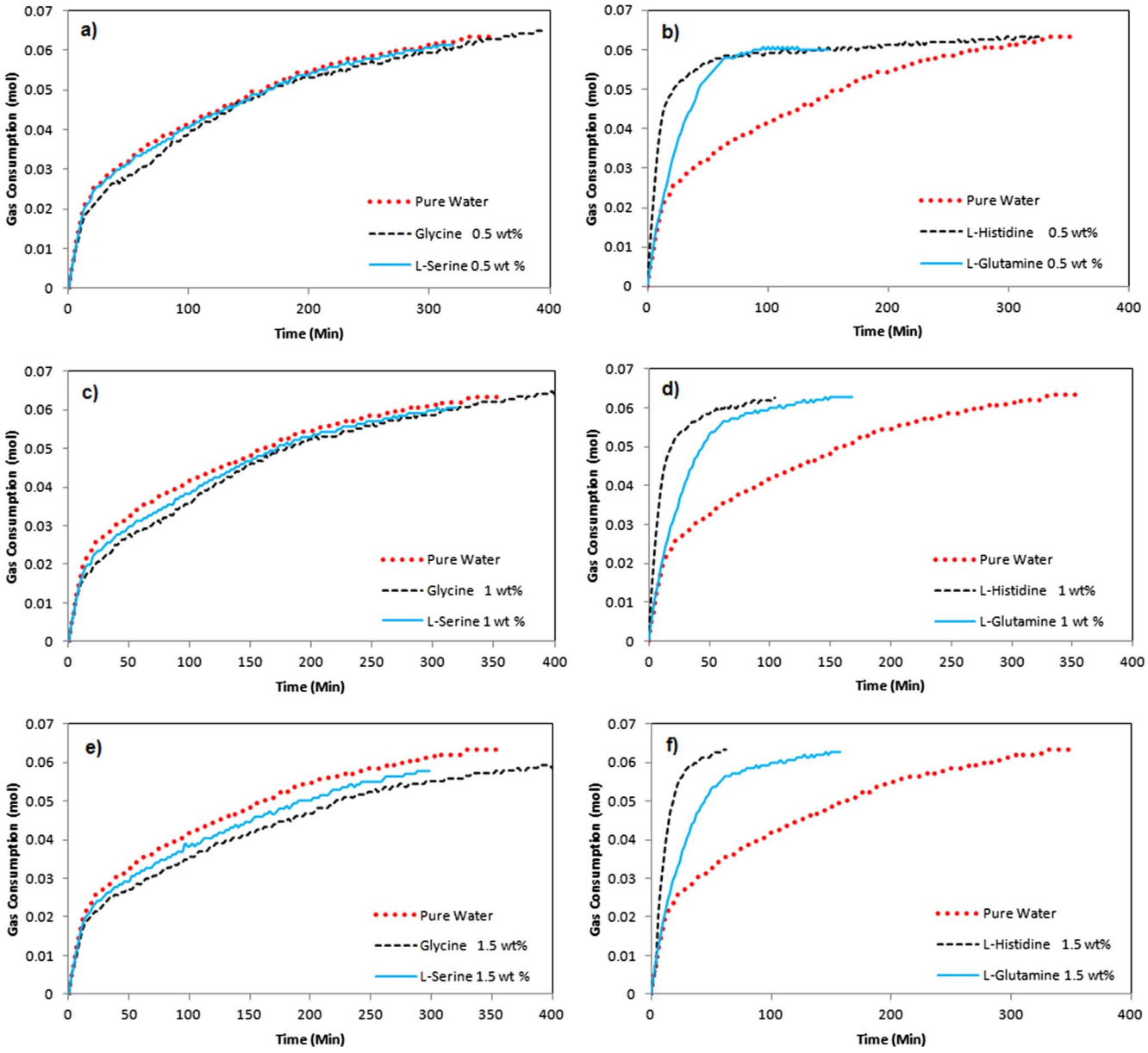

Fig. 4. The dual effect of hydrophobic and hydrophilic amino acids on the growth rate of gas hydrate in the methane + propane + water system.

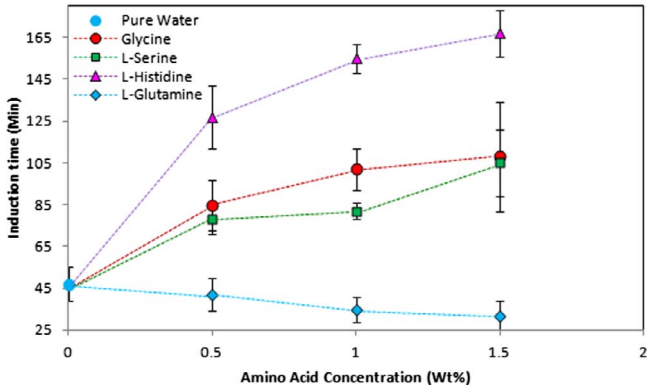

Fig. 5. The average induction time values for methane/propane hydrate formation in the presence of hydrophobic and hydrophilic amino acids.

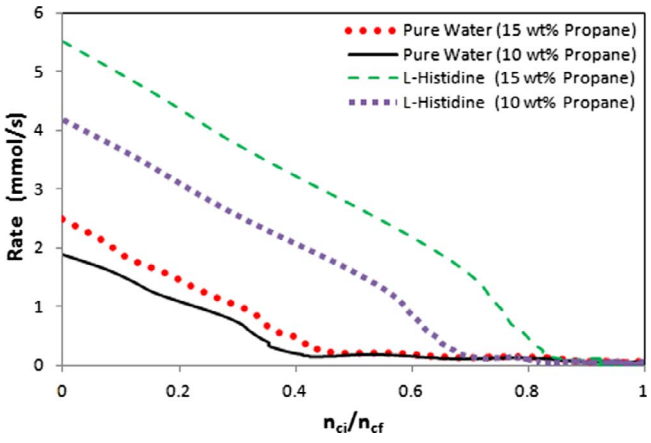

Fig. 6. The growth rate of hydrate in different gas samples (10 and 15 mol% propane) with or without L-histidine.

methane and 10 mol% propane. Fig. 6 compares the effect of L-histidine on hydrate growth rate in methane + propane + water system with different concentrations of propane (10 and 15 mol% propane). The results confirm that the hydrate growth rate in the test gas mixture containing 90 mol% methane and 10 mol% propane (mixture B) is also prompted by L-histidine. A comparison of the results showed that with increase in propane concentration from 10 to 15 mol%, the initial growth rate of hydrate with pure water increased from 1.9 to 2.4 mmol/s. However, in the presence of 0.5 wt% of L-histidine, it increased from 4.1 to 5.6 mmol/s. In fact, when the concentration of propane is high, the promotion effect of L-histidine on the growth of the methane/propane hydrate becomes more significant. In previous study, it was proved that L-histidine has an inhibitory effect on CO_2 hydrate growth rate [30]. This shows that the dual effect of L-histidine depends on the guest gas and the system. In fact, it seems that L-histidine has a promotion effect on hydrate growth in the presence of hydrophobic hydrate former such as ethane, methane and propane. For a better understanding of these results, the effects of amino acids on methane + THF + water system which contains a hydrophilic hydrate former (THF) was also analyzed.

3.3. The effects of hydrophobic, hydrophilic and charged amino acids on nucleation and growth rate of gas hydrate in methane + THF + water system

Fig. 7(a) shows gas consumption during methane hydrate formation in the presence of THF and amino acids. It shows that all amino acids reduced the rate of hydrate growth, although L-glutamine is almost ineffective. In fact, L-histidine has a promotion effect on hydrate growth in ethane + water and methane + propane + water systems, while it showed a weak inhibitory effect on the growth of hydrate in methane + THF + water system. On the other hand, hydrophobic amino acids have inhibitory effects on all the systems. The values of average induction time also indicate that hydrophobic amino acids can be used to retard the nucleation, although their inhibitory effects on the nucleation are less in comparison with L-histidine (Fig. 7(b)). The average induction time of hydrate formation in the presence of L-histidine is 5.8 times greater than that of hydrate formation with pure water, while in the presence of glycine and L-serine, it is 4.8 and 3.5 times greater, respectively.

3.4. Analysis of the results and investigation on the possible mechanisms

The results of this work showed the dual effect of L-histidine on the nucleation and growth rate of hydrate. Also, the effects of hydrophilic amino acids were different in the studied systems. So, the possible mechanism should be investigated for a better understanding of the effects of amino acids on hydrate formation. First, the effects of amino acids on the nucleation of hydrate were described (in different systems). The experiments showed that the average induction time increased in the presence of hydrophobic amino acids (in all systems), but decreased in the presence of L-glutamine (as a hydrophilic amino acid). Also, L-histidine as a hydrophilic and charged amino acid increased the average induction time. The possible reason may be the different structural organization of water near the hydrophobic, hydrophilic and charged groups of amino acids. It should be noted that the amine (-NH2) and carboxylic acid (-COOH) functional groups in amino acids are hydrophilic, while the side chain may be hydrophobic (glycine and L-serine), hydrophilic (L-glutamine and L-histidine) and charged (L-histidine) [36]. Also, the water molecules adjacent to the hydrophilic groups have a better ordering and are more clustered in comparison with the hydrophobic groups [37–39]. On the other hand, the number of water-water hydrogen bonds close to the hydrophilic groups is lower [38]. So, the structure and ordering of water molecules adjacent to the hydrophilic and hydrophobic groups are different. Accordingly, hydrophobic amino acids retard nucleation as a result of the different structural organization of water molecules near the two hydrophilic groups and the hydrophobic side chain. On the other hand, the different structural organization of water molecules is not significant in the presence of L-glutamine (with three hydrophilic groups). Therefore, the nucleation is not retarded. In this regard, Fig. 8 also confirms that the average induction time increased (the nucleation is more retarded) with increase in the amino acid hydrophobicity. On the other hand, the experimental results of average induction time for hydrate formation in the presence of L-histidine (with three hydrophilic groups) may seem inconsistent with this analysis, because L-histidine increased the average induction time (even more than glycine and L-serine). However, the role of the charged side chain of L-histidine should not be forgotten. In fact, the ordering of water molecules around two hydrophilic groups is considerably different in comparison with the structural organization of water near the charged side chain.

The effects of amino acids on hydrate growth rate can also be described based on the side chain properties of amino acids. Their effects are also dependent on hydrate former and the system. The results showed that glycine and L-serine in the examined systems (ethane + water, methane + propane + water and methane + THF + water systems) reduced the growth rate of hydrate, while L-glutamine and L-histidine showed a dual effect on the growth rate of hydrate in different systems (weak inhibitory effects on the growth rate of hydrate in methane + THF + water system, and promotion effects in ethane + water, methane + propane + water systems). The interesting finding is shown with categorization of the hydrate formers in

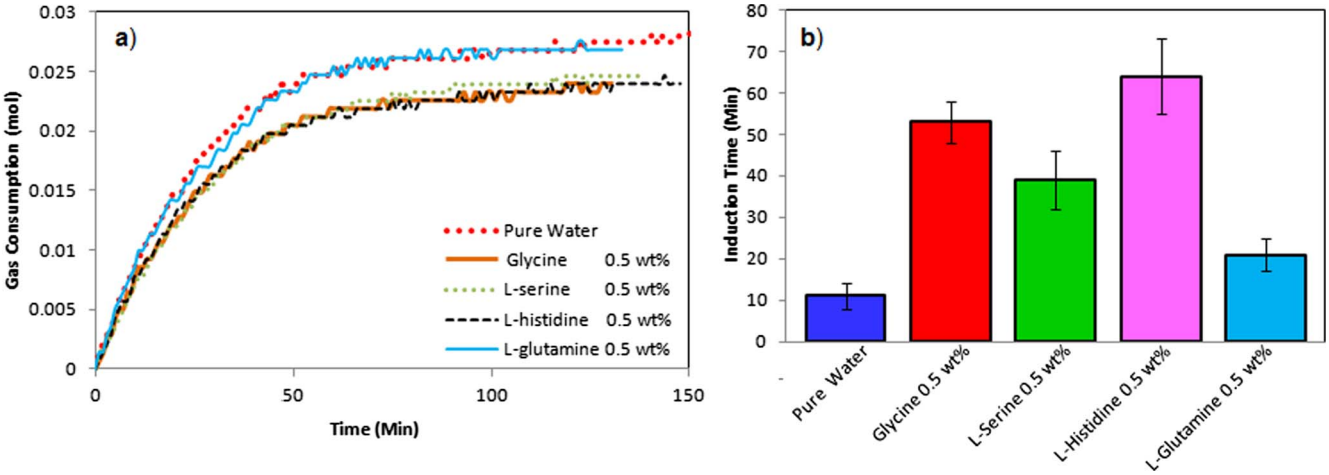

Fig. 7. The effects of hydrophobic and hydrophilic amino acids on the growth rate of hydrate (a) and the nucleation (b) in methane + THF + water system.

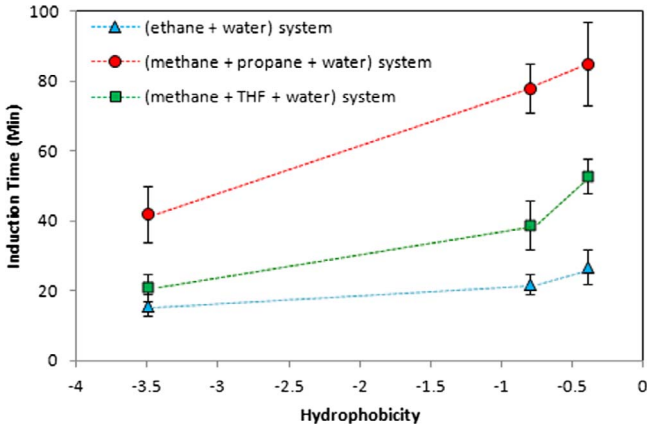

Fig. 8. The variation of average induction time with the hydrophobicity values of amino acids.

Table 2
The hydrophobicity and hydrophilicity of the applied hydrate formers in this work.

Hydrate former	*Ln B*	Hydrophobic/hydrophilic
Methane	-3.3	Hydrophobic
Ethane	-3.1	Hydrophobic
Propane	-3.4	Hydrophobic
THF	5.8	Hydrophilic

If Ln B be negative, then the solute is hydrophobic [40].
B was defined based the dimensionless Henry's Law constant in Ref. [40].

hydrophobic and hydrophilic components. The hydrophobicity and hydrophilicity of the applied hydrate formers are shown in Table 2. The negative values of "*Ln B*" show that the hydrate former is hydrophobic. Also, the positive values indicate that the hydrate former is hydrophilic [40]. So, it was interestingly found that the growth rate of hydrate is reduced by hydrophobic amino acids in the systems including only hydrate formers with hydrophobic nature (ethane, methane and propane), while hydrophilic amino acids show promotion effects in these systems. On the other hand, the hydrophobic and hydrophilic amino acids play the inhibition role, if the system includes a hydrate former with hydrophilic nature (THF). Also, results analysis showed that the effect of hydrophilic amino acids is more significant in the system with two hydrophobic hydrate formers (propane and methane) in comparison with the system with only one hydrophobic hydrate former (ethane).

The probable reason for the promotion effects of hydrophilic amino acids on growth rate may be the local increase of ethane, methane and propane concentrations in the hydrate growth sites. Oostenbrink and Gunsteren [41] found that urea (with hydrophilic groups of NH_2 and CO) can enhance methane cluster formation by reducing the hydrophobic effect. In fact, they concluded that urea pushes methane into the water bulk and increases the local concentration of methane, thereby promoting cluster formation. The molecular structure of urea is close to that of hydrophilic amino acids. Its molecular structure includes two NH_2 groups and a CO group. In fact, NH_2 and CO are the same functional groups in urea and amino acids. On the other hand, the hydrophilic side chain of hydrophilic amino acids and the extra NH_2 group of urea are also hydrophilic. Therefore, it can be imaged that L-histidine and L-glutamine as hydrophilic amino acids push the ethane, methane and propane into the growth sites on the crystal surface of hydrate and then increase the hydrate growth rate. However, it is considered that this mechanism is not dominant in the methane + THF + water system, when a component with high hydrophilic property is present in the system (THF). These results can also be analyzed based on the studies of Takeya et al. [42] who found that hydrates formed within hydrophilic beads are more stable in comparison with hydrophobic beads. In fact, they showed that the tendency to grow is more in the presence of hydrophilic beads. Therefore, it may also be a possible reason for the promotion effects of hydrophilic amino acids on the hydrate growth rate.

Based on these descriptions, a probable mechanism can be suggested for the promotion effects of hydrophilic amino acids on the hydrate growth. In fact, this mechanism is presented based on the observations of Oostenbrink and Gunsteren, and Takeya et al. on hydrate formation with hydrophobic gas molecules such as methane, ethane, propane and their mixtures. According to Fig. 9, the mechanism can be described. In the first step, hydrophilic amino acids are adsorbed on the crystal surface of hydrate. In fact, the NH_2 and CO functional groups of amino acids can form hydrogen bonds with the hydrate surface. In the second step, local concentrations of ethane, methane and propane (in the hydrate growth sites) increased due to the presence of hydrophilic amino acids on the hydrate surface. In fact, hydrophilic amino acids push the hydrophobic gas molecules into hydrate growth sites and incomplete cavities of the hydrate surface. Consequently, more gas molecules are trapped in the hydrate cavities and the hydrate growth rate becomes increased. In the third step, the hydrophilic amino acids surround the hydrate structure due to the hydrophilic nature of its surface, thereby making the formed cavities to become more stable. On the other hand, the structured water molecules in the neighborhood of hydrophilic amino acids became increased. Therefore, the hydrate growth (with a higher rate) is oriented in the direction of the surrounding amino acids. In addition, the works of Wang et al. [43] and Perfeldt et al. [44] can also help in a better understanding of the different effects of amino acids (hydrophobic or hydrophilic) on hydrate growth in the presence of different hydrate formers. Wang et al. [43] performed hydrate formation experiments in glass tubes (with hydrophobic and hydrophilic surfaces) and found that methane hydrate growth was oriented towards the hydrophilic surface. Also, Perfeldt et al. [44] showed that when their crystallizer (for hydrate formation) was coated with a hydrophobic layer, the methane hydrate growth significantly reduced. Therefore, it was confirmed that, when hydrophobic hydrate formers (such as methane, ethane and propane) are present in the system, the hydrate growth is oriented towards the hydrophilic surface and the hydrate growth rate is increased, while in the presence of a hydrophobic surface, the hydrate growth is limited. Similarly, when the hydrate is formed by a hydrophobic hydrate former such as methane, ethane and propane, the hydrophilic amino acids are adsorbed on crystal surface, and increase the hydrate growth rate in the direction of their hydrophilic surface. On the other hand, in the presence of hydrophobic amino acids, the hydrate growth rate is decreased due to less growth towards the hydrophobic surface. However, it seems that these probable mechanisms are not dominant in the presence of THF (as a hydrophilic hydrate former) due to the possible competition between hydrophilic THF and hydrophilic amino acids for adsorption on hydrate surface. This competition between components has been pointed out by some researchers [33,45] and in this work, may result in the decrease of THF concentration (as hydrate former) in the hydrate cavities, and subsequently lead to the decrease in hydrate growth rate.

3.5. Comparison of the effect of amino acids with PVP and SDS

In this work, for the performance evaluation of hydrophobic and hydrophilic amino acids, their inhibition and promotion effects on hydrate formation were compared with PVP and SDS, respectively. Fig. 10(a,b) indicates that glycine has a weak inhibitory effect on hydrate growth rate in comparison with PVP (in ethane + water and methane + propane + water systems). Also, L-histidine is not an effective promoter in comparison with SDS (in ethane + water system), while its effect is significant in promoting growth rate of hydrate in methane + propane + water system. In fact, the initial growth rate (in ethane + water system) increased from 1.2 to 1.4 mmol/s when L-histidine was added to the system, but it was enhanced from 2.4 to 5.6 mmol/s in the methane + propane + water system. Although, the

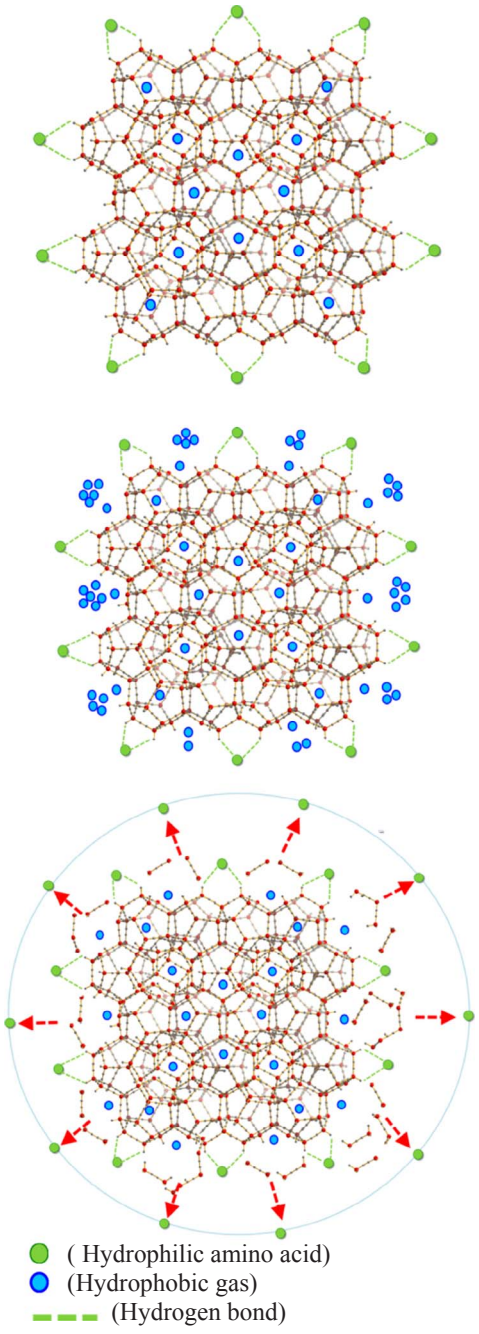

Fig. 9. Probable mechanism for promotion effects of hydrophilic amino acids on the hydrate growth.

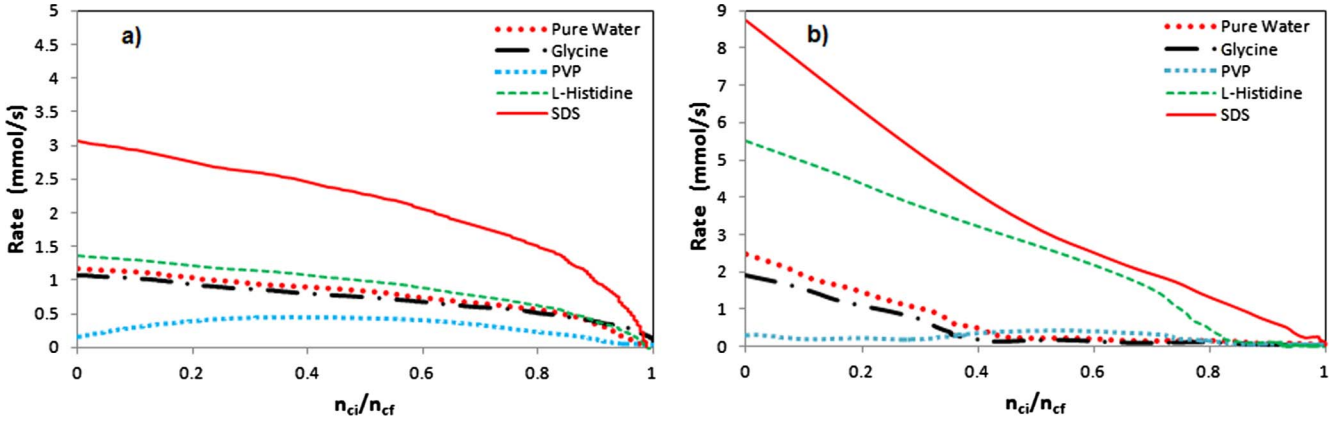

Fig. 10. Comparison of the effect of amino acids with that of PVP and SDS (on the growth rate of hydrate) in ethane + water system (a) and methane + propane + water system (b).

Table 3
The ratio of average induction times (additives to pure water, PVP and SDS) for hydrate formation in the ethane + water system.

	Average induction time Additives/Pure water	Effects	Average induction time Additives/PVP	Average induction time Additives/SDS
Glycine 0.5 wt%	1.50	Inhibition effect	0.42	3.86
Glycine 1.5 wt%	2.67	Inhibition effect	0.75	6.86
L-Serine 0.5 wt%	1.22	Inhibition effect	0.34	3.14
L-Serine 1.5 wt%	2.00	Inhibition effect	0.56	5.14
L-Histidine 0.5 wt%	2.89	Inhibition effect	0.81	7.43
L-Histidine 1.5 wt%	4.17	Inhibition effect	1.17	10.7
L-Glutamine 0.5 wt%	0.89	Promotion effect	0.25	2.29
L-Glutamine 1.5 wt%	0.83	Promotion effect	0.23	2.14
SDS 0.1 wt%	0.39	Promotion effect	0.11	1.00
PVP 0.5 wt%	3.56	Inhibition effect	1.00	9.14

Table 4
The ratio of average induction times (additives to pure water, PVP and SDS) for hydrate formation in the methane + propane + water system.

	Average induction time Additives/Pure water	Effects	Average induction time Additives/PVP	Average induction time Additives/SDS
Glycine 0.5 wt%	1.81	Inhibition effect	0.61	9.44
Glycine 1.0 wt%	2.17	Inhibition effect	0.73	11.3
Glycine 1.5 wt%	2.30	Inhibition effect	0.77	12.0
L-Serine 0.5 wt%	1.66	Inhibition effect	0.56	8.67
L-Serine 1.0 wt%	1.74	Inhibition effect	0.59	9.11
L-Serine 1.5 wt%	2.23	Inhibition effect	0.75	11.7
L-Histidine 0.5 wt%	2.70	Inhibition effect	0.91	14.1
L-Histidine 1.0 wt%	3.30	Inhibition effect	1.11	17.2
L-Histidine 1.5 wt%	3.55	Inhibition effect	1.19	18.6
L-Glutamine 0.5 wt%	0.89	Promotion effect	0.30	4.67
L-Glutamine 1.0 wt%	0.74	Promotion effect	0.25	3.89
L-Glutamine 1.5 wt%	0.68	Promotion effect	0.23	3.56
SDS 0.1 wt%	0.19	Promotion effect	0.06	1.00
PVP 0.5 wt%	2.98	Inhibition effect	1.00	15.6

results show that L-histidine can be introduced as a promoter in the methane + propane system, its effect is less in comparison with SDS. The effects of applied amino acids on hydrate nucleation were also compared with that of PVP and SDS. Tables 3 and 4 show the average induction time values of amino acids in comparison with water, PVP and SDS (in ethane + water and methane + propane + water systems). The inhibition and promotion effects of additives can be determined based on the ratio of average induction times (hydrate formation with additives to hydrate formation with pure water). These values confirm that glycine, L-serine, L-histidine and PVP have inhibitory effects on the nucleation in ethane + water and methane + propane + water systems, while L-glutamine and SDS can promote the nucleation of hydrate. With investigation on the ratio of average induction times (additives to PVP, and additive to SDS), the performance of amino acids on the nucleation can be evaluated. These results show that the average induction time values for glycine and L-serine are 34–75 and 61–75% of the value of average induction time in the presence of PVP, for hydrate formation in the ethane + water and methane + propane + water systems, respectively. In fact, they have suitable performance on the hydrate nucleation, although they are poor inhibitors for hydrate growth. Also, the effect of glycine and L-serine on the nucleation is more in the methane + propane + water system. The results also show that the effect of L-histidine (at a concentration of 0.5 wt%) on the induction time of hydrate formation is close to that of PVP, although the average induction time in the presence of 1.0 and 1.5 wt% L-histidine is 1.11–1.19 times greater than that of PVP (in methane + propane + water system). Among the applied amino acids, L-glutamine decreased the average induction time, although its effect on the nucleation is not high in comparison with SDS.

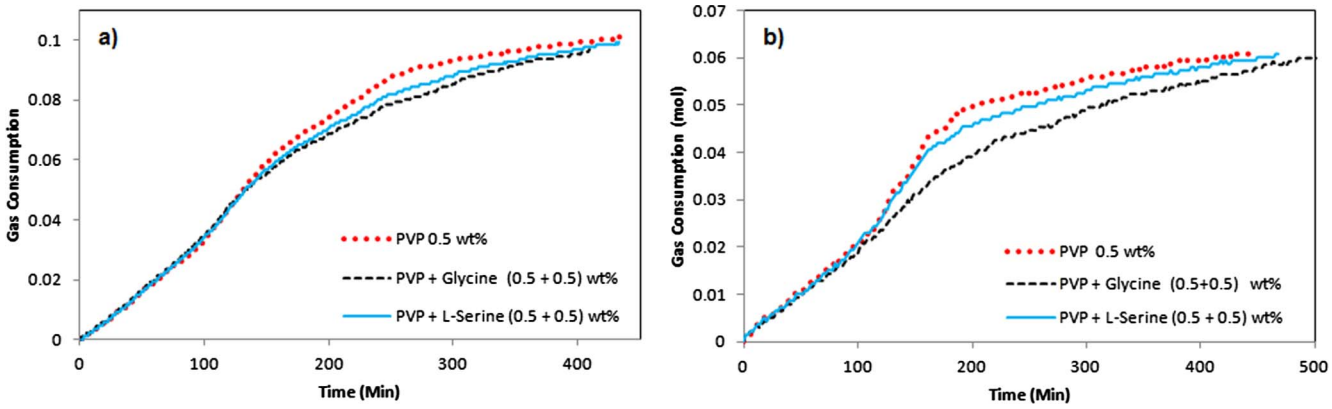

Fig. 11. The effect of hydrophobic amino acids as synergists on hydrate formation with PVP in ethane + water system (a) and methane + propane + water system (b).

3.6. The effect of hydrophobic amino acids as synergists on the kinetic hydrate inhibitor (PVP)

The performance of hydrophobic amino acids (glycine and L-serine) as synergists for PVP was also examined. As shown in Fig. 11(a), glycine and L-serine enhance the strength of PVP to prevent ethane hydrate growth. The results show that the synergistic effect of glycine is more than that of L-serine. The synergistic performance of glycine and L-serine on methane/propane hydrate growth was also tested. Fig. 11(b) shows that glycine and L-serine have synergistic effects on the decrease of hydrate growth by PVP. In addition, glycine and L-serine synergize the effect of PVP to retard the nucleation in ethane + water and methane + propane + water systems. The results show that glycine and L-serine increase the average induction time from 22 to 41% for hydrate formation with PVP. These results can be useful in the development of new synergists with good biodegradability properties.

4. Conclusions

In this study, the effects of hydrophobic and hydrophilic amino acids on the nucleation and growth rate of gas hydrate in ethane + water, methane + propane + water and methane + THF + water systems were investigated. The following conclusions can be drawn based on the experimental results.

(1) Glycine and L-serine (as hydrophobic amino acids) decreased the growth rate and retarded the nucleation of hydrate in all the studied systems. In fact, the average induction time was 1.22–2.67 times greater than the average induction time of hydrate formation with pure water (in ethane + water system), but it was 1.66–2.2 and 3.5–4.8 times greater in methane + propane + water and methane + THF + water systems, respectively.
(2) The performance of hydrophilic amino acids depended on the system. Interestingly, they acted as promoters of the growth of hydrate in ethane + water and methane + propane + water systems, while they showed inhibitory effects in the methane + THF + water system.
(3) L-glutamine and L-histidine as hydrophilic amino acids had different effects on the nucleation. L-histidine retarded nucleation in all the systems, while L-glutamine promoted nucleation in ethane + water, and methane + propane + water systems. Analysis of the obtained results showed that nucleation was more retarded with increasing amino acid hydrophobicity.
(4) Comparison of the effects of amino acids with that of SDS and PVP confirmed that hydrophobic amino acids have weak inhibitory effects on hydrate growth, while hydrophilic amino acids can be introduced as new promoters for hydrate growth (depending on the system).
(5) The experimental results indicated that glycine and L-serine with hydrophobic properties can also be introduced as new synergist inhibitors.

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