Inhibition properties of new amino acids for prevention of hydrate formation in carbon dioxide–water system: Experimental and modeling investigations

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

ABSTRACT

In the present work, the effect of new structures of amino acids is studied for prevention of hydrate formation in the carbon dioxide–water system. These amino acids consist of L-proline (as amino acid with nonpolar side chain), L-serine and L-glutamine (as amino acids with polar side chain), and L-histidine (as amino acid with charged side chain). The inhibition effects of these amino acids were compared with glycine, L-threonine, and poly-N-vinylpyrrolidone (PVP). Experiments were performed in the concentration range of 0.5–2 wt.%. Investigation on the experimental results shows that inhibition properties of amino acids in an aqueous solution was due to hydrophobicity, the net charge of amino acid, and electrically charge of the side chain. Based on the experimental results, the ranking of amino acids (to decrease the hydrate growth rate) is as follows: L-histidine > glycine > L-proline ≈ L-serine ≈ L-threonine > L-glutamine, although the inhibition effect of some amino acids is not significant. In addition, the inhibition effects of these amino acids are quantitatively described by the chemical affinity model. The predicted results confirm that some of the applied amino acids decrease CO_2 hydrate formation rate.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Gas hydrates are crystalline solid compounds, composed of water and certain gas molecules (such as methane, ethane, propane, and carbon dioxide). The water molecules link to each other through hydrogen bonds and form a cage-like structure around gas molecules [1]. Depending on the molecular size of the hydrate former, the water molecules in hydrate crystal can be stabilized into the three main structures (sI, sII, and sH).

Carbon dioxide is the primary greenhouse gas, which can form hydrate crystals. For example, in the CO_2 capture process (during CO_2 injection and transportation), CO_2 hydrate crystals may cause blockage in pipelines [2,3]. CO_2 hydrate formation in gas reservoirs containing CO_2 is also introduced [4]. Similarly, CO_2 hydrate may be formed during CO_2 injection into cold saline aquifers [5]. Thus, prevention of CO_2 hydrate formation is of key importance in the aforementioned fields [6,7].

Inhibitor injection is the most common method to prevent gas hydrate formation [8,9]. Thermodynamic hydrate inhibitors (THIs) such as salts, alcohols, and glycols are the first group of inhibitors, which change the pressure/temperature of hydrate formation to higher pressure and lower temperature. These inhibitors are used at high concentrations (40–60 wt.%) [1]. Thus, the use of these inhibitors often requires significant quantities for injection. In the 1990s, low dosage hydrate inhibitors (LDHIs) were introduced, which can be divided into two groups: kinetic hydrate inhibitors (KHIs or KIs) and anti-agglomerants (AAs). They are used at low concentrations (below 1 wt.%). KHIs retard nucleation and slow down the growth of hydrate crystals, while AAs keep small hydrate particles dispersed and prevent from hydrate agglomeration [1,10]. Although water-soluble polymers such as PVP, PVCap, and Gaffix VC-713 are the most common type of KHIs, the main problem is the poor biodegradability of these inhibitors [1,10]. Thus, researchers focused on KHIs with more environmentally friendly.

Antifreeze proteins (AFPs) and antifreeze glycoproteins (AFGPs) were the main group of green inhibitors [1]. Al-Adel et al. [11] investigated the effect of type I antifreeze proteins (AFPs) in comparison to poly(VP/VC). They reported that these inhibitors decrease methane hydrate formation rate, while their performance was similar. Daraboina et al. [12] also tested the effect of two antifreeze proteins (type I and type III) on the formation kinetics of methane/ethane/propane hydrate. Their results showed that the hydrate growth was delayed in the presence of these inhibitors. Gordienko et al. [13] tested the effects of AFPs on tetrahydrofuran (THF) hydrate and natural gas hydrates. They found that AFPs are superior inhibitors compared to PVP. Bagherzadeh et al. [14] presented the mechanism of the winter flounder AFP

(wf-AFP) to prevent methane hydrate formation by molecular dynamics simulation. They observed that wf-AFP was bound to the water molecules of methane hydrate by the methyl side chain of L-threonine and L-alanine. In fact, their results demonstrated that the L-threonine and L-alanine (as amino acid) play a significant role to prevent hydrate growth, although the experimental results of Perfeldt et al. [15] showed that L-threonine is ineffective on methane hydrate formation.

It should be noted that kinetic hydrate inhibitors are more used for natural gas or a mixture of hydrocarbons, but for prevention of CO_2 hydrate formation, some types of structures were tested as KHIs. The most important of these structures are ionic liquids and some amino acids. For example, Chun and Jaafar [16] showed that the tested ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) works as a kinetic inhibitor for CO_2 hydrate formation. Also, Sa et al. [17] tested the effects of five hydrophobic amino acids (including glycine, L-alanine, L-valine, L-leucine, and L-isoleucine) on CO_2 hydrate formation and found that amino acids with shorter alkyl side chains (glycine and L-alanine) were better KHIs. On the other hand, some amino acids were known as environmentally friendly corrosion inhibitors in acidic solutions such as the water-CO_2 system [18,19]. Thus, the study of the potential of these amino acids for prevention of CO_2 hydrate formation can be useful in evaluation of their dual application in the water–CO_2 system. Amino acids were also investigated on THF hydrate formation. Naeiji et al. [20,21] investigated the effect of glycine and L-leucine on THF hydrate formation. Their results showed that glycine is more effective KHIs.

Amino acids are organic compounds composed of amine and carboxylic acid with a specific side chain [22]. They are biodegradable and environmentally friendly [17,20]. Also, some amino acids (such as glycine and L-threonine) are the main part of antifreeze proteins (AFPs). Thus, investigation of inhibition effects of new structures of amino acids with different properties of the side chain can be useful for the development of environmentally friendly inhibitors.

In this work, for preventing CO_2 hydrate formation, four new structures of amino acids (including L-proline, L-serine, L-glutamine, and L-histidine) are selected based on different properties of amino acids, such as hydrophobicity, net charge of amino acid or electrically charge of the side chain. The performance of amino acids in an aqueous solution is examined and described based on these properties. Also the effects of glycine, L-threonine and PVP are examined for preventing CO_2 hydrate formation in comparison to the presented structures. In addition, the performance of amino acids for decreasing CO_2 hydrate formation rate is discussed and modeled by the chemical affinity model.

2. Experimental

2.1. Materials

CO_2 (99.9 vol% purity) is utilized for hydrate formation with double distilled water or aqueous solution of amino acids. The amino acids (including glycine, L-proline, L-serine, L-threonine, L-glutamine, and L-histidine) are supplied by Merck. The structures and properties of these amino acids are tabulated in Table 1. Also PVP with a molecular weight of 10 000 g/gmol is provided from Sigma Aldrich.

2.2. Apparatus

The schematic of the used apparatus is shown in Fig. 1. The experimental apparatus is a jacketed batch reactor with a capacity of 655 cm³ (with the uncertainty of ±4 cm³) and design pressures of 0–60 bar. The reactor temperature is controlled by the cooling system. It consists of a coolant bath with controllable circulator that is utilized to circulate the coolant (water/ethylene glycol) through the jacket. The temperature of the reactor is measured by a PT100 thermometer with the uncertainty of ±0.1 K. The reactor pressure is measured by a pressure transmitter with an uncertainty of ±0.1 bar. The pressure and temperature data are recorded by the data acquisition system connected to a computer.

2.3. Experimental procedure

First, the reactor was washed and rinsed three times using distilled water and evacuated by a vacuum pump. It was subsequently charged with 300 cm³ of liquid sample (including aqueous solution of the amino acids). It was pressurized up to 30 bar at 285.15 K with a stirring rate of 300 rpm. The system was allowed to reach the equilibrium state under these conditions and then was cooled to 275.15 K without agitation. When the temperature was adjusted (at the constant temperature of 275.15 K), the mixer was turned on at 300 rpm for CO_2 hydrate formation. The pressure change in reactor was recorded until equilibrium pressure was reached. The moles of gas consumed during CO_2 hydrate formation were calculated by Eq. (1), which the Peng–Robinson equation of state was used for calculating compressibility factor [23].

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

Table 1
The structure and properties of applied amino acids [19,29].

Amino acids	Molecular structure with side chain	pKa$_1$ (—COOH)	pKa$_2$ (—NH$_2$)	pKa (side chain)	Hydrophobicity
Glycine (Gly)	H$_2$N—CH—COOH / H	2.34	9.60	–	−0.4
L-Proline (L-pro)	HN—CH—COOH / H$_2$C CH$_2$ / CH$_2$	1.99	10.60	–	−1.6
L-Serine (L-ser)	H$_2$N—CH—COOH / CH$_2$—OH	2.21	9.15	–	−0.8
L-Threonine (L-thr)	H$_2$N—CH—COOH / HO—CH—CH$_3$	2.09	9.10	–	−0.7
L-Glutamine (L-gln)	H$_2$N—CH—COOH / CH$_2$—CH$_2$—C—NH$_2$ // O	2.17	9.13	–	−3.5
L-Histidine (L-his)	H$_2$N—CH—COOH / CH$_2$ / (imidazole ring) NH N	1.82	9.17	6.04	−3.2

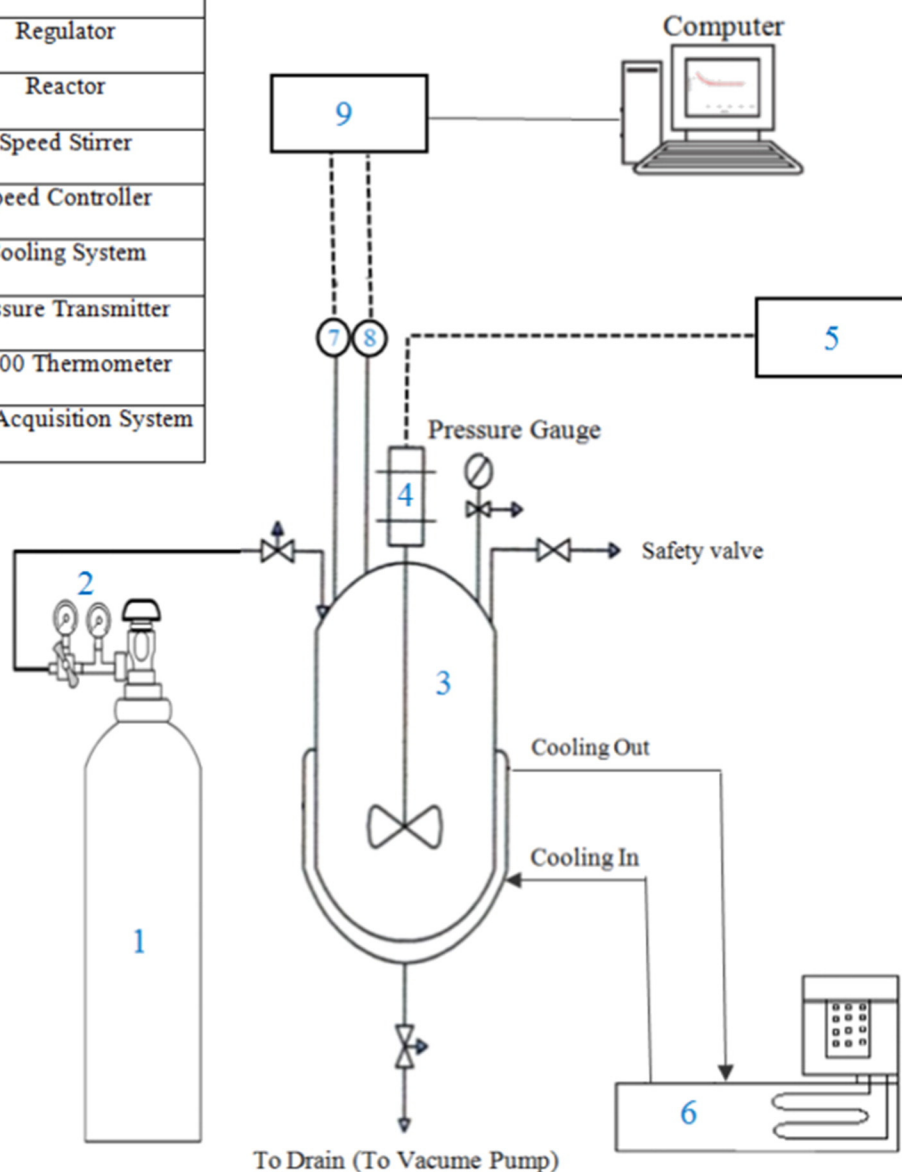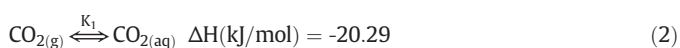| No	Description
1	Gas Cylinder
2	Regulator
3	Reactor
4	Speed Stirrer
5	Speed Controller
6	Cooling System
7	Pressure Transmitter
8	PT100 Thermometer
9	Data Acquisition System

Fig. 1. Hydrate formation apparatus.

3. Net charge of amino acids in CO$_2$-saturated water

The net charge calculation of amino acids in CO$_2$-saturated water can be useful for analysis of their inhibition effects. The net charge of amino acids in CO$_2$-saturated water is related to pH. On the other hand, the reaction of CO$_2$ with water and the temperature and pressure variations of the system (in the range from 275.15 to 285.15 K and 15.8 to 30 bar, respectively) change the pH, and consequently, change the net charge of amino acids. So for calculation of the net charge, the reaction of CO$_2$ with water and the temperature and pressure variations must be considered.

The characteristic equilibrium reactions for CO$_2$ in water can be considered according to the following equations [2].

$$CO_{2(g)} \overset{K_1}{\Longleftrightarrow} CO_{2(aq)} \quad \Delta H(kJ/mol) = -20.29 \tag{2}$$

$$CO_{2(aq)} + H_2O_{(l)} \overset{K_2}{\Longleftrightarrow} H_2CO_{3(aq)} \quad \Delta H(KJ/mol) = -0.02 \tag{3}$$

$$H_2CO_{3(aq)} \overset{K_3}{\Longleftrightarrow} HCO_{3\ (aq)} + H^+_{(aq)} \quad \Delta H(kJ/mol) = 7.66 \tag{4}$$

$$HCO_{3\ (aq)} \overset{K_4}{\Longleftrightarrow} CO_3{}^{2-}{}_{(aq)} + H^+_{(aq)} \quad \Delta H(kJ/mol) = 14.85 \tag{5}$$

Equilibrium constants for reactions were calculated by the van't Hoff equation at 275.15 and 285.15 K. The calculated results are presented in Table 2. Also for calculation of pH in the negligible concentration of CO$_3^{2-}$ the following equation can be used [2]. Accordingly, obtained pH values were variable from 3.77 (285.15 K, 30 bar) to 4.06 (275.15 K, 15.8 bar).

$$pH = -0.5 \log \left(10^{-14} + \frac{K_2 \times K_3}{K_1} \times P_{CO_2} \right) \tag{6}$$

Table 2
Equilibrium constants of the characteristic reactions for CO_2 in water.

Equilibrium constant			
	At 298.15 K	At 285.15 K	At 275.15 K
K_1	3.4×10^{-2}	4.9×10^{-2}	6.7×10^{-2}
K_2	1.7×10^{-3}	1.7×10^{-3}	1.7×10^{-3}
K_3	4.5×10^{-7}	3.9×10^{-7}	3.5×10^{-7}
K_4	4.7×10^{-11}	3.6×10^{-11}	2.8×10^{-11}

The net charge of applied amino acids at different pH values can be calculated by Eq. (7) [24]. This equation demonstrates that the net charge of amino acids is obtained by summing the charge of each group. The first term of this equation is considered for negative charge groups of amino acids (—COO—) and the second term is for positive charge groups (—NH_3^+ or charged side chain of L-histidine) [24]. The obtained results from the net charge of amino acids are tabulated in Table 3.

$$\text{Net } Z = \sum_{j=1}^{m} \left(\frac{-1}{10^{-(pH-pK_j)} + 1} + \frac{+1}{10^{(pH-pK_j)} + 1} \right) \tag{7}$$

4. Modeling

In current work, the chemical affinity was used for the kinetic study of CO_2 hydrate formation with amino acids. For obtaining kinetic parameters of this model (t_k and $-A_r/RT$) the following equation was derived in previous work [25].

$$\frac{A_i}{RT} = -\frac{A_r}{RT} \left[-\ln \left(\frac{t_i}{t_k} \exp \left(1 - \frac{t_i}{t_k} \right) \right) \right] \tag{8}$$

where

$$\frac{A_i}{RT} = -\ln \frac{n_{ci}}{n_{cf}}. \tag{9}$$

The presented algorithm in Fig. 2 can be used to obtain kinetic parameters (t_k and $-A_r/RT$) of Eq. (8). Also, for prediction of gas consumption (n_{ci}) the following equation can be used [25]:

$$\frac{n_{ci}}{n_{cf}} = \left[\left(\frac{t_i}{t_k} \exp \left(1 - \frac{t_i}{t_k} \right) \right) \right]^{\frac{-A_r}{RT}}. \tag{10}$$

5. Results and discussion

5.1. Experimental results and discussion

The experiments for investigation of the effect of amino acids on CO_2 hydrate formation kinetics were performed at concentrations of 0.5–2 wt.%. The first test was performed with L-proline. Fig. 3 shows the effect of L-proline on growth rate of CO_2 hydrate. The gas consumption rate was decreased with L-proline in comparison to pure water. In

Table 3
The net charge of amino acids under experimental conditions.

Amino acids	Net charge at pH = 3.77 (285.15 K, 30 bar)	Net charge at pH = 4.06 (275.15 K, 15.8 bar)
Glycine (Gly)	0.036	0.019
L-Proline (L-pro)	0.016	0.008
L-Serine (L-ser)	0.026	0.014
L-Threonine (L-thr)	0.020	0.011
L-Glutamine (L-gln)	0.024	0.013
L-Histidine (L-his)	1.005	0.995
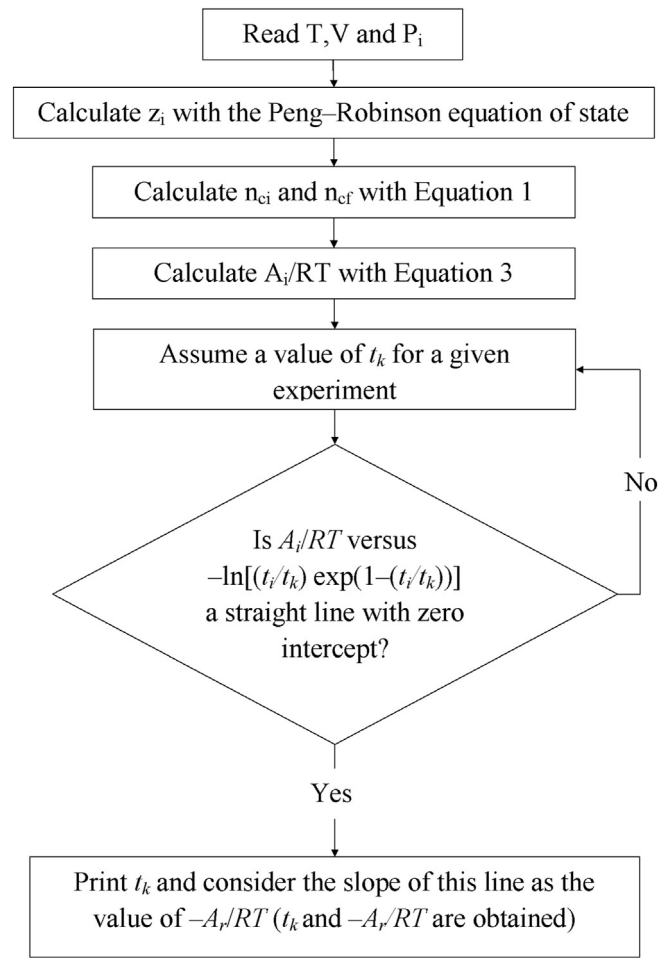
Fig. 2. The algorithm for calculation of kinetic parameters (t_k and $-A_r/RT$).

fact, the rate of gas consumption reflects the growth rate of CO_2 hydrate [26]. On the other hand, the growth rate of hydrate decreases with increasing of concentration from 0.5 to 1.5 wt.%, while the inhibitory effects are almost the same in concentrations of 1.5 and 2 wt.%. Fig. 4 shows the effect of L-serine on CO_2 hydrate formation kinetics. It also decreases the gas consumption rate. The experimental results for L-glutamine and L-histidine are shown in Figs. 5 and 6, respectively. The results demonstrate that the effect of L-glutamine on decreasing of CO_2 hydrate formation rate is negligible, while the effect of L-histidine is more significant. In fact, it seems that L-histidine is more effective than other amino acids for preventing CO_2 hydrate formation, although the inhibition effect of these new green structures must be compared together. In addition, the performance of these amino acids
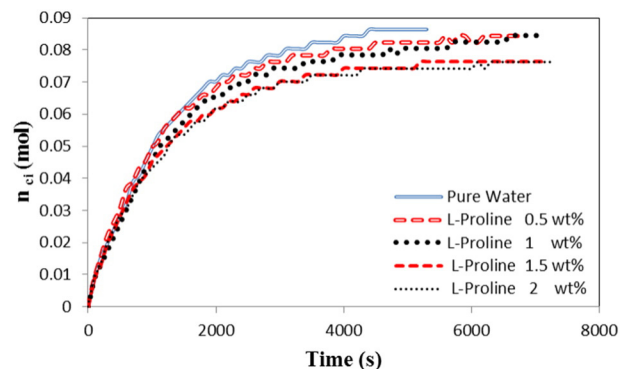
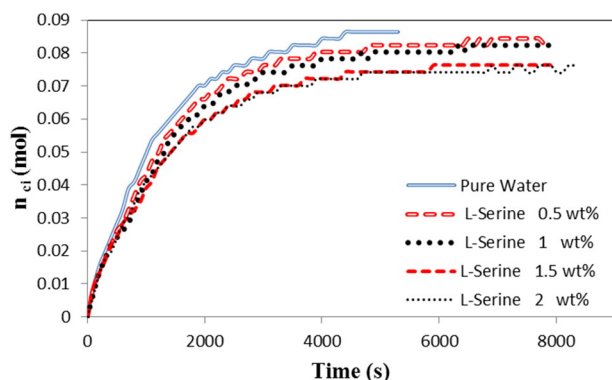Fig. 3. The effect of L-proline on CO_2 hydrate formation rate.

Fig. 4. The effect of L-serine on CO_2 hydrate formation rate.
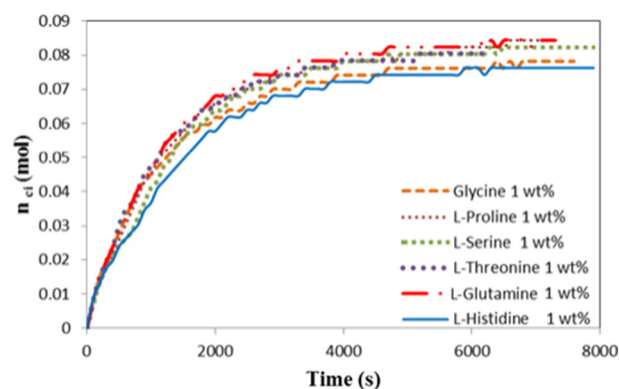

Fig. 7. The effect of used amino acids at concentration of 1.0 wt.%.

can be compared to glycine and L-threonine. Thus, experiments were also performed with glycine and L-threonine. It should be noted that glycine was selected as the best introduced inhibitor of amino acids in literatures [17,20]. On the other hand, some literatures reported that L-threonine has a significant role in the inhibition mechanism of some antifreeze proteins [14]. Also, the inhibition effect of L-threonine on CO_2 hydrate formation is not reported in references.

Figs. 7 and 8 show the effects of new structures of amino acids in comparison to glycine and L-threonine at concentrations of 1 and 1.5 wt.%. The results demonstrated that the inhibition effect of L-histidine is higher than glycine, while the effects of L-proline, L-serine, and L-threonine are less than glycine. Also, L-glutamine has the lowest inhibition effect on CO_2 hydrate formation rate.

Based on experimental results, the ranking of amino acids (to decrease the hydrate growth rate) is as follows: L-histidine > glycine >

L-proline ≈ L-serine ≈ L-threonine > L-glutamine. In fact, the inhibition effect of L-histidine with charged side chain is more than uncharged side chain amino acids with polar or nonpolar side chain. On the other hand, the inhibition effect of glycine is more than other amino acids with polar or nonpolar side chain (uncharged side chain), while L-glutamine is the least effective amino acid. Also the inhibition effects of L-proline, L-serine, and L-threonine are almost the same. It should be noted that L-threonine decreased CO_2 hydrate formation rate, while according to some reports, it was ineffective on methane hydrate formation [15]. For analysis of these results the inhibition mechanism and inhibition properties of amino acids must be investigated.

The inhibition mechanism of amino acids is probably related to two main reasons. First, the oxygen atoms of carbonyl in amino acids form hydrogen bonds with water molecules of hydrate surface. Second, the side chain of amino acid (usually hydrophobic group or charged side chain) forms a van der Waals interaction or electrostatic interactions with crystal surface. Therefore, they interrupt nucleation and disrupt further growth of the hydrate crystals [10,27,28].

According to these notifications, the inhibition properties of amino acids for preventing CO_2 hydrate formation can be analyzed. One of the main properties of amino acids is hydrophobicity of side chain. Hydrophobicity values of applied amino acids are presented in Table 1. The comparison of these values with experimental results shows that the inhibition effect of uncharged side chain amino acids is decreased with reducing hydrophobicity values, thus L-glutamine with the minimum value of hydrophobicity is the least effective amino acid and glycine with maximum hydrophobicity is the most effective one. However, with reducing hydrophobicity value of L-proline in comparison to L-serine and L-threonine the inhibition effect is not varied. The effect of the hydrophobic group was also investigated in some literatures. Recently Bagherzadeh et al. [14] reported that wf-AFP can be bound to the water molecules of methane hydrate by the hydrophobic methyl
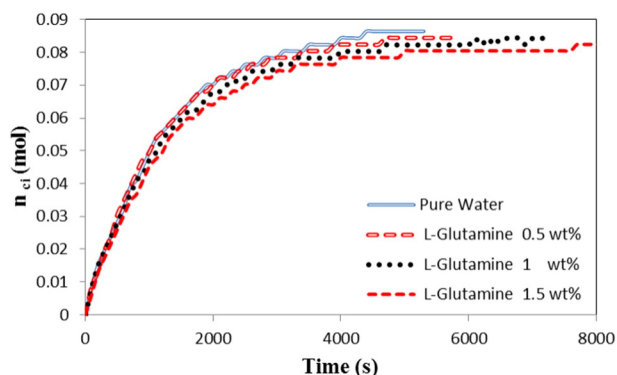

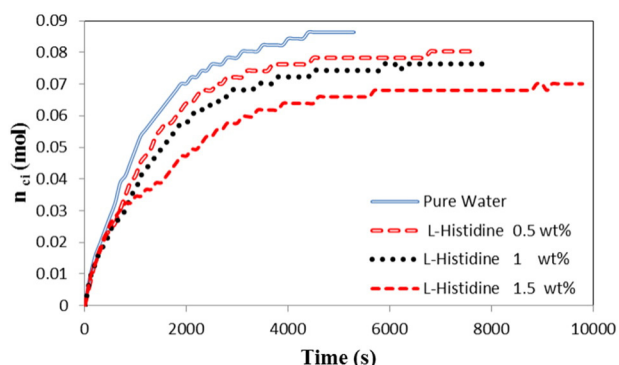**Fig. 5.** The effect of L-glutamine on CO_2 hydrate formation rate.

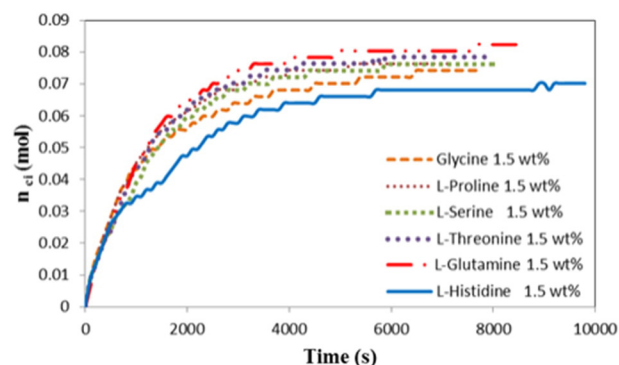**Fig. 6.** The effect of L-histidine on CO_2 hydrate formation rate.

Fig. 8. The effect of used amino acids at concentration of 1.5 wt.%.

side chain of L-threonine and L-alanine. In fact, they found that hydrophobic groups block the empty hydrate half cages, while the hydrate surface is stabilized via hydrophobic interaction of the side chain with the surrounding water molecules. So the inhibition effects of applied amino acids are increased with increasing the values of hydrophobicity.

The net charge of amino acids is also one of the main properties of amino acids for prevention of CO_2 hydrate formation. The net charges of amino acids were calculated under experimental conditions. The obtained results are presented in Table 3. Based on the obtained values the net charge of L-histidine is very high in comparison to other applied amino acids. Thus the inhibition effect of L-histidine is more than other applied amino acids. In fact, high net charge (charged side chain) of L-histidine causes the stronger interactions with water molecules of hydrate surface. In addition, the polar water molecules around charged molecules or charged side chain of L-histidine are less ice-like. Therefore, the rate of nucleation and growth of CO_2 hydrate is decreased. Also it can be seen that the net charge of glycine is more in comparison to L-proline, L-serine, L-threonine, and L-glutamine. Thus more inhibition effect of glycine in comparison to these amino acids may be due to the net charge.

5.2. Modeling results and discussion

The performance of applied amino acids to decrease the hydrate growth rate can be described quantitatively by the chemical affinity model. In fact, the main purpose is the calculation of kinetic parameters for performance evaluation of amino acids as KHIs for the development of environmentally friendly inhibitors. According to the presented algorithm in Fig. 2 the kinetic parameters (the values of $-A_r/RT$ and t_K) can be calculated. For example, A_i/RT versus $-\ln[(t_i/t_k)\exp(1-(t_i/t_k))]$ is plotted in Fig. 9 for CO_2 hydrate formation with L-histidine. The linear relation with zero intercept confirms that the value of t_k is assumed correctly. Also, the slope of this line can be considered as the value of $-A_r/RT$. The values of $-A_r/RT$ and t_K for other experiments were calculated similarly, as listed in Table 4. On increasing the amino acid concentration from 0.5 to 2.0 wt.%, the values of $-A_r/RT$ are decreased. These results confirm that the rate of CO_2 hydrate formation is decreased with increasing the amino acid concentration. The minimum value of $-A_r/RT$ is obtained for L-histidine at a concentration of 1.5 wt.%, while this value is higher for glycine and the other amino acids at all concentrations (even at concentration of 2 wt.% of glycine). These values confirm that the inhibition effect of L-histidine is more than glycine. Also, these values for glycine are less than amino acids with uncharged side chain. On the other hand, these values for L-glutamine are close to pure water and show that the inhibition effect of L-glutamine is almost negligible. Also Fig. 10 shows that the average values of $-A_r/RT$ in concentration of 0.5, 1, and 1.5 wt.% are decreased with increasing hydrophobicity values. Thus the results of model also confirmed that the
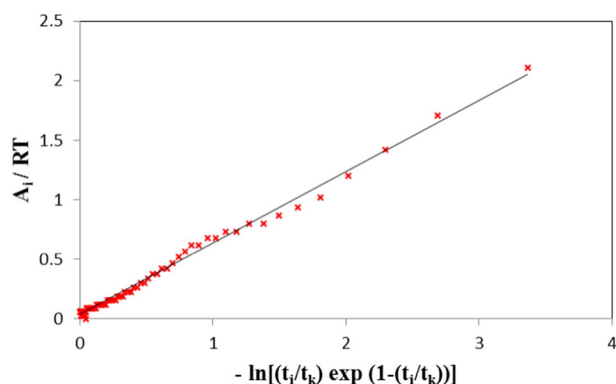
rate of CO_2 hydrate formation is reduced with increasing hydrophobicity of uncharged side chain amino acids. The obtained values of t_k are also presented in Table 4. These values show that CO_2 hydrate formation is slower in the presence of amino acids rather than pure water.

The obtained kinetic parameters (t_k and $-A_r/RT$) can be used for calculation of gas consumption (n_{ci}) by Eq. (10). Fig. 11 shows the results of the chemical affinity model for prediction of gas consumption during CO_2 hydrate formation in the presence of amino acids (in concentration of 1 wt.%). The results are in good agreement with experimental data and confirm that the chemical affinity model can be applied for investigation of the inhibition effect of amino acids on CO_2 hydrate formation.

5.3. The inhibition effect of PVP in comparison to applied amino acids and analyzing on potential of applied structure as KHIs

The experiments were also performed with PVP. Fig. 12 shows the effect of PVP in comparison to glycine and L-histidine (which had the best inhibitory effect among applied amino acids). In concentrations of 1 and 1.5 wt.% the effect of PVP is more than glycine while in concentration of 1 wt.% the effect of PVP and L-histidine is almost alike. Also in
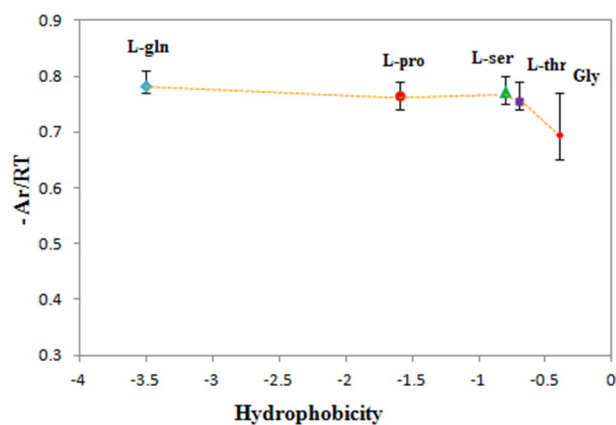
Table 4
Obtained kinetic parameters of the chemical affinity model for applied amino acids in the concentration range of 0.5–2 wt.%.

Amino acids	Concentration (wt.%)	Model parameters	
		$t_k(s)$	$-A_r/RT$
Pure		4562	0.81
Glycine	0.5	4649	0.77
Glycine	1.0	5484	0.67
Glycine	1.5	7016	0.65
Glycine	2.0	7174	0.64
L-Proline	0.5	4848	0.79
L-Proline	1.0	5100	0.77
L-Proline	1.5	5142	0.74
L-Proline	2.0	5984	0.72
L-Serine	0.5	5089	0.80
L-Serine	1.0	5411	0.77
L-Serine	1.5	5445	0.75
L-Serine	2.0	5588	0.75
L-Threonine	0.5	4585	0.79
L-Threonine	1.0	4643	0.74
L-Threonine	1.5	6182	0.74
L-Threonine	2.0	6249	0.73
L-Glutamine	0.5	4235	0.81
L-Glutamine	1.0	4876	0.77
L-Glutamine	1.5	5070	0.77
L-Histidine	0.5	5004	0.76
L-Histidine	1.0	5660	0.67
L-Histidine	1.5	7780	0.60

Fig. 9. A_i/RT versus $-\ln[(t_i/t_k)\exp(1-(t_i/t_k))]$ for CO_2 hydrate formation with L-histidine at concentration of 1.5 wt.%.

Fig. 10. Average values of $-A_r/RT$ in concentrations of 0.5, 1, and 1.5 wt.% versus hydrophobicity (for CO_2 hydrate formation in the presence of uncharged side chain amino acids).
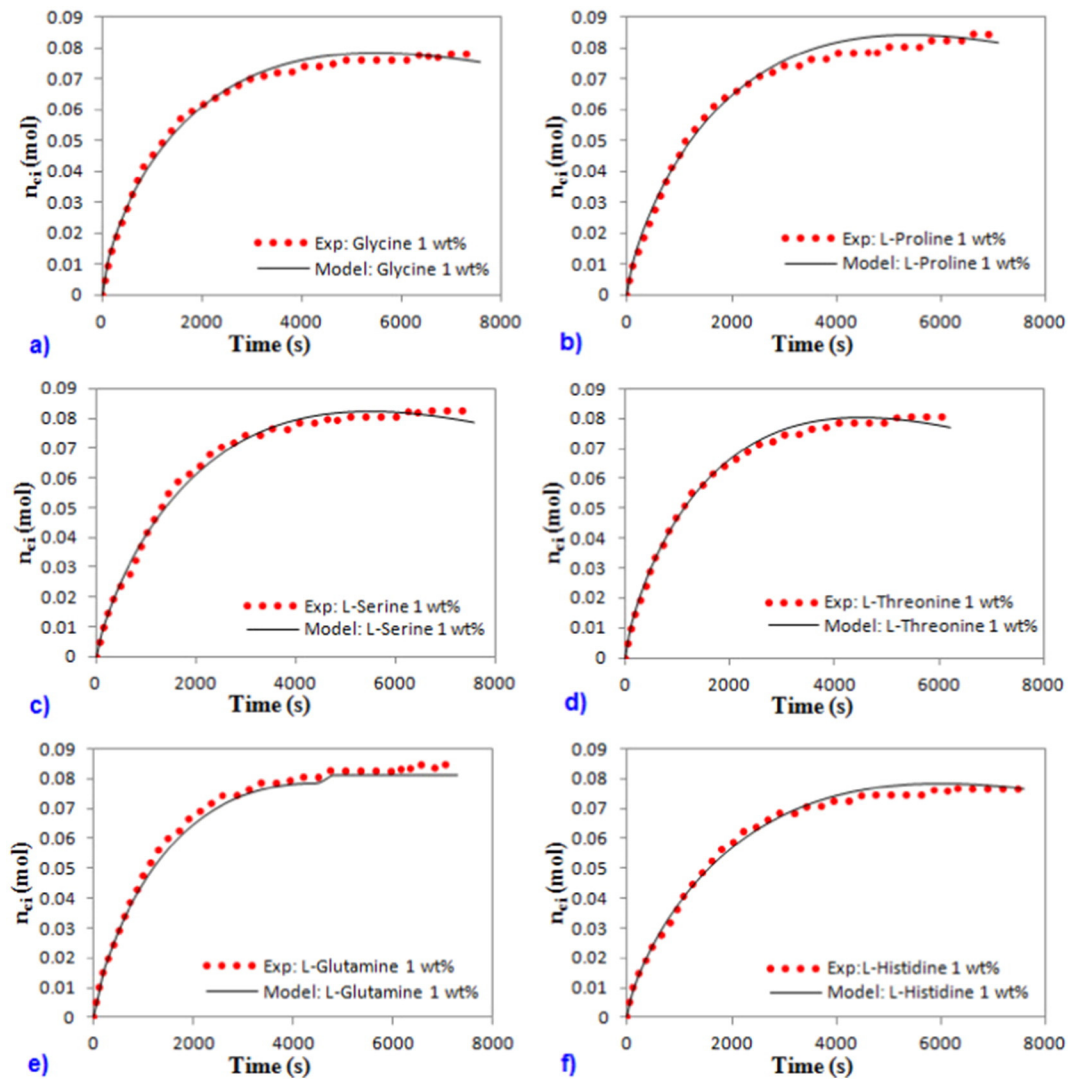
Fig. 11. Comparison between the calculated and the experimental gas consumption (n_{ci}) in the presence of amino acids (in concentration of 1 wt.%).

concentration of 1.5 wt.% the effect of L-histidine is more than PVP. A characterization of CO_2 hydrate formation in the presence of additives is introduced which can be useful for better understanding the effect of amino acids on CO_2 hydrate growth. Zhang et al. [30] showed that under high carbonate (CO_2) concentrations, the effect of additives on formation rate of CO_2 hydrate may be insignificant. In fact, additive (promoters or inhibitors) for appropriate performance should be

adsorbed on the crystal surface of hydrate, but in high concentration of CO_2 a competitive adsorption between additives and CO_2 will affect the performance of additive. This is more effective in initial times of CO_2 hydrate formation, because the concentration of CO_2 is higher and adsorption of the applied structure on crystals of CO_2 hydrate is insignificant. Thus, the inhibition effect of amino acids or PVP on the initial rate of CO_2 hydrate formation is insignificant. While, CO_2 hydrate formation
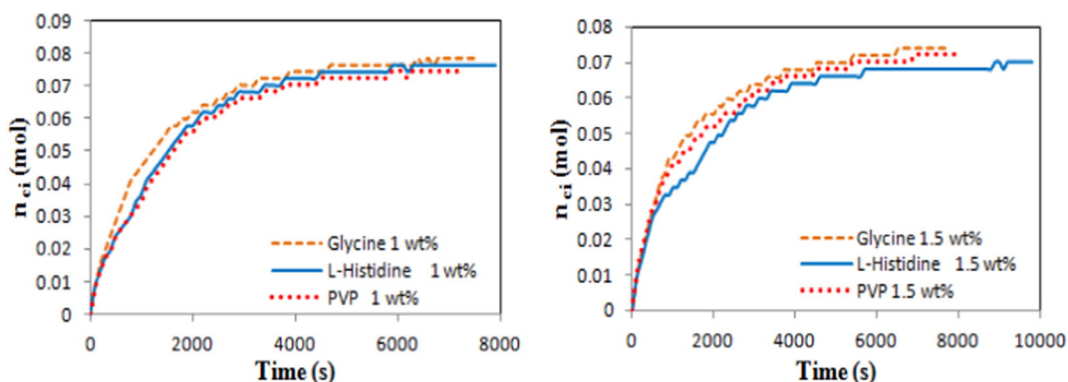

Fig. 12. Comparison between PVP, glycine, and L-histidine in concentrations of 1 and 1.5 wt.%.

is continued the concentration of CO_2 (around the crystal surface of CO_2 hydrate) is decreased and amino acids and PVP can be more adsorbed on the crystal surface. Therefore, the inhibition effect of these structures is more significant with time. Consequently, charged and ionic structures as promoter or inhibitor (such as ionic liquid) are more effective on kinetics of CO_2 hydrate formation. The reason may be due to more adsorption of these structures on crystals of CO_2 hydrate in a competitive adsorption with CO_2 and thus for the same reason, the effect of L-histidine may be more in comparison to PVP (in concentrations of 1.5 wt.%). In fact, according to Table 3 the net charge of L-histidine is very higher than other amino acids and may be a key reason for more inhibition effect of L-histidine on CO_2 hydrate formation.

6. Conclusions

The results of the experiments show that applied amino acids decrease CO_2 hydrate formation rate, and their inhibition effect is more at higher concentrations. L-Histidine was more effective than glycine, PVP, and other amino acids. In fact, the effect of L-histidine with charged side chain and high net charge is more than uncharged side chain amino acids with low net charge. Furthermore, the experimental results demonstrate that the inhibition effects of uncharged side chain amino acids increase with increasing hydrophobicity values. Consequently, the inhibition effect of glycine is more than L-proline, L-serine, and L-threonine, while L-glutamine has the lowest inhibition effect on CO_2 hydrate formation rate. Also, the obtained kinetic parameters of the chemical affinity model ($^{-}A_r/RT$ and t_K) confirm that the rate of CO_2 hydrate formation is reduced in the presence of amino acids.

Nomenclature

A_i	the chemical affinity at state i
A_r	proportionality constant in Eq. (8) which denotes the affinity rate constant
K	equilibrium constant
n_{ci}	moles of gas consumed up to time t_i
n_{cf}	total moles of consumed gas
n_o	initial moles of gas in the reactor
n_i	moles of gas at time t_i in the reactor
P	pressure
P_{CO2}	partial pressure of CO_2
R	universal gas constant
T	temperature
t	time
t_i	time required to reach state i
t_k	time required to reach equilibrium conditions
V	volume of gas in the reactor
Z	compressibility factor

Subscripts

o	initial value
i	state i
j	arbitrary component

References

[1] E.D. Sloan, C. Koh, Clathrate Hydrates of Natural Gases, third ed. Taylor & Francis, 2007.
[2] J.H. Sa, B.R. Lee, D.H. Park, K. Han, H.D. Chun, K.H. Lee, Amino acids as natural inhibitors for hydrate formation in CO_2 sequestration, Environ. Sci. Technol. 45 (2011) 5885–5891.
[3] D.Y.C. Leung, G. Caramanna, M.M. Maroto-Valer, An overview of current status of carbon dioxide capture and storage technologies, Renew. Sust. Energ. Rev. 39 (2014) 426–443.
[4] Y. Feng, S. Hu, X. Liu, G. Luo, G. Zhu, Prevention and disposal technologies of gas hydrates in high-sulfur gas reservoirs containing CO_2, J. Nat. Gas Sci. Eng. 19 (2014) 344–349.
[5] T. Ding, Y. Liu, Simulations and analysis of hydrate formation during CO_2 injection into cold saline aquifers, Energy Procedia 63 (2014) 3030–3040.
[6] L.V. Lim, A.V. Lloren, R.B. Lamorena, The effect of urea in the nucleation process of CO_2 clathrate hydrates, J. Mol. Liq. 194 (2014) 245–250.
[7] B. ZareNezhad, M. Mottahedin, F. Varaminian, Effects of process variables on the initial gas hydrate formation rate: the case of ethane hydrate formation in the absence or presence of SDS kinetic promoter, J. Mol. Liq. 198 (2014) 57–62.
[8] J. Yang, B. Tohidi, Characterization of inhibition mechanisms of kinetic hydrate inhibitors using ultrasonic test technique, Chem. Eng. Sci. 66 (2011) 278–283.
[9] M.A. Kelland, F.T. Reyes, K.W. Trovik, Tris(dialkylamino)cyclopropenium chlorides: tetrahydrofuran hydrate crystal growth inhibition and synergism with polyvinylcaprolactam as gas hydrate kinetic inhibitor, Chem. Eng. Sci. 93 (2013) 423–428.
[10] M.A. Kelland, History of the development of low dosage hydrate inhibitors, Energy Fuel 20 (3) (2006) 825–847.
[11] S. Al-Adel, J.A.G. Dick, R. El-Ghafari, P. Servio, The effect of biological and polymeric inhibitors on methane gas hydrate growth kinetics, Fluid Phase Equilib. 267 (2008) 92–98.
[12] N. Daraboina, I.L. Moudrakovski, J.A. Ripmeester, V.K. Walker, P. Englezos, Assessing the performance of commercial and biological gas hydrate inhibitors using nuclear magnetic resonance microscopy and a stirred autoclave, Fuel 105 (2013) 630–635.
[13] R. Gordienko, H. Ohno, V.K. Singh, Z. Jia, J.A. Ripmeester, V.K. Walker, Towards a green hydrate inhibitor: imaging antifreeze proteins on clathrates, PLoS One 5 (2) (2010) e8953.
[14] S.A. Bagherzadeh, S. Alavi, J.A. Ripmeester, P. Englezos, Why ice-binding type I antifreeze protein acts as a gas hydrate crystal inhibitor, Phys. Chem. Chem. Phys. 17 (2015) 9984–9990.
[15] C.M. Perfeldt, P.C. Chua, N. Daraboina, D. Friis, E. Kristiansen, H. Ramløv, J.M. Woodley, M.A. Kelland, N. Solms, Inhibition of gas hydrate nucleation and growth: efficacy of an antifreeze protein from the longhorn beetle rhagium mordax, Energy Fuel 28 (2014) 3666–3672.
[16] L.K. Chun, A. Jaafar, Ionic liquid as low dosage hydrate inhibitor for flow assurance in pipeline, Asian J. Sci. Res. 6 (2) (2013) 374–380.
[17] J.H. Sa, G.H. Kwak, B.R. Lee, D.H. Park, K. Han, K.H. Lee, Hydrophobic amino acids as a new class of kinetic inhibitors for gas hydrate formation, Sci. Rep. 3 (2013) 2428.
[18] G. Gece, S. Bilgic, A theoretical study on the inhibition efficiencies of some amino acids as corrosion inhibitors of nickel, Corros. Sci. 52 (2010) 3435–3443.
[19] J. Fu, S. Li, Y. Wang, L. Cao, L. Lu, Computational and electrochemical studies of some amino acid compounds as corrosion inhibitors for mild steel in hydrochloric acid solution, J. Mater. Sci. 45 (2010) 6255–6265.
[20] P. Naeiji, A. Arjomandi, F. Varaminian, Amino acids as kinetic inhibitors for tetrahydrofuran hydrate formation: experimental study and kinetic modeling, J. Nat. Gas Sci. Eng. 21 (2014) 64–70.
[21] P. Naeiji, A. Arjomandi, F. Varaminian, Optimization of inhibition conditions of tetrahydrofuran hydrate formation via the fractional factorial design methodology, J. Nat. Gas Sci. Eng. 21 (2014) 915–920.
[22] F.A. Carey, R.M. Giuliano, Organic Chemistry, eighth ed. McGraw-Hill, 2010.
[23] A. Danesh, PVT and Phase Behaviour of Petroleum Reservoir Fluids, Elsevier Science, 1998.
[24] D.S. Moore, Amino acid and peptide net charges: a simple calculational procedure, Biochem. Educ. 13 (1) (1985) 10–11.
[25] H. Roosta, S. Khosharay, F. Varaminian, Experimental study of methane hydrate formation kinetics with or without additives and modeling based on chemical affinity, Energy Convers. Manag. 76 (2013) 499–505.
[26] H. Roosta, F. Varaminian, S. Khosharay, Experimental study of CO_2 hydrate formation kinetics with and without kinetic and thermodynamic promoters, Sci. Iran. C 21 (3) (2014) 753–762.
[27] A.K. Norland, M.A. Kelland, Crystal growth inhibition of tetrahydrofuran hydrate with bis- and polyquaternary ammonium salts, Chem. Eng. Sci. 69 (2012) 483–491.
[28] M.F. Mady, J.M. Bak, H. Lee, M.A. Kelland, The first kinetic hydrate inhibition investigation on fluorinated polymers:poly(fluoroalkylacrylamide)s, Chem. Eng. Sci. 119 (2014) 230–235.
[29] J. Kyte, R.F. Doolittle, A simple method for displaying the hydropathic character of a protein, J. Mol. Biol. 157 (1982) 105–132.
[30] J.S. Zhang, C. Loa, P. Somasundaran, J.W. Lee, Competitive adsorption between SDS and carbonate on tetrahydrofuran hydrates, Int. J Colloid Interface Sci. 341 (2010) 286–288.