Effects of New Amino Acids as Green Inhibitors on CO_2 Hydrate Formation Kinetics

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Abstract

In this study, new amino acids were examined as green inhibitors to prevent CO_2 hydrate formation. The tested amino acids consisted of glycine and L-proline (as amino acids with nonpolar side-chain), L-serine and L-threonine (as amino acids with polar side-chain). The inhibition effects of new amino acids were compared with glycine, which was introduced as good inhibitors in literatures. Experiments were performed in the concentration range of 0.5-2 wt%. The experimental results showed that improvement in inhibition properties of amino acids was due to hydrophobicity of the side chain.

Keywords: CO_2 hydrate; Kinetics; Green inhibitors; Amino acids

Introduction

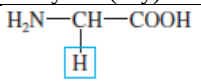
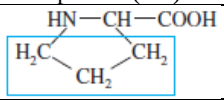
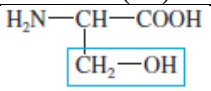
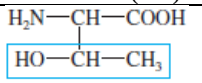
Gas hydrates are ice-like solid compounds, composed of water and certain gas molecules. The water molecules form a network of cages by hydrogen bonds. Under low temperature and high pressure, these cages can trap gas molecules [1]. Interest in gas hydrates began in 1934 when Hammerschmidt discovered that they caused blockages in gas and petroleum pipelines [2]. Thus, it was focused on developing methodology for preventing hydrate blockages in pipelines [3]. The inhibitor injection into the pipeline is the most common method for prevention of hydrate. Inhibitors are divided into two groups: Thermodynamic hydrate inhibitors (THIs) and low dosage hydrate inhibitors (LDHIs). Also LDHIs are segmented into two groups: kinetic hydrate inhibitors (KHIs or KIs) and anti-agglomerants (AAs). But the main problem was the poor biodegradability of these inhibitors [2]. Thus, researchers focused on KHIs with more environmentally friendly. Recently, amino acids were applied as green inhibitors. Sa et al. [4] introduced hydrophobic amino acids as a new class of KHIs and investigated the effect of these inhibitors on CO_2 hydrate formation. They tested hydrophobic amino acids with different lengths of alkyl side chains and

found that amino acids with shorter alkyl side chains were better KHIs. In addition, Naeiji et al. [5] investigated the effect of glycine and L-leucine on THF hydrate formation. In the mentioned literatures [4, 5], hydrophobic amino acids with nonpolar side-chain were tested, while the effects of amino acids with polar side-chain were not investigated. In this work, the effects of two amino acids with nonpolar side-chain and two amino acids with polar side-chain were examined and investigated for preventing CO_2 hydrate formation.

Experimental

In this work, CO_2 (99.9 vol% purity) was utilized for hydrate formation with double distilled water or aqueous solution of amino acids. The amino acids were supplied by Merck. The structures and properties of these amino acids are tabulated in Table 1.

Table 1. The structure and properties of applied amino acids [6]

Amino acids	Glycine (Gly)	L-proline (Pro)	L-serine (Ser)	L-threonine (Thr)
Molecular structure				
Hydrophobicity	−0.4	−1.6	−0.8	−0.7

The experimental apparatus used for the experiments were consisted of a jacketed batch reactor with a capacity of 655 cm^3. A PT100 thermometer with the uncertainty of ±0.1 K was connected to the reactor for measurements of the temperature. The reactor pressure was also measured using a pressure transmitter with an uncertainty of ±0.1 bar. In every experiment, the reactor was rinsed three times using distilled water and evacuated by a vacuum pump. The reactor was subsequently charged with 300 cm^3 of liquid sample (including water or 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 changes of reactor were 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.

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

n_{ci}, n_o, and n_i represent the moles of gas consumed up to time t_i, initial moles of gas in the reactor, and moles of gas at time t_i in the reactor, respectively. Also P, V, Z, R, and T represent the pressure, volume of gas in the reactor, compressibility factor, universal gas constant and temperature, respectively.

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 experiments were first carried out with

glycine. Fig. 1 (a) shows the effect of glycine on CO_2 hydrate formation rate. The gas consumption rate was decreased with glycine in comparison with pure water. In fact, the rate of gas consumption reflects CO_2 hydrate formation rate. On the other hand, the rate of hydrate formation decreases with increasing of concentration from 0.5 to 2 wt%. It should be noted that glycine was introduced as the best inhibitor of amino acids in literatures [4, 5]. Thus, it was selected for comparison with new amino acids in this work. The first test with new amino acids was performed with L-proline, as results shown in Fig. 1 (b). L-proline decreases CO_2 hydrate formation rate, while it is more effective to prevent hydrate formation in higher concentrations. Figs. 1 (c) and (d) show the effects of L-serine and L-threonine on CO_2 hydrate formation kinetics, respectively. They also decrease the gas consumption rate.

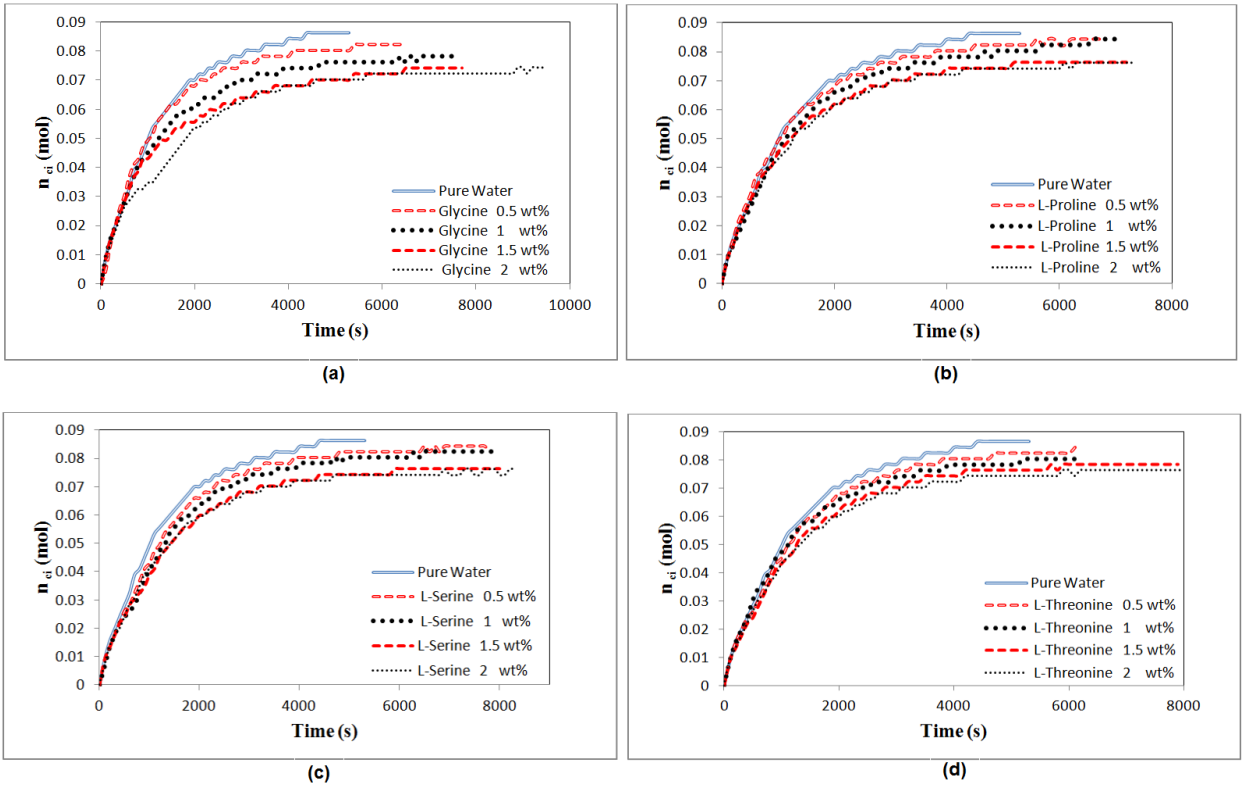


Fig. 1. The effect of glycine, L-proline, L-serine, and L-threonine on CO_2 hydrate formation rate

Therefore, the new amino acids used in this work, may be introduced as new inhibitor for hydrate formation, although the effect of these inhibitors must be compared with glycine (as the best inhibitor of amino acids up to now). Fig. 2 shows the effects of new amino acids in comparison with glycine at concentration of 2 wt%. The analysis of results at concentrations of 2 wt% shows that the inhibition effect of of L-proline, L-serine, and L-threonine are less than glycine. Based on experimental results, the ranking of amino acids as green inhibitors (to prevent CO_2 hydrate formation) is as follows: glycine > L-proline ≈ L-serine ≈ L-threonine. In fact, the experimental results show that glycine is better inhibitor than other amino acids with polar or nonpolar side-chain. Hydrophobicity values of applied amino acids are presented in Table 1. It shows that glycine with maximum hydrophobicity is the most effective one. In fact, 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 effect is increased.

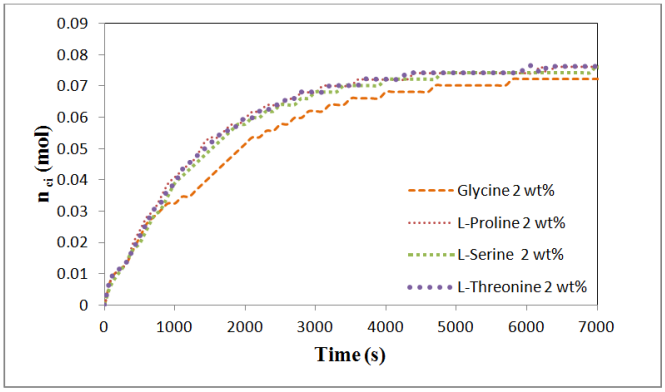


Fig. 2. The effect of used amino acids at concentration of 2.0 wt%

Conclusions

The results of the experiments showed that applied amino acids decrease CO_2 hydrate formation rate, and their inhibition effects are more at higher concentrations. Furthermore, the experimental results demonstrated that the inhibition effect of amino acids was due to hydrophobicity of the side chain. Consequently, the inhibition effect of glycine was more than L-proline, L-serine, and L-threonine.

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