Excellent synergy effect on preventing CH₄ hydrate formation when glycine meets polyvinylcaprolactam

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Abstract

The inhibitory performance of glycine and its synergistic potentiality for poly N-vinylcaprolactam (PVCap) was studied by evaluating subcooling temperature, induction time and crystal growth inhibition respectively. Glycine could not inhibit CH₄ hydrate formation alone but it could enhance the inhibitory performance of PVCap. The subcooling temperature of PVCap increased by 4.1 °C and the induction time also increased by 16-fold after blending the glycine with PVCap. Simultaneously, the performance of PVCap inhibiting hydrate crystal growth became more powerful in the presence of glycine. The rapid growth region of PVCap was totally avoided even at 13.5 °C subcooling with the help of glycine, leading crystal growth rate decreasing by 80%. The biggest difference between glycine and common synergists was that 1.0% mass fraction glycine could equivalently replace PVCap in the same amount, leading 40.8% lower cost and 23.4% higher biodegradability. Furthermore, the relationship between outstanding synergistic effect of glycine and its hydrophilic structure was studied.

1. Introduction

Gas hydrate is an ice-like solid based on water molecules, which is formed by host molecules (H₂O) and small guest gas (CH₄, C₂H₆, etc.) under proper thermodynamic condition [1,2]. Due to small guest molecules trapped into the three-dimensional lattice structure of hydrogen-bonded water molecules, gas hydrate is a good material for storage methane, separation of gas mixture or sequestration of greenhouse gases (CO₂, CH₄) [3–7]. However, natural gas hydrate formation is also recognized as a flow assurance challenge for the oil and gas industry, causing blockage of production pipeline and economic loss [8,9].
Kinetic hydrate inhibitor (KHIs) is a popular method to solve hydrate blockage problems. Poly N-vinylcaprolactam (PVCap), as a commercial kinetic hydrate inhibitor, is the most commonly used KHI in gas and oil field. PVCap is limited by its insufficient tolerant subcooling and it is usually applied in moderate conditions (<10 °C subcooling) [10,11]. To enhance the inhibition effectiveness of PVCap on delaying hydrate formation, various synergists of PVCap emerge. These synergists mainly consist of small molecules like alcohols (glycol [12,13], butoxy ethanol [14]), some salts (quaternary ammonium-based salts [15–17], tris-(dialkyl-amino) cyclopropenium chloride [18], hexa-alkyl guanidinium salts [19,20]), some polymers [21,22] (polyethylene oxide, polyethylene glycol) and ionic liquids [23,24] (1-alkyl-3-methylimidazolinium and so on).

Synergists can enhance PVCap inhibition effectiveness greatly. For example, butoxy ethanol, a typical alcoholic synergist for PVCap, could prolong the induction time of PVCap up to 30 times [14]. In term of quaternary ammonium-based salts, tetra (iso-hexyl) ammonium bromide (TiHexAB) performed outstandingly among them as a synergist for PVCap with 0.25% mass fraction. TiHexAB with 0.25% mass fraction decreased the onset temperature of PVCap by 6.2 °C [15]. As a typical alkylguanidinium salt, hexa-butylguanidinium bromide with 0.25% mass fraction increased the subcooling of PVCap by 6.5 °C when combined with PVCap [20]. Besides, ionic liquids are also synergists for PVCap. The induction time of PVCap with 0.5% mass fraction was prolonged from 22.8 min to 120.3 min when PVCap is mixed with 0.5% mass fraction of [EMIM][BF₄] (1-butyl-3-methylimidazolium) and so on. Among current synergists of PVCap, quaternary ammonium-based synergists and their derivations are outstanding. However, these excellent synergists are faced with inaccessible properties.

The activity of amino acids, the cheap and green material, as hydrate inhibitors has been investigated. Sa et al. [26] proved that glycine and L-alanine had a good prospect as thermodynamic inhibitors for CO₂ hydrate formation. Sa et al. [27] also studied that the kinetic effect of hydrophobic amino acids on CO₂ hydrate formation. The results demonstrated that glycine and alanine performed kinetic effect on delaying the CO₂ hydrate formation, which is weaker than that of poly N-vinylpyrrolidone (PVP). Varaminian et al. [28] studied the ability of glycine, L-serine, and L-histidine on preventing CO₂ hydrate formation. The result proved that only L-histidine manifested the effectiveness of kinetic inhibition though not significant. Moreover, the molecular simulation showed that only asparagine could suppress hydrate growth [29].

Although amino acid as kinetic hydrate inhibitors has been investigated, the inhibitory performance of amino acid is not good. Amino acids, possessing amine and carboxylic acid groups, can decrease the activity of water molecules by forming hydrogen bond, which may be a potential synergist of typical KHIs. Hence, the synergy effect of glycine for PVCap in the CH₄/H₂O system is investigated in this paper.

2. Experimental section

2.1. Materials

PVCap, whose molecular weight was about 1500 Da, was synthesized by free-radical polymerization of N-vinyl-2-pyrrolidone in diethylene glycol monobutyl ether [30]. Glycine with 99.9% mass fraction was obtained from Aladdin Co. Ltd. (Shanghai, China). Methane with 99.9% mass fraction was supplied by Guangzhou Zhuozheng Gas Industry Co. Ltd. Distilled water used in all experiments was weighed on an electronic balance with an accuracy of ±0.1 mg.

2.2. Apparatus

The induction time test was carried out in autoclaves, consisting of six identical magnetic-stirred steel cells each measuring 100 ml in volume. Detailed schematic and description of the setup had been demonstrated in our previous literatures [8,30]. The subcooling temperature and CGI region were conducted on the designed 310 ml autoclave where temperature was controlled by a thermostat bath (Huber CC805) and it is shown in Fig. 1. In both apparatus, the allowable operational temperature and pressure ranges for the vessels were −50.0 °C to 250.0 °C and 0.0 MPa to 30.0 MPa, respectively. The platinum resistance thermometers (PT100) with an accuracy of ±0.1 °C was placed inside vessels to measure the temperatures. A pressure transducer with an accuracy of ±0.01 MPa was used to measure internal pressure of vessels. The results were recorded by a data logger (Agilent 34970A).
2.3. Methods

The isothermal cooling method [31] was used to measure the induction time. Detailed test procedures also could be found in our previous studies [8,30,32]. In the beginning, the temperature was adjusted to (1 to 2) °C above equilibrium points at the corresponding pressure in the experiment. Then the temperature of vessel was cooled down to 1.5 °C and after that it was kept for 48.0 h. There were 5 parallel experiments for testing induction time.

The constant cooling method [33,34] was used to test the subcooling temperature of inhibitors. The cooling rate was usually 1 °C/h to induce hydrate formation at initial temperature (25.0 °C). The onset temperature where the hydrate nucleus first occurred was recorded as \( T_0 \). The subcooling temperature was defined by the difference between phase equilibrium temperature and the \( T_0 \). The typical test procedure could be found anywhere [33–38].

The crystal growth inhibition (CGI) method was used to evaluate hydrate growth rates in the presence of a small amount of hydrate crystal. The CGI method was developed by Anderson et al. of Herriot Watt University [39] and it was proved to be a reliable technique [40,41] in practice. The procedures consisted of several cycles of hydrate growth-dissociation in the presence of hydrate crystal. With the initial temperature of 25 °C, the system was cooled for inducing hydrate formation at 11.6 MPa, of which the corresponding equilibrium temperature was 14.0 °C [42]. With abundant hydrate presenting in cell, temperature would be increased to dissociate the hydrate until there was a small amount of hydrate (<0.5% mass fraction water converted as hydrate). In order to confirm the results, several cooling/heating were conducted in the presence of small hydrate. Both the detailed test process and divided standard of inhibition region (shown in Table 1) could be found in many literatures [13,30,41]. Crystal inhibition regions can be divided into such four parts as complete inhibition region (CIR), slow growth region (SGR), rapid growth region (RGR) and slow dissociation region (SDR). The divided standard of different inhibition regions was shown in Table 1.

<table>
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KHI induced CGI region and typical hydrate growth rates.

<table>
<thead>
<tr>
<th>CGI region</th>
<th>Typical growth rates ( V_g ) (%/h)</th>
<th>Growth rate description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIR</td>
<td>0</td>
<td>No growth</td>
</tr>
<tr>
<td>SGR(S)</td>
<td>0.1 (0 &lt; ( V_g &lt; 0.5 ))</td>
<td>Slow growth</td>
</tr>
<tr>
<td>SGR(M)</td>
<td>1 (0.5 ( \leq V_g &lt; 5.0 ))</td>
<td>Medium growth</td>
</tr>
<tr>
<td>RGR</td>
<td>10 (5.0 ( \leq V_g ))</td>
<td>Rapid growth</td>
</tr>
<tr>
<td>SDR</td>
<td>Dissociation rate one order of magnitude less</td>
<td>Abnormally dissociation</td>
</tr>
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3. Results and discussion

3.1. Hydrate nucleation process

The typical curve of pressure and temperature in testing subcooling temperature of KHIs was shown in the Fig. 2. Maximum subcooling temperature that glycine could reach were shown in Fig. 3. The system without additive was regarded as a blank test and the subcooling temperature of the blank test was 3.2 °C. The subcooling temperature of glycine with 1.0% mass fraction was 3.3 °C, nearly equal to that in the blank test. Even though the mass fraction of glycine exceeded 7.0%, the subcooling temperature was merely 6.5 °C. Glycine had negligible kinetic inhibitory performance.

![Fig. 2. The typical curve obtained by constant cooling test with PVCap and 1.0% mass fraction glycine.](image)

![Fig. 3. The subcooling degree of glycine with different concentration.](image)
However, glycine could improve the subcooling temperature of PVCap. The results shown in Fig. 4 proved that the synergetic effect of glycine for PVCap became more obvious with the increase of glycine concentration. Glycine with 1.0% mass fraction slightly increased the subcooling temperature of PVCap while 5.0% mass fraction and 7.0% mass fraction glycine would improve it by 2.6°C and 4.1°C respectively. The synergistic effect of glycine for PVCap in terms of increasing subcooling temperature was due to thermodynamic inhibition. Sa et al. [32] proved that glycine could decrease the phase equilibrium temperature of CO2 hydrate. Glycine possessed both amine and carboxylic acid groups in its molecular structure. The hydrophilic nature of glycine decreased the activity of water molecules through hydrogen bonds. Mixing PVCap with glycine, the effective groups from PVCap as well as glycine would form more hydrogen bonds with water molecules, leading to stronger disruption of water structures. As a result, the subcooling temperature of PVCap would be improved.

The induction time of combination inhibitors consisting of PVCap and glycine was summarized in Fig. 5. The results from induction time tests showed that glycine with 1.0% mass fraction could equivalently replace PVCap in the same amount. For comparison, the induction time of PVCap with 0.5% mass fraction was measured (5.0 h). At both subcooling temperatures (10.0°C and 12.0°C), induction time of 0.5% mass fraction PVCap and 1.0% mass fraction glycine was longer than that of 1.5% mass fraction PVCap alone. It seemed that the enhancement of inhibitory effectiveness brought by 1.0% mass fraction glycine equaled to that of 1.0% mass fraction PVCap. Besides, glycine with high concentration could further prolong the induction time of the PVCap. The induction time of combination inhibitor containing PVCap and glycine exceeded 48.0 h once the mass fraction of glycine exceeded 5.0%, which was as 16.0 times long as that without glycine. As a small molecule with hydrophilic group, glycine might easily approach to water molecules, disrupting the liquid water structure around PVCap polymers. Both glycine and PVCap interacted with water molecules so that it required more time for water clusters to aggregate as nuclei. Hence, the induction time of PVCap would be improved significantly when PVCap was used with glycine together.

The CGI method was used to determine the crystal growth boundaries of PVCap in the presence of glycine. By this means, hydrate stochastic nucleation process was avoided. Crystal growth rates represented the ability of the KHIs to retard crystal growth. At first, the crystal growth rates in the presence of glycine were tested. Fig. 6 showed pressure & temperature curves for CH4 with glycine aqueous solutions in the presence of 0.21% hydrate during the cooling and heating experimental process. The results showed that glycine had no capacity in retarding hydrate crystal growth. Once the pressure and temperature entered hydrate formation
zone, the hydrate crystal in glycine aqueous solution started growing at a rate of 4.61%/h, which was almost as fast as the growth rate in pure water system.

Fig. 7 showed pressure & temperature curves during cooling and heating experimental process for CH₄ with 1.5% mass fraction PVCap and combination inhibitor containing 0.5% mass fraction PVCap and 1.0% mass fraction glycine. For PVCap with 1.5% mass fraction, the nucleation occurred at 4.8 °C on the first cooling run. Next, the cell was heated rapidly to dissociate the hydrate until only 0.42% water remained as hydrate. Then, two cooling and heating cycles were conducted. The result (Figure in 7a) showed that the hydrate growth rate was very rapid (2.98%/h) when it crossed over slow growth region. As a result, 9.65% of water in the cell converted into hydrate when the temperature reached 1.0 °C in the presence of 1.5% mass fraction PVCap. The inhibitory performance of combination inhibitor was close to that of 1.5% mass fraction PVCap. The hydrate crystal in the system containing 0.5% mass fraction PVCap plus 1.0% mass fraction glycine occurred relatively earlier but grew slower than in the system with 1.5% mass fraction PVCap (shown in Fig. 7b). Ultimately, the amount of hydrate was approximately equivalent in two systems at the same condition.

Subsequently, the influence of the concentration of glycine on inhibition performance of PVCap was also investigated. The CGI
tests were conducted for the systems under 0.5% mass fraction PVCap plus 3.0% mass fraction or 5.0% mass fraction glycine, respectively. Fig. 8 showed temperature & pressure curves during three cooling and heating cycles for CH₄ system with 0.5% mass fraction PVCap plus 3.0% mass fraction glycine. The phase curve of methane hydrate was shown for comparison [42]. In the presence of 0.32% hydrate, no hydrate growth was detected until the temperature reached 6.2 °C. Then hydrate crystal grew at the rate of 0.25%/h when the temperature cooled from 6.2 °C to 5.5 °C. At the temperature of 5.5 °C, crystal growth rate suddenly increased from 0.31%/h to 0.68%/h. At the end of the cooling process, the maximum growth rate was no more than 1.51%/h although the subcooling temperature reached 12.5 °C. Interestingly, when the temperature in the cell was heated 2.6 °C higher than phase equilibrium temperature, the hydrate dissociation continued at the speed of 0.07%/h, which was only 5% of decomposition rate with no additives. From the similar growth patterns in three cycles, four growth regions were apparently obtained. The boundary of CIR, SGR(S), SGR (M) and SDR were as follows: ΔTs-I = -7.8 °C, ΔTs-I = -8.4 °C, ΔTs-I = -13.2 °C, ΔTs-I = +2.6 °C.

As it is shown in Fig. 9, the PVCap mixed with 5.0% mass fraction glycine could powerfully hinder hydrate growth. Maximum hydrate growth rate did not exceed 1.1%/h in the experimental process. The CIR, SGR(S), SGR (M) and SDR boundaries of 0.5% mass fraction PVCap plus 5.0% mass fraction glycine were as follows: ΔTs-I = -7.9 °C, ΔTs-I = -9.6 °C, ΔTs-I = -13.5 °C, ΔTs-I = +2.4 °C, respectively.

The subcooling extents of inhibitors-induced the CGI regions of 0.5% mass fraction PVCap plus glycine with different concentrations were summarized in Fig. 10. For comparison, the CGI regions of 0.5% mass fraction PVCap were measured, which were similar with the literature value [40]. Glycine itself could not retard the hydrate crystal growth whereas it could remarkably improve the inhibitory strength of PVCap as a synergist. After introducing 1.0% mass fraction glycine, the completed inhibition region of PVCAp extended 1.8 °C to low temperature zone. Besides, the rapid growth region (RGR) of PVCap was completely replaced by slow growth region (SGR) even the subcooling reached 13.5 °C. Additionally, the synergistic effect of glycine was in positive correlation to its concentration in the range tested. The subcooling ceiling of CIR and SGR(S) of PVCap increased by 1.8 °C and 1.6 °C when the mass fraction of glycine increased from 1.0% to 3.0%. Similarly, the very slow growth region of PVCap shifted 1.2 °C to lower temperature region when the mass fraction of glycine increased from 3.0% to 5.0%.

As we know, the multilayer adsorption of PVCap on hydrate surface was not dense and some capillary channel would form between different layers where the hydrate former could freely pass [43]. Due to capillary channel, the kinetic inhibitors did not successfully inhibit the crystal growth or even promote the crystal growth, which had been reported in literatures [23,35]. Glycine as a small molecule might easily penetrate into spaces that polymer chains could not cover, resulting in occupying the channel that hydrate formers got through. The possible process of PVCap plus glycine interacted with hydrate crystal was shown in Fig. 11. Therefore, this behavior of glycine could help PVCap more effectively retard crystal growth by reducing the diffusion of CH₄ or water molecules from the bulk phase to cluster where the crystal preferred to grow.

### 3.3. Biodegradability and economy

The measurement of BOD₅ and COD were carried out based on HJ 505-2009 standards and GB/T 11914-1989 standards of China. The wastewater was usually considered as hardly biodegradable when the value of BOD₅/COD was less than 0.20 [44]. From the above point, BOD₅/COD value of 0.25% mass fraction PVCap was 0.249, which was not easy to be biodegraded. Biodegradability of 0.25% mass fraction PVCap plus 0.75 mass fraction was 0.325. Glycine could improve the biodegradability of PVCap by 23.4%. Besides, compared with the commercial PVCap ($23.52/kg), 1.0% pectin can replace 1.0% PVCap, whose usage can save almost $22,359 per ton producing water and make the cost decreased by 40.8%.

### 4. Conclusion

Glycine itself was not a good kinetic hydrate inhibitor, which could not inhibit the CH₄ hydrate formation. However, the capacity of glycine as a synergist of PVCap was outstanding. The subcooling temperature of PVCap would increase by 4.1 °C and the induction
time would increase to 16-fold in the presence of glycine. Besides, both CIR and SGR(S) of PVCap extended more than 1.8 °C in the presence of glycine. And the rapid growth region of PVCap was completely controlled even at the subcooling temperature of 13.5 °C, which also decreased the hydrate crystal growth rate by 80%. It was striking that glycine could equally replace PVCap in the same amount when glycine was used with PVCap together. The inhibitory effect of 0.5% mass fraction PVCap with 1.0% mass fraction glycine was equivalent to the inhibitory activity of 1.5% mass fraction PVCap. Glycine would decrease the cost of PVCap by 40.8% and increase the biodegradability by more than 23.4%. The hydrophilic nature of glycine might help the polymer to disrupt more water molecules and enhanced the strength of PVCap delaying hydrate nucleation. What’s more, glycine as a small molecule could easily approach to the places where macromolecule polymer could not cover, forming additional transfer resistance when CH₄ or water molecules transported toward hydrate clusters. Hence, the hydrate growth rate would be reduced when PVCap was used with glycine together.

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References


