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Full Length Article

Excellent synergy effect on preventing CH_4 hydrate formation when glycine meets polyvinylcaprolactam

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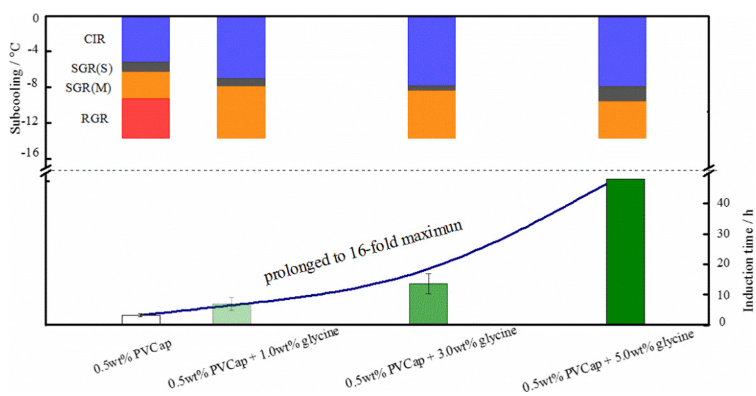
HIGHLIGHTS

- Glycine had weak inhibitory effect while cloud enhance the performance of PVCap.
- The induction time of PVCap increased 16-fold with the help of glycine.
- The rapid growth region of PVCap was avoided in the presence of glycine.
- Glycine significantly decrease the cost and improve biodegradability of PVCap.

GRAPHICAL ABSTRACT



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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 CH_4 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 (H_2O) and small guest gas (CH_4, C_2H_6, CO_2, C_3H_6, 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 (CO_2, CH_4) [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].

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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 alkylguanidium 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 [EMIM][BF_4] (1-butyl-3-methylimidazolium) with 0.5% mass fraction [24,25]. Among current synergists of PVCap, quaternary ammonium-based synergists and their derivations are outstanding. However, these excellent synergists are faced with inaccessible to obtain or toxic problems.

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 CO_2 hydrate formation. Sa et al. [27] also studied that the kinetic effect of hydrophobic amino acids on CO_2 hydrate formation. The results demonstrated that glycine and alanine performed kinetic effect on delaying the CO_2 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 CO_2 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 CH_4/H_2O 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 apparatuses, 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).

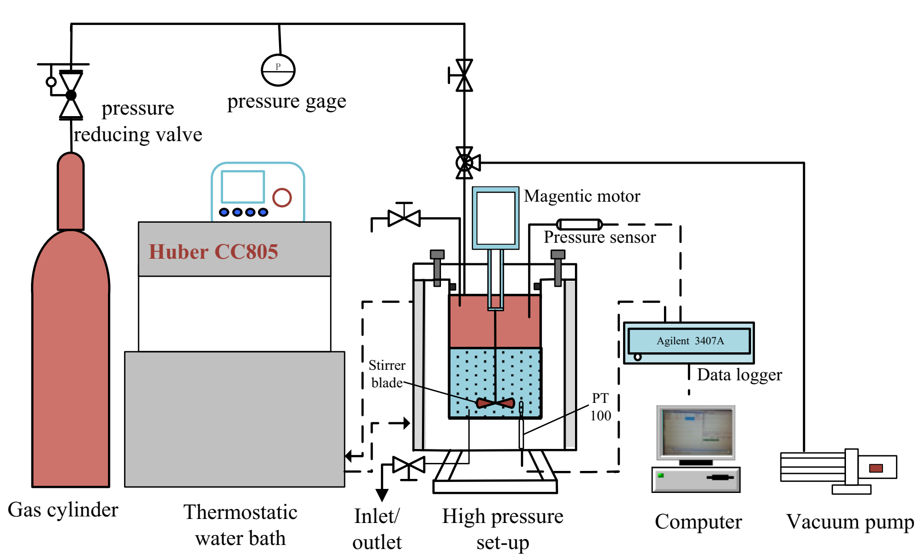

Fig. 1. Schematic illustration of the 310 mL autoclave used in experiments.