

Recovery of monoethylene glycol combined with kinetic hydrate inhibitor



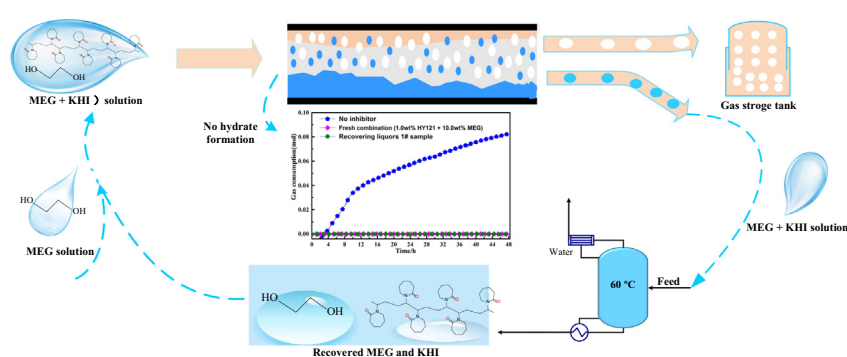
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HIGHLIGHTS

- The recovery rate of MEG was affected by the temperature rather than HI-121.
- HI-121 could be recovered along with MEG under proper recovery conditions.
- HI-121 with various polymer chain lengths reduced the *TIE* of the recovered MEG.
- The solution recovered under milder conditions retained good inhibitory performance.
- Adding 5 wt% MEG restored the recovered solution performance to original levels.

GRAPHICAL ABSTRACT



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ABSTRACT

Kinetic hydrate inhibitors (KHIs) combined with thermodynamic inhibitors (THIs) such as monoethylene glycol (MEG) have been good additives for the prevention of hydrate blockages in oil and gas industry operations. The regeneration and recycling of MEG are conventional process steps used to reduce costs. However, the recovery of THIs in the presence of KHIs or the recovery of the KHIs alone has rarely been investigated. In this paper, a series of experiments was designed to study the recovery of both a KHI based poly (N-vinylcaprolactam) and MEG. The results showed that the MEG recovery rate was closely related to the recovery temperature, but was not influenced by the KHI. The MEG recovery rate from solutions consisting of MEG and the KHI was as high as 94.52%, and the KHI was recovered along with the MEG. The polymer structure of the KHI was rarely changed when the recovery temperature was close to its polymerization temperature. The presence of the KHI had a negative impact on the thermodynamic inhibition efficiency of the MEG. The KHI performance of the recovered solution obtained at the KHI polymerization temperature could reach the level of the fresh combination inhibitor, but the recovered solutions obtained at temperatures far above the KHI polymerization temperature demonstrated worse inhibitory performance. The kinetic performance could be restored by adding 5.0 wt% fresh MEG. MEG enabled a subcooling temperature decrease into the range in which KHI which could play its role effectively, leading to the improved kinetic performance of the recovered solution.

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1. Introduction

Natural gas hydrates are ice-like crystalline solids that contain small guest molecules in cages formed by hydrogen-bonded water molecules (Sloan and Koh, 2008; Sum et al., 2009). Under appropriate conditions of temperature (typically less than 30.0 °C) and pressure (typically greater than 2.0 MPa), gas hydrates can form anywhere that water molecules coexist with potential guest molecules such as methane, carbon dioxide, or nitrogen (Igboanusi and Opara, 2011; Perrin et al., 2013). Consequently, natural gas hydrates have posed serious problems in oil and gas production systems, because clogging of the gas and oil transmission pipelines by the hydrates can lead to safety risks and financial loss (Perrin et al., 2013; Sloan et al., 2011). To solve this problem, a variety of methods such as thermal heating, depressurization, and mechanical elimination have been suggested. The injection of hydrate inhibitors into the pipelines has become the most popular approach in the gas and oil industries (Sloan and Koh, 2008; Sa et al., 2015).

Hydrate inhibitors can be generally classified as thermodynamic inhibitors (THIs) or low-dosage hydrate inhibitors (LDHIs). Historically, THIs such as methanol, monoethylene glycol (MEG), and a variety of salts have been widely used in deep-water drilling operations (Sa et al., 2011). These agents shift the thermodynamic conditions of hydrate formation outside the temperature and pressure ranges used during operation, leading to the complete prevention of hydrate formation. Nowadays, instead of the typical methanol inhibitor, MEG has become a popular choice for its environmental friendliness (Brustad et al., 2005). However, this inhibitor is expensive, because large amounts of MEG must be injected into the pipeline (20–60 wt% of the water produced) (Creek, 2012). To reduce operating costs, the MEG is usually recovered and recycled. The most common regeneration system for monoethylene glycol is a MEG recovery unit (MRU) (Allenson and Scott, 2010). Although the MRU affords an economical method for MEG recovery, the system is bounded by an upper limit in terms of how much MEG can be recovered. Consequently, the operator must limit production by shutting down high water-producing wells or adding fresh MEG. In an industrial production process, either option will severely impact the cost profile. Hence, the more desirable solutions to reducing the costs of high MEG injection dosages are the LDHIs.

Kinetic hydrate inhibitors (KHIs), a type of LDHI, are water-soluble polymers which delay hydrate nucleation and growth for a certain amount of time under particular subcooling conditions (Luna-Ortiz et al., 2014). Typical KHIs are polymers based on 5- and 7-membered-ring *N*-vinyl lactams, such as poly(*N*-vinylpyrrolidone) (PVP) and poly(*N*-vinylcaprolactam) (PVCap) (Cha et al., 2013; Kim et al., 2011; Kang et al., 2013; Sharifi et al., 2014; Reyes and Kelland, 2013). One of the main advantages of KHIs is that the effective dosage is 0.5–2.0 mass% of the water produced, which is one percent of THIs. However, KHIs are not the best solution for hydrate prevention because the current commercial inhibitor requires effective subcooling below 12.0 °C in field applications (Lou et al., 2012; Xu et al., 2015; Sun, 2012; Clark and Anderson, 2007). This could be an issue, for example, the subcooling required in offshore deep-water or ultra-deep-water systems as high as 20.0 °C (Lovell and Pakulski, 2002; Argo et al., 2000; Budd et al., 2004; Rithauddeen and Al-Adel, 2014; Higgins et al., 2006). In such systems, hydrate prevention cannot be optimally controlled using KHIs alone.

Fortunately, the use of combined KHI/THI treatments has provided a solution for overcoming these problems, by improving the subcooling requirements for the KHIs and reducing the THI dosages. Thus, the THIs can modulate the subcooling temperature

into the range appropriate for KHI application, while the KHIs can significantly reduce the THI injection amounts. Thus, composite inhibitors consisting of KHIs and THIs have become active areas of research (Allenson and Scott, 2010; Cha et al., 2013; Kim et al., 2014; Mozaffar et al., 2016; Mitchell and Talley, 1999; Swanson et al., 2005). In laboratory-based testing, the good performance of a composite inhibitor that included a KHI and THI has been confirmed. Kim et al. (Kim et al., 2014) indicated that replacing a high dose of MEG with 0.2 wt% KHI was a good option, reducing the injection of MEG by 20.0 wt%. Mozaffar et al. (Mozaffar et al., 2016) proved that MEG has a very positive effect on PVCap as hydrate inhibitor and the combination of MEG + PVCap or MeOH + PVCap offers far better inhibition by mass/volume inhibitor than MEG or MeOH alone. In field applications, it is rare to use inhibitor combinations consisting of KHIs and THIs; successful cases have only injected a KHI or THI. Table 1 summarizes the applications of KHIs replacing THIs in the oil and gas fields.

In oil and gas industry applications, THIs are usually recovered to a large extent due to their mature recovery processes, whereas the low doses of KHIs are directly discharged. However, this lack of KHI recovery may result in fouling of the produced water. To reduce the pollution caused by KHI discharge, Anderson et al. (Anderson et al., 2016) introduced a method to remove them from the produced water, achieving a KHI removal rate of 90.0% by solvent extraction. In an actual field application, special techniques such as centrifugal separation or filtration must be included in water treatment processes, which may incur extra operational expenses and even alter the process. Compared with the KHI removal method, other approaches such as the recycling of both the KHI and THI would be convenient and less costly, if the recycling measures were feasible. The recovery of THIs in the presence of KHIs or the recovery of KHIs alone has been rarely investigated. It is not clear whether both kinds of inhibitors can be recovered or the inhibitory performance of the recovered inhibitors would be good. These problems must be addressed to advance the industrial application of combined KHI/THI inhibitors to prevent hydrate formation.

In this work, the recovery efficiency of MEG and a KHI was studied under different operating conditions. The thermodynamic performance of the recovered MEG was also evaluated in a high-pressure autoclave. Additionally, the kinetic inhibitory performance of recovered solutions consisting of MEG and the KHI was investigated systematically. Finally, the thermodynamic and kinetic inhibitory performance properties were studied with a multicomponent gas having the same composition of the natural gas distributed in the South China Sea. These studies will lead to a completely new understanding of the recovery and reuse of combined MEG/KHI hydrate inhibitors.

2. Experimental section

2.1. Materials

A proprietary KHI (HI-121; number-average molecular weight, $M_n = 1120$) was synthesized by the free-radical polymerization of *N*-vinylcaprolactam in diethylene glycol monobutyl ether (Yang et al., 2012). MEG with a minimum purity of 99.9 mol% was obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetone and methanol were obtained from Aladdin Co., Ltd. (Shanghai, China). The composition of the synthetic gas which was supplied by the Guangzhou Zhuozheng Gas Industry Co. Ltd. is shown in Table 2. The simulated formation water used in all experiments was weighed on an electronic balance with an accuracy of ± 0.1 mg, its composition is shown in Table 3.

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