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# Relationship between the interfacial tension and inhibition performance of hydrate inhibitors



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## HIGHLIGHTS

- Kinetic inhibition behavior and gas/liquid interfacial tension were investigated in parallel with respect to different hydrate forming systems.
- Lower interfacial tension corresponds to higher kinetic inhibition performance.
- New insights into the mechanisms of both kinetic inhibition of KHIs and synergic effect of alcohols were presented.
- New rule for developing KHI or screening KHI synergist was proposed and triglycol was found to be a good synergist.

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## ABSTRACT

In this study, we tried to establish the relationship between the kinetic inhibition performance of KHIs and their effects on interfacial properties, such as the interfacial tension between hydrate-forming gases and aqueous solutions. The hydrate onset time and gas/liquid interfacial tension for systems composed of the same natural gas and aqueous phases containing different kinetic hydrate inhibitors (KHIs) and KHI synergists were measured in parallel. Five amide class KHIs, PVP-E, PVP-A, PVP-BP developed by our group, as well as PVP and Inhibex 501 were tested. Four familiar alcohols, methanol, ethanol, glycol and triglycol, were used as synergists. All of the experimental results with different types or dosages of KHIs and synergists show that a lower interfacial tension corresponds to a longer onset time, i.e., a better kinetic inhibition performance. We therefore suggested a lowest gas/liquid interfacial tension rule for developing amide class KHIs or KHI synergists as well as for determining their suitable applied dosages. Additionally, triglycol was found to be a good synergist for PVP-BP, and its best applied dosage is 2.3 wt% or so. Finally, we proposed new insights into the mechanisms of both the kinetic inhibition of KHIs and the synergistic effect of alcohols.

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## 1. Introduction

Gas hydrates are types of non-stoichiometric, ice-like crystalline compounds that are formed through combinations of water with suitably sized guest species under suitable temperatures and pressures (Sloan and Koh, 2008; Eslamimanesh et al., 2011). Gas hydrates can lead to both benefits and hazards for humans. *In situ* natural gas hydrates widely found beneath the ocean floor and in the permafrost region might become new potential energy resources. By contrast, the formation of gas hydrates in gas and oil pipelines or other petroleum production and transport equipment may lead to serious hazards, such as plugging (Sloan, 2003). Since hydrate plugging was first identified by Hammerschmidt in 1934 (Wu et al., 2007; Hammerschmidt, 1934), petroleum industries

have paid considerable attention to the inhibition of hydrate formation in their facilities. Traditionally, hydrate formation was prevented by injecting thermodynamic inhibitors, such as methanol and glycol at a high dosage so that the hydrate equilibrium phase boundary is shifted to significantly lower temperature and higher pressure conditions (Mohammadi and Richon, 2010; Li et al., 2006; Sun et al., 2012). Considering the economic and environmental concerns, the development and application of low-dosage hydrate inhibitors (LDHIs) has drawn an increasing amount of attention in recent decades (Kelland, 2006). LDHIs usually refer to kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). KHIs are usually water-soluble polymers. They inhibit hydrate formation not by changing the thermodynamic formation conditions for the hydrate because of their low dosage (< 1 wt%), but by prolonging the onset time and dramatically decreasing the growth rate of hydrate crystals (Chen et al., 2015). AAs prevent facilities from plugging by controlling the morphology of the hydrate to be

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fine particles that can act as a fluid (Yan et al., 2014; Flourey et al., 2000; Zerpa et al., 2011; Peng et al., 2012).

Until now, the inhibition mechanisms of KHIs have not been very clear. Scientists are very interested in what happens between KHIs and the hydrate nuclei or particles. Additionally, KHIs are often used in conjunction with synergists that can significantly enhance the kinetic inhibition performance of KHIs (Perrin et al., 2013). However, the synergistic mechanisms are not clear.

Most KHIs are water-soluble polymers such as PVP, Gaffix VC-713, Inhibex 501. It is believed that the adsorption of KHI molecules on the surface of hydrate nuclei plays a critical role in inhibiting the hydrate formation (Lederhos et al., 1996). Certainly, these KHI molecules may also be absorbed by the surface of aqueous phase and therefore affecting the gas/liquid interfacial properties. Considering both surfaces of aqueous phase and hydrate are dominated by water molecules, we think one can learn the adsorption behavior of KHI molecules on the surfaces of hydrate nuclei indirectly by investigating gas/liquid interfacial properties. In the literature, interfacial tension data near the hydrate formation conditions are relatively scarce. The majority of the data in the literature (Slowinski et al., 1957; Massoudi and King, 1975; Sachs and Meyn, 1995) have been measured at temperatures above 296 K, as Schmidt et al. (2007) summarized. For cases with surfactants, Watanabe et al. (2005) reported the interfacial tension of methane/water with sodium dodecyl sulfate (SDS) near the hydrate-formation conditions. In our lab, Peng et al. (2009) measured the interfacial tension of a methane/aqueous VC-713 solution within temperature and pressure ranges of 274.2–282.2 K and 0.1–20 MPa. Sun et al. (2004) measured the interfacial tension of methane/water with sodium dodecyl sulfate (SDS) in the temperature range of 273.2–298.2 K and pressures of up to 10 MPa. Liu et al. (2009) measured the interfacial tension of methane/water with kinetic inhibitors, Inhibex 301, and Inhibex 501 within temperature and pressure ranges of 274.2–282.2 K and 0.1–20.1 MPa. However, no kinetic data for the formation of hydrates accompanied these interfacial tension data. These kinetic data are very important to pursue the inherent relationship between kinetic inhibition behavior and interfacial properties.

In this work, we investigate the kinetic inhibition mechanism together with the synergic effect of several alcohols by measuring both the onset times of hydrate formation and the gas/liquid interfacial tensions with respect to a series of systems composed of natural gas and aqueous solutions with different types or dosages

of kinetic additives. The experimental results show that the performance of kinetic inhibition strongly depends on the interfacial tension. Based on these results, some new insights into the mechanisms of both the kinetic inhibition of KHIs and synergic effect of alcohols were obtained.

## 2. Materials and methods

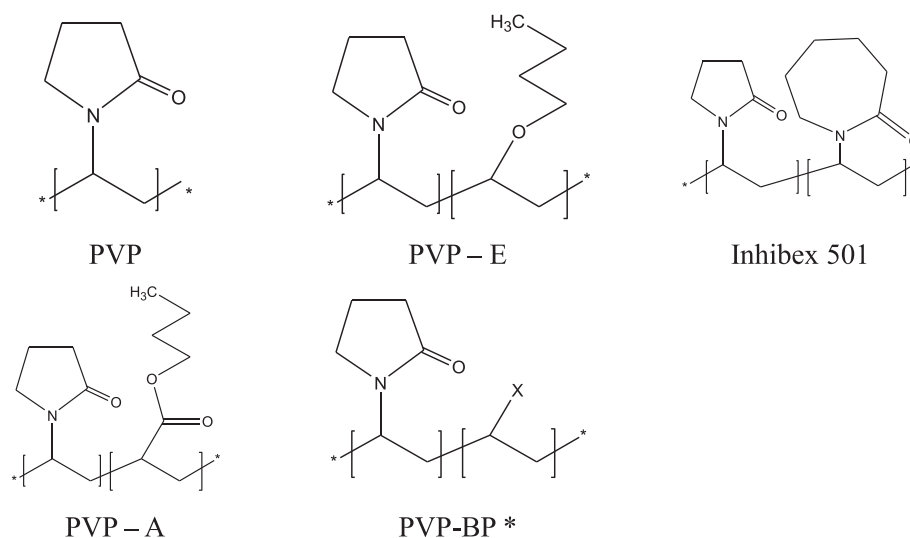
### 2.1. Materials

Hydrate kinetic inhibitors, PVP-BP, PVP-E and PVP-A were all produced in our laboratory (Qin et al., 2015). The Inhibex 501 was obtained from ISP (International Specialty Products), Inc. USA. PVP was bought from Sigma-Aldrich. The KHIs used in the study belong to the same amide class, which are all the ramification of PVP. Their molecular structures are shown in Fig. 1. Methanol, ethanol, glycol, triglycol and petroleum ether were all analytical reagent (AR) grade and purchased from Aladdin Industrial (United States). The natural gas used to form hydrates was supplied by Beijing Beifen Gases Industry Co., Ltd. Its composition was determined three times by an HP 7890 gas chromatograph, and the average value is shown in Table 1. The equilibrium formation conditions of the natural gas hydrate in aqueous solutions were predicted by the Chen–Guo hydrate model (Chen and Guo, 1996; 1998) and were used to determine the subcooling of hydrate formation systems.

### 2.2. Hydrate inhibition performance test

In this work, the kinetic inhibition performances of KHIs together with the synergists were tested in a high-pressure sapphire cell that has been described in previous papers (Chen et al., 2009; Wang et al., 2009; Zhang et al., 2005; Zhang et al., 2006). A schematic of the apparatus is shown in Fig. 2. The main part of the apparatus is a transparent cylindrical sapphire cell with a maximum working pressure of 40 MPa. This cell is mounted in an air bath with a view window and is equipped with a magnetic stirrer for mixing gases and liquids. The uncertainties of the temperature and pressure measurements are  $\pm 0.10$  K and  $\pm 0.01$  MPa, respectively. The temperature of the air bath is stable within  $\pm 0.10$  K.

Before each experimental run, the transparent cell was soaked and rinsed with ethanol and then with petroleum ether to remove possible residual impurities. Subsequently, it was dried by purging



\*X refers the group containing phenyl group

Fig. 1. Molecular structure of KHIs.

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