



The synergism of the binary and ternary solutions of polyethylene glycol, polyacrylamide and Hydroxyethyl cellulose to methane hydrate kinetic inhibitor



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ABSTRACT

This study investigates the hydrate inhibition performance of three polymers, polyethylene glycol (PEG), polyacrylamide (PAM) and hydroxyethyl cellulose (HEC), with a well-known kinetic inhibitor, polyvinylpyrrolidone (PVP), to retard the hydrate onset as well as decelerating the crystal growth rate of methane hydrate. A high-pressure reactor with experimental operation conditions of temperature of 275.15 K, initial pressure of 6 MPa and stirring speed of 900 rpm has been utilized. It is observed that the addition of PEG, PAM or HEC to the PVP solution enhances inhibition efficiency, so that it causes a more increase (about 2–8 times) in the induction time and hydrate growth rate become slower than that of the inhibitor alone. The same concentrations of three additives (PEG, PAM and HEC) have represented different effects on the PVP solution. HEC and PAM solutions have respectively showed the highest induction time and the lowest crystal growth rate compared to other solutions. Also, it has been found that ternary solution of inhibitors can be better selection than binary solution of them to increase the hydrate inhibition performance, so that these solutions can prolong the hydrate nucleation up to 20 times and slow significantly down the crystal growth rate by 70% compared to the inhibitor alone.

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1. Introduction

Natural gas hydrates are crystalline solids, in which small gas molecules are trapped inside hydrogen bonded water cages (Carroll, 2002; Sloan and Koh, 2008). Gas hydrates are considered as a challenging problem for oil and gas industry since they plug pipelines requiring costly remedies (Sun et al., 2011). The studies related to the problematic side of gas hydrates are attempting to find the methods for gas hydrate inhibition (Ng and Robinson, 1994; Niang et al., 2010). Many mechanical methods to prevent hydrate formation (like insulated flow lines and active heating) can be expensive, impractical or ineffective under some conditions (Patel and Russum, 2010). The most common way to prevent gas hydrate formation is chemical inhibition. The traditional hydrate inhibitors are thermodynamic inhibitors such as methanol and glycols, which use of these chemicals is more costly since their effective concentration may be as high as 30–50% on the free water basis (Keshavarz Moraveji, 2012; Roosta et al., 2013).

Replacing these traditional thermodynamic inhibitors with a low dosage hydrate inhibitors can lead to very substantial cost savings. Kinetic hydrate inhibitors (KHIs) are now a well-known low dosage hydrate inhibitor, which are water soluble polymers designed to delay hydrate nucleation and growth (Chua et al., 2011a; Kelland, 2011; Kelland, 2006). Most classes of KHI polymers are vinylic polymers such as polyvinylpyrrolidone (PVP), polyvinylcaprolactam (PVCap) and co-polymers thereof (Kelland, 2011, 2006; Villano et al., 2010). (Kelland, 2006, 2011) discussed the type and properties of these KHIs. The PVP and PVCap, respectively containing the 5- and 7-ring lactam, can be adsorb on the hydrate lattice and alter the rate of gas hydrate, while some other polymer may prevent hydrate nucleation by disturbing the bulk water structure (Kang et al., 2014; Naeiji et al., 2014a, 2014b; Tang et al., 2010). The effects of methanol, PVP and PVCap on both nucleation and growth of methane hydrate have been studied by Ke et al. (2013). Their results showed that methanol has insignificant effect on nucleation, while PVP and PVCap decrease average nucleation rate and increase the induction time of gas hydrate formation (Ke et al., 2013). Chua et al. (2011a) investigated the ability of poly(N-vinyl piperidone) (PVPip), containing the 6-

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ring lactam, to inhibit the growth of sll hydrate crystals. In comparison with PVP and PVCap, PVPip showed an intermediate growth inhibition performance at similar polymer molecular weights (Chua et al., 2011a).

It has been also determined that poly(*N,N*-dialkylacrylamide)s perform well as KHIs (Colle et al., 1996; Conrad et al., 2010; Kelland et al., 2000). Chua et al. (2011b) tested poly(*N*-isopropylacrylamide)s (PNIPAMs), and poly(*N*-isopropylmethacrylamide)s (PNIPMAMs) for their structure II gas hydrate KHI performance. In constant cooling, PNIPAM performed significantly better than a commercial KHI polymer, Luvicap 55W (Chua et al., 2011b). Villano et al. (2010) carried out hydrate KHI tests on the several poly(*N,N*-dialkylacrylamide)s. They found that polymer tacticity does affect the performance of this class of polymers, so that isotactic polyacryloylpyrrolidine (PAP) give shorter induction time than atactic PAP and different tacticity poly(*N,N*-dimethylacrylamide)s (PDMAA)s are poorer nucleation inhibitors than the PAPs (Villano et al., 2010).

Since different inhibitor groups have different characteristics, functionality and inhibitory mechanisms, the binary compositions or more kinds of inhibitors is adopted. The inhibition performance of KHI polymers often improve with added synergists. Small molecules of alcohols and glycol ethers may have synergistic effect on polymers, for example, butyl glycol ether is synergist of PVCap (Cohen et al., 1998a). Cha et al. (2013) investigated the hydrate formation in the presence of both mono-ethylene glycol (MEG) and PVP. Their results showed that hydrate onset time is further delayed due to synergistic inhibition effect of two inhibitors (Cha et al., 2013). A formulation of polyethylene glycol (PEG) drilling fluid with KHI added has been developed to drill in gas hydrate bearing sediments by Jiang et al. (2011). They found when a small amount of kinetic inhibitor such as PVP is added into the PEG drilling fluid, it can considerably inhibit hydrate nucleation and aggregation (Jiang et al., 2011). Surfactants can be also used as synergists with KHI polymers. Hu et al. used PVP and a novel kind of KHI copolymer poly(*N*-vinyl-2-pyrrolidone-co-2-vinyl pyridine)s in conjunction with tetrabutylammonium bromide (TBAB) to increase their performances on hydrate inhibition (Hu et al., 2012). Sometimes, organic molecules such as polyethylene oxide (PEO) are accompanied with KHIs to increase their inhibition performance. Keshavarz Moraveji (2012) studied the impact of PEO on the performance of PVP, so that it enhances the percentage of inhibition and induction time of kinetic inhibitor. Besides, different KHIs may be joined together to promote each other performance (Kelland et al., 2000; Rivers and Crosby, 2004).

The main focus of this paper is to investigate experimentally the effect of polyethylene glycol (PEG), polyacrylamide (PAM) and hydroxyethyl cellulose (HEC) as synergists with polyvinylpyrrolidone (PVP) on the formation kinetics of methane hydrate, in particular to observe their ability in hydrate inhibition performance.

2. Materials and methods

2.1. Materials

The name, chemical formula, purity and supplier of the material used in this work are given in Table 1. Also chemical structure of these materials is shown in Fig. 1. The methane gas which would form structure I hydrates with a purity of 99.5% from Technical gas services has been utilized to test the KHIs performance. In all of the experiments, deionized and distilled water purchased from Iran Bahrezolal Co. has been used to make aqueous solutions containing kinetic hydrate inhibitors.

2.2. Apparatus and procedure

In this work, a high-pressure system has been used to produce gas hydrate. A schematic diagram of the experimental apparatus is given in Fig. 2. A cylindrical high-pressure reactor, which can withstand pressures up to 90 bars, made of stainless steel with total available volume of 990 cm³ has been utilized. To provide temperature control, a jacket of the reactor is connected to a temperature bath. A PT100 thermocouple with an accuracy of ± 0.1 K and a Druck PTX1400 pressure transducer with an accuracy of about $\pm 0.25\%$ of the scale (0.05 MPa) have been inserted into the cell to measure its temperature and pressures, respectively. They are connected to a data acquisition system and a personal computer to acquire the temperature and pressure in the cell as functions of time. For the sake of mixing and homogeneity of solution in the reactor, a stirrer shaft controller at a maximum speed of 900 rpm has been applied.

For starting an experiment, a vacuum pump has been used to evacuate the high-pressure cell. Then, the aqueous solution containing water and additive at 500 ml has been prepared and charged to the reactor. For the sake of removing the effect of solubility stage on hydrate formation, methane gas has been injected into the reactor at given pressure which is below the methane hydrate equilibrium pressure (Sloan and Koh, 2008). After reaching temperature (about 275 K) and pressure equilibrium, the reactor has been pressurized to the given experimental pressure (about 6 MPa) and stirrer has been started at a speed of 900 rpm. Temperature and pressure of the solution during hydrate formation process has been recorded until equilibrium condition is achieved.

3. Results and discussion

Hydrate formation comprises of hydrate nucleation and crystal growth processes. Hydrate nucleation is the process that the hydrate nucleuses grow to achieve critical size for continued growth, while hydrate crystal growth is the process that the small hydrate nucleuses begin to grow up to macroscopic crystals (Ohtake et al., 2005). Nucleation process is affected by several cases such as water memory effect, physical properties, impurities and mechanical agitation. Several hypotheses have been advanced that mechanical agitation can increase nucleation rate by altering incipient nuclei to favor crystallization sites, but it does not suppress the inherent stochastic nature of nucleation (Dai et al., 2014). Since agitation has been held at a maximum speed of 900 rpm, its effect is ignored in this paper. KHIs as impurities are proposed to affect both the hydrate nucleation and crystal growth processes. Therefore, several criterions have been considered to evaluate KHIs performance in the present study. First criterion is induction time of hydrate formation in certain subcooling, which related to the hydrate nucleation process. Initial and average rate of hydrate growth are evaluated as second and third criterions, which can be determined as follows:

$$rate_{ini} = \frac{\Delta P}{\Delta t} = \frac{P_1 - P_2}{2000} \quad (1)$$

$$rate_{ave} = \frac{\Delta P}{\Delta t} = \frac{P_1 - P_2}{36000} \quad (2)$$

where P_1 and P_2 are the reactor pressures corresponding to hydrate formation at the onset of growth process and at 2000 or 36,000 s after it, respectively.

Figs. 3–5 show the change in reactor pressure versus time curves for the solutions of binary compositions containing 0.5 wt% PVP and three polymeric additives of PEG with 5–100 ppm, PAM

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