



Synergistic effects of nonylphenol ethoxylates and polyethylene glycols on performance of gas hydrate kinetic inhibitor



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ABSTRACT

In this work, the kinetic inhibition effect of two non-ionic surfactants, nonylphenol ethoxylates (NPEs) and polyethylene glycols (PEGs) has been investigated on both nucleation and growth of ethane hydrate in the presence of a known kinetic inhibitor, polyvinylpyrrolidone (PVP). The results have been compared to experiments done without PVP at the same condition. Moreover, a kinetic model based on mass transfer has been applied to predict the kinetic coefficient. Experiments have been performed in an isochoric bath reactor under constant conditions with temperature of 275.15 K, initial pressure of 2.2 MPa and aqueous solutions of containing either 100 ppm NPE/PEG or 100 ppm NPE/PEG plus 1 wt.% PVP. The addition of NPEs and PEGs has extended the induction time remarkably and it has been prolonged about 2–6 times compared to pure water system. It has also been observed that inhibition efficiency is enhanced in the presence of PVP, so that it causes a more increase (about 4–20 times) in the induction time and decrease in the initial rate. With varying surfactant length included NPEs (NPE6, NPE10, NPE30 and NPE40) and PEGs (PEG200, PEG300, PEG400 and PEG600), NPE6 and PEG400 have shown the best inhibition performance. The results showed that NPE solutions was generally more effective than PEG on the induction time (increasing up to 16,000 s), while PEG solutions considerably reduce the rate of hydrate crystal growth and kinetic constant obtained by model.

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1. Introduction

Gas hydrates are ice like and non-stoichiometric crystalline solids composed of hydrogen-bonded networks of water molecules and small gas molecules such as methane, ethane, CO₂, etc. [1–3]. Hydrate formation conditions (moderately low temperature and relatively high pressure) are usually occurred in oil and gas production operations, so that they can obstruct flow lines, valves and wellheads, causing serious safety problems. Thus, many researchers have been interested to develop various ways to prevent hydrate formation [4–6]. The current technology for preventing gas hydrate formation in pipelines consists of injecting the chemical inhibitors, which they are classified as thermodynamic hydrate inhibitors (THIs) and low-dosage hydrate inhibitors (LDHIs) as kinetic inhibitors (KIs) and anti-agglomerates (AAs). Since THI concentrations may be as high as 30–50% on the free water basis, there has been a shift toward LDHI, which cause a reasonable delay in the growth of hydrate crystals with relatively low concentration [7,8]. Furthermore KHIs, in concentrations only a few hundreds of parts per million, slow the rate of hydrate nucleation and growth rate of hydrate crystals. Thus transportation of fluids through the facilities would be occurred without hydrate formation.

In contrast, AAs allow hydrates to form while avoiding accumulation into large masses [9,10]. The common KHIs are polymers with lactam rings such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap) [11]. The PVP and PVCap, well dissolve in water and adsorb on the hydrate lattice and alter the rate of gas hydrate, whereas some other polymer can prevent nucleation of gas hydrate by disturbing the bulk water structure [5].

Ke et al. presented the effects of methanol, PVP and PVCap on both nucleation and growth of sl methane hydrate. They found that methanol had no significant effect on nucleation, while PVP and PVCap reduced average nucleation rate and increased the induction time of gas hydrate formation [12]. Kang et al. studied the effect of PVP and PVCap on the induction time of natural gas hydrate. Their results indicated that the induction time would be increased from 1.8 to 470 times larger than pure water. [5].

Both KHIs and AAs are usually polymers with surfactant properties [13]. While polymers are principally considered as KHIs, surfactants exhibit diverse agglomerated characteristics [7,14,15]. Karaaslan and Parlaktuna investigated different types of surfactant solutions to produce natural gas hydrates. They found that an anionic surfactant such as linear alkyl benzene sulfonic acid would increase the hydrate formation rate as well as some of cationic surfactant (quaternary ammonium salt). Although, cationic and anionic surfactants were pronounced as promoters, the non ionic surfactant such as nonylphenol ethoxalate (NPE) has not been clarified [13]. Dai et al. investigated the performance

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Table 1
Materials used for this work.

Material	Chemical formula	Purity
NPE6	C ₁₅ H ₂₄ O(C ₂ H ₄ O) ₆	>98%
NPE10	C ₁₅ H ₂₄ O(C ₂ H ₄ O) ₁₀	>98%
NPE30	C ₁₅ H ₂₄ O(C ₂ H ₄ O) ₃₀	>98%
NPE40	C ₁₅ H ₂₄ O(C ₂ H ₄ O) ₄₀	>98%
PEG200	H(C ₂ H ₄ O) ₄ OH	>98%
PEG300	H(C ₂ H ₄ O) ₆ OH	>98%
PEG400	H(C ₂ H ₄ O) ₉ OH	>98%
PEG600	H(C ₂ H ₄ O) ₁₃ OH	>98%
PVP k-25	(C ₆ H ₉ NO) _n	>93%
Ethane	C ₂ H ₆	99.99%

of many kinds of surfactants such as anionic surfactant (SDBS), cationic surfactant (CTAB) and non-ionic surfactant (PEG) on hydrate formation rate. It was concluded that some of surfactants could reduce the surface tension of gas–water interfacial, so that the solubility of gas in liquid would be increased. Comparing with the pure water, SDBS and CTAB solution have shown the acceleration effect on the induction time, while the effect of PEG and ionic solution was not obvious [16]. Hao et al. used ethylene glycol to study the kinetic of hydrate formation. It is known that ethylene glycol and its derivatives are good inhibitive additives as anti-low temperature [17]. Jiang et al. also developed a formulation of PEG drilling fluid with KHI added to drill in gas hydrate bearing sediments. They found that the addition of a small amount of kinetic inhibitor such as PVP into the PEG drilling fluid can considerably inhibit hydrate nucleation and aggregation [18].

As mentioned before, non-ionic surfactants such as ethylene glycols, ethoxylates, propoxylates or mixed ethoxylate–propoxylates of primary and secondary aliphatic alcohols are the most preferable type to prevent hydrate formation. Some of these substances are solids, while others are liquids and waxy nature. In this work, the main focus is investigating the effect of nonylphenol ethoxylates (NPEs) and polyethylene glycols (PEGs) as non-ionic surfactants on the nucleation and formation kinetics of ethane hydrate. Also, the synergistic effect of a known kinetic inhibitor, PVP, on the inhibition performance of NPEs (NPE6, NPE10, NPE30 and NPE40) and PEGs (PEG200, PEG300, PEG400 and PEG600) has been studied. Finally, a model based on mass transfer has been applied for prediction of the kinetic data and determination of kinetic coefficient.

2. Materials and methods

2.1. Materials

The purities and supplier of the material used in this work are given in Table 1. The deionized and distilled water from Iran Bahrezolal Co. has also been used in the preparation of solutions. The chemical structure of NPEs, PEGs and PVP are displayed in Fig. 1 and some physical properties of them are also given in Table 2. NPEs and PEGs are made by repeating ethylene oxide group (C₂H₄O).

Table 2
Preliminary physical properties of material used in this work.

Material	Avg. EO ^a mole	Appearance at 25 °C	Molecular weight (g/mol)	HLB	Density at 25 °C (g/cm ³)	Viscosity at 25 °C (cP)
PVP k-25	–	powder	25,000		1.2	5000–20,000
NPE6	6	Liquid	486	10.9	1.041	252
NPE10	9.7	Liquid	649	13.2	1.060	278
NPE30	30	Solid	1542	17.1	SOL ^b	SOL ^b
NPE40	40	Solid	1982	17.8	SOL ^b	SOL ^b
PEG200	4	Liquid	190–210	17.5 ^c	1.124	51
PEG300	6	Liquid	275–315	17.5 ^c	1.125	70
PEG400	9	Liquid	380–420	19.8 ^c	1.125	89
PEG600	13	Liquid	570–630	19 ^c	1.125	136

^a EO: ethoxylate.

^b It is determined in the solution.

^c Calculated by equations available in Ref. [19].

2.2. Apparatus

The schematic diagram of the apparatus used in this work, is shown in Fig. 2. Its main part is a stirred batch reactor made of stainless steel with volume of 990 cm³ which can withstand pressures up to 90 bars. The jacket of the reactor for heat transfer is connected to a temperature bath. A PT100 thermometer with an accuracy of ±0.1 K and a Druck PTX1400 pressure transmitter (0–0.002 MPa) with an accuracy of about ±0.25% inserted into the cell are used for temperature and pressure measurements, respectively. The signals of temperature and pressure are acquired by a data acquisition system. A magnetically coupled stirrer shaft and stirring motor speed controller at a speed of 900 rpm has been applied for mixing and homogeneity of solution in the reactor.

2.3. Procedure

For starting an experiment, the cell has been evacuated with a vacuum pump. The aqueous solution (water + additive) of 500 ml has been prepared and charged to the reactor. This solution consists of 100 ppm NPE (or PEG) and 1 wt.% PVP. Ethane gas has been injected into the reactor at pressure below the ethane hydrate equilibrium pressure at given experimental temperature (about 275.15 K) [3]. When the solution reached to experimental temperature and became stable, the reactor has been pressurized to the given experimental pressure (about 2.2 MPa). Stirring has been started and pressure of the solution during process has been recorded until equilibrium condition is achieved.

3. Kinetic modeling for ethane hydrate formation and calculation of the kinetic constant

Daimaru et al. [20] proposed a model for the hydrate formation kinetics with chemical potential difference as the driving force of hydrate formation. Considering to their model, the apparent gas consumption rate can be expressed as:

$$\left(-\frac{dn}{dt}\right) = aK^* (\mu_g - \mu_{eq}) \quad (1)$$

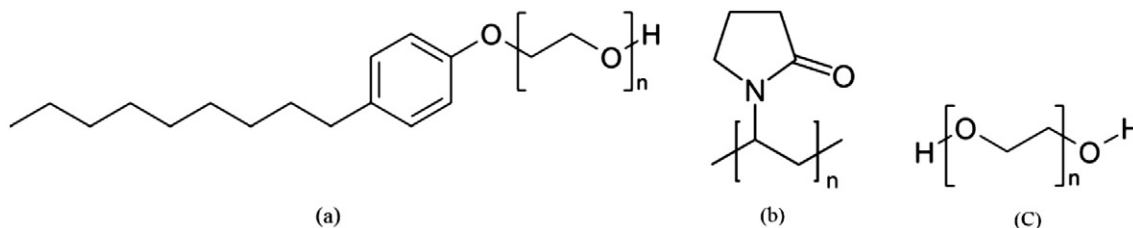


Fig. 1. Chemical structure of NPEs (a), PVP (b) and PEGs (c).

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