



Application of various water soluble polymers in gas hydrate inhibition



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ABSTRACT

Formation of hydrates in gas transmission lines due to high pressures and low temperatures is a serious problem in the oil and gas industry with potential hazards and/or economic losses. Kinetic hydrate inhibitors are water soluble polymeric compounds that prevent or delay hydrate formation. This review presents the various types of water soluble polymers used for hydrate inhibition, including conventional and novel polymeric inhibitors along with their limitations. The review covers the relevant properties of vinyl lactam, amide, dendrimeric, fluorinated, and natural biodegradable polymers. The factors affecting the performance of these polymers and the structure–property relationships are reviewed. A comprehensive review of the techniques used to evaluate the performance of the polymeric inhibitors is given. This review also addresses recent developments, current and future challenges, and field applications of a range of polymeric kinetic hydrate inhibitors.

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1. Introduction

Gas hydrates are solid crystalline ice-like compounds in which gas (guest) molecules are trapped in polyhedral water cavities at low temperatures (typically less than 27 °C) and moderate pressures (typically more than 0.6 MPa) [1–7]. Although the appearance is similar to that of ice, their structure is completely different from that of ice and they can exist at temperatures far above the ice point. The trapped gas molecules may include propane, methane, ethane, isobutene, cyclopentane, and carbon dioxide [8–16]. In nature, they are found undersea in the continental shelves and the permafrost regions [17,18]. Methane hydrates are the most common among gas hydrates [19–23].

Based on the geometries of the gas molecules in the water cages, hydrates are classified as structure I (sI), structure II (sII), and structure H (sH) [24–28]. Another less common form of hydrates is known as sT hydrates. Structure I hydrates have a body-centered cubic structure and are found in nature. On the other hand, sII hydrate has a diamond type lattice within a cubic framework, which commonly occurs in artificial systems, such as oil and gas pipelines [29]. sH hydrates have a hexagonal crystal structure while sT hydrates have a trigonal structure. The type of the crystal structure depends on the size of the guest molecule; e. g., methane and ethane form sI hydrates, propane forms sII hydrates, and the combination of CH₄ and larger guest molecules such as cyclopentane form sH hydrates. Dimethyl ether forms sT hydrates. A general notation Xⁿ is used to describe these water cages, where X is the number of sides of a face of a cage and n is the number of faces of a cage. Unit structures of common hydrates are shown in Fig. 1.

Hydrates were first discovered by Sir Humphrey Davy in 1810. The studies that followed Davy's discovery were mainly academic until 1930. In this period, overcoming the problem of large scale hydrate formation in gas pipelines became a major challenge to the gas industry [30,31]. The formation of gas hydrates during the transportation and treatment of natural gas poses many problems such as clogging of gas pipelines, plugging blowout preventers, and jeopardizing the foundations of deep water platforms [32,33]. In the worst-case scenario, pipelines can explode causing extensive economic and environmental damage in addition to posing a threat to personnel safety [34–42]. In deep water drilling operations, low temperature and high pressure conditions favor hydrate formation in drilling fluids [43,44].

Oil/gas industry uses a range of methods to prevent the formation of hydrates, such as pipeline insulation, water removal from the gas/oil streams, maintaining the operational parameters outside the hydrate formation zones, and injection of chemicals [45–47]. Insulation of pipelines and the removal of water from gas/oil streams are expensive processes [48]. Addition of chemicals to the fluid stream is the most promising and economical method to inhibit hydrate formation. These chemicals are referred to as "hydrate inhibitors". Hydrate inhibitors, discussed in the following sections, are mainly of the following types: kinetic hydrate inhibitors (KHIs), thermodynamic hydrate inhibitors (THIs), and anti-agglomerates (AAs).

Reviews that cover some aspects of hydrate formation and their inhibition are available elsewhere. Koh reviewed the

physicochemical techniques and methods used to obtain a fundamental understanding of hydrate formation and their inhibition [49]. Her review focused on the studies of phase equilibria of gas hydrates, macroscopic time resolved measurements, mechanistic models, and molecular simulation techniques. Kelland et al. reviewed the history of the development of low dosage hydrate inhibitors (LDHIs) where research efforts on the development of LDHIs by well-known companies are highlighted [50]. Perrin et al. reviewed the chemistry of LDHIs [51]. They discussed the structure–property–performance relationship of polymeric inhibitors.

The first part of this review highlights the major classes of gas hydrate inhibitors, followed by the evaluation and screening techniques of inhibitors. The aim of including these two sections is to introduce the readers to common types of inhibitors, their relative advantages and disadvantages, and to provide an understanding about the evaluation of the performance of inhibitors. Subsequent sections discuss the different classes of polymeric inhibitors, current and future challenges, and field applications.

2. Major classes of hydrate inhibitors

2.1. Thermodynamic hydrate inhibitors

THIs alter the thermodynamic conditions by changing the temperature and pressure to values where hydrates are not stable, thus hydrate formation is not favored [52–58]. Typical THIs include alcohols (methanol), glycols (monoethylene glycols), and electrolytes (NaCl) [59–65]. This method is expensive as high concentrations of THIs have to be used (10–50 wt%) [66–68]. More than \$500 million is spent annually for methanol injection to prevent hydrate formation [69]. As production and exploration move to deeper waters, conditions become more severe, requiring much higher concentration of THIs to prevent hydrate formation. Additionally, large quantities of THIs pose storage and handling problems, particularly in the offshore environment, due to limited space availability [70,71]. A considerable vaporization loss caused by supercritical gases is another issue associated with THIs. Due to environmental, technical, and economic issues, the gas industry is shifting towards using LDHIs which include AAs and KHIs [72].

2.2. Anti-agglomerates

In order to distinguish between KHIs and AAs, it is necessary to understand the mechanism of gas hydrate formation. Gas hydrate formation is initiated by a nucleation process which finally reaches the crystal growth state when gas–water clusters grow to a critical size [73]. Even though AAs do not prevent the formation of hydrates, they prevent the agglomeration of hydrates and ensure that hydrates are formed as finely suspended slush, which can be swept away from the gas pipelines [74–78]. Amine oxides such as tripropylamine oxide, tri-n-pentylamine oxide, tri-isopentylamine oxide, tri(ethylenedibutylamine oxide)amine oxide, tetrabutyl-1,10-decanediamine bis-oxide, tetrabutyl-1,7-heptanediamine bis-oxide, pentabutyl diethylenetriamine tris-amine

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