The influence of corrosion inhibitors on hydrate formation temperature along the subsea natural gas pipelines

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ABSTRACT

Pipeline industry annually invests millions of dollar on corrosion inhibitors in order to minimize corrosion's implication on flow assurance; however, attention has never been focused on the possibilities of these chemicals to promote hydrate formation along deepwater pipeline which is also a flow assurance problem. Five inhibitors were investigated in this study at different concentrations and pressures in a cryogenic sapphire cell at static condition. The changes in the formation temperature established that all the inhibitors promote hydrate but at different rates while their hydrate formation patterns also differ from one another. Their ability to promote hydrate could be attributed to their hydrogen bonding properties which is required for hydrate formation. Also, the difference in the promotion rate is attributed to their different sizes and structures, active functional groups and affinity for water molecules which determine the type of hydrogen bonding exhibited by each inhibitor while in solution. The structure and size of each inhibitor also affect its electronegativity and ionization energy since the active electrons of some of the inhibitors have direct exposure to the nucleus while for others; the active electrons at the outermost shell have been shielded from direct influence of the attractive force. Furthermore, the active functional groups obeys electronegativity trend of periodic table to determine whether the resulting bond type will be polar ionic, covalent or ionic with some covalent characteristic in nature. Though, all the inhibitors are foamy; dodecylpyridinium chloride (DPC) was however the foamiest. DPC also exhibited its highest promotion ability at 200 ppm and exhibited specific behaviour at 5000 ppm to suggest a change in the hydrate formation rate beyond the Critical Micelles Concentration (CMC). Again, increase in agitation rate prolonged the complete solidification time of the hydrates probably due to the gas solubility. Finally, the feasibility of using this chemical as an additive at high concentrations for natural gas transportation and storage in slurry form was observed due to some exhibited properties, this however requires further investigations.

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1. Introduction

Inhibition of corrosion along the inner wall of pipelines during natural gas transportation is a major investment in the gas industry due to the implications of the corrosion problems on flow assurance. In fact, natural gas pipelines, which are vastly manufactured from low-carbon steel materials for cheaper cost implications (Papavinasam et al., 2007) are susceptible to sweet corrosion due to availability of the carbon-dioxide and water molecules within the gas flows (Gaverick, 1994). This corrosion type is responsible for 60% of oil and gas field failures (Lopez et al., 2003) while the annual global cost on economic and capital losses from corrosion is estimated to be in excess of AU$2.2 trillion. In view of this, to minimize the impacts on flow assurance, corrosion inhibitors are injected as different chemical compounds into the pipelines during the gas transportations and various researches have been funded to improve the performance of these chemicals.

Corrosion inhibitors are generally organic and inorganic compounds and they operate by being either anodic or cathodic in nature (Aljourani et al., 2009). While the anodic inhibitors form a passivation layer on the metal surface thus preventing its oxidation, the cathodic inhibitors retard the corrosion by inhibiting the reduction of water to hydrogen gas. The suitability of each chemical depends on the pipe's material of construction, the gas composition and the operating conditions. The efficiency of each inhibitor is influenced by the operating conditions and material properties (Doner et al., 2011).

Nomenclature

V	volume (l)
L	pipe length (km)
D_{ft}	desired film thickness (ml)
M_1	concentration of available Inhibitor (ppm)

M_2	concentration of required solution (ppm)
V_1	volume of inhibitor (ml)
V_2	volume of solution (ml)
T_{Blank}	formation temperature for the blank experiment (°C)
T_{New}	formation temperature for the (blank+inhibitor) experiment (°C)

The operating conditions influence the corrosion rate and the inhibitor properties determine its effectiveness. The operating conditions include temperature, pressure, pH, inhibitor concentration, flow rate and CO_2 concentration (Abdel-Gaber and Saadawy, 2013; Liu et al., 2013) and the inhibitor properties include the alkyl chain length, ring size, type of head, bond type, bond strength, contact angle, and unit cell structure and parameters (Shaban et al., 2013).

Corrosion inhibitors generally possess surfactants properties (El-Mahdy et al., 2013) and surfactants have been established to aid hydrate formation (Mandal and Laik, 2008). Hydrate formation is one of the major flow assurance problems in pipeline engineering; it annually costs the gas industry millions of dollars for its minimization and billions of dollars on the eventual consequences (Obanijesu et al., 2011). Gas hydrates are ice-shaped, crystal lattice, solid compounds formed by the physical combination of water molecules with small paraffinic homologous hydrocarbon molecules (C_1–C_4) and the non-hydrocarbon components (CO_2, H_2S, N_2, etc.) at high pressure and low temperature due to the weak Van der Waals forces and the hydrogen bonding properties of water (Chapoy et al., 2010; Zhang et al., 2011). The crystalline compound is stabilized by the encapsulated smaller molecular diameters guest such as CH_4 and C_2H_6 (Sloan and Koh, 2007) which are trapped in the microcavities of a crystal lattice provided by the host water. Gas hydrate formation during deepwater transportation is aided by the favourable thermodynamic conditions of the producing environment. If not quickly removed, the hydrate grows and accumulates along the line to block the inner orifice of the pipe thus leading to pressure build-up and eventual pipeline rupture.

Several studies have been carried out on properties and efficiencies of various corrosion inhibitors (Bentiss et al., 2000; Aljourani et al., 2009) but none of the existing literature have investigated the ability of these chemicals to promote hydrate formation (Sloan, 2003; Gabitto and Barrufet, 2009; McConnell et al., 2012) hence, the significance of this study is to select five of the most regularly used inhibitors as listed in Table 1 to investigate the capability of them for promoting hydrate formation along deepwater gas pipelines.

2. Methodology

2.1. Reagent, materials and equipment

The corrosion inhibitors investigated are presented in Table 1 while Table 2 shows the natural gas as prepared by BOC Gases, Australia (based on the authors' specifications) so as to maintain constant composition throughout the experiment. Purified water was obtained from a reverse osmosis system (Milli-Q†) as the double-distilled, ultrapure laboratory grade (MQ-H_2O). The five inhibitors were prepared from their various fresh stocks and each experiment was conducted at static condition inside a cryogenic sapphire cell (Fig. 1).

The cryogenic sapphire cell equipment is made up of piston pump, pneumatic pump, sapphire cell unit, valves, two cameras and other fittings. The equipment was manufactured by Sanchez Technology (ST) in France and operates at a temperature range of −160 °C to 60 °C (with accuracy of ±0.10 °C) and pressure range of 1–500 bar (with accuracy of ±0.5 bar). The cell uses the already in-built softwares (namely, Falcon-E4378-Curtin-Cryogenic Cell, Workbench V-5-Gas pump-Pressure software and Texmate Meter Viewer) to monitor and regulate the operating temperature and pressure of the system.

The sapphire cell unit (Fig. 2) is an inner glass cell of 60 ml for liquid/gas interaction and has a magnetic stirrer which could be regulated to a desired speed. A thermocouple is placed on the top of the cell to read the gas phase temperature (or TOP TEMPERATURE) and another to the bottom to read the liquid phase temperature (or BOTTOM TEMPERATURE) during an experiment. For each experiment, the cell was properly cleaned and vacuumed in order to drastically minimize experimental errors. To achieve this, the cell is firstly depressurized by direct venting to the atmosphere followed by opening the cell door to critically clean the glass cell with MQ-H_2O. The internal wall of the glass cell was then completely dried with air using an air blower in order to minimize water retention and the glass cell was finally secured with nuts at both ends. The cell door was then closed and securely locked while the whole cell was vacuumed and the inlet valves tightly closed.

Table 2
Composition of the studied natural gas

Component	Concentration (mol%)
CH_4	70.90
C_2H_6	5.00
C_3H_8	3.00
n-C_4H_{10}	0.94
n-C_5H_{12}	0.10
N_2	0.06
CO_2	20.0

Table 1
The list of inhibitors used for the study

Inhibitor	Abbreviation	Molecular formula	Mol. wt. (g/mol)
2-Mercapto pyrimidine	MP	$C_4H_4H_2S$	112.15
Cetylpyridinium chloride	CPC	$C_{21}H_{38}NCl \cdot H_2O$	358.07
Dodecylpyridinium chloride	DPC	$C_{17}H_{30}ClN$	283.88
Thiobenzamide	TB	$C_6H_5CONH_2$	121.14
Benzl dimethyl hexadecylammonium chloride	BDHC	$CH_3(CH_2)_{15}N(CH_3)_2CH_2C_6H_5 \cdot Cl$	396