Effect of acid gases on kinetic hydrate inhibitors

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ARTICLE INFO

ABSTRACT

While kinetic hydrate inhibitors (KHIs) have seen increasing use in the hydrocarbon production industry as a cost effective hydrate mitigation strategy, there is still a lack of understanding concerning inhibition mechanisms and the underlying factors, which influence this. For example, little is known about the effect of gas composition even though this plays a major role, with lean acid gases presenting a particular challenge to KHIs. In this study, a Crystal Growth Inhibition (CGI) method previously developed in-house has been used to examine the effect of acidic gases on KHI performance. Using poly-n-vinylcaprolactam (PVCap) as the KHI, the effect of CO_2 and H_2S on different gas mixtures has been measured in detail for pressures up to ~14.0 MPa. In addition, the effect of a low pH resulting from hydrochloric, acetic and citric acids on PVCap methane hydrate inhibition has been investigated for comparison. Based on experimental results and thermodynamic modelling, it is concluded that hydrate growth from dissolved gas – a significant factor for water miscible H_2S and CO_2 – does not appear to play a major role in KHI performance. Likewise, a pH reduction itself does not seem to have a notable influence. Instead, results point to changes in cage occupancy patterns/guest gas composition a function of pressure as having the greatest effect on KHI inhibition, potentially by changing the strength of polymer absorption on different hydrate crystal faces.

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1. Introduction

In hydrocarbon production operations, gas hydrate mitigation can be associated with significant capital (CAPEX) and operating expenditure (OPEX), particularly when it comes to challenging conditions such as large subcoolings and high water cuts. To reduce the costs involved in hydrate inhibition, kinetic hydrate inhibitors (KHIs) have become increasingly popular in recent years [1–3]. However, despite offering impressive CAPEX and OPEX advantages over traditional thermodynamic inhibitors (THIs, e.g. methanol or ethylene glycol), our limited understanding of KHI mechanisms and sensitivity to different factors (e.g. water, gas and liquid hydrocarbon composition, presence of other production chemicals, pH) continues to restricts usage.

Studies have shown that hydrate crystals formed from gas mixtures have a much more complex behaviour compared to those formed from single gaseous or liquid hydrate formers [4–6]. The addition of KHIs to such systems adds yet another layer of complexity. Previously, as part of a Joint Industrial Project (JIP) at Heriot-Watt Institute of Petroleum Engineering, extensive work was conducted on the effect of guest gas and hydrate structure on aqueous PVCap performance using a recently developed Crystal Growth Inhibition (CGI) method [7]. Due to the complex behaviour noted, experiments started on single component gas systems before moving to binary, ternary, quaternary and finally multicomponent real natural gases. The results of this work have shown that gas composition plays a crucial role in governing KHI performance, most notably as a function of pressure, with CO_2 content highlighted as a significant factor in this [7]. Studies of various types of KHI polymer in different gas systems also confirms the crucial impact of gas composition on inhibition performance [8–10].

Trends in the industry towards increasing production of acid/sour gases means this issue is of growing importance; KHIs being favoured as a hydrate inhibition solution for gas and gas condensate systems. Data on KHI performance in sour gas systems is somewhat limited, although studies have shown that these can offer a challenging environment for KHIs, especially in terms of compatibility with other pipeline chemicals such as corrosion inhibitors [11–13]. There are number of factors that can potentially make sour systems difficult for KHIs. For example, sour gases are commonly quite lean (low in heavier s-II forming components such

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as propane and butane), meaning structure-I can be the most stable hydrate structure, posing a problem for KHIs that are designed primarily for inhibition of s-II hydrates. Then there is the issue of H_2S and CO_2 themselves; these can form quite high fractions of the gas phase and evidence suggests they are important factors in KHI performance, whether this be due to acidity or other fundamental processes such as cage occupancy patterns vs polymer surface adsorption strength. Finally, acidic solutions can change aqueous polymer conformation [14]; this could potentially cause coagulation and precipitation, so reduce hydrate inhibition performance while encouraging fouling problems.

While considerable improvements have been achieved in KHI performance in recent years, less consideration has been paid to understanding precise inhibition mechanisms and the effect of different system parameters [15], with testing often still very much trial and error. However, when it comes to investigating the fundamentals of KHI polymer hydrate inhibition, using reliable and proven methods is vital. In this work, a relatively new Crystal Growth Inhibition (CGI) technique [16,17], originally developed in this laboratory, has been used to study the effects of acidic CO_2 and H_2S on KHIs for various different gas mixtures. In addition, the effect of a low pH resulting from hydrochloric, acetic and citric acids on PVCap methane hydrate inhibition has been investigated for comparison, while a thermodynamic model has been used to assess the potential impact of changes in aqueous gas solubility with pressure. The results of this work are reported here.

2. Experimental materials and methods

All experiments described here (except tests on H_2S containing gases) were conducted using in-house designed and built autoclave cells with a volume of ~280 ml. These autoclaves can be operated up to maximum pressure of 41.0 MPa over a temperature range between 233.0 K and 323.0 K. Cells are made of either stainless steel or titanium (salt compatible). H_2S experiments were carried out at the Hydrafact Ltd. sour gas lab in similar high-pressure, ~280 ml volume, acid gas compatible (hastelloy) stirred autoclaves. Temperature control of autoclave cells is achieved by circulating coolant from a programmable cryostat through an insulated jacket surrounding the cells. Cell internal temperature is determined by platinum resistance thermometers (PRT, ±0.1 K), while pressure is measured by either strain standard gauge (±7 kPa) or precision Quartzdyne (±0.07 kPa) transducers, which are regularly calibrated against a dead weight tester. Pressure and temperature of the cells are continually monitored and recorded by a computer. A magnetic motor stirrer with moderate mixing rate of ~500 rpm is used to mix cell fluids creating the most favourable conditions for hydrate growth, promoting stable or metastable equilibrium, and thereby presenting the conservative testing conditions for KHIs. A schematic illustration of autoclaves has been previously presented by Anderson et al. [16].

Aqueous solutions were prepared gravimetrically using PVCap as the KHI polymer, which was Luvicap-EG base polymer (K value = 25–8, average MW = 7000) supplied by BASF, with the ethylene glycol solvent removed by vacuum oven drying. Deionised water was used to prepare solutions. Purity of the gases used in the experiments and in preparing the gas mixtures was: methane 99.995%, ethane 99.5%, propane 99.5%, and CO_2 99.995%. Gas mixtures were prepared gravimetrically with compositions checked by GC where appropriate. Natural gas compositions used in tests are provided in Table 1. All the multicomponent natural gases and mixtures containing H_2S were supplied by BOC. Purity of citric and acetic acid powders used to prepare solutions was 99.5 mass%, with these supplied by Sigma-Aldrich. The purity of hydrochloric acid used was 10.0

Table 1
Composition of natural gases used in CGI experiments on PVCap in a previous study [16] and the gas with 12.0 mol% CO_2 used in this study.

Component	Mole%	
	Previous study	This study
Methane	89.4	79.0
Ethane	5.1	5.4
Propane	1.5	1.8
i-Butane	0.2	0.2
n-Butane	0.3	0.3
i-Pentane	0.1	–
CO_2	1.6	12.0
Nitrogen	1.9	1.3
n-Pentane	0.1	–

mass% HCl aqueous. The pH of acidic solutions was measured with a VWR pH110 pH meter calibrated using manufacturer-supplied buffer solutions.

Hydrate phase boundaries used in this study are either predicted by Hydrafact/Heriot-Watt University HydraFLASH® 2.2 [18] thermodynamic model or measured experimentally using a standard isochoric step-heating method [19].

As noted, a Crystal Growth Inhibition (CGI) based method previously developed in-house has been used in all experiments. In this method, which is described in detail in papers by Anderson et al. [16] and Mozaffar et al. [17], KHI evaluation is based on the measurement of four fixed, repeatable (and transferable between different set-ups) crystal growth inhibition and dissociation pressure-temperature (PT) regions. These regions, as shown in Table 2, are classified based on orders of magnitude change in hydrate growth rates (% water converted to hydrate per hour). To define boundaries for these CGI regions, the following standard procedures [16,17] were followed:

1. Initial rapid cooling of the system to a high subcooling to form hydrates while generating a 'no-hydrate' (water + gas only) PT baseline
2. Heating the system in steps to leave only a small fraction of hydrates (around < 0.5% of water converted), while defining the extent of any possible slow dissociation region (SDR)
3. Cooling the system down again at a constant rate of 1.0 K/hour, observing clear changes in growth rate to determine slow growth regions
4. Cooling the system 0.5–1.0 K steps, likewise with a small fraction of hydrate still present, to delineate the extent of the complete inhibition region (CIR)

3. Results and discussion

Analysing the effect of acidic gases on kinetic hydrate inhibitor performance could be quite challenging as there are potentially up to three main factors that may play a role, including aqueous phase

Table 2
CGI regions definition based on change in hydrate growth rate. Characteristics of the hydrate slow dissociation region (SDR) are also shown.

Region name		% Water converted to hydrate/h[a]	Growth rate
CIR		0.00	No growth
SGR	(VS)	0.01 (<0.05)	Very slow
	(S)	0.1 (≥0.05 to <0.5)	Slow
	(M)	1 (≥0.5 to <5)	Medium
RGR		10 (≥5)	Rapid
SDR		Dissociation rate one order of magnitude less than for no KHI	(Abnormally) Slow dissociation

[a] Growth rate order of magnitude.