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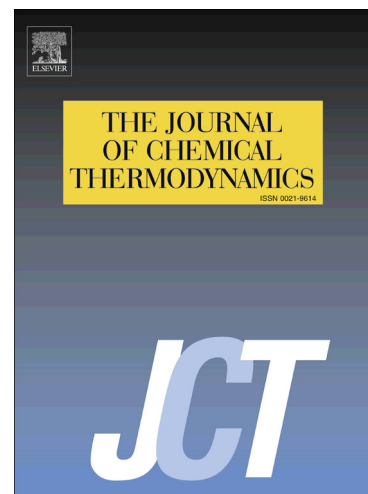
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Effect of Acid Gases on Kinetic Hydrate Inhibitors

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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 CO₂ and H₂S 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 H₂S and CO₂ – 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.

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 CO₂ 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 [8,9,10].

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 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 H₂S and CO₂

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 CO₂ and H₂S 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 H₂S 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). H₂S 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 CO₂ 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 H₂S 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 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].

Table 1 Composition of natural gases used in CGI experiments on PVCap in a previous study [16] and the gas with 12.0 mole% CO₂ 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	-

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)

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 / hr ^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

^aGrowth rate order of magnitude

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 acidity, increased propensity for hydrate formation from dissolved gas (due to much higher CO₂ / H₂S solubility in the aqueous phase compared to hydrocarbons / N₂), and hydrate cage occupancy patterns (thus strength of polymer adsorption) as a function of composition / pressure. Due to difficulties associated with considering all these factors at the same time, in this work, CGI experiments were carried out at different concentrations of CO₂ and H₂S to see the effect of cage occupancy patterns on KHI performance, while effect of acidity was examined independently by working with hydrocarbon gases only (very low aqueous solubility and no pH effect) for aqueous solutions of known pH. Modelling studies using HydraFLASH® 2.2 thermodynamic model [18] were also undertaken to examine gas solubility changes.

3.1 Methane-ethane-propane-carbon dioxide mixture with PVCap

Results of previous studies in this laboratory [7] showed that the CO₂+C₂H₆+CH₄ combination in natural gas (NG) seems to result in stronger PVCap hydrate inhibition at higher pressures, although CO₂ is apparently responsible for the significant reduction in inhibition observed at lower pressures. To examine the effect of CO₂ more precisely, while at the same time working towards the composition of a real natural gas, PVCap induced CGI behaviour in methane-ethane-propane-CO₂ systems were measured in this study.

Figure 1 shows CGI data and interpreted regions for the tested 91.5 mole% methane / 4.9 mole% ethane / 2.0 mole% propane / 1.6 mole% CO₂ gas mixture with 0.5 mass% PVCap aqueous. Consistent with other nominally s-II forming binary and multicomponent gas systems [7], CGI boundaries for this system appear related primarily through subcooling to the s-I phase boundary for the gas, i.e. initial hydrate growth on cooling is apparently the result of s-I formation.

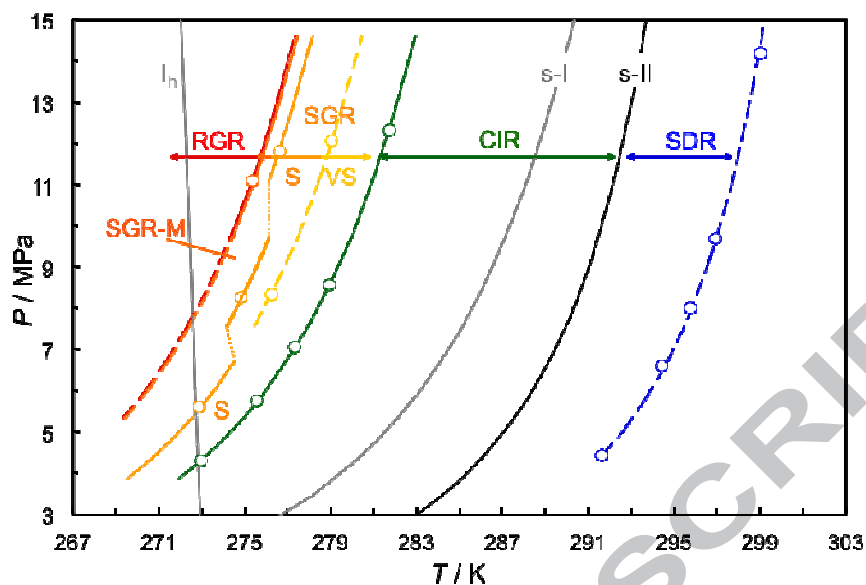


Figure 1 CGI data and interpreted regions for the 91.5 mole% methane / 4.9 mole% ethane / 2.0 mole% propane / 1.6 mole% CO₂ gas mixture with 0.5 mass% PVCap aqueous.

The addition of CO₂ to the CH₄-C₂H₆-C₃H₈ system results in an overall significant improvement in PVCap performance (Figure 4); the CIR region is the largest observed for all the systems shown in Figure 4, extending apparently to $\Delta T_{s-I} = \sim 7.2$ K across the pressure range studied (~ 5.0 to 13.0 MPa). Likewise, the SGR region is also the largest in extent observed; with CGI properties extending up to 12.8 K subcooling from the s-I boundary for the CH₄-C₂H₆-C₃H₈-CO₂ mixture. However, while the addition of CO₂ clearly improves PVCap performance compared to the CH₄-C₂H₆-C₃H₈ system, a modest reduction in PVCap performance is still observed for the CH₄-C₂H₆-C₃H₈-CO₂ system below ~ 10.0 MPa (SGR[VS] lost and SGR[S-M] boundary at lower subcoolings). Therefore, data would support previous conclusions that CO₂ content plays an important role in PVCap performance, increasing PVCap CGI properties at higher pressures, but with this being offset somewhat by it reducing performance modestly at lower pressures for the system described.

3.2 CO₂-rich natural gas with PVCap

In addition to the above, CGI studies have also been undertaken on 0.5 mass% PVCap in a natural gas system with high CO₂ (12.0 mole%). Figure 2 shows example CGI method cooling and heating curves and interpreted CGI boundaries for the 12.0 mole% CO₂ natural gas with 0.5 mass% PVCap aqueous. As shown, for 12.0 mole% CO₂, PVCap inhibition is apparently stronger at lower pressures compared to higher pressures. This is opposite to the case for multicomponent systems where CO₂ is modest

(e.g. 1.6 mole% CO₂ natural gas [16] and the CH₄-C₂H₆-C₃H₈-1.6 mol% CO₂ mixture, as shown in Figure 4). However, while for example the CIR region at 12.0 mole% CO₂ is comparable in subcooling extent to that for natural gas with 1.6 mol% CO₂ at $\Delta T_{s-I} = \sim 5.2$ K, the total extent of the SGR region is reduced for 12.0% at both high and low pressures, supporting a generally common negative effect of CO₂.

In conclusion, results suggest that CO₂ plays an important role in PVCap performance, in particular with respect to the common changes in CGI inhibition seen from lower ($P < 7.0$ MPa) to higher ($P > 10.0$ MPa) pressures. However, while CO₂ is commonly associated with a negative effect, this is not ubiquitous across all gas systems at all pressures. Rather, the effect depends on the CO₂ concentration and other gas components in the system, speculatively due to associated cage occupancy patterns and so strength of polymer adsorption on hydrate crystal surfaces.

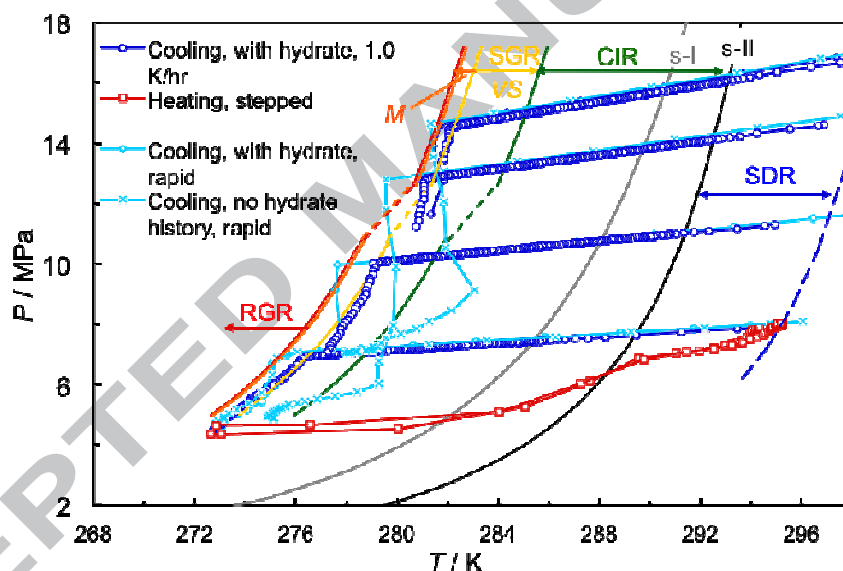


Figure 2 Interpreted CGI regions and example CGI method cooling and heating curves for 12.0 mole% CO₂ natural gas with 0.5 mass% PVCap aqueous.

3.3 Methane-carbon dioxide with PVCap

Following tests on nominally s-II forming natural gas systems with different CO₂ contents (12.0 mole% CO₂ to compare with exiting data for 1.6 mole%), CGI experiments were subsequently carried out on a 90.0 mole% CH₄ / 10.0 mole% CO₂ binary mixture at pressures up to 14.0 MPa to observe the effect of CO₂ in a s-I forming gas system, particularly as a function of pressure. Figure 3 shows determined CGI regions for this gas mixture.

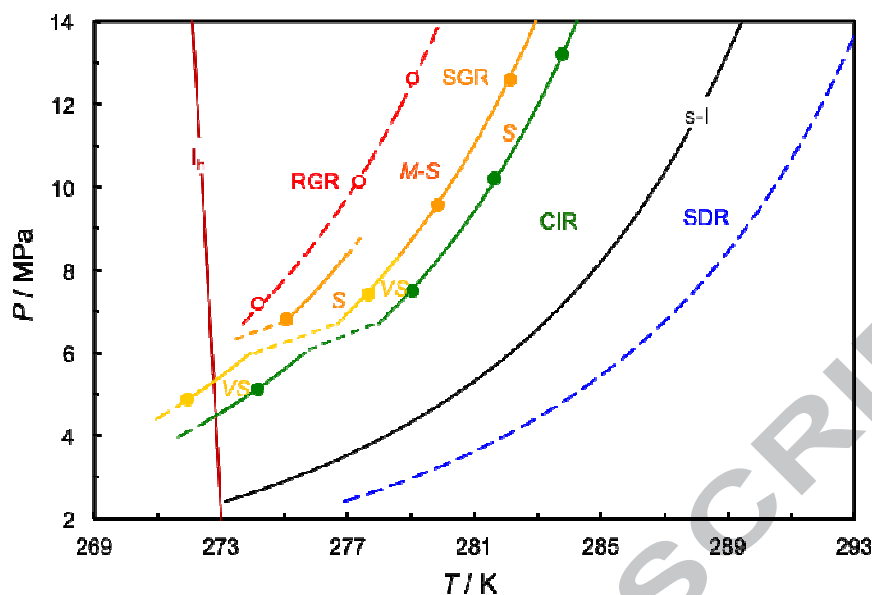


Figure 3 Determined CGI regions for 0.5 mass% PVCap with the 10.0 mol% CO₂ / 90.0 mol% CH₄ gas mixture.

As can be seen in Figure 3, PVCap performance reduces with increasing pressure in the 10.0 mole% CO₂ / 90.0 mole% CH₄ system. This reduction in extent of CGI regions occurs at around 6.0-7.0 MPa, beyond which regions become largely constant in terms of subcooling.

Figure 4 shows a comparison of subcooling extents of CGI regions from the s-I phase boundary for different gas systems presenting the effect of CO₂. The small negative effect of modest CO₂ content fractions (1.6 mole%) systems at lower pressures contrasts that for higher CO₂ in both the natural gas (12.0 mole%) and CH₄-CO₂ systems where PVCap inhibition is stronger at lower pressures. This means that for standard natural gases of modest CO₂ content (e.g. up to 5.0 mole%), CO₂ is unlikely to be the primary source of the reduction in performance commonly observed at lower pressures. Instead, it seems more likely the combination of CO₂ and ethane is causing a positive effect at higher pressures. This can be seen in Figure 4; when ethane and CO₂ are both present alongside methane, the highest CGI subcooling extents are observed (important CIR and SGR[VS] specifically). Both of these are dominant s-I large cavity occupiers; ethane in particular only occupying the large 5¹²6² cavity. H₂S is similar, albeit of slightly lower molecular diameter, but this feature is the main one common to the three gases, which seem to have the most influence on PVCap CGI performance in terms of gas composition and pressure.

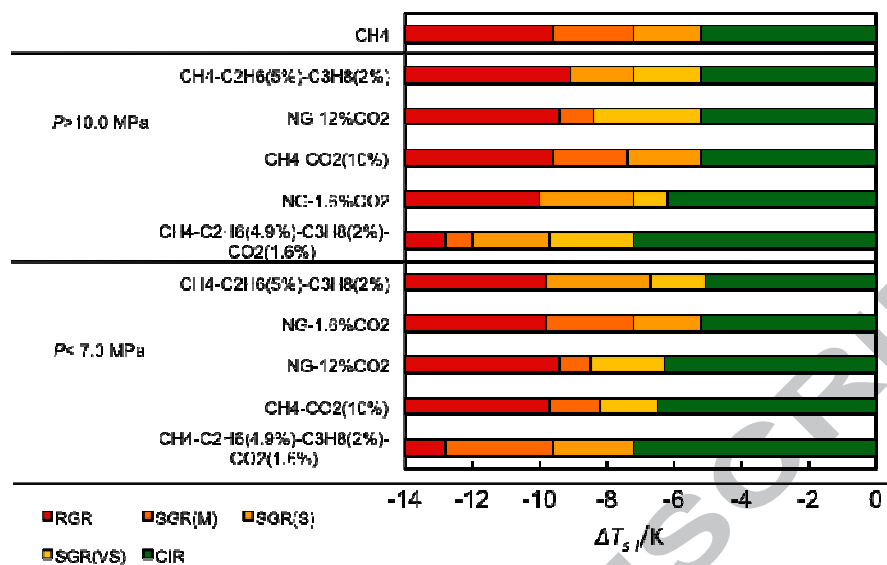


Figure 4 Comparison of subcooling extents of CGI regions from the s-I phase boundary (measured or predicted) for different gas systems showing the effect of CO₂. The plot sorts the data as a function of CIR region extent at pressures lower than 7.0 MPa and higher than 10.0 MPa. NG compositions are given in Table 1. Data for CH₄ and NG-1.6 mole% CO₂ from Anderson et.al. [16], data for CH₄-C₂H₆(5.0 mole%)-C₃H₈(2.0 mole%) from Mozaffar [7].

The causes of this behaviour still remain somewhat elusive, although based on findings to date, hydrate cage occupancy patterns (as determined by gas composition and pressure) have emerged as the most likely controlling factor; investigations into gas solubility and acidity, as discussed below, suggesting the former does not have an obvious influence and the latter actually increases PVCap inhibition (Sections 3.5 and 3.6).

3.4 Effect of hydrogen sulphide on KHI performance

Hydrogen sulphide is acidic gas which, like CO₂, poses a challenge for KHIs. As part of this study, two gas mixtures of 5.0 and 10.0 mole% H₂S with methane were studied to see the effect of H₂S on PVCap performance. A further mixture containing both CO₂ (5.0 mole%) and H₂S (5.0 mole%) with methane was then investigated. Figure 5 shows a comparison of determined subcooling extents of 0.5 mass% PVCap aqueous induced hydrate CGI regions for various single and binary/ternary mixtures of CH₄, CO₂ and H₂S studied.

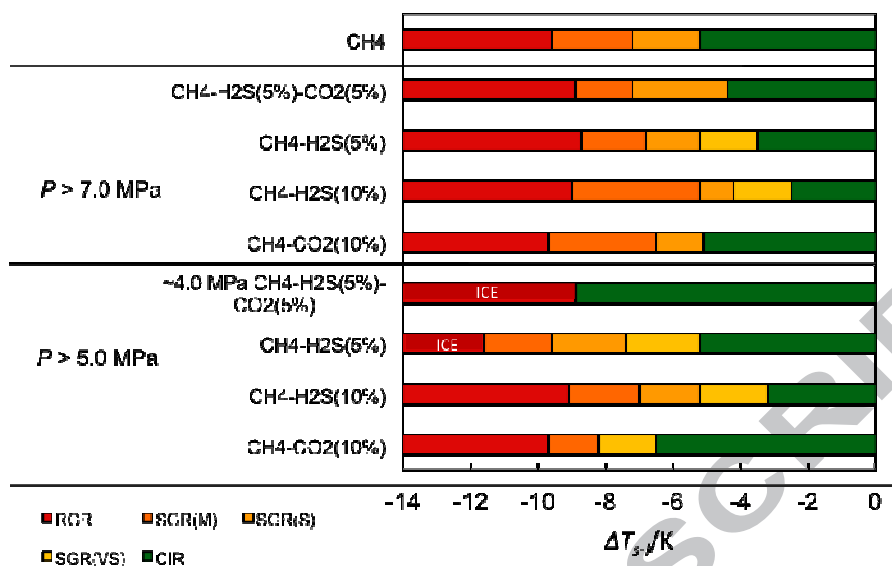


Figure 5 Comparison of determined subcooling extents of 0.5 mass% PVCap aqueous induced hydrate CGI regions for various single and binary/ternary mixtures of CH₄, CO₂ and H₂S. CH₄ data from Anderson et al. [16].

As can be seen in Figure 5, data suggest H₂S has a negative effect on PVCap performance when compared with pure methane. At both 5.0 and 10.0 mole% H₂S concentrations, the total extent of CGI behaviour is reduced compared to those for methane by up to ~1 °C subcooling. Furthermore, the higher the H₂S content, the more the complete inhibition region (CIR) is reduced. Likewise, at both H₂S concentrations, PVCap performance reduces with pressure up to around 7.0-8.0 MPa, beyond which CGI region extents become largely constant.

The effect of H₂S somewhat is similar to that for 10.0 mole% CO₂ with methane. As noted, the negative effect of H₂S increases with pressure, which was also the case for 10 mole% CO₂ with methane. In natural gases, an opposite case apparently applies for CO₂, at least at lower concentrations (1.6 mole%); at higher concentrations (e.g. 12.0 mole%) pressure likewise has negative effect. In the ternary CO₂-H₂S-CH₄ mixture, CGI performance is very high at low pressures – the CIR extending at least to 8.9 K subcooling – but reduces markedly above ~7.0 MPa. In both pressure ranges, adding CO₂ to H₂S-CH₄ mixture improves PVCap inhibition properties compared to the 5.0 mole% H₂S / 95.0 mole% CH₄, which is more pronounced at lower pressure (~4.0 MPa).

3.5 Modelling studies on the effect of gas solubility

For acidic gases, gas solubility in the aqueous phase is a further factor that could potentially explain the significant changes in PVCap performance as a function of pressure. To examine this, modelling studies were undertaken as part of this work using the HydraFLASH[®] 2.2 [18] thermodynamic model. The Cubic-Plus-Association (CPA) equation of state (EoS) was used; this combines the cubic SRK EoS with an association (chemical) term which takes into account the specific molecular site-site interactions due to hydrogen bonding [20]. For hydrate-forming conditions the model uses the solid solution theory of van der Waals and Platteeuw [21].

Figure 6 shows predictions for equilibrium aqueous H₂S solubility in the presence of hydrate as a function of subcooling and pressure for the 10.0 mole% H₂S / 90.0 mole% CH₄ system. As can be seen, as the pressure increases along the phase boundary (zero subcooling), so does the gas solubility in equilibrium with hydrate. However, this increase largely stops above 8.0 MPa. Clearly, at all pressures, as subcooling increases, so the equilibrium solubility of H₂S in the presence of hydrate reduces, thus the driving force for hydrate formation from dissolved gas increases.

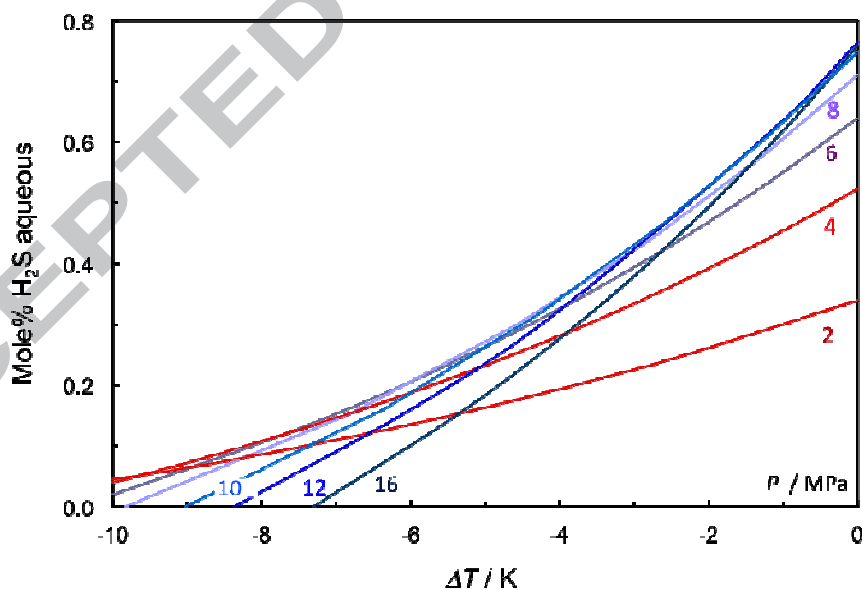


Figure 6 HydraFLASH[®] 2.2 predictions for equilibrium aqueous H₂S solubility in the presence of hydrate as a function of subcooling and pressure for the 10.0 mole% H₂S / 90.0 mole% CH₄ system.

Predictions do therefore suggest increasing propensity for hydrate formation from dissolved gas as pressure is increased up to around 8.0 MPa, at which point this starts to

stabilise. Likewise, as subcooling is increased, so the driving force for hydrate formation from dissolved gas increases. Such patterns could fit with experimental results for the $\text{H}_2\text{S}-\text{CH}_4$ system if it is assumed that hydrate formation from dissolved gas is a problem for PVCap; inhibition performance reducing as pressure increases up to around 8.0 MPa then stabilising, i.e. increasing formation from dissolved gas reduces performance then this largely stops as the driving force for it reduces at higher pressures. However, this is not supported by results for CO_2-CH_4 .

Figure 7 shows predictions for equilibrium aqueous CO_2 solubility in the presence of hydrate as a function of subcooling for 10.0 mole% CO_2 / 90.0 mole% CH_4 system. A similar pattern to that for the H_2S system is observed; as pressure increases, so does the solubility of CO_2 in the presence of gas hydrate at the phase boundary. Likewise, as subcooling is increased, so CO_2 solubility in the presence of hydrate decreases, thus propensity for hydrate formation from dissolved gas increases.

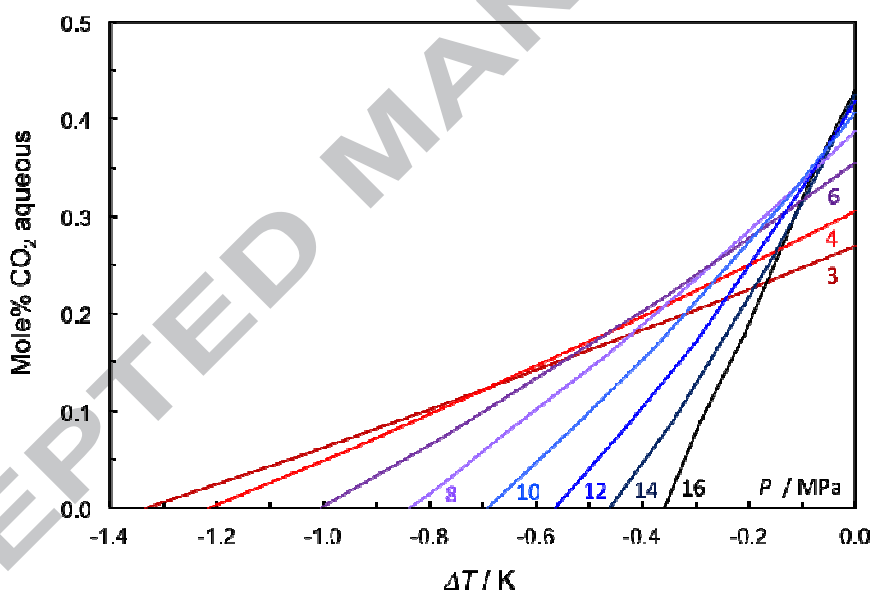


Figure 7 HydraFLASH[®] 2.2 predictions for equilibrium aqueous CO_2 solubility in the presence of hydrate as a function of subcooling for 10.0 mole% CO_2 / 90.0 mole% CH_4 system.

However, there is a clear difference in the CO_2-CH_4 system; minimal CO_2 solubilities in the presence of hydrate – thus maximum propensity for formation from dissolved gas – occur at less than 1.4 K subcooling for all pressures compared to over 10.0 K subcooling for the H_2S system. At the highest pressure condition modelled of 16.0 MPa, values are lower than 0.4 K subcooling for the CO_2 system and higher than 7.0 K subcooling for the H_2S system. This would imply that, if hydrate formation from dissolved gas is an issue for PVCap, then performance should be worse in CO_2-CH_4

systems (driving force for hydrate formation from dissolved gas peaks at much lower subcoolings) and worsen with pressure in both H₂S-CH₄ systems and CO₂-CH₄ systems, with the negative effect of CO₂ being greater than that for H₂S. This is not apparently the case though; instead PVCap performance improves with pressure in natural gases with lower levels of CO₂, while the negative effect of pressure for other CO₂ containing systems is less apparent than is the case for H₂S containing systems. Results therefore do not clearly support theoretically ‘less hindered’ growth from dissolved gas having a strong negative effect on PVCap performance.

3.5 Effect of pH and acidity on PVCap performance

The effect pH may have on KHI performance is not well established. The primary concern is acidity / low pH, namely that resulting from the aqueous dissolution and partial ionic dissociation of CO₂ (forming carbonic acid, $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$) and H₂S (forming hydrosulfuric acid, $\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$) from natural gases. Changing pH is known to cause changes in polymer conformation [14], this potentially leading to coagulation / precipitation which could result in a reduction in hydrate inhibition performance and/or fouling problems. As earlier noted, to examine the effect of acidity independently of gas composition and solubility, we have looked at the general effect of pH by working with hydrocarbon gases only (very low aqueous solubility and no pH effect) with aqueous solutions of known pH.

Three different acidic solutions, all with the same pH, were tested with methane for this purpose. Citric acid was chosen initially due to it being a mild acid with no particular corrosion risk (chelating agent for metals), and with a molecular diameter too large to potentially be involved in whole or partial hydrate enclathration. Furthermore, its weak, organic nature also makes arguably similar to naturally-occurring organic acids that may be found in hydrocarbon reservoir produced waters. To further investigate the effect of pH, acetic acid (which is also common to reservoir waters) and hydrochloric acid were tested to see if behaviour was the same as for citric acid.

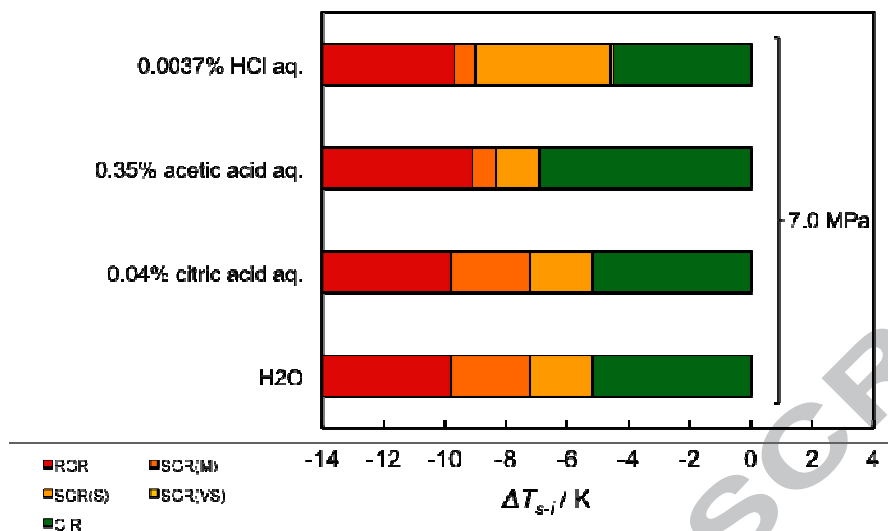


Figure 8 Comparison of subcooling extents of CGI regions from the s-I boundary for 0.5 mass% aqueous PVCap with deionised water and with 0.04 mass % citric acid, 0.35 mass % acetic acid and 0.0037 mass % hydrochloric acid tests with methane. CH₄-H₂O data from Anderson et al. [16].

Figure 8 shows a comparison of subcooling extents of CGI regions (from the s-I boundary) for 0.5 mass% aqueous PVCap with deionised water and with 0.04 mass % citric acid, 0.35 mass % acetic acid and 0.0037 mass % hydrochloric acid, all tested with methane and all at a moderately acidic pH of 3.0.

CGI behaviour for PVCap in the citric acid system is effectively indistinguishable from that for deionised water, with region boundaries identical. There was some evidence that growth rates were slightly slower in the SGR(S) region in the citric acid system, but not enough to warrant changing region classification. Thus, if anything, the acidic nature of the aqueous phase at pH 3.0 was slightly positive with respect to PVCap inhibition.

With respect to a slight positive effect, during preparation of citric acid solutions, it was noted that at higher citric acid concentrations / lower pH, polymer drop-out occurred (cloud point ~3.5 mass% citric acid at a pH of ~2.0). This ties in with the general rule of thumb that components dissolved in the aqueous phase which encourage polymer drop-out (e.g. salts, glycol ethers), unless levels actually cause precipitation, tend to have a positive effect on PVCap performance. A simple explanation for this is that hydrate crystal surface adsorption is more favoured when polymer miscibility with water is increasingly tenuous.

In case of acetic acid however, the positive effect clearly can be observed at least in terms of CIR and SGR(VS) extents from Figure 8. Both CIR and SGR(S) regions are increased to -7.1 and -8.4 K respectively, but there is a slight reduction in total CGI inhibition extent. In a similar case to citric acid, it was observed that at higher acetic acid concentrations / pH, polymer drop-out occurred (cloud point ~7.2 mass% acetic acid at a pH of ~2.3). For these two tested systems, results therefore suggest that pH may not be a major factor in KHI performance, at least in terms of having a negative effect, and can even enhance inhibition.

Similar to what was observed for citric and acetic acids, hydrochloric acid at a pH of 3.0 did not show a significant effect on PVCap CGI behaviour for methane hydrates. There is a slight reduction in CIR extent, which is -4.6K compared to -5.2K for PVCap in deionised water. Despite this slight negative effect on the CIR, the SGR(S) region extent is increased to -9.0 K, while a very narrow SGR(VS) region was introduced. The rapid growth region (RGR) boundary was however unchanged at ~-9.7 K.

4. Conclusions

For evaluation of the effect of acidic gases on KHI performance, three possible controlling factors were investigated for PVCap with various CO₂ and H₂S containing gas mixtures. Based on results, it is concluded that the effect of guest gas composition and presumably cage occupancy patterns [7] seems to play an important role in KHI inhibition, notably as a function of pressure, although the specific mechanisms involved are unclear. In terms of the effect of cage occupancy, it is speculated that the more stable the hydrate structure, the more stable the 'hydrate-polymer' complex formed following surface adsorption, so the better the PVCap performance in terms of CGI. Obviously, the stability of a hydrate depends on guest gas and occupancy; some formers need small cavities to be occupied in addition to the large cages (e.g. methane) whilst others do not (such as ethane).

Results of tests on CO₂ containing systems clearly suggest an important role for this acidic gas in PVCap CGI performance, particularly from lower ($P < 7.0$ MPa) to higher ($P > 10.0$ MPa) pressures. However, while CO₂ is commonly associated with a general negative effect on PVCap inhibition, this is not ubiquitous across all gas systems at all pressures. Rather, the effect depends on the CO₂ concentration and other gas components in the system.

CGI studies on a 91.5 mole% methane / 4.9 mole% ethane / 2.0 mole% propane / 1.6 mole% CO₂ gas mixture with 0.5 mass% PVCap aqueous confirm that the addition of CO₂ to the CH₄-C₂H₆-C₃H₈ mixture causes a significant improvement in PVCap induced crystal growth inhibition, notably at higher pressures ($P > 10.0$ MPa), however it also introduces the pattern of reduced (relatively, compared to higher pressures) CGI extents/PVCap performance at lower pressures, supporting the theory that CO₂ is likely responsible for this in natural gas systems. However, overall the performance of PVCap is better in this mixture than for a real natural gas [16], suggesting that while CO₂ is responsible for reduced PVCap performance in NGs at low pressure, it alone is not the sole cause of this.

Addition of high CO₂ (12.0 mole%) to natural gas results in PVCap performance being better at lower pressures compared to higher pressures; the opposite case for when CO₂ is modest (1.6 mole%). However, the presence of 12.0 mole% CO₂ does still reduce the overall total extents of CGI regions compared to 1.6 mole% CO₂, supporting a generally negative CO₂ effect. For 10.0 mole% CO₂ with methane, a similar trend to H₂S is observed, with the extent of CGI regions decreasing with pressure. Overall, CO₂ is less negative than H₂S, with PVCap performance more comparable to simple methane systems with even a slight improvement in inhibition at lower pressures.

Based on CGI studies of PVCap inhibition in 5.0 and 10.0 mole% H₂S with CH₄ systems, H₂S appears to have a markedly negative effect on PVCap performance, most notably as pressure increases past ~8.0 MPa, although above this pressure CGI region extents become constant. This is a similar pattern to what is seen for CO₂-CH₄ systems. PVCap performance in H₂S containing systems is improved by adding carbon dioxide; 5.0 mole% H₂S / 5.0 mole% CO₂ being more comparable with 10.0 mole% CO₂ / 90 mole% CH₄ and showing particularly strong PVCap CGI inhibition at lower pressures, although again with region extents markedly reduced at higher pressures ($P > 7.0$ MPa).

Initial modelling studies of gas solubility in the presence of hydrate vs subcooling and pressure do not show clear support for hydrate formation from dissolved gas – a second possible controlling factor on KHI performance – being a notable problem for KHIs. Likewise, studies on the effect of pH do not suggest that acidity, at least moderate acidity (pH 3.0) has a negative effect. Thus, speculatively, with acidity and hydrate formation from dissolved gas looking not to be major factors, this would leave cage occupancy patterns – and presumably how that affects the strength of polymer

adsorption on hydrate crystal surfaces / stability of polymer-hydrate complexes – as the most likely factor controlling PVCap performance in terms of CGI, particularly as a function of pressure.

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Highlights

The effect of acidic gases on KHI performance is investigated by means of a Crystal Growth Inhibition (CGI) method

For different CO₂ and H₂S containing gas systems, three possible controlling factors are evaluated

It is concluded that guest gas composition and cage occupancy patterns seem to play the most important role

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