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Effect of Diethanolamine, Mono-ethanolamine and Polyvinylpyrrolidone on Gas Hydrate Formation in a Simulated Offshore Environment

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Abstract- ***Gas hydrate formation remains a major flow assurance challenge in natural gas production and transportation systems, particularly under high-pressure and low-temperature conditions typical of offshore environments. This study investigates the combined effects of monoethanolamine (MEA), diethanolamine (DEA), and polyvinylpyrrolidone (PVP) on gas hydrate inhibition using a controlled hydrate flow-loop system. The work also considers the influence of iron filings as a representative corrosion-derived contaminant to simulate realistic pipeline conditions. Experimental evaluations were conducted at low inhibitor dosages (0.01–0.05 wt%) across multiple inhibitor combinations. The uninhibited system exhibited typical hydrate behaviour, characterised by rapid pressure decline and significant exothermic temperature increase, confirming hydrate nucleation and growth. The results showed that PVP, acting as a kinetic hydrate inhibitor, effectively delayed hydrate formation, while ethanolamine-based inhibitors contributed to thermodynamic suppression through interaction with water molecules. Among the tested systems, the MEA–DEA–PVP hybrid formulation demonstrated the highest inhibition performance under clean conditions, achieving a maximum inhibition efficiency of approximately 71% at 0.02 wt%, indicating strong synergistic interaction at low dosage. The MEA–PVP system also showed significant inhibition, with optimal performance at 0.02 wt%, while PVP alone achieved peak performance at a slightly higher concentration of 0.04 wt%. These findings confirm that hydrate inhibition is strongly concentration-dependent and that optimal performance occurs within a narrow low-dosage range. The introduction of iron filings reduced inhibition efficiency across all systems to approximately 60–62%, indicating that corrosion-derived particles promote heterogeneous nucleation and weaken inhibitor effectiveness. However, MEA-containing systems showed comparatively better performance under contaminated conditions, suggesting greater resilience to nucleation enhancement. Overall, the study demonstrates that hybrid thermodynamic–kinetic inhibitor systems provide effective low-dosage hydrate suppression, but their performance is significantly influenced by pipeline contamination. These findings provide important insights for optimising hydrate management strategies in real gas pipeline systems.***

Index Terms- ***Monoethanolamine, Diethanolamine, Polyvinylpyrrolidone, Hydrate.***

I. INTRODUCTION

Gas hydrate formation remains a critical challenge in the production and transportation of natural gas, particularly in deepwater and high-pressure pipeline systems. Gas hydrates are crystalline inclusion compounds formed when water molecules create cage-like structures that trap light hydrocarbon gases such as methane under conditions of low temperature and high pressure [1], [2]. These conditions are commonly encountered in subsea pipelines, where ambient temperatures are low and operating pressures are high. The formation and accumulation of hydrates can lead to partial or complete blockage of pipelines, posing significant safety risks and resulting in substantial economic losses due to production downtime and remediation efforts [3].

The thermodynamic and kinetic processes governing hydrate formation are influenced by several factors, including pressure, temperature, gas composition, water availability, and system disturbances. One of the most important parameters is subcooling, defined as the difference between the system temperature and the hydrate equilibrium temperature at a given pressure. Increased subcooling enhances the driving force for hydrate nucleation and growth, thereby accelerating hydrate formation [2], [4]. In practical pipeline operations, transient conditions such as shutdowns and restarts further exacerbate hydrate risks by promoting water accumulation and rapid cooling within the system [3].

To mitigate hydrate formation, several strategies have been developed, including thermal insulation, depressurisation, dehydration, and chemical inhibition. Among these, chemical inhibition is widely regarded as the most practical and cost-effective approach, especially in offshore environments where mechanical intervention is limited [5]. Traditional thermodynamic hydrate inhibitors (THIs), such as methanol and monoethylene glycol (MEG), function by shifting the hydrate equilibrium conditions to lower temperatures or higher pressures. However, these inhibitors typically require high concentrations (10–60 wt%), leading to increased operational costs, logistical challenges, and environmental concerns [2], [6].

In response to these limitations, research has increasingly focused on low-dosage hydrate inhibitors (LDHIs), including kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). KHIs, such as polyvinylpyrrolidone (PVP) and polyvinylcaprolactam (PVCap), operate by delaying hydrate nucleation and crystal growth rather than altering thermodynamic equilibrium [7], [8]. These polymers adsorb at the hydrate–water interface, disrupting hydrogen bonding and inhibiting the formation of stable hydrate structures. Although KHIs are effective at low concentrations, their performance is sensitive to operating conditions such as subcooling, salinity, and flow dynamics [9].

In addition to hydrate inhibitors, corrosion inhibitors are routinely injected into natural gas systems to protect pipeline integrity from degradation caused by acidic gases such as CO_2 and H_2S. Compounds such as monoethanolamine (MEA) and diethanolamine (DEA) are widely used in gas processing and corrosion control due to their ability to interact with acidic species and form protective films on metal surfaces [10]. However, the presence of these inhibitors introduces additional chemical complexity into the system. Their interaction with hydrate inhibitors and their potential influence on hydrate formation behaviour are not yet fully understood.

Furthermore, corrosion processes generate solid by-products such as iron particles and iron sulfide scales, which remain suspended in the fluid stream. These particles can act as heterogeneous nucleation sites, lowering the energy barrier required for hydrate formation and accelerating crystallisation [11]. Despite this, most laboratory studies on hydrate inhibition are conducted under relatively clean conditions, neglecting the influence of such contaminants. This gap limits the applicability of experimental findings to real-field pipeline environments, where corrosion and particulate matter are unavoidable.

Damages caused by hydrate formation most times are catastrophic and cause repairs worth millions of dollars to remedy, hence it is way cheaper to plan and prevent these issues than to repair [13], [14], [15].

Recent studies have emphasised the need for integrated approaches that consider both thermodynamic and kinetic inhibition mechanisms, as well as the role of contaminants in hydrate formation [3], [9]. Hybrid inhibitor systems combining thermodynamic and kinetic components have shown potential for achieving improved performance at reduced dosages, but systematic experimental evaluation of such systems, particularly in the presence of corrosion-derived particles, remains limited.

Therefore, this study investigates the combined effects of monoethanolamine (MEA), diethanolamine (DEA), and polyvinylpyrrolidone (PVP) on gas hydrate inhibition under controlled flow-loop conditions. In addition, the influence of iron filings as a representative corrosion contaminant is examined to simulate realistic pipeline environments. The objective is to provide a clearer understanding of the synergistic and contamination-dependent behaviour of these inhibitors, thereby contributing to the development of more effective and reliable hydrate management strategies in natural gas systems.

II. IDENTIFY, RESEARCH AND COLLECT IDEA

Hydrate inhibition experiments were conducted using a laboratory-scale gas hydrate flow loop designed to simulate pipeline operating conditions. The system allowed continuous monitoring of pressure and temperature during hydrate formation under controlled conditions. A baseline (uninhibited)

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experiment was first performed to establish the characteristic hydrate formation behaviour, identified by a sharp pressure decline and a corresponding temperature increase due to exothermic hydrate crystallisation.

Subsequently, inhibition experiments were carried out using monoethanolamine (MEA), diethanolamine (DEA), and polyvinylpyrrolidone (PVP), applied individually and in hybrid combinations. The inhibitor concentrations investigated ranged from 0.01 to 0.05 wt%, consistent across all test conditions. The selected formulations corresponded to the study objectives, including MEA–PVP, MEA–DEA–PVP, and combinations involving iron filings to simulate corrosion-contaminated pipeline environments.

For experiments involving contamination, iron filings were introduced into the system to represent corrosion-derived particulates commonly present in field pipelines. This enabled the evaluation of inhibitor performance under both clean and contaminated conditions.

During each experimental run, pressure–time and temperature–time data were recorded continuously. Hydrate formation onset was identified by a sustained pressure drop and a simultaneous temperature rise. The effectiveness of each inhibitor system was assessed by comparing its performance against the uninhibited baseline.

Inhibition efficiency (IE) was used as the primary performance metric and was determined based on the relative suppression of hydrate formation compared to the control experiment. It is expressed as:

$$IE(\%) = \frac{(P_{inhibited} - P_{control})}{P_{control}} \times 100$$

where $P_{inhibited}$ represents the system pressure under inhibited conditions and $P_{control}$ represents the pressure under uninhibited conditions at corresponding time intervals.

Higher inhibition efficiency values indicate better hydrate suppression, reflected by delayed nucleation, reduced pressure decline, and moderated temperature excursions. The comparative analysis across different inhibitor systems and concentrations enabled identification of optimal formulations and assessment of the impact of corrosion contaminants on hydrate inhibition performance.

III. FINDINGS

The experimental results demonstrate clear differences in hydrate inhibition performance across the various inhibitor systems and concentrations evaluated. The uninhibited (control) experiment exhibited classical hydrate formation behaviour, characterised by a rapid pressure decline and a distinct temperature rise, confirming hydrate nucleation and growth within the flow loop.

In the presence of inhibitors, all systems showed measurable suppression of hydrate formation, evidenced by delayed pressure drop, extended induction time, and reduced temperature spikes. However, the degree of inhibition varied significantly with both concentration and inhibitor composition. The relation with DEA, MEA, PVP is shown in Fig, 1.

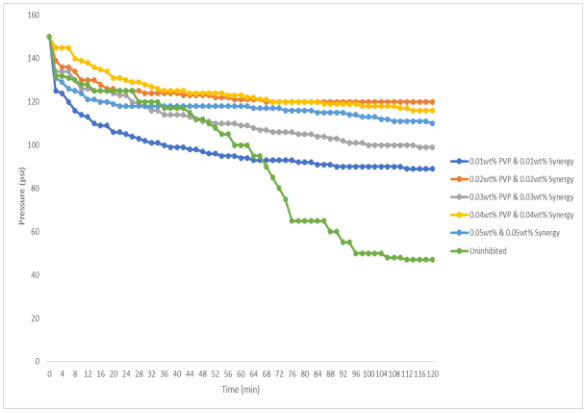

Fig. 1. Effect of DEA, MEA and PVP

For the MEA–PVP system, inhibition performance improved with concentration up to an optimum at 0.02 wt%, where a maximum inhibition efficiency of approximately 69% was achieved. Beyond this concentration, performance declined slightly, indicating a concentration-dependent behaviour typical of hybrid inhibitor systems. PVP alone also demonstrated effective inhibition, achieving its peak performance at 0.04 wt% with an inhibition

efficiency of about 70%, confirming its role as an effective kinetic hydrate inhibitor at slightly higher dosage.

The three-component MEA–DEA–PVP system exhibited the highest overall performance under clean conditions, attaining a maximum inhibition efficiency of approximately 71% at 0.02 wt%. This result indicates a synergistic interaction between thermodynamic and kinetic inhibition mechanisms at low dosage.

When iron filings were introduced, inhibition performance decreased across all systems. The maximum inhibition efficiencies dropped to a narrower range of approximately 60–62%, reflecting the influence of corrosion-derived particles in promoting heterogeneous nucleation. Despite this reduction, inhibited systems still performed significantly better than the control, confirming that hydrate suppression remained effective even under contaminated conditions.

Comparatively, systems containing MEA maintained more stable performance under contamination, while DEA-dominant systems showed slightly greater performance reduction. This behaviour is consistent with the observed pressure–time and temperature–time profiles, where MEA-containing systems exhibited slower pressure decline and less pronounced temperature excursions.

Overall, the results confirm that hydrate inhibition is strongly dependent on inhibitor composition, concentration, and system contamination. Optimal performance was consistently observed at low dosage (around 0.02 wt%) in hybrid systems, while contamination by iron filings reduced efficiency but did not eliminate inhibitor effectiveness.

VI. CONCLUSION

This study demonstrates that gas hydrate formation can be effectively suppressed using low-dosage inhibitor systems combining monoethanolamine (MEA), diethanolamine (DEA), and polyvinylpyrrolidone (PVP). The experimental results confirm that inhibition performance is strongly dependent on both concentration and inhibitor composition, with optimal performance consistently observed at 0.02 wt% for hybrid systems. The MEA–DEA–PVP blend exhibited the highest inhibition efficiency under clean conditions, indicating a synergistic interaction between thermodynamic and kinetic inhibition mechanisms.

The introduction of iron filings, representing corrosion-derived contaminants, reduced inhibition efficiency across all systems, highlighting the significant influence of heterogeneous nucleation on hydrate formation. Despite this reduction, all inhibitor systems maintained measurable suppression compared to the uninhibited condition, confirming their effectiveness under realistic pipeline scenarios.

Overall, the findings establish that hybrid inhibitor systems offer improved hydrate mitigation at low concentrations, while also demonstrating that pipeline contamination must be considered in inhibitor selection and optimisation.

APPENDIX

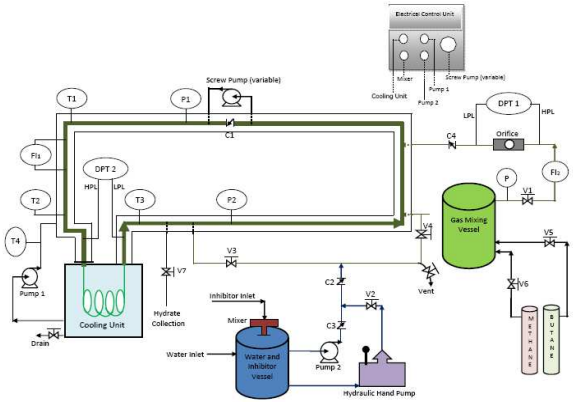

Fig. 2. Schematic of the gas hydrate flow loop [12]

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